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STUDIES IN THE PROPERTIES OF IONIC CRYSTALS

BY

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I.

THE DIELECTRIC CONSTANT OF ALKALINE EARTHS

DETERMINED BY AN IMMERSION METHOD DEPENDING ON THE VARIATION WITH TEMPERATURE OF THE DIELECTRIC CONSTANT OF THE IMMERSION LIQUID

BY

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Introduction and Summary.

In order to elucidate the relationship between the dielectric constant and the structure of solid compounds, it is best to proceed on a definite plan, for instance based on the periodic system of the elements. Binary uni-univalent compounds of course constitute the simplest cases, by now the dielectric constants of nearly all alkali-halides have been measured by many investigators, and a comprehensive compilation of data and references is given in LANDOLT-BÖRNSTEIN's tables[1]. In our present work dielectric constants of KCl, RbCl, RbBr and RbI at about 70° C. have been determined; at lower temperatures these had been determined earlier by the writer as well as by other investigators as will be seen from table 3. The temperature coefficients have small positive values.

Proceeding next to di-divalent compounds, it is observed that only very few of these have been investigated earlier. The dielectric constant of ZnS was extrapolated from infrared by LIEBISCH and RUBENS[2], and the dielectric constant of MgO was measured by GÜNTHERSCHULZE and KELLER[3] (see later). In the present work the determination of dielectric

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[1] LANDOLT — BÖRNSTEIN: Tabellen; Erg. Bd. III; 194 h-r. p. 1889—98.

[2] LIEBISCH T. and RUBENS H.: Sitzber. Preuss. Akad. d. Wiss. XLVIII (1919).

[3] GÜNTERSCHULZE A. and KELLER F.: ZS. f. Physik. **75,** 82 (1932).

constants for the alkaline earths was regarded the main object. Various samples of BeO, MgO, CaO and SrO were investigated. Beryllium compounds were prepared in a pure state following a method given by HÖNIGSCHMIED and BIRKENBACH, and strontium compounds following a method by S. P. L. SØRENSEN.

The alkaline earths are obtained nearly always as fine powders consisting of porous particles, hence resort must be taken to an immersion method. The special type of immersion method proposed by the writer[1] was found particularly suited for the purpose. According to this method, powder and a suitable immersion liquid were mixed and boiled for an hour in vacuo in order to remove occluded air. The mixture was transferred to the dielectric cell which was heated or cooled to a suitable temperature and then inserted into a Dewar vessel. During the subsequent slow temperature variation, the capacity of the dielectric cell was determined at intervals, and a curve, recording the variation of capacity with temperature, was plotted in a diagram. Afterwards the mixture was filtered, and the filtrate put into the dielectric cell, whereupon the measurements were repeated, and a new curve plotted in the same diagram. Where these two curves intersect, i. e. at that temperature, the dielectric constants of mixture, liquid and solid are equal, and if the dielectric constant of the liquid is known, that of the solid is hereby determined.

The present dielectric cell was calibrated by the standard values of dielectric constant for certain pure liquids determined by HARTSHORN and OLIVER, and by SUGDEN (see later).

Similar methods have been proposed for the purpose of

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[1] HØJENDAHL K.: ZS. physik. Chem. B. **20**, 54 (1933).

determining the refractive index or the density of a powder, but have not met with success, because these properties vary little with temperature. The dielectric constant of a polar liquid, however, varies a great deal with temperature, as will be seen from the diagram (Fig. 6) in which it is demonstrated, that the dielectric constant of acetylene tetrachloride varies from 4.5 to 14 inside the liquid region.

In an older method of STARKE[1] the dielectric constant was varied by altering the composition of the immersion liquid, which in that case was a mixture. The present method, however, is considered advantageous not only because it is easier, but also for other reasons. In the present method the dielectric cell is kept closed during the measurements, no moisture or carbon dioxide being allowed in; that would hardly be possible by the old method. In the present method the rapidity of measurements is hampered by the slow heat transfer inside the dielectric cell, in the old method the rapidity would be even more hampered by the slow diffusion of the liquid added into the pores of the particles.

The capacity of the dielectric cell was measured by means of a resonance apparatus which is described in detail. The wave-lengths used were 120, 134 and 142 meters. By means of switches the dielectric cell was substituted by a capacity box, which was adjusted until resonance was again obtained. Then the capacity of the dielectric cell was equal to that of the capacity box. The effect on the dielectric constant, arising from the electrical conductivity of the cell contents, is computed and in actual cases this effect is found to be negligible.

Chlorobenzene, ethylene dichloride, acetylene tetrachloride and mixtures of benzene with nitrobenzene or ethyl

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[1] STARKE H.: Wied. Ann. **60**, 629 (1897).

alcohol were used for immersion liquids. As a rule, the liquids were purified by means of silica gel and distillation. In the case of acetylene tetrachloride, few and conflicting data are found in the literature, therefore a number of its properties were investigated. Its melting point, determined in two ways, was found to be — 44° C. From the variation of boiling point with pressure the latent heat of evaporation was evaluated. The variation with temperature and frequency of the dielectric constants of liquid and solid acetylene tetrachloride was investigated, the resultant curves being given in Fig. 6. Just below the melting point solid acetylene tetrachloride exhibits anomalous dispersion, i. e. the dielectric constant varies considerably with frequency as well as with temperature.

The Apparatus used for Measuring Dielectric Constants.

In principle the apparatus was similar to the earlier apparatus[1] used at Universitetets kemiske Laboratorium and at Landbohøjskolens kemiske Laboratorium, both in Copenhagen; and to the apparatus used in the Physikal.-chem. Abt. des Chemischen Instituts der Universität Würzburg[2].

A number of improvements, however, have been introduced in the course of time. The present apparatus is shewn diagramatically in Fig. 1. The double set of switches S_3 and S_4 enabled measurements to be performed either by the substitution method or by the compensation method. When S_3 was in the upper position marked 'in', the adjustable capacity box C_3 was thrown into the oscillation circuit of

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[1] Højendahl K.: Studies of Dipole Moment (Dissertation). Copenhagen. (1928) p. 69.

[2] Højendahl K.: ZS. physik. Chem. B. **20**, 55 (1933).

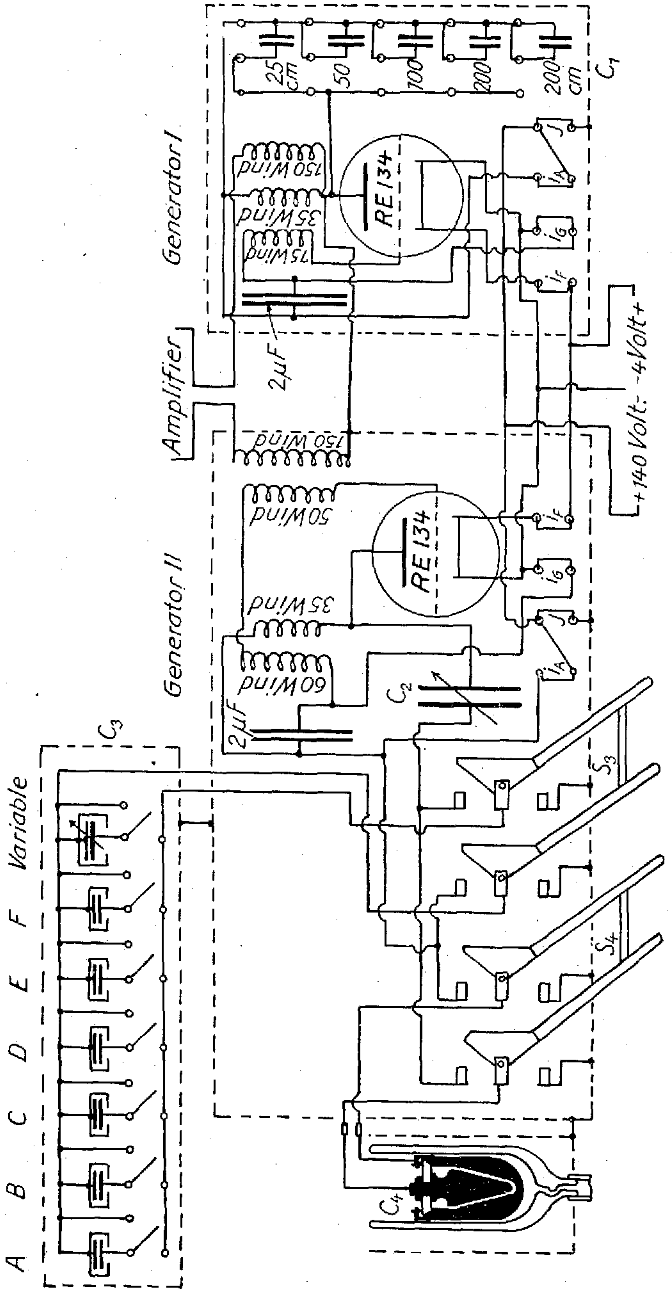

Fig. 1. Dielectric Apparatus.

generator II. When S_3 was in the opposite position marked 'out', C_3 was thrown out and both sides were short-circuited to the screen. Similarly when S_4 was 'in', the capacity C_4 of the dielectric cell was thrown into the oscillation circuit, whereas if S_4 was 'out' both sides of C_4 were connected to the screen.

In the substitution method the two switches were moved alternately. By this means the unknown capacity C_4 was replaced by the known adjustable capacity C_3. The advantage of this method was, that if C_3 was adjusted to almost the exact value the interchange could be performed in such a short time that the frequency of the generator II had no time to drift. This drift being caused by variation in the heating current of the valve or by draughts. In the compensation method the switch S_3 was constantly 'in', hence the capacity box C_3 was always part of the circuit. By moving the switch S_4 the capacity C_4 of the dielectric cell was thrown either in or out. The increase in capacity, following the introduction of C_4, was compensated by adjusting C_3 until the frequency of generator II was the same as before; then the capacity C_4 should be equal to the change in C_3. The compensation method was employed to determine small capacities, such as those of the empty condenser, its parts and the leads. Otherwise the substitution method was found to be the more advantageous. During the interchange, care must be taken that the oscillations are never interrupted. The two switches must therefore not simultaneously be 'out'. In order to define the capacity of the switch, it must always be moved 'in' or 'out' to the limit of impact.

The dielectric cell or substance condenser shewn in Fig. 2, was essentially the same as that used in Würzburg. It was in the main symmetrical about an axis of rotation.

The outer part U and the inner part I were chromium plated brass. The earlier silver plating had been mechanically worn off. The agate disk A was bolted to the inner part and ground to fit closely against the outer part. By means of the nut M the position of the agate disk and thereby the position of the inner part with respect to the outer part was secured. A well defined gap, about 3 mm. wide, was thereby ensured, into which gap the mixture to be investigated was placed.

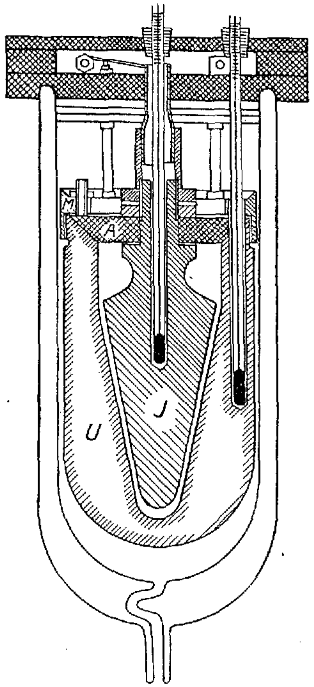

Fig. 2. Dielectric Cell.

As earlier the entire condenser was inserted in an unsilvered Dewar vessel, but now this vessel has an inlet at the bottom through which hot or cold air could be injected in order to obtain a regulated temperature variation of the condenser. The massive metal ensured uniform temperature in the entire outer part. Difficulties of some importance might arise due to the imperfect heat transfer between the inner and the outer part of the condenser, therefore the temperature variation must be a slow one. In later experiments the stream of air was stopped, and subsequent readings made when the temperatures of inner and outer parts were equal. The temperatures were read on two nerol or toluene thermometers. — The mutual capacity of two mercury thermometers would cause disturbances. — These thermometers were calibrated by comparison with standard thermometers, and in particular by the melting points of ice and mercury. The region of temperature considered was from —60° to +100° C. It was often sufficient to consider temperatures either above or below room temperature. If the entire region from —60 to 100° was to be considered, the condenser was cooled to —60° by means of CO_2-ether, whereupon it was placed in the Dewar vessel and allowed to warm slowly up to 0° C., taking about 5 hours to do so. During that time readings of capacity and temperature were taken at regular intervals. At a temperature just below zero it was found expedient to increase the rate of heating by injection of hot, dry air; the dry air was also injected for the purpose of evaporating and thereby removing any ice (rime), before it melts. Liquid water of course, was a danger to the contents of the condenser. When room temperature was attained, the research was generally interrupted over night. During the next day the temperature was gradually raised to 100° C., by further injection of hot air. In order to investigate higher temperatures the condenser was heated on a gas burner to 150° C., and placed in the Dewar vessel and allowed to cool slowly. Moderately low temperatures were obtained by means of common salt and ice, or better still, by placing the condenser in a dessicator in the open air on a cold winter night. Compressed air was procured from the plant of the college; it was dried through calcium chloride and heated in an electric oven.

As will be seen from Fig. 2 the condenser was suspended in the 'nokait' lid by means of three bolts of German silver (small thermal conductivity). One of these bolts was connected to one terminal and formed one lead. The second lead is directly visible in the figure; it consisted of bushing and plug, because the connected parts must be able to turn independently. The plug, which was perforated to take the thermometer, was connected to the second terminal. The 'nokait' lid fitted against the Dewar vessel, but it did not rest on it. It rested on a metal box, (not visible in the Fig. 2) forming a metal shield round the condenser. In this box the Dewar vessel was seated on a 'suberite' ring. The entire box with all could be tipped round a horizontal axis. In this way the terminal plugs of the condenser or dielectric cell could be removed from the corresponding bushings in the shield of generator II, whereupon the dielectric cell could be lifted out of the Dewar vessel and box. By turning the nut *M* with respect to the outer part *U* the condenser or dielectric cell could be taken into three pieces, namely 1) the nut *M* with nokait lid and terminals, 2) the outer part *U* and 3) the inner part *I* with agate disk and bushing. The dielectric cell was closed by the opposite operation, but care must be taken that the different holes for the thermometers are in alignment. This was ensured by means of a rod of dimensions similar to those of the thermometers.

The adjustable capacity box C_3 was built similar to a resistance box, from a set of six 'Baltic' air block condensers and a small variable condenser. It is, however, far more difficult to ensure independent additivity of capacities than of resistances. In order to secure additivity each component condenser was enclosed in a separate metal box. These boxes were connected together and connected to one terminal of the capacity box. One side of each component condenser was always connected to the box. The second side was brought through an opening in the box, and connected to a bushing in the ebonite top plate. By means of a special double plug or bridge, connection could be made, either to bushings connected to the second terminal in which case the capacity considered was 'in', or connection could be made to bushings connected to the first terminal in which case the condenser considered was short circuited and 'out'. In the above manner a capacity box which can be accurately set and read can be constructed from ordinary commercial radio articles. The entire capacity box was surrounded by a separate metal shield connected to the other shields of the apparatus.

The generators I and II were built from commercial radio articles when these were still abundant. Some parts were taken over from an older apparatus. The circuits will be seen from the diagram (Fig. 1). The valves were 'Telefunken R.E. 134'. The coils were 'Reactone Low Loss'. The variable condenser C_2 in generator II was an adjustable 'Torotor' condenser. In generator I a system of 'Baltic' block condensers was used for capacity. They could be thrown 'in' and 'out' from the outside in a similar way to those of the capacity box.

By this means it was ensured that the measurements were performed not at any frequency, but at a number of definite frequencies. The frequencies most often used correspond to the wave-lengths 120 m., 134 m., and 142 m.[1].

Each generator was placed in a separate box. Such a box consisted of front plate, bottom plate and framework of ebonite. The framework was rigidly bolted together by means of corners of brass plate. On top, bottom and three sides zinc plates were bolted on. The front plate was covered by a window fitted with brass network. The zinc plates and the brass network formed a closed Faraday cage or shield, which was connected to the shields mentioned before.

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[1] The wave meter was kindly lent to me by Mr. J. P. Christensen, Telephone and Telegraph Department of the Technical Highschool, Copenhagen.

If need be, the zinc plates could be removed to give access to the interior. Valves, coils etc. were mounted on the bottom plate. The front plate contained a number of control knobs, allowing the generator to be operated from the outside. The leads were all placed in the space between bottom and front plate, and hence they were all visible as soon as the zinc plates were removed. The leads were made of thick wire soldered on and drawn as far as possible straight through the intervening space from one support to another. The leads must be rigid and as remote as possible from everything else, in order that mechanical vibrations shall cause the smallest possible capacity or frequency changes (quivering).

The frequency of the electric oscillation set up in a generator depends largely on the effective capacity and inductance of the dominant oscillatory circuit, which in this case was placed in the anode circuit. In the case of generator II this dominant circuit was composed of a coil with 35 windings and the capacities C_2 and C_3 (or C_2 and C_4) in series. The use of capacities in series instead of in parallel gives the possibility of generating a larger variety of frequencies by means of the same condensers.

Auxiliaries. The two generators were coupled together by means of a link circuit, and the interference note set up was eventually made audible by means of a commercial radio receiver with loud speaker (Unica). If the frequencies of the two generators are close, an audible note will be heard in the loud speaker. The closer the frequencies, the more bass the note. The note will eventually be so bass that it becomes inaudible over a narrow interval. The two borders of this interval were used in the measurements in a manner similar to the borders of the sound minimum employed in the telephone-bridge method for determination of resistances. The procedure in the substitution method was then the following: A definite frequency or wave-length, say 142 m. was set up in generator I by throwing the 100 cm. condenser in the oscillation circuit of this generator. With the dielectric cell C_4 in, and the capacity box C_3 out of the oscillation circuit of generator II, the condenser C_2 was adjusted to one of the borders of the silent interval. C_4 was then replaced by C_3 which was adjusted to the two borders of the silent interval. The settings of these were read. Afterwards the procedure was repeated with C_2 set on the second border of the silent interval. The mean value of these four readings on the capacity box C_3 measured the capacity of the dielectric cell C_4.

The heating current for generators and receiver was supplied by an accumulator battery. The anode current for the receiver was taken from a high tension battery; that for the generators from a stabilizer (Fig. 3) the most important part of which was a discharge potential divider from G.m.b.H. Stabilovolt. The potential across the divider is nearly independent of the current passing through. This was combined with an iron-in-hydrogen resistance Fe., having just the opposite character in so far as the potential increases steeply with the current. The combination of these suppressed slow variations in the potential of the town supply to such an extent that the potential variations of the stabilized potential were found not to exceed 3 per cent. of those of the supply. In order to suppress oscillations as well, a filter chain consisting of chokes L and block condensers K were also introduced. The stabilizer was mounted in a box similar to those of the generators.

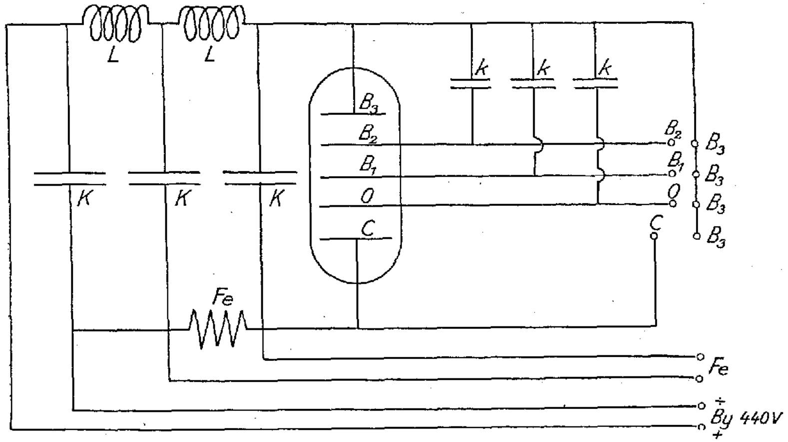

Fig. 3. Stabilizer.

Calibration of the Apparatus.

The calibration of the adjustable capacity box was undertaken in a manner similar to the calibration of weights. The different block condensers A, B, etc. were expressed in terms of the degrees on the scale of the variable condenser. An unknown capacity x was measured by two different combinations of component condensers. For instance:

$$x = C + F + 14.8 = C + 88.1$$

from which was found: $F = 73.3$ degrees on scale

Similar equations were written down for other combinations. The different values varied due to the experimental error, which was up to 3 degrees on the scale, but there was no definite trend. As a mean value of 9 determinations it was found: $F = 71.2$ degrees on scale. In a similar manner the difference $E—F$ was found from 10 determinations to be 72.9 and hence E was equivalent to 144.1

degrees on the scale and so on. That no definite trend was observed is a proof that the component capacities were independently additive within the experimental error. Furthermore by means of the standard instruments of the electrical laboratory of Nordisk Kabelfabrik the corresponding capacities were expressed in cm.[1]. As a result the following values for the different component condensers were obtained:

Table 1.

	degrees on scale	capacity in cm.
A	1093.0	222.2
B	1065.0	219.2
C	564.5	115.6
D	288.0	62.1
E	144.1	32.8
F	71.2	13.9
	1° equals	0.205 cm.

The calibration of the dielectric cell was undertaken to determine the true capacity of the cell. The apparent capacity of the cell was considered to consist of two parts, namely the true capacity which varied proportional to the dielectric constant of the contents, and the lead capacity which was constant. Four independent determinations were made:

1) By direct measurement of lead capacity. The capacity of the dielectric cell filled with air including leads to the switch S_4 was measured by the compensation method. It was found to be equivalent to 223.3 degrees on the scale or 45.7 cm. Afterwards the outer part was removed, i. e. it was screwed out of the nut M. The capacity of what was left was considered to be that of the leads. It was found to be equivalent to 102.2 degrees on the scale or 20.9 cm. The difference of 121.1 degrees on the scale or 24.8 cm. was the true capacity of the dielectric cell.

2) Using benzene as a standard liquid. The purification of standard liquids is considered later. The capacity of the dielectric cell with benzene, leads included, by the compensation method was equivalent to 373.3 degrees on the scale at 17° C. According to the most accurate determination of Hartshorn and Oliver[2], the dielectric constant of benzene at 20° C. is 2.282, and at 17° C. it is 2.288. From this and the foregoing measurement on air one unit of dielectric constant was found to correspond to:

$$\frac{373.3-223.3}{2.288-1.001} = 116.6 \text{ degrees on the scale.}$$

3) Using chlorobenzene as a standard liquid. By now the most accurate value of the dielectric constant of chlorobenzene is presumably that of Sugden[3], i. e. $\varepsilon_{25^\circ} = 5.612$, whereas Ulich and Nespital[4] found $\varepsilon_{25^\circ} = 5.605$ and $\varepsilon_{20^\circ} = 5.685$. With the same temperature coefficient the Sugden value becomes 5.690 at 20° C., which was taken as a standard value. The capacity of the cell with chlorobenzene at 20° C. measured by the compensation method was found to be equivalent to 779.8 degrees on the scale. In a manner similar to that given for benzene it was found that one unit of dielectric constant corresponds to 118.7 degrees on the scale.

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[1] I therefore wish to express my thanks to Mr. J. Møllerhøj.

[2] Hartshorn L. and Oliver D. A.: National Physical Laboratory. Collected Researches Vol. **22**, p. 342 (1930).

[3] Sugden S.: J. Chem. Soc. (1933) p. 773.

[4] Ulich H. and Nespital W.: ZS. physik. Chem. B. **16**, 229 (1932).

4) The above calibrations were carried out by the compensation method, the great majority of the measurements, however, were carried out by the substitution method. The dielectric constants measured were as a rule larger than that of chlorobenzene. Therefore a calibration was also carried out by the substitution method, using chlorobenzene and ethylene dichloride as standard liquids. Measurements on these two liquids were in fact carried out repeatedly during the entire series of measurements, in order to control the constancy of the true capacity of the dielectric cell. The following 16 readings referred to 20° C. were obtained on chlorobenzene in the course of time:

607.4; 609.1; 608.4; 611.9; 616.8; 616.9; 600.0; 600.8;

604.5; 605.2; 606.3; 606.3; 605.9; 611.0; 608.3 and 605.3.

all in degrees on the scale of the capacity box. It is seen that definite changes occur, which are somewhat larger than the hap-hazard error. The reason is the following:

The mixture of powder and liquid was sometimes so tough, that a certain violence was necessary in order to close the dielectric cell. On one occasion, towards the end of the series of researches, the pressure was so large, that a bit of the agate disk was broken off. The agate disk was mended by means of dental cement in a manner similar to the filling of a tooth. The change in capacity following this mishap, however, was not the largest. Other changes were caused by the giving way of the tin packings between the inner part *I* and the agate disk *A*, and by wear and tear on the different parts, which necessitated readjustment of the screws bearing against the upper surface of the agate disk.

Originally it was the intention to use the individual measurements on chlorobenzene to correct for these changes in the true capacity of the dielectric cell. This, however, was abandoned, since it was found that the dielectric constants of solids could not for other reasons be reproduced to more than 2—5 per cent. Hence the mean value of 607.7 at 20° C. was considered the standard reading for chlorobenzene.

In a similar manner the value of 1175.2 at 20° C. was obtained as an average of eight measurements on ethylene dichloride. The most accurate value of the dielectric constant of this compound as determined by Sugden: loc. cit. is: $\varepsilon = 10.36$ at 25° C., whereas Ulich and Nespital: loc. cit. found $\varepsilon = 10.24$ at 25° C. and $\varepsilon = 10.50$ at 20° C. Hence the value $\varepsilon = 10.62$ was taken as the standard value at 20° C. according to Sugden.

The difference in dielectric constant

$$10.62 - 5.69 = 4.93$$

corresponds to the difference in readings

$$1175.2 - 607.7 = 567.5.$$

The true capacity i. e. the number of degrees on the scale corresponding to one unit on dielectric constant therefore becomes:

$$\frac{567.5}{4.93} = 115.2 \text{ degrees on the scale}$$
$$\text{or } 115.2 \times 0.205 = 23.6 \text{ cm.}$$

As this value was obtained from repeated measurements by the more accurate substitution method it was taken as the standard value. The agreement with values obtained in other ways showed, that it was essentially correct and furthermore that linear inter- and extrapolation was allowable.

By such extrapolation the reading corresponding to zero dielectric constant was found to be —48 degrees on the scale. This was the difference in capacities of leads leading to C_3 and C_4, it includes the capacity of the capacity box with all block condensers out, and the scale of the variable condenser at zero.

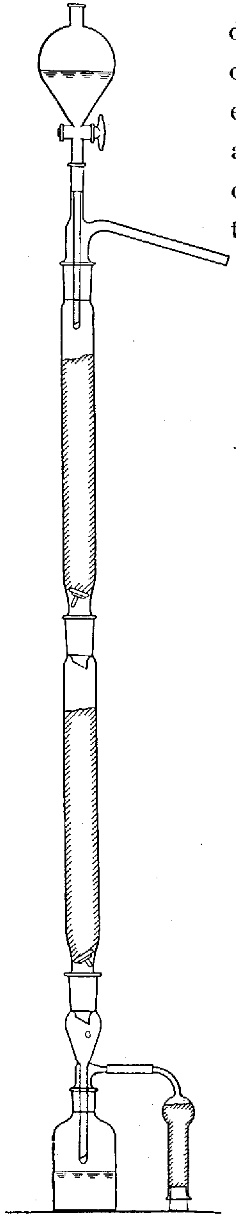

Fig. 4. Purification of Liq. by means of Silica Gel.

Immersion Liquids.

In addition to the standard liquids mentioned above namely chlorobenzene and ethylene dichloride, we used acetylene tetrachloride and mixtures of benzene with nitrobenzene or ethyl alcohol as immersion liquids. These mixtures were used in order to evade an eventual decomposition of ethylene dichloride by the reactive compounds SrO and CaO.

Of the above liquids, benzene, chlorobenzene, ethylene dichloride, acetylene tetrachloride and nitrobenzene were purified by practically the same method. They were allowed to ooze through silica gel as proposed by Grimm and Wolff[1]. By selective adsorption more polar impurities such as water were retained on the gel. The adsorption apparatus was built from standard grounded parts (Normal Schliff), see Fig. 4. It was found convenient to have two columns (Hempel columns) one on top of the other. When the silica gel in the upper column was saturated, and the column therefore removed in order to refill it, the lower column was raised to the top and the refilled column attached below. In this manner a good purification could be obtained by means of the smallest amount of silica gel.

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[1] Grimm H. G. and Wolff H.: ZS. angew. Chem. **41**, 98 (1928).

The liquids were afterwards distilled in the same distillation apparatus as used by Lannung[1] in his research on the solubilities of alkali-halides in alcohols and acetone. The apparatus is described and a figure is given by Lannung. The liquid containers were also those constructed by Lannung. They were stored in the dark and served their purpose well.

Nitrobenzene was distilled twice in a cheaper apparatus by slow surface evaporation in a vacuum of 20 mm. Hg.

The pure liquids were characterized by the following constants:

Benzene	melting point	5.10° C.
Nitrobenzene	melting point	5.76° C.
Chlorobenzene	refractive index n_D =	1.5224 at 23.6° C.
Ethylene dichloride	refractive index n_D =	1.4427 at 23.4° C.

Ethyl alcohol was purified by the method of Lund and Bjerrum[2] using magnesium and iodine. When it was due to be used the ethyl alcohol was distilled directly from the magnesium ethylate.

Various properties of acetylene tetrachloride were given special attention. Thus the refractive index for the D line was found to be 1.4937 at 22.0° C.[3].

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[1] Lannung A.: ZS. physik. Chem. A. **161**, 256 (1932).

[2] Lund H. and Bjerrum J.: Ber. D. Chem. Ges. **64**, 210 (1931).

[3] This value supercedes the value n_D = 1.4988 at 23° C. given by the writer in Kemisk. **16**, 54 (1935).

The melting point from the fusion curve is — 43° C. (thermometers calibrated by means of melting points of mercury and ice), but owing to the small heat of fusion and the slight heat conductivity of acetylene tetrachloride the melting point as determined from the fusion curve, i. e. temperature — time curve, is not very definite. A more definite value of — 44.5° C. is found from the variation of dielectric constant with temperature as will be considered later. The above values of the melting point agree well with that determined by Timmermans[1], namely — 43.8° C., but not with that found by Herz and Rathmann[2], namely — 36° C. The latent heat of vaporization of acetylene tetrachloride can be determined from the variation of boiling point with pressure. The above distillation apparatus used for the purification of the liquids was employed for the measurements. It was connected to a mercury-gauge. By the adjustment of the taps leading to the vacuum of a water jet aspirator and to dry air at atmospheric pressure, various pressures could be maintained, and the corresponding values of pressure and boiling point could be determined. Such values are plotted in diagram 5. Two samples were investigated. The crosses + + + refer to a purified sample and the circles to a still further purified sample. This second sample was the middle fraction obtained during the distillation of the first one. It is seen that there is no marked difference between the data obtained for the two samples, which indicates that these were sufficiently purified. The triangles represent earlier data of Herz and Rathmann[3], and the diamond data of Walden and Swinne[4]. In order to determine the latent heat of vaporization, Briggsian logarithms of pressure are plotted as ordinates against the reciprocals of the absolute temperatures as abcisses. The X's are the values obtained from the first sample and the filled circles those obtained from the second sample. The data can be represented by a straight line within the experimental error, hence they can be expressed by the following "August" equation:

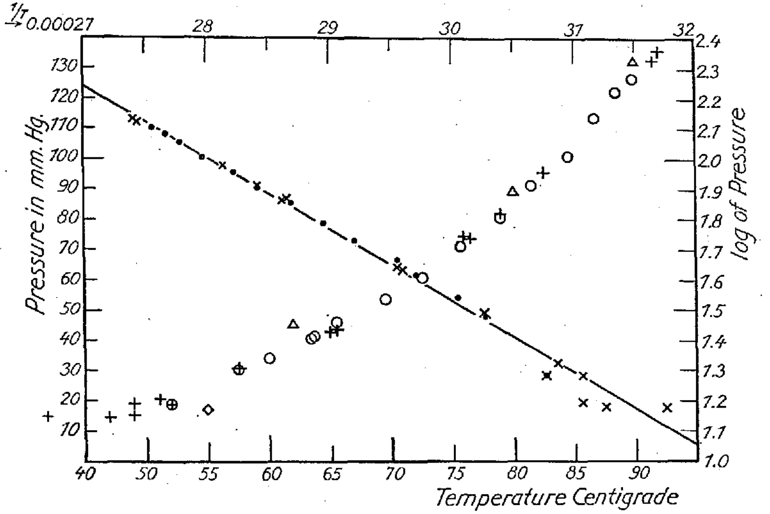

Fig. 5. Vapour Pressure of Acetylene Tetrachloride.

$$\log_{10} p = -\frac{A}{T} + B = -\frac{2375}{T} + 8.655;$$

According to the Clausius-Clapeyron relation the latent heat of evaporation is equal to:

$$l = \frac{A \times R}{\log e} = \frac{2375 \times 1.986}{0.4343} = 10850 \text{ cal/Mol.}$$

This is the value for a range of temperature around 70° C.;

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[1] Beilstein: Handbuch org. Chem. Ergbd. I. p. 25.

[2] Herz W. and Rathmann W.: Chem. Zeitung, 37, 621 (1913).

[3] Herz W. and Rathmann W.: Chem. Zeitung. 36, 1417 (1912).

[4] Walden P. and Swinne R.: ZS. physik. Chem. 82, 281 (1913).

Herz and Rathmann loc. cit. found 9134 cal/Mol at about 140° C.

The dielectric constant of acetylene tetrachloride in the liquid state was determined by the substitution method, whereas the dielectric constant in the solid state up to a value of about nine was determined by the compensation method. The measurements were performed in the following manner. Acetylene tetrachloride was freed from air by boiling in vacuo, whereupon it was placed in the dielectric cell which afterwards was cooled to — 70° C. in carbon dioxide-ether. The cooled dielectric cell was placed in the Dewar vessel of the measuring apparatus, and measurements were carried out during the gradual warming of the dielectric cell; later on the temperature was raised by injection of hot air. Close to the melting point the dielectric constant of the solid increases rapidly with temperature, and therefore in the present research with time. Hence the readings were taken by setting the condensers C_2 and C_3 at definite positions. In a short time the entire scale of notes was heard, and the temperatures corresponding to the two borders of the silent interval were read on the thermometers. The mean value of these readings gives the temperature corresponding to the setting of the condenser. Four series of measurements were carried out. In diagram 6 the resultant dielectric constants are plotted as ordinates against the (corrected) temperatures as abcisses. Data at 142 m. wave-length are denoted by triangles, those at 134 m. wave-length by X's, and those at 120 m. wave-length by circles.

Note that the dielectric constant varies considerably with temperature, and somewhat with frequency. The pointed maximum represents the melting point of — 44.5° C. The decrease of the dielectric constant of the liquid with rise of

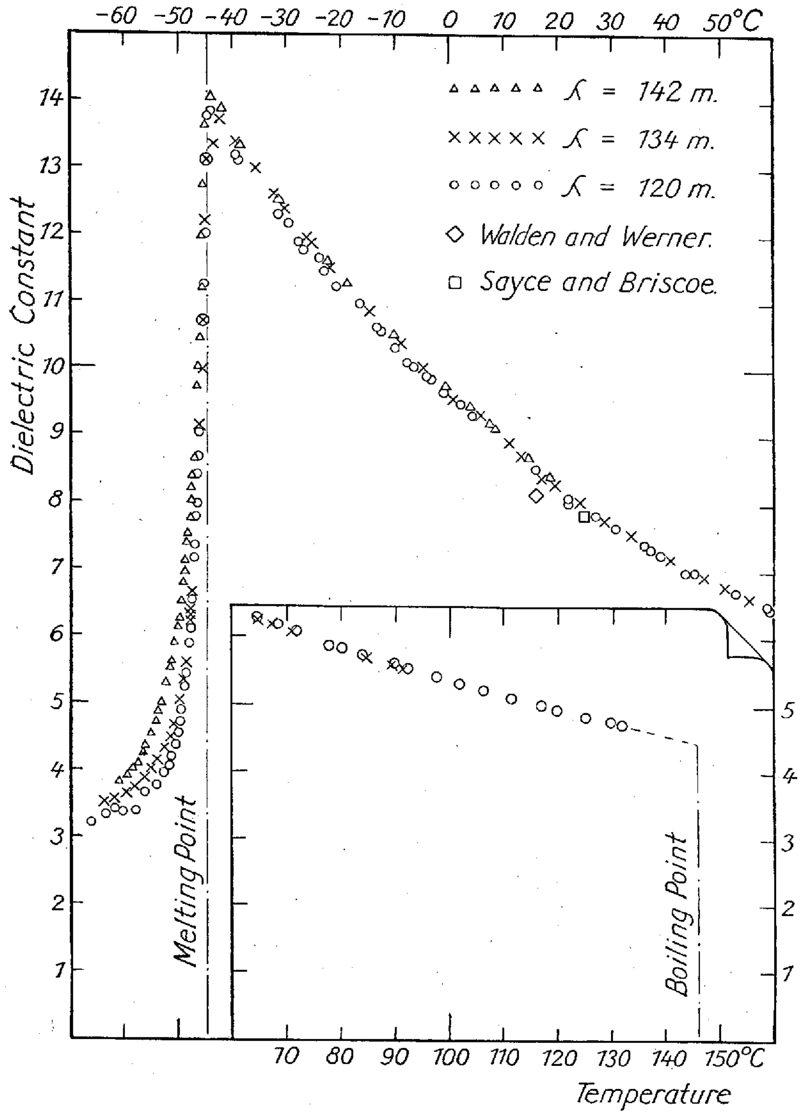

Fig. 6. Dielectric Constant of Acetylene Tetrachloride.

temperature is considerable. Furthermore the liquid region is wide, ranging from — 44.5° C. to 146° C. As a consequence of this the region of dielectric constant encompassed by liquid acetylene tetrachloride is unusually large, ranging from 14 down to 4.5. This great range makes acetylene tetrachloride especially suited as an immersion liquid for the present powder method. At and above room temperature the data at different wave-lengths fall practically on a single curve, i. e. there is no dispersion. At low temperatures there seems to be a slight dispersion also in the liquid, but hardly outside the experimental error. The divergency of the different points would seem to indicate an experimental error of about one per cent. This, however, is not the total error; there are systematic errors as well which will be considered later. The total error is presumably of the order two per cent. at room temperature, and up to five per cent. at the highest and lowest temperatures. Within this error the dielectric constant of liquid acetylene tetrachloride, at least below 100° C., can be expressed by the following empirical equation:

$$\varepsilon = 9.7 - 7.7 \times 10^{-2}\, t + 3.4 \times 10^{-4}\, t^2;$$

where t is the temperature in degrees Centigrade.

The dielectric constant of acetylene tetrachloride has been determined earlier by WALDEN and WERNER[1], who found the value 8.15 at room temperature (about 16°). In diagram 6 this is denoted by a diamond, lying somewhat below the data of the writer. The temperature given by WALDEN and WERNER, however, is not well defined. A determination has also been carried out by SAYCE and BRISCOE[2], who found a value of 7.83 at 25° C. This is denoted in diagram 6 by a square lying close below the data of the writer. The difference is of the same order of magnitude as our experimental error.

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[1] WALDEN P. and WERNER O.: ZS. physik. Chem. **111**, 469 (1924).

[2] SAYCE L. A. and BRISCOE H. V. A.: Journ. Chem. Soc. 2626 (1926).

The dielectric constant changes abruptly on fusion for many polar compounds. In the present case, however, this change is not so abrupt as is generally found. It looks like a continuous transition existing between the dielectric constant of the solid and that of the liquid. The slope of the curve for the dielectric constant of the solid in vicinity of the melting point is steep, but it is not perpendicular. It furthermore depends on the frequency or wave-length in such a manner that the shorter wave gives the steeper slope.

This behaviour can be explained by a theory outlined by DEBYE[1]. According to this theory a polar molecule in a crystal lattice can occasionally turn round and take up another orientation. The number of molecules oriented in a given direction is determined by the BOLTZMANN distribution law, in virtue of which the orientation is affected by an external field. The induced moment obtained by orientation of dipoles depends on frequency or wave-length, because at the longer wave the molecule gets more time to await an opportunity for turning round. It depends on temperature, because it is the thermal energy of the molecules which overcomes the potential barriers involved in turning the molecule with respect to the surrounding molecules.

Experimental results similar to the above have been obtained by many investigators. Notably ERRERA[2], and SMYTH and HITCHCOCK[3]. It is found from the work of SMYTH and HITCHCOCK in particular, that traces of impurities have

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[1] DEBYE P.: Polare Molekeln, (Polar Molecules). Hirzel. Leipzig (1929). Paragraph 21. pp. 118—124.

[2] ERRERA J.: Journ. de Physique et le Radium. (6) **5**, 304 (1924).

[3] SMYTH C. P. and HITCHCOCK C. S.: Journ. Amer. Chem. Soc. **54**, 4631 (1932).

a considerable influence on the shape of the curve. This influence is such that the purer sample shows a more abrupt change in dielectric constant on fusion. As an explanation it is suggested that the molecules turned by the field in particular are those situated at places in the crystal where the continuity of the lattice is disturbed, for instance by the presence of foreign molecules.

Preparation and Analysis of solid Compounds.

KCl (Kahlbaum zur Analyse) was dried. RbCl, RbBr and RbI were those samples, which we had used earlier, recovered by recrystallization from water and dried[1]. They were prepared following a method by Lannung[2].

The beryllium compounds were prepared in a pure state following the method given by Hönigschmied and Birkenbach[3]. Commercial $Be(OH)_2$ was dissolved in acetic acid and the basic acetate formed was recrystallized twice in Soxhlet's apparatus from pure acetic acid. The crystals of basic beryllium acetate were placed in a tube of hard glass which was inserted into a larger glass tube placed in an electric oven. The basic acetate was sublimed from the narrow tube into the wider one at a vacuum of 10 mm. Hg in a stream of pure air. The sublimate was found to be free from iron. It was decomposed by nitric acid. From the beryllium nitrate, pure beryllium carbonate was prepared by precipitation with pure ammonium carbonate. By ignition of the hydroxide, the nitrate or the carbonate, different samples of beryllium oxide were obtained.

MgO (Kahlbaum zur Analyse) was analysed. A trace of

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[1] Højendahl K.: ZS. physik. Chem. B, **20**, 61 (1933).

[2] Lannung A.: ZS. physik. Chem. A, **161**, 259 (1932).

[3] Hönigschmied O. and Birkenbach L.: Ber. D. chem. Ges. **55**, 6 (1922).

carbonate and as much as 0.01 per mille chloride was found, but nothing else. The magnesium oxide was ignited. In one case the nitrate was formed by dissolving the oxide in nitrid acid. By ignition of the nitrate a special sample of magnesium oxide was obtained.

$CaCO_3$ (Merck pro Analysi) was analysed. No barium was found by the finest test of Sørensen (see later). A slight precipitate with $CaSO_4$ solution revealed a trace of strontium. A minute trace of iron and a minute trace of chloride were found, but nothing else. Calcium oxide was obtained by ignition.

SrO 'Kahlbaum', which had been ignited for four hours at 1000—1100° C., was analysed. Traces of $Cl-$ and $Fe+++$ were found. The dry residue of soluble sulphates amounted to 2.16 per cent. 2.8 per cent. CO_2 was found[1]. By spectral analysis about 1 per cent. Ca and rather less Ba were estimated to be present. Two series of measurements were carried out on the above SrO, whereas the subsequent two series were carried out on SrO purified following the method of Sørensen[2]. By this method iron and other metals were removed by heating an aqueous solution of strontium chloride and hydroxide with chlorine and filtering the ferric hydroxide formed. If large amounts of barium had been present, they could have been precipitated as barium chloride by addition of hydrogen chloride in the cold. In order to remove all other metals but barium, calcium, and lead, the sulphate was precipitated and washed. The sulphate was decomposed by ammonium carbonate and the carbonate by nitric acid. Barium was removed by fractional

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[1] I am indebted to Dr. K. J. Pedersen for using his apparatus which is described in: Journ. Amer. Chem. Soc. **53**, 20 (1931).

[2] Sørensen S. P. L.: ZS. anorg. Chem. **11**, 375 (1896).

precipitation of the sulphate from the nitrate solution. The remaining strontium nitrate solution was dried, and the residue repeatedly extracted with alcohol. Calcium nitrate, being considerably more soluble than strontium nitrate, was removed, and we were left with pure strontium nitrate. From this the carbonate was obtained by precipitation with ammonium carbonate. Different samples of strontium oxide were obtained by ignition of nitrate, carbonate, or hydroxide (obtained from oxide).

The pure strontium nitrate was analysed for barium and calcium by the finest tests given by Sørensen. No precipitate of barium chromate was visible after two days, which shows that the product contained less than 0.2 per mille barium. A slight precipitate of $CaNH_4AsO_4$ showed the presence of about 3 per mille calcium. On ignition strontium oxide was found to corrode the platinum crucible. The ignited product was gray, due to the platinum content, which was found to be about one per mille.

The ignition of the different compounds was performed in two electric furnaces. The first of these was a crucible furnace from Heraeus in which a temperature of 1000° C. could be attained. The second furnace was procured for the purpose. It was built by Sieverts in Stockholm and fitted with 'Globar' heating elements of carborundum. In this furnace a temperature of 1400° C. could be attained. The temperature was measured by means of a platinum — platinum-rhodium thermo-couple. The crucibles were generally of platinum except in the case of magnesium oxide where a magnesium oxide crucible of course was used. In order to avoid the formation of hydroxide or carbonate, due to the moisture and carbon dioxide in the air, and furthermore to prevent the formation of strontium peroxide, due to oxygen, a stream of pure nitrogen was conducted through the furnace until it was so cold that the crucible could be removed and placed in a dessicator.

Preparation of the Mixture of Powder and Immersion Liquid.

The ignited product was pulverized in a porcelain mortar. In the cases of calcium- and strontium oxide the mortar was placed in a manipulation chamber through which a stream of pure air was conducted. This chamber was similar to those in which balances are sheltered. Three openings, closed by shutters, are just large enough to allow a hand to be put into the chamber to perform the manipulation without introducing sensible amounts of moisture and carbon dioxide. The same chamber was also used for some of the following operations where moisture and carbon dioxide should likewise be avoided.

The powdered product was placed in a flask, belonging to the intermixture apparatus (Fig. 7). This was built similar to a vacuum distillation apparatus from standard ground parts — Greiner and Friedrich Normalschliff. — It consisted of a round flask heated on an electric air bath. This was surmounted by an empty Hempel column, which served to catch the splashes — contrary to ordinary practice bumping is wanted. The column was attached to an Asher condenser, in the thermometer joint of which the leg of a tap-funnel was inserted. Through this tap-funnel the immersion liquid was introduced. The condenser was attached to a receiver, which in turn was connected to a water-jet aspirator. By tilting the apparatus the condenser could act as a reflux condenser.

The procedure was as follows: The powder — in particular the alkali-halides which were not dried in other ways — was dried by heating to about 200° C. in the highest vacuum attainable i. e. some 20 mm. Hg. After cooling the liquid was added, and the mixture boiled in vacuo — bumping — for two hours. By this operation occluded air should as far as possible have been removed from the powder. Finally the superfluos liquid was distilled off into the receiver, and pure air was allowed in. In the cases of strontium and calcium oxide, the immersion liquid was in most cases a mixture of nitrobenzene in benzene. To avoid heating the oxides with the less resistant nitrobenzene, the oxide was mixed with benzene in the above manner, and nitrobenzene was subsequently added. It was found necessary to allow the mixture to stand for some time, preferably over night, so that nitrobenzene might diffuse into the pores of the oxide.

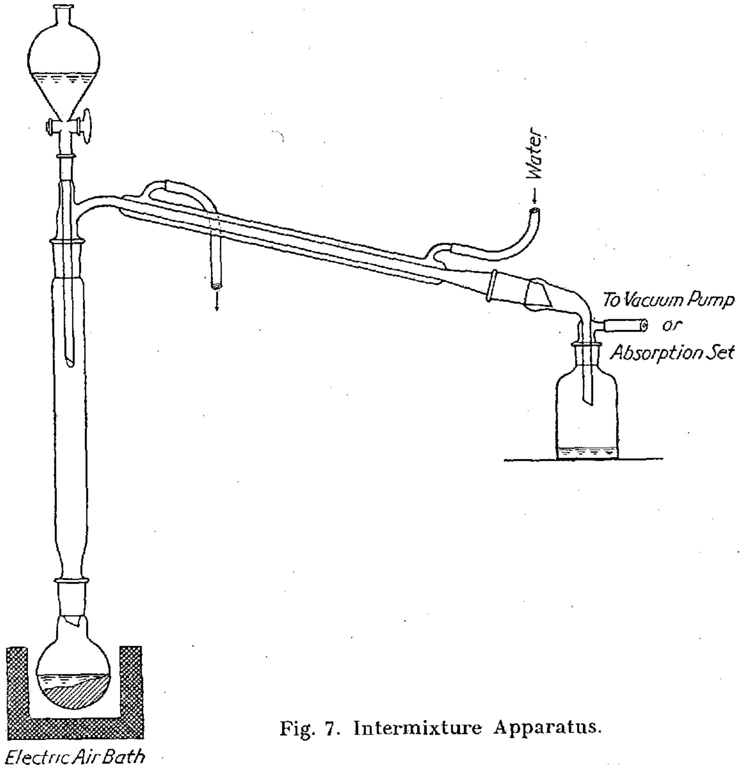

Fig. 7. Intermixture Apparatus.

The flask containing the mixture was placed in the manipulation chamber, and there the contents were poured into the outer part of the dielectric cell. The powder was allowed to precipitate to a certain degree, in so far this could be accomplished in a reasonable time, and the surplus liquid was drained off by means of a special pipette, having a plate of ebonite fixed on. By means of a libella this plate was placed level with the brim of the outer part of the dielectric cell, and by suction the liquid above a certain level was removed. The liquid drained off was employed later on. The inner part of the dielectric cell, filled to the defined height, contained 35 cubic centimeters of the mixture. The mixture was stirred, and the inner part of the dielectric cell was introduced. This was rocked and turned until the ground parts fitted together, and the nut *M* (see Fig. 2) could be screwed into the proper position. In order that the dielectric cell could be closed properly without violence, the fraction of solid powder must not exceed 30 per cent by volume of the mixture. This fraction of solid in the mixture was determined as follows: The amount of solid substance was originally weighed in the flask, and subsequently the liquid was added and mixed with the powder, whereupon the contents were poured into the dielectric cell. Here the powder precipitated, and the surplus liquid was drained off. It is now assumed that the total amount of solid was transferred into the dielectric cell, and knowing the density of the solid and the volume of the dielectric cell i. e. 35 cubic centimeter, the percentage by volume of solid in the mixture could be calculated. This percentage is not very definite, however, even if the solid could be quantitatively transferred, because the solid precipitated in the dielectric cell to an unknown extent.

Determination of the Dielectric Constant of Solids.

The dielectric cell was cooled as described on page 12, and then inserted into the Dewar vessel. During the subsequent slow rise in temperature, readings were carried out by the substitution method as described on page 10. The readings on the scale of the variable condenser in the capacity box were plotted against the corresponding readings on the thermometers. Such plots are given in the following diagrams.

The key is as follows:

△ ——— △ i. e. the triangles denote measurements on the mixture at a wave-length of 120 meters;

\+ ——— + i. e. the crosses, the same at a wave-length of 134 meters;

□ —·— □ i. e. the squares, the same at a wave-length of 142 meters.

Curves, usually straight lines, have been drawn through the points of each set. Various combinations of block condensers were generally used, each combination giving a separate curve in the diagram. Such a curve for instance is denoted $A + F$, which means that, besides the variable condenser, the block condensers A and F were in the circuit.

After these measurements were finished the contents of the dielectric cell were filtered on a dry filter. The filtrate, together with the liquid drained off by the pipette (see

page 35), was placed in the dielectric cell, and the capacities and temperatures were measured exactly as above. The readings have again been plotted in the diagram.

The key is as follows:

○ ——— ○ i. e. circles, denote measurements on the filtrate or the pure liquid at a wave-length of 120 meters;

× ——— × i. e. X's, the same at a wave-length of 134 meters;

◇ —·— ◇ i. e. diamonds, the same at a wave-length of 142 meters.

Curves (straight lines) have again been drawn through the points of each set. Where the corresponding curves for mixture and filtrate intersect, the dielectric constants of solid and liquid are equal. As described, the determination was made with the use of a single combination of block condensers only; by considering more combinations of block condensers, the accuracy was improved in the following manner: In a separate part of the diagram, the differences between corresponding readings on the scale for liquid and mixture, have been plotted against the readings on the thermometers. The temperature at which this difference was zero, records a much more accurate value of the intersection temperature, and the corresponding reading on the scale was found from the curve for the liquid (or mixture). The dielectric constant was then calculated in the following manner: To the reading on the scale of the variable condenser was added, 1) the value of the block condensers in scale degrees (see page 18), and 2) the value 48, representing the lead capacity (see page 22). The total, expressed in scale degrees, was divided by 115.2 (see page 21), whereby the dielectric constant of liquid and solid at the temperature of

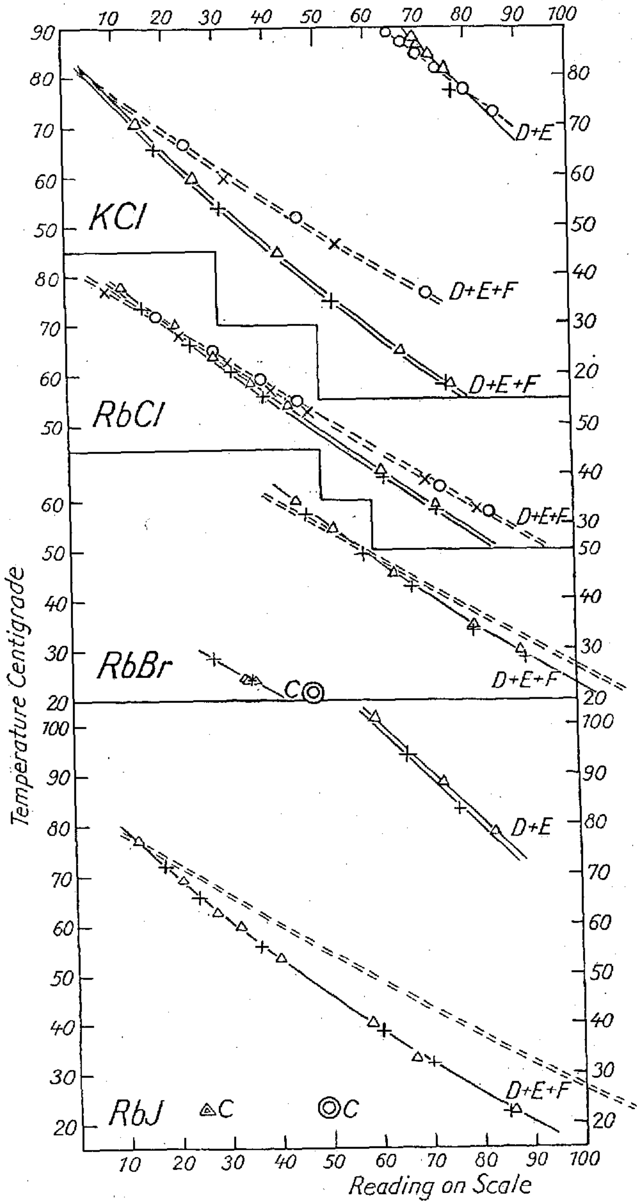

Fig. 8. Alkali Halides in Chlorobenzene.

intersection was determined. Above zero the thermometers gave the temperature in degrees centigrade with sufficient accuracy, but below zero a correction was found to be necessary. This correction was based on the melting points of ice and mercury. In the tables the corrected temperatures are quoted either in brackets or in a special column.

Data for alkali halides are given in diagram 8 and in table 2. The key is explained in the foregoing pages.

Table 2.

	Origin	Vol. per cent solid	Liquid	Wave-length	Intersection temperature	Condenser readings			Dielectric constant
						variable	fixed	total	
KCl	Kahlbaum	19.2	C_6H_5Cl	120	77.5	79.5	480.1	559.6	4.86
„	zur Anal.	same sample		120	80.0	4.8	551.3	556.1	4.83
„	„			134	80.0	5.8	551.3	557.1	4.84
RbCl	purified	8.6	C_6H_5Cl	120	68.7	23	551	574	4.99
„	„	same sample		134	68.9	22	551	573	4.97
RbBr	purified	19.9	C_6H_5Cl	120	52.0	55	551	606	5.26
„	„	same sample		134	51.2	55	551	606	5.26
RbI	purified	17.7	C_6H_5Cl	120	77.5	12	551	563	4.89
„	„	same sample		134	75.8	14	551	565	4.90

The dielectric constant of KCl has been accurately determined by Eucken and Büchner[1] whose measurements were carried out on plates cut from large single crystals. They found a value of 4.68 at 20° C. with a temperature coefficient $\frac{1}{\varepsilon}\frac{d\varepsilon}{dT} = 30.3 \times 10^{-5}$. This determination is considered the most accurate, and my determination above is only to be considered as a test of the total error involved

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[1] Eucken A. and Büchner A.: ZS. physik. Chem. B, **27**, 321 (1934).

in the present method. According to Eucken and Büchner the dielectric constant at 80° C. will be 4.77 which is about 1.5 per cent. smaller than the above values.

The dielectric constants of rubidium halides have likewise been determined earlier, and the different data have been compared in table 3.

Table 3.

	New dielectric constant	At temperature	Old dielectric constant	At temperature	Temperature coefficient	Dielectric constant at room temperature found by other investigators
RbCl	4.98	69	4.78[4]	1	6×10^{-4}	5.20[1]; 4.95[2]; 4.68[3]
RbBr	5.26	52	5.16[4]	—14	3×10^{-4}	4.70[1]; 4.87[2];
RbI	4.90	77	4.51[4]	12	13×10^{-4}	4.81[1]; 5.58[2];

[1] Errera J.: ZS. Elektrochemie. **36**, 818 (1930).
[2] Kyropoulos S.: ZS. f. Physik. **63**, 849 (1930).
[3] Schupp P.: ZS. f. Physik. **75**, 100. (1932).
[4] Højendahl K.: ZS. physik. Chem. B. **20**, 63 (1933).

There is fair agreement between my old and new values when it is remembered that there is a temperature difference of about sixty degrees. Old and new values are employed for the determination of temperature coefficients $\frac{1}{\varepsilon}\frac{d\varepsilon}{dT}$ which, however, cannot be considered accurate, because the error on the individual measurements is 2 per cent, giving rise to an error of some 50 per cent. on the temperature coefficient. The agreement between the data of the different investigators is not particularly good. I am aware that the plate method as developed by Eucken and Büchner is capable of greater accuracy than the powder methods; granted of course that sufficiently large crystals can be obtained. This is presumably the case with the alkali-halides, and therefore I suggest that any further measurements on these should be carried out by the plate method. But there are many cases where large single crystals cannot be obtained, and here the powder method in its present form will be of value. Such for instance is the case with most oxides.

BeO. Six mixtures of BeO of different origins and with different immersion liquids were investigated. For one of these mixtures the actual readings have been plotted into a diagram, Fig. 9. The diagrams for the other mixtures were

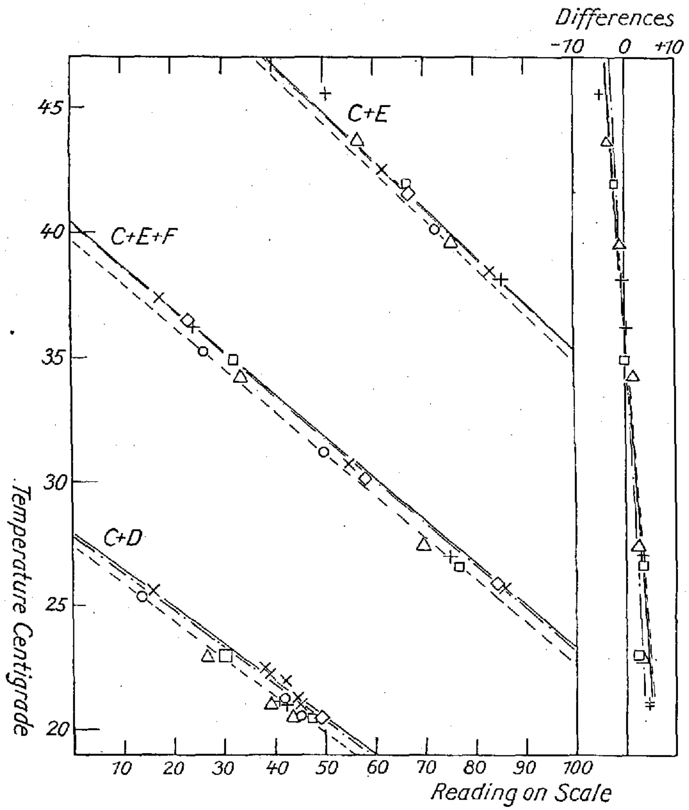

Fig. 9. BeO_{III} in $C_2H_2Cl_4$.

similar, and therefore they have been left out in order to save space, and only the intersection temperatures and the corresponding condenser readings are given in table 4. The sample considered in the diagram is the third one in the table. The key is largely as given earlier; 'pure' means purified as described on page 30; the ignition temperature is given in degrees Centigrade, and the duration of the ignition was some hours.

Table 4.

	Origin	Ignition temperature	Vol. per cent solid	Liquid	Wave-length	Intersection				Dielectric constant
						Temperature	Condenser reading			
							variable	fixed	total	
BeO_I	Be(OH)$_2$	950		C$_2$H$_4$Cl$_2$	120	79	8	900	908	7.89
,,	Merck	,,	same sample		134	84	— 16	900	884	7.68
BeO_{II}	BeCO$_3$	950	4.5	C$_2$H$_4$Cl$_2$	120	82	— 14	900	886	7.70
,,	pure	,,	same sample		134	79	3	900	903	7.84
BeO_{III}	BeCO$_3$	950	4.2	C$_2$H$_2$Cl$_4$	120	36	21	828	849	7.37
,,	pure	,,	same sample		134	36	26	828	854	7.41
,,	,,	,,	same sample		142	36	26	828	854	7.41
BeO_{IV}	Be(NO$_3$)$_2$	950	7.8	C$_2$H$_2$Cl$_4$	120	35	32	828	860	7.46
,,	pure	,,	same sample		134	36	29	828	857	7.44
BeO_V	BeCO$_3$	1400	13.6	C$_6$H$_5$Cl	120	— 40 (— 48)	130	684	814	7.06
BeO_{VI}	same as BeO_V			C$_2$H$_4$Cl$_2$	134	83	55	828	883	7.67

In diagram 10 the dielectric constants have been plotted against the corresponding temperatures. It will be observed that the dielectric constant increases with temperature, whilst no definite variation with frequency or ignition temperature is evident. It may be remarked that the greatest deviation, i. e. the highest value of the dielectric constant was found for the less pure sample at 120 meters wave-length, but the corresponding value for 134 meters wave-length does not deviate, and hence we are not allowed to infer that impurities cause an increase in the dielectric constant. The value of the temperature coefficient is: $\frac{1}{\varepsilon}\frac{d\varepsilon}{dT} = 7 \times 10^{-4}$, as determined from the slope of the line drawn in the diagram, Fig. 10.

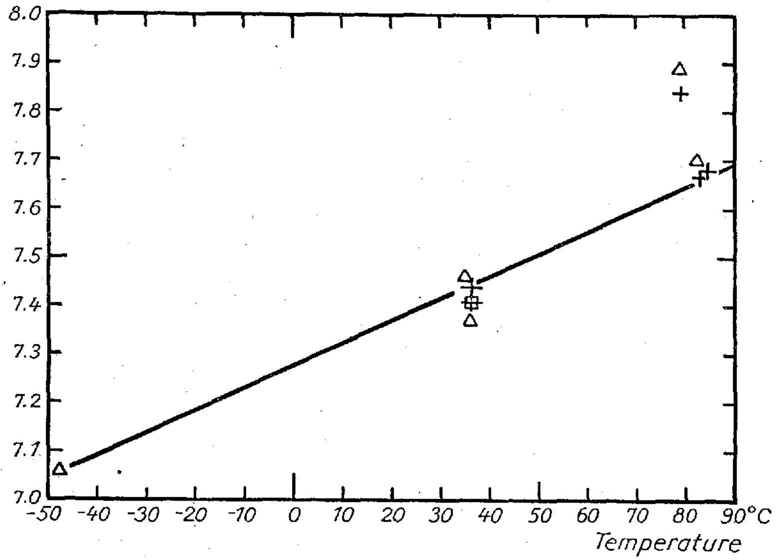

Fig. 10. Dielectric Constant of BeO.

Data for MgO are given in table 5. In the case of the third sample the actual measurements are plotted into diagram 11. The key is as above.

It is observed that the dielectric constants obtained differ somewhat, and the agreement becomes still worse if the value 8.2 found by GÜNTHERSCHULZE and KELLER[1] is compared with the above values. It is possible, that the dielectric constant of MgO depends on the manner of preparation, or

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[1] GÜNTHERSCHULZE A. and KELLER F.: ZS. f. Physik. **75**, 82 (1932).

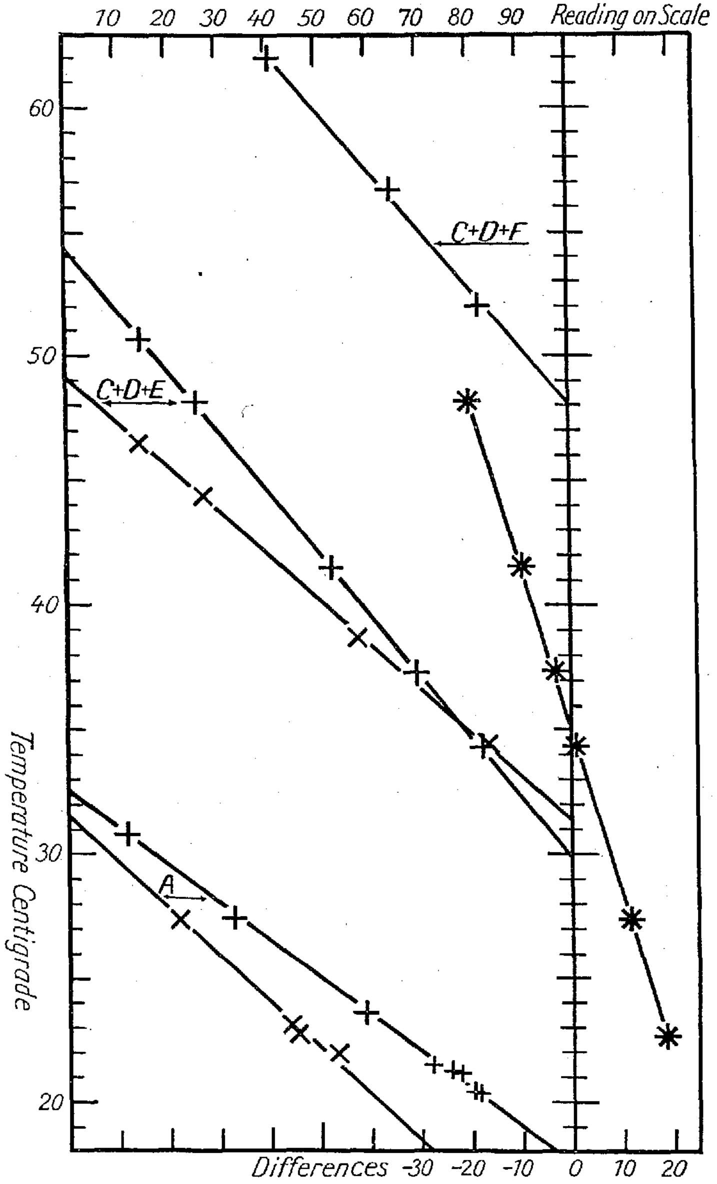

Fig. 11. MgO in $C_2H_4Cl_2$.

Table 5.

	Origin	Ignition temperature	Vol. per cent solid	Liquid	Wave-length	Intersection				Dielectric constant
						Temperature	Condenser reading			
							variable	fixed	total	
MgO$_{\text{I}}$	$Mg(NO_3)_2$	960	6.8	$C_2H_4Cl_2$	120	43.3	30	1045	1075	9.33
„	„	„	same	sample	134	45.8	21	1045	1066	9.25
MgO$_{\text{II}}$	Kahlbaum	950	(6)	$C_2H_4Cl_2$	120	32.5	93	1045	1138	9.87
„	z. Analyse	„	same	sample	134	33.0	99	1045	1144	9.93
MgO$_{\text{III}}$	Kahlbaum z. Analyse	1400	18.5	$C_2H_4Cl_2$	134	35.1	79	1045	1124	9.76

to be more precise on the size and regularity of the individual crystals, but this is not very likely in view of the small deviations encountered in the case of BeO. It will be necessary to carry out further measurements before this problem can be settled. Quite recently it has become possible to obtain large single crystals of MgO. It would be valuable if the dielectric constant of such crystalline MgO could be determined. Meanwhile I consider 9.8 the most likely value for the dielectric constant of MgO.

Data for CaO are given in table 6. The key is similar to that used in the foregoing cases, but now the immersion liquid is a mixture, and hence the table has been extended by the introduction of separate columns for the two liquids, and a column recording the percentage by weight of liquid II in the liquid mixture. Diagram 12 records two sets of measurements, made on two samples of the same mixture. The data of the first sample are denoted in the usual manner, whilst the data of the second sample are surrounded by circles, and lines are dotted. As it is not known in what proportion the powder distributes itself in the two samples,

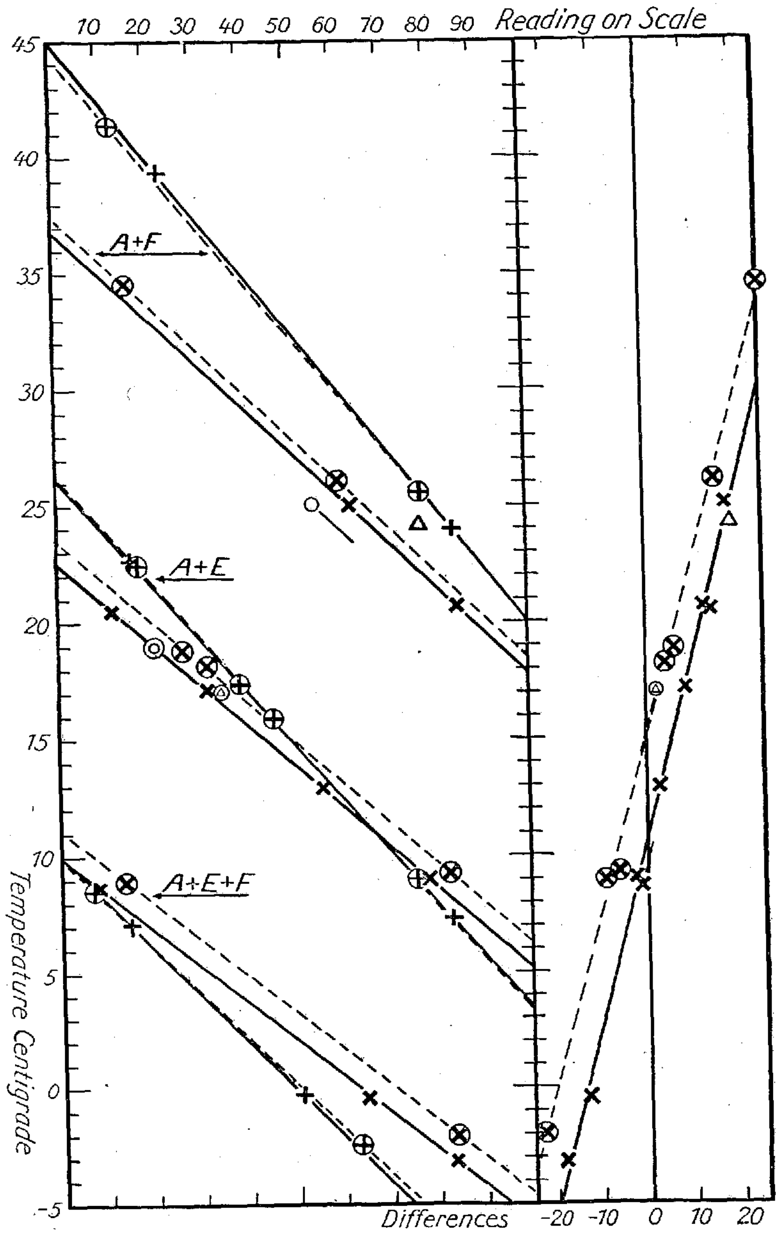

Fig. 12. CaO in Mixture of 45.0 % $C_6H_5NO_2$ and C_6H_6.

the percentage by volume of solid in the mixture have been left out. They are presumably about 27 per cent. in both cases.

Table 6.

	Origin	Ignition temp-erature	Vol. per cent solid	Liquid I	Liquid II	Per cent by weight of II
CaO_{I}	$CaCO_3$	1300	30	C_6H_6	$C_6H_5NO_2$	40.2
CaO_{II}	$CaCO_3$	1300		C_6H_6	C_2H_5OH	
CaO_{III}	$CaCO_3$	1300		C_6H_6	$C_6H_5NO_2$	45.0
CaO_{IV}	$CaCO_3$	1300	same mixture as CaO_{III}			

	Wave-length	Intersection					Dielectric constant
		Temperature		Condenser reading			
		read	correct	variable	fixed	total	
CaO_{I}	134	— 18	— 22	175	1212	1387	12.04
CaO_{II}	134	13	13	3	1429	1432	12.44
CaO_{III}	120	9.8	9.8	74	1285	1359	11.80
,,	134	10.7	10.7	68	1285	1353	11.74
CaO_{IV}	120	15.0	15.0	49	1285	1334	11.58
,,	134	15.0	15.0	49	1285	1334	11.58

The data for the second sample are considered less safe because of a mishap; on closing the dielectric cell a bit of the agate disk was broken off. The mixture was then poured back into the flask and stored in a dessicator, whilst the agate disk was mended by means of dental cement. The effective capacity of the mended cell was checked as mentioned on page 20, whereupon the mixture was introduced anew, and measurements carried out. Owing to this mishap the percentages have not been quoted. Leaving this second sample out of consideration, the mean value 11.8 ± 0.3 is regarded as the best value of the dielectric constant at 10° C. of CaO prepared by igniting pure $CaCO_3$ at 1300° C.

The electrical conductivity of the filtrate was determined. 0.7×10^{-8} mho's was found for the first sample, and 60×10^{-8} mho's was found for the second sample. The considerably larger conductivity in the latter case was due to the presence of alcohol. According to the calculations in the appended paper, the conductivity causes an error which can be shown to be negligible, even in the case of the second sample. The residue of CaO obtained by the filtration was analysed for carbonate — due to air, and for nitrate — formed by decomposition of nitrobenzene. The residue was placed in the distilling flask of the apparatus (Fig. 7), and heated in vacuo to dryness, whereupon the dry residue was weighed in the flask. Afterwards an absorption system was connected to the outlet, the Hempel column was removed, and the apparatus was reconnected in such a way that the leg of the tap-funnel came close to the bottom of the flask. A sufficient amount of dilute hydrochloric acid was introduced, and a stream of CO_2-free air was injected through the tap-funnel. This air bubbled through the boiling solution in the flask, and drove the carbon dioxide into the absorption system; the absorbed carbon dioxide was then weighed. The contents of CO_2 in the different samples were as follows: in CaO_I 1.5 per mille, in CaO_{II} 1.5 per mille, in CaO_{III} 1.1 per mille. The solution in the flask was tested for nitrate or nitrite by means of concentrated sulphuric acid and ferrous sulphate, but no reaction was detected.

Data for SrO are given in table 7. The key is the same as for CaO.

Table 7.

	Origin	Ignition temperature	Vol. per cent solid	Liquid I	Liquid II	Per cent by weight of II
SrO_I	"Kahlbaum"		11.5	C_6H_6	$C_6H_5NO_2$	40.3
SrO_{II}	"Kahlbaum"		15.4	C_6H_6	$C_6H_5NO_2$	47.4
SrO_{III}	$Sr(NO_3)_2$	1350	13.4	C_6H_6	$C_6H_5NO_2$	49.7
SrO_{IV}	$Sr(OH)_2$	1350	21.5	C_6H_6	$C_6H_5NO_2$	44.8

	Wave-length	Intersection					Dielectric constant
		Temperature		Condenser reading			
		read	correct	variable	fixed	total	
SrO_I	134	— 18.5	— 23	179	1212	1391	12.08
SrO_{II}	134	25	25	39	1356	1395	12.12
SrO_{III}	134	10	10	118	1429	1547	13.43
SrO_{IV}	134	— 7	— 10	86	1429	1515	13.16

The readings are in the cases of SrO_{III} and SrO_{IV} given in the diagrams 13 and 14. The above samples of $Sr(NO_3)_2$ and $Sr(OH)_2$ were purified following Sørensen's method (see page 31). It will be seen that the values found for the dielectric constant are considerably higher in the case of the purified SrO than in the case of SrO "Kahlbaum". This discrepancy is explicable when it is borne in mind that, according to the analysis described on page 31, SrO "Kahlbaum" contains a large percentage of impurities, whereas, according to the analysis described on page 32, the purified

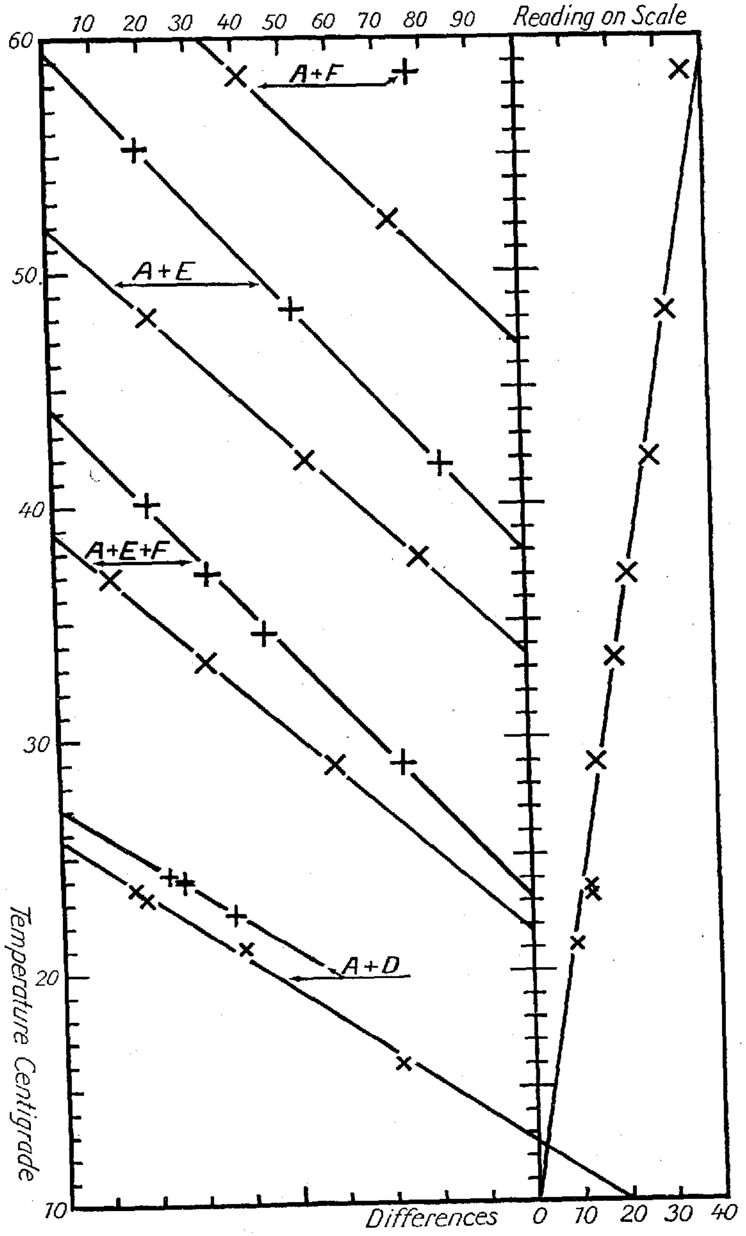

Fig. 13. SrO in Mixture of 49.7 % $C_6H_5NO_2$ in C_6H_6.

SrO contains only 3 per mille Ca and 1 per mille Pt. These data refer to the fresh SrO; after the measurements, however, the residual SrO was analysed for CO_3^{--} and NO_3^{-} in the same manner as described in the case of CaO; 1 per mille CO_2 and a faint trace of nitrate were found. The conductivity of the filtrate from SrO_{IV} was 1×10^{-8} mho's. It is evident that the purified strontium oxide is considerably purer than the "Kahlbaum" product, and hence the mean value of the two determinations on the purified compound, i. e. 13.3 ± 0.3 at 0° C. is regarded the most likely dielectric constant of strontium oxide.

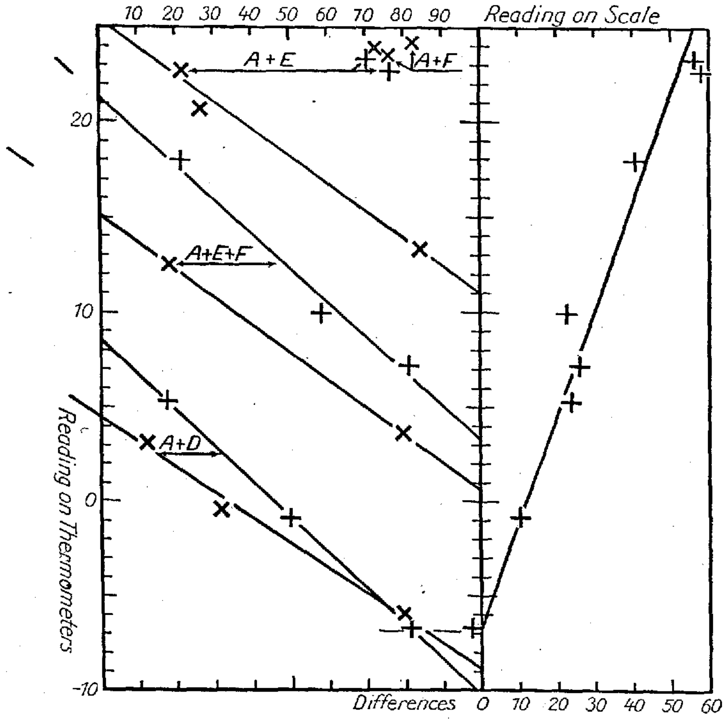

Fig. 14. SrO in Mixture of 44.8 % $C_6H_5NO_2$ in C_6H_6.

A few, mainly preliminary, measurements have been omitted, either because of too far an extrapolation, or because of discrepancies which presumably were caused by air bubbles.

Conclusion.

The dielectric constants of the alkaline earths have been collected in the following table:

Table 8.

	Temperature	Dielectric constant	Error	Difference
BeO	20° C.	7.35	0.2	2.45
MgO	35° C.	9.8	0.5	2.0
CaO	10° C.	11.8	0.3	1.5
SrO	0° C.	13.3	0.3	

It will be observed that the dielectric constant increases steadily down the series, but the differences become smaller; those between the values for consecutive members decreasing by 0.5. Assuming this relationship to hold for the difference between SrO and BaO as well, we may foreshadow a value of 14.3 for the dielectric constant of BaO.

As regards the experimental procedure, the present immersion method, which depends on the variation with temperature of the dielectric constant of a polar liquid, has proved efficient. It is presumably the method to be used in the case of a powder consisting of porous particles. If single crystals of a reasonable size could be obtained, the plate method would be more accurate; and this method, using a compressed slug, may also be advantageous in the case of an extremely reactive compound such as barium oxide, for which it is difficult to find a sufficiently resistant immersion liquid.

Inability to reproduce the dimensions of the dielectric cell is probably the more important source of error; the order of magnitude being 2 per cent. as found on page 20. In order to reduce this error, a new dielectric cell has been constructed, but it is premature to judge how far this new cell is preferable to the old one, and further particulars are therefore postponed. The errors due to setting and reading scales of condensers in the apparatus are less important and have been largely eliminated by repetition. It is questionable whether the use of the capacity box in place of a variable precision condenser is advantageous or not. The capacity box has the advantage that it can be built in the laboratory workshop from commercial condensers, and also ones eyes are not strained by reading scales. The disadvantage lies in the complication involved in the calculation and representation of data. A larger capacity of the variable condenser or a smaller capacity of the dielectric cell would be preferable in order that one combination of fixed condensers might suffice for the determination of the point of intersection. The substitution method enables accurate measurements to be made even when the frequencies of the generators are drifting. At present methods for maintaining the frequency are known; still, the use of the substitution method enabled us to build an accurate apparatus at comparatively small expense.

Appendix.

Estimation of the Error caused by the Electrical Conductivity of the Contents of the Dielectric Cell.

In the case of a circuit as complicated as that of generator II in Fig. 1, it is not feasible to calculate exactly the effect on the dielectric constant determination arising from the electrical conductivity of the medium. In the present instance, however, we only want to know, whether such an effect may be neglected or not, and for that purpose we can simplify the problem considerably. We will therefore consider the simple circuit formed from a coil with the inductance L in series with a leaky condenser with capacity C and resistance R. In this circuit a sinusoidal potential is induced, and we are going to determine the conditions for resonance.

Similar problems have, of course, been treated in the literature previously, and the present calculation is based on that given by Jaeger in the Handbuch der Physik[1].

The induced potential V gives rise to a current i which results in a potential v across the leaky condenser and a potential v_1 across the inductance. The leaky condenser is considered to be composed of a capacity C and a resistance R in parallel, consequently the current can be written as the sum of two parts; one, a conduction current through the resistance and the other a displacement current through the condenser:

$$i = \frac{v}{R} + C\frac{dv}{dt}; \tag{1}$$

The induced potential V is counterbalanced by the potentials v and v_1, the latter being given by the usual expression. Hence:

$$V = L\frac{di}{dt} + v; \tag{2}$$

or eliminating i:

$$V = LC\frac{d_2 v}{dt^2} + \frac{L}{R}\frac{dv}{dt} + v; \tag{3}$$

This equation will be simplified in the manner proposed by Jaeger using a new unit of time defined by:

$$\tau = \omega_0 t \text{ where } \omega_0 = \sqrt{\frac{1}{LC}}; \tag{4}$$

The modified equation then becomes:

$$V = \frac{d_2 v}{d\tau^2} + \frac{1}{R}\sqrt{\frac{L}{C}}\frac{dv}{d\tau} + v; \tag{5}$$

$$\text{Putting } \frac{1}{2R}\sqrt{\frac{L}{C}} = \alpha;\ v = x;\ \text{and } V = \varphi(\tau); \tag{6}$$

the standard form of Jaeger's equation (10) is obtained, i. e.

$$(10) \qquad \frac{d_2 x}{d\tau^2} + 2\alpha\frac{dx}{d\tau} + x = \varphi(\tau); \tag{7}$$

and from now on the treatment is concordant with his. Jaeger's equation numbers are given at the front of the equations.

The sinosoidal potential induced in the circuit is:

$$V = \varphi(\tau) = A\sin(\varkappa\tau + \delta); \tag{8}$$

where A is the amplitude; δ the phase; and $\varkappa = \frac{\omega}{\omega_0}$ the pulsatance (on the new unit of time). The advent of this

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[1] Handbuch der Physik. **16**, chapter 7 by Jaeger W. pp. 201—224. (1927).

potential gives rise initially to complicated fluctuations of current and potentials in the circuit, but these are eventually damped, and the remaining potential across the condenser becomes a sinusoidal potential which can be written:

(50) $$v = x = \frac{A}{N}\sin(\varkappa\tau + \delta + \chi); \qquad (9)$$

where N is the ratio between the amplitude values of V and v. The expressions (8) and (9) are inserted in equation (7), and at the times $\tau = -\frac{\delta}{\varkappa}$ and $\tau = -\frac{\delta+\chi}{\varkappa}$ two expressions for the difference in phase χ are derived:

$$\tan\chi = -\frac{2\,\alpha\varkappa}{1-\varkappa^2}; \text{ and } \sin\chi = -\frac{2\,\alpha\varkappa}{N}; \qquad (10)$$

On elimination of χ is obtained:

(51) $$N^2 = (1-\varkappa^2)^2 + 4\,\alpha^2\varkappa^2; \qquad (11)$$

Resonance, i. e. a maximum value of v for a given value of V, will be obtained when N and also N^2 attain minimum values with respect to $\varkappa$, α being maintained constant. From the differentiation

(57) $$\frac{d(N^2)}{d(\varkappa^2)} = 0; \text{ it is found: } \varkappa_m = \sqrt{1-2\,\alpha^2}; \qquad (12)$$

In the substitution method the leaky condenser with resistance R and capacity C was replaced by a perfect condenser of immense resistance and with capacity C_1, the latter condenser being adjusted until the pulsatance $\omega_1 = \sqrt{\frac{1}{LC_1}}$ was the same as that of the damped circuit. This is determined by the above resonance value $\varkappa_m$ or, reverting to the usual unit of time, by $\varkappa_m\,\omega_0$. Hence:

$$\varkappa_m = \frac{\omega_1}{\omega_0}; \qquad (13)$$

Considering the definition of ω_1 given above and of ω_0 given by equation (4), and introducing the value of α from equation (6):

$$\varkappa_m = \frac{\omega_1}{\omega_0} = \sqrt{\frac{C}{C_1}} = \sqrt{1-\frac{L}{2\,R^2C}}; \qquad (14)$$

Eliminating L by means of the relation (4): $LC = \frac{1}{\omega_0^2}$ we obtain:

$$\frac{C}{C_1} = 1 - \frac{1}{2\,R^2C^2\,\omega_0^2}; \qquad (15)$$

For practical purposes this expression is modified by the introduction of the dielectric constant ε in place of the capacity C; the specific electrical conductivity l in mho's in place of the resistance R, and the wave-length λ in cm. in place of the pulsatance ω. Thus the relative error in the dielectric constant, arising from the conductivity of the cell contents is determined as:

$$\frac{\Delta\varepsilon}{\varepsilon} = \frac{1800\,l^2\lambda^2}{\varepsilon^2}; \qquad (16)$$

For correction purposes this expression is only strictly applicable to the idealized circuit considered, but it will give us the order of magnitude of any such error in our experimental circuit, and we shall see that a small conductivity has negligeable effect on our results.

As an illustration, consider the case of CaO in a mixture of benzene and ethyl alcohol for which the measured conductivity was by far the greatest, i. e. $l = 6 \times 10^{-7}$ mho's; $\varepsilon = 12.2$, and $\lambda = 13400$ cm.

$$\frac{\Delta\varepsilon}{\varepsilon} = \frac{1800 \times 6^2 \times 10^{-14} \times (1.34)^2 \times 10^8}{(12.2)^2} = 8 \times 10^{-4}. \quad (17)$$

Even in this exceptional case the error is negligible, although we are close to the limit.

Substances with larger conductivities should not in my opinion be measured by the interference note method, but by a bridge method.

The conductivities of the liquids (filtrates) were determined by means of direct current from an accumulator battery which passed through resistances, a conductivity cell and a galvanometer. The method was calibrated by means of conductivity water of known conductivity.

The conductivity was only measured when it was anticipated to be great. Thus from earlier measurements I knew the conductivity of chlorobenzene saturated with alkali halide to be of the order 10^{-10} mho's, and therefore the conductivity of these solutions were not measured. Similarly it was argued that BeO and MgO are chemically so resistant that any considerable rise in conductivity of the immersion liquid was not to be anticipated.

A similar circuit having capacities in parallel was considered by SUGDEN[1] who found the following expression for the deviation of a leaky condenser:

$$C = C\,\mathrm{obs}\left(1 - \frac{1}{R^2 \omega^2 C^2} \cdot \frac{C}{C_0}\right); \quad (18)$$

The capacity of the dielectric cell C is smaller than the measured value C obs by a magnitude similar to that found above.

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[1] SUGDEN S.: Journ. Chem. Soc. (1933) p. 774.

II.

ON THE RELATIONSHIP BETWEEN DIELECTRIC CONSTANT, REFRACTIVE INDEX, ABSORPTION AND REFLECTION MAXIMA AND MINIMA IN THE FAR INFRA-RED, AND COMPRESSIBILITY OF REGULAR IONIC CRYSTALS

BY

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TABLE OF SYMBOLS

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a	amplitude	80	A	area	73
b	constant	96	B	constant ratio	101
c	velocity of light	83	C	numerical constant	112
d	distance in free space	114	D	proportionality factor	101
e	electronic charge	66			
f	elastic force	109	F	Faraday charge	83
g	lattice dimension	106	G	Cation	66
h	height	74	H	Anion	66
j	Madelung's constant	99	I	strength of the inner field of force	66, 76
k	number of neighbours	99	K	proportionality factor	81, 110
k_1	number of next neighbours	99			
l	change in ionic distance	97	L	distance between (neighbour) ions	97, 115
m	mass of one molecule (ion)	80	M	molecular weight	73, 91
n	refractive index	77, 91	N	Avogadro's number	73
o	constant ratio	98			
p	polarization	113	P	molar polarization	127
p_A	atomic polarization	113			
p_E	electronic polarization		P_E	molar refraction	127
	or refraction	113	P_E^+, P_E^-	molar refraction of ions	122
p	pressure	102	Q	density of charge	74
r	radius	74	R	reflection ratio	86
r	distance	96			
r	ionic radius	114, 122			
s	displacement	66, 103			
t	time	80			
u	number of cations in molecule	66	U	electric moment of 1 cc.	73
v	number of anions in molecule	66	V	volume	101
x y z	components of displacement	104, 107	X Y Z	coordinates	104, 107

		page
α	polarizability	66
α_A	atomic polarizability	67
α_{A_0}	atomic polarizability (long waves)	82
α_E	electronic polarizablt.	66
$\alpha_E^+\ \alpha_E^-$	„ „ of ions	66
β	Heckmann's parameter	76, 120
γ	number of outer electrons	126
δ	density	73, 91
ε	dielectric constant	75, 91
ϕ	total potential energy	100
φ	potential energy of repulsive forces	97
$\varphi, \varphi' \varphi''$	coefficients in the Taylor series of the potential energy of repulsive forces between neighbours	97
$\psi \psi' \psi''$	coefficients between next neighbours	98
$\varphi_{(B)}$	(Born)potential energy	97
$\varkappa$	compressibility	102, 116
λ	wave-length	83
μ	electric moment induced in a molecule	66
ν	valency of an ion	66
ω	frequency or pulsatance	80
ϱ	constant distance	97
θ	angle	73

Introduction.

Two classes of insulators have structures sufficiently simple to be amenable to theoretical treatment. The dilute gas, and to a certain extent the dilute solution (in non-polar solvents) fall in the first class. The dielectric constant and related properties of gases and dilute solutions were considered by DEBYE[1] in his theory of dipole moments. Ionic crystals form the second class; a theory of ionic crystals was worked out by BORN and co-workers in a number of papers. A survey is given in the Handbuch der Physik[2]. In these papers a number of relations between measurable properties were derived; at present a relation between the dielectric constant, the refractive index and the wave-length of the absorption or reflection maximum in the far infra-red (residual ray) interests us. Such a relation was first derived by DEHLINGER[3], and afterwards developed by BORN[4] and by HECKMANN[5]. Further contributions to the theory and to the experimental data were given by ERRERA[6] and by EUCKEN and BÜCHNER[7].

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[1] DEBYE P: Polar Molecules. Chemical Catalogue Company. New York.
„ „ Polare Molekeln. Hirzel. Leipzig. (1929))

[2] BORN M. and BOLLNOW O. F.: Hdb. d. Physik. **24**, 370 (1927).
BORN M. and GÖPPERT-MAYER M.: Hdb. d. Physik. (2 Aufl.) **24**, 11 (1933).

[3] DEHLINGER W.: Physik. ZS. **15**, 276 (1914).

[4] BORN M.: Physik. ZS. **19**, 539 (1918).

[5] HECKMANN G.: ZS. f. Kristall. **61**, 250 (1925).

[6] ERRERA J.: ZS. Elektrochemie. **36**, 818 (1930).

[7] EUCKEN A. and BÜCHNER A.: ZS. physik. Chem. B. **27**, 321 (1935).

As emphasized by Heckmann in particular, the above relation is subject to an inherent uncertainty originating in the 'Lorentz force'. It is the object of the present exposition to investigate from a theoretical, as well as from an experimental point of view, this uncertainty or deviation of the Lorentz force. In addition a further relation (also subject to the uncertainty of the Lorentz force) will be derived, connecting the dielectric constant, the refractive index and the compressibility[1]. A test of the theory and an evaluation of the deviations due to the Lorentz force can be made by means of this latter relation in particular, because of the large amount of experimental data available.

The theory is rendered as simply as possible; this simplicity is achieved by making at the start such assumptions as earlier investigators have been obliged to make in the course of their calculations. This also implies the advantage that the limitation of the deduction is clearly seen. The following are the necessary preliminary assumptions and restrictions.

1) *The ions must be arranged in a regular diagonal lattice. The NaCl, CsCl, ZnS and CaF_2 lattices are the only ones complying with this requirement.*
2) *The charge of an ion must be a whole multiple of the electronic charge. This means that there must be no sharing of electrons between the ions.*
3) *The lattice shall be perfect and the ions devoid of thermal motion. Actually the latter is not the case even at the absolute zero of temperature, but the amplitudes are generally small.*

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[1] An approach was made by the writer in 'Leipziger Vorträge' (1929) p. 114, or in English: 'The dipole moment and chemical structure' (1931) p. 108, both edited by P. Debye.

4) *The forces between the ions can be separated into two types. a) the electrostatic force which follows Coulomb's law, and b) a short range intrinsic repulsive force which keeps the ions apart.*
5) *This intrinsic repulsive force is assumed to be central, and this implies that the electron cloud of the ion has spherical symmetry.*
6) *Since the intrinsic repulsive forces are short range, only such forces between neighbours and eventually between next neighbours need consideration.*
7) *Dissipative forces are disregarded, i. e. the damping of the ionic motion is neglected.*
8) *Classical mechanics and not quantum mechanics are employed.*

By means of the above restrictions and assumptions an idealized state is defined for which certain relations can be derived. These relations, however, will only hold with approximation to the actual ionic crystal. The theory may be refined by omitting certain of the restrictions, but as long as the uncertainty of the Lorentz force remains, much better agreement cannot be expected.

Induced Moments and Polarizabilities.

If the ionic lattice as considered above is placed in an electric field it will suffer deformation arising from two different causes.

The first effect to be considered takes place inside each ion. The applied field causes the electrons in the ion to be displaced relative to the nucleus. By the displacement forces between electrons and nucleus come into play, which eventually will balance the external force. The displacement of charges gives rise to an electric moment, the "charge-centre" of the electrons no longer being situated at the nucleus. The displacement of the charge-centre relative to the nucleus multiplied by the total charge of the electrons is defined as the electric moment induced in the ion in question. It is an assumption verified by experiment, that for the small field strengths commonly used, the displacement, and thereby the induced moment, is proportional to I the strength of the electric field of force. Hence we will write:

$$\mu_E^+ = I\,\alpha_E^+ \text{ and } \mu_E^- = I\,\alpha_E^-; \qquad (1)$$

for the moments induced in cation and anion respectively, α_E^+ and α_E^- are the constant "internal or electronic polarizabilities" of the ions. The total electronic moment of the molecule $G_u\,H_v$ is the sum:

$$\mu_E = I\,\alpha_E = I\,(u\alpha_E^+ + v\,\alpha_E^-); \qquad (2)$$

The second effect consists of a deformation of the lattice itself. The ion considered as an entirety is a charged body. Owing to the action of the electric field, positive ions retire from negative ions on one side, whilst approaching them on the other side and vice versa. Due to the change in distance forces of the types considered in assumption 4) come into play. These forces will eventually balance the external force.

The electric moment arising when the ion of charge $+\nu e$ is displaced the distance s is:

$$\mu_A^+ = \nu e s; \qquad (3)$$

Again the displacement and the induced moment is assumed to be proportional to the force. This is so much more likely

because the same forces come into action when the body is externally deformed, and then the deformation is known to be proportional to the force applied. The reason for the proportionality is considered on pages 106 and 109, it is found to be valid for small displacements only. Hence for ordinary small displacements we have:

$$\mu_A^+ = I\,\alpha_A^+; \qquad (4)$$

where α_A^+ is the constant "atomic polarizability"[1]. The moment induced in the molecule $G_u\,H_v$ is the sum of those of the constituent ions. Hence:

$$\mu_A = I\,\alpha_A = I\,(u\,\alpha_A^+ + v\,\alpha_A^-); \qquad (5)$$

By superposition of the two types of moment the total moment induced in a molecule is obtained:

$$\mu = \mu_E + \mu_A = I\,(\alpha_E + \alpha_A); \qquad (6)$$

This is only allowable if these moments are independent of each other, which is only true to a certain degree. The considerations on pages 124—28 have some bearing on this question.

By the ionic shift considered above it is mainly the distances between unlike ions that are altered. In some cases, however, the distances between like ions are changed as well. This means that the dimensions of the crystal are altered by the field, or from the converse point of view, that the crystal is piezoelectric. Piezoelectricity in itself is an important property, the theory of which has been elucidated by BORN and HECKMANN. To the present exposition it means

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[1] This mode of designation was proposed by L. EBERT: ZS. physik. Chem. **113**, 1 (1924).

a complication, which, however, can be eliminated by a simple experimental artifice.

If the electric field applied is alternating, the values of the polarizabilities α_E and α_A will vary with the frequency or wave-length of the electric field. The variation is due to the inertia of the electrons, the ions or the entire crystal. The inertia of the vibrating parts depends mainly on their masses which are very different in magnitude, thus the mass of an ion is some thousand times as large as that of the electron, and the parts vibrating in the piezoelectric crystal contain a huge number of ions. Due to these great differences in mass and inertia, the natural frequencies of the different vibrations are widely separated in the spectrum.

In the vicinity of the natural frequency, the polarizability or the dielectric constant or the refractive index (these are related as will be shown later) vary much to both sides; and at a frequency which is considerably higher than the natural frequency in question, the corresponding part of the polarizability vanishes. The shape of the dispersion curve in the vicinity of the natural frequency of the ionic vibration will be considered in details on pages 78—90.

The lowest natural frequencies are those of the vibrations arising in piezoelectric crystals. It is well known that piezoelectric quartz crystals are employed in the broadcasting stations for adjusting the frequency. The natural acoustic frequencies depend on the rigidity and the size of the crystal, they are often close to the ordinary radio frequencies of 10^6. At frequencies considerably higher than this the acoustic vibrations vanish, for instance this is the case at a frequency of 10^8. At such a frequency we are also far from the natural frequency of the vibration of positive and negative ions in the crystal. This natural frequency which manifests itself in the residual ray is of the order 10^{13}. The dispersion is only great close to the natural frequencies. If therefore the dielectric constant of a piezoelectric crystal (which shall be large) is measured at a suitable frequency of the order 10^8 or wave-length of some meters, the effect of piezoelectricity will be eliminated. This means that the dimensions of the crystal and furthermore the distances between like ions are not altered during the vibration. It is this value of the dielectric constant which has to be introduced in the following formulae. It is evident that this is not necessarily the same as the static value which means that the dielectric constant of piezoelectric crystals shows dispersion at radio frequencies. This is probably one of the reasons why the dielectric constants of solids hitherto have not been determined with conformity.

At a sufficiently high frequency α_A vanishes and only α_E is left. α_E has remained nearly constant throughout the entire range of frequency encountered so far, its natural frequency being situated in the ultra-violet region. In the visible region there is a sensible dispersion known of old, but α_E determined in the near infra-red at a frequency of 10^{14} is considered a good representative of the static value.

The Lorentz Force.

We require to find the electric force I which acts on the charges inside the body. The electric force, however, is defined as the force exerted on a unit charge of electricity situated in empty space; hence to measure the electric force inside a body, we must make a small cavity surrounding the point at which the unit charge is placed. It is now observed that the force obtained depends on the shape of the cavity. For a continuum or an isotropic body it is reasonable to assume that a spherical cavity gives the correct value of the force. Seen from the centre the sphere is isotropic i. e. it has the same properties in all directions which is not the case with any other surface. Furthermore the force at the centre does not depend on the dimensions of the spherical cavity. This is most easily realized by an argument given by N. Bohr:

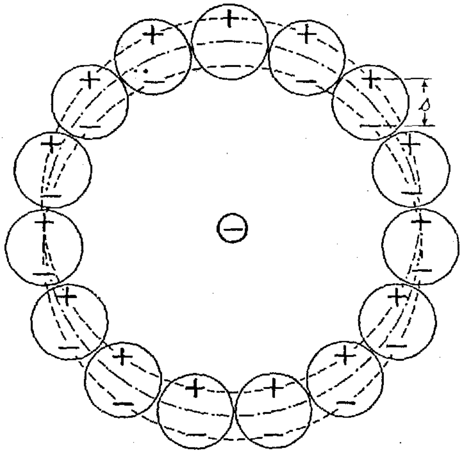

Fig. 1.

Consider a spherical shell, for instance one molecule thick, cut out of the bulk of polarized substance. (Fig. 1). In each molecule a moment is induced which can be considered as two charges at a small distance s. As the centres of the molecules lie on the surface of a sphere it is seen that the positive and the negative charges respectively lie on two spheres mutually displaced the distance s. Both of these spheres surround the measuring charge placed at the centre of the first sphere. Now in the interior of a sphere with evenly distributed charge the force is zero, hence it will be realized that this also is the case at the centre of a spherical polarized shell.

Similar considerations can also be applied to the regular crystals. If an arbitrary ion in the lattice is considered the "central ion", it is seen that the surrounding substance can be divided up into concentric shells, each shell containing a number of four or more ions all having the same distance from the central ion. The ions in such a shell have like charges, and they are regularly and to a certain extent also evenly distributed on a sphere. By the action of a homogeneous field of force the ions are displaced, furthermore dipoles are induced in them. We remark however, that the different charges still form regular polyhedra having the "central ion" pretty close to the centre. Now the electric force close to the centre of a regular configuration of charges is not quite zero, but it is negligibly small. Later, on page 109 this will be shewn to be the case for certain important regular configurations.

In this manner it is realized that we are not altering sensibly the force on the central ion, if shell by shell we remove the surrounding ions, thus forming a spherical cavity around the central ion. This is the basis of the classical theories of Clausius-Mosotti and Lorenz-Lorentz as given by Debye[1].

Hechmann[2], however, discards the above argument for the following reason: The ion is an extended structure, the distance between the nucleus and one of the outer electrons is comparable to the distance between the ions. The nuclei of the neighbouring ions form a regular polyhedron around the nucleus of the central ion which even if displaced remains close to the centre. Hence the argument is valid as regards the nuclei. The outer electrons in the central ion however, are often remote from the nucleus and thereby also from the centre of the polyhedron of neighbouring ions. Therefore the above argument is not valid as regards the electrons. This can also be expressed in another manner:

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[1] Debye P.: Polare Molekeln. p. 4.

[2] Heckmann G.: ZS. f. Kristal. **61**, 253 (1925).

The field of force due to the neighbouring ions is inhomogeneous. We are not allowed to consider the strength of the field where the electrons move to be given by the value at the centre of the polyhedron i. e. close to the nucleus. That there is a deviation is evident, the question is, how great is it, and on what does it depend? To evaluate the deviation from theory alone is not feasible as it would require an intimate knowledge of the distribution and motion of electrons in the ions. What is attempted is an empirical investigation regarding the manner in which the deviation varies from compound to compound, especially in the system of alkali-halides. We should expect the deviation to depend on the dimensions of the ions and on their internal polarizabilities. On page 122 in table 7 we find that actually it depends mainly on the internal polarizability of the anion. As a measure of the deviation the proportionality factor β proposed by Heckmann can be employed (see later).

Onsager[1] likewise discards the classical theory of Clausius-Mosotti, his problem however, is a different one. He computes the action of a dipole molecule on its surroundings and vice versa, and concludes that the strength of the electric field due to the surroundings must not in general be averaged into the familiar Lorentz force. In the present theory dipoles are not considered, hence the problem treated by Onsager does not appear.

We are now changing from an atomic to a continuous viewpoint, and will calculate how the strength of the field of force inside a spherical cavity of macroscopic dimensions depends on the induced moment.

Inside the body there are equal amounts of positive and negative electricity in any space element, hence uncompensated charges will appear on interfaces only. To determine the density of charge on such an interface, two cylinders are cut out of the bulk of polarized substance (see Fig. 2). They are bounded by the same cylinder surface which is a tube of force. The only difference is that in one case the flat ends are perpendicular to the lines of force forming its curved surface, and in the other cases the flat ends are inclined to them at an angle θ. Since they have the same diameter and height d, their volumes will be the same and equal to Ad where A is the area of cross section perpendicular to the lines of force. All the electric moments induced in the constituent molecules are parallel to the lines of force and consequently they are simply additive. Considering expression (6) the moment of one cubic centimeter becomes:

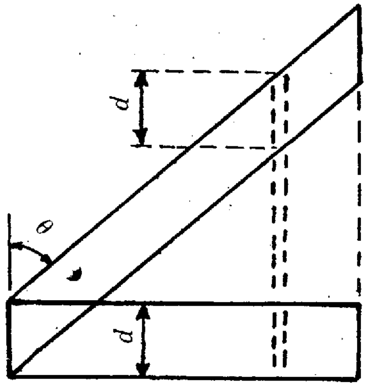

Fig. 2.

$$U = \frac{\mu N \delta}{M} = \frac{I N \delta}{M} (\alpha_E + \alpha_A); \tag{7}$$

where δ is the density; M the molecular weight; N Avogadro's number; μ the moment induced in one molecule; I the strength of the electric force; α_E the electronic polarizability and α_A the atomic polarizability. The total moment of each cylinder becomes the same, and each is equal to UAd. The cylindrical bounding surfaces are not charged, since they are parallel to the lines of force and thereby to the induced moments. The only uncompensated charges are to be found

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[1] Onsager L.: J. Amer. Chem. Soc. 58, 1486 (1936).

on their end surfaces. As the distances between corresponding charges are always d, it is seen that the total charges on the end surface in both cases becomes UA. The area of the inclined end is $\frac{A}{\sin\theta}$, and the density of charge therefore becomes: $U\sin\theta$. The area of the perpendicular end is A, hence the density of charge becomes U.

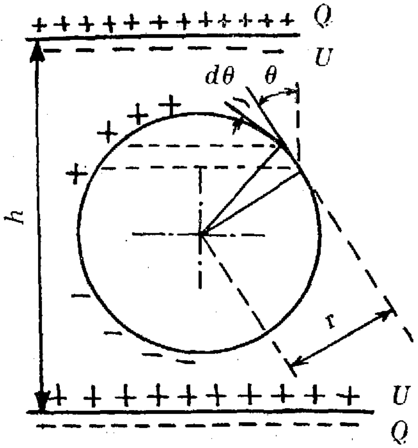

Fig. 3.

The induced moments and polarizabilities are not directly measurable. What can be measured is the dielectric constant and the refractive index. The dielectric constant is generally measured by means of a condenser which can be used as a convenient mental picture in the following deduction (see Fig. 3). The metal plates are charged with electricity of density Q. Thereby a homogeneous field of force is set up which induces the moment U in each cubic centimeter of the dielectric placed between the plates. As argued above, the interface between metal plate and dielectric is charged with electricity of density U. These charges are very close to those of the plates themselves and of opposite sign. Seen from the outside there are no charges within the bulk, and so from the outside the condenser behaves like an empty condenser charged with electricity of density Q—U. This also holds with regard to the potential. For the condenser the potential is proportional to this apparent charge, and the dielectric constant ε of the dielectric is the ratio between the amount of electricity required to

give the condenser a certain potential, when the dielectric fills it, and the amount to give it the same potential when empty. Hence:

$$\varepsilon = \frac{Q}{Q-U}; \tag{8}$$

This is how the polarization manifests itself outside the dielectric.

To evaluate the field of force at a point within the dielectric in addition to the force arising from external charges Q and from polarization charges on the external surface of the dielectric U, we have forces due to the polarization charges on the walls of the spherical cavity. The forces due to the molecules removed from the cavity were discussed on p. 70—72. To evaluate the forces from the spherical cavity the surface of the sphere is divided up in rings, the boundaries of such a ring being given by the angles θ and $\theta + d\theta$ see Fig. 3. The area of this ring surface is:

$$2\pi r \cos\theta r d\theta;$$

As considered earlier the density of charge on an inclined surface is $U\sin\theta$. Each element of the ring reacts upon the measuring unit at the centre with a Coulomb force, and the components of this force in the direction of the external field, when added together give the force arising from the ring, i. e.

$$\frac{2\pi r^2 \cos\theta\, d\theta\, U\sin\theta \sin\theta}{r^2} = 2\pi U \sin^2\theta \cos\theta\, d\theta;$$

The total force due to the charges on the sphere is found by integration over the total surface of the sphere.

$$2\pi U \int_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} \sin^2\theta \, d(\sin\theta) = 2\pi U \left| \frac{\sin^3\theta}{3} \right|_{-\frac{\pi}{2}}^{+\frac{\pi}{2}} = \frac{4\pi}{3} U; \qquad (9)$$

This is the classical Lorentz force, but according to HECKMANN it is not necessarily the force acting on the electrons in an ion. The uncertainty may be expressed by multiplying the Lorentz force by a proportionality factor β. This β is an average value regarding the different electrons and nuclei. It is doubtful whether β is independent of frequency, any change will probably affect α_E and α_A to different degrees. The assumption that β is independent of frequency is presumably equivalent to HECKMANN's[1] assumption that $\beta_1 = \beta_2 = \beta$, at all events it leads to the same result. Adding to this modified Lorentz force, the forces arising from the true charge density Q on the plates and the polarization charge density U on the dielectric interface, we get for the total strength of the inner field of force:

$$I = 4\pi(Q - U) + \frac{4\pi U\beta}{3}; \qquad (10)$$

Using (8) to eliminate Q we obtain:

$$I = 4\pi U\left(\frac{\varepsilon}{\varepsilon - 1} - 1 + \frac{\beta}{3}\right) = 4\pi U \frac{1 + \frac{\beta}{3}(\varepsilon - 1)}{\varepsilon - 1}; \qquad (11)$$

This gives an expression for the ratio U/I, the same ratio can be found from equation (7):

$$\frac{U}{I} = \frac{\varepsilon - 1}{4\pi\left[1 + \frac{\beta}{3}(\varepsilon - 1)\right]} = \frac{N\delta}{M}(\alpha_E + \alpha_A);$$

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[1] HECKMANN G.: ZS. f. Kristal, **61**, 254 middle of the page (1925).

Hence:

$$\alpha_E + \alpha_A = \frac{M}{4\pi N\delta} \cdot \frac{\varepsilon - 1}{1 + \frac{\beta}{3}(\varepsilon - 1)}; \qquad (12)$$

Two important cases are to be considered:
When $\beta = 1$; the classical CLAUSIUS-MOSOTTI equation is obtained:

$$\alpha_E + \alpha_A = \frac{3M}{4\pi N\delta} \cdot \frac{\varepsilon - 1}{\varepsilon + 2}; \qquad (13)$$

and when $\beta = 0$, i. e. no Lorentz force whatever, we get:

$$\alpha_E + \alpha_A = \frac{M}{4\pi N\delta}(\varepsilon - 1); \qquad (14)$$

MAXWELL[1], in his work on the electromagnetic theory of light, deduced the relation:

$$n^2 = \varepsilon; \qquad (15)$$

between the refractive index n and the dielectric constant ε. The relation has been verified by many investigators, notably by DRUDE[2, 3] but n and ε must be measured at the same frequency, and the damping must be negligible.

If MAXWELL's relation is introduced in equation (12) the following expression is derived:

$$\frac{M}{4\pi N\delta} \cdot \frac{n^2 - 1}{1 + \frac{\beta}{3}(n^2 - 1)} = \alpha_E + \alpha_A \text{ at high frequency } = \alpha_E; \qquad (16)$$

If β is equal to unity the familiar LORENZ-LORENTZ ex-

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[1] MAXWELL J. C.: Treatice on Electricity and Magnetism. **2**, 396 (1881).

[2] DRUDE P.: ZS. physik. Chem. **23**, 267 (1897).

[3] In Fysisk Tidsskrift (1936) 86, the writer has given a simple derivation of Maxwell's relation based on Drude's first method.

pression results. The refractive index is generally measured at the frequency of visible light, and as argued on page 69. α_A vanishes at such a frequency, when only α_E remains. Now in the visible region there is sensible dispersion of n and α_E, we therefore extrapolate them to zero frequency. Plotting n against the square of frequency, we expect and find an almost straight line. Instead of extrapolating, we may use directly the value of n in the near infra-red, where it has become almost constant. Hence if (16) represents the value of α_E when n is measured at a suitable infra-red frequency, and (12) the value of $\alpha_E + \alpha_A$ when ε is measured at a frequency considerably lower than the natural frequency of the atomic vibration, the value of α_A can be obtained by subtracting (16) from (12).

$$\begin{aligned}\alpha_A &= \frac{M}{4\pi N\delta}\left[\frac{\varepsilon-1}{1+\frac{\beta}{3}(\varepsilon-1)} - \frac{n^2-1}{1+\frac{\beta}{3}(n^2-1)}\right] \\ &= \frac{M}{4\pi N\delta}\cdot\frac{\varepsilon-n^2}{\left[1+\frac{\beta}{3}(\varepsilon-1)\right]\left[1+\frac{\beta}{3}(n^2-1)\right]};\end{aligned} \tag{18}$$

From which again two important values are derived namely:

$$\text{for } \beta = 1; \qquad \alpha_A = \frac{9M}{4\pi N\delta}\cdot\frac{\varepsilon-n^2}{(\varepsilon+2)(n^2+2)}; \tag{19}$$

$$\text{and for } \beta = 0; \qquad \alpha_A = \frac{M}{4\pi N\delta}(\varepsilon-n^2); \tag{20}$$

Dispersion in the Infra-Red Region.

As stated on page (68) the shape of the dispersion curve in the vicinity of the natural frequency of the ionic vibration will be given a special consideration. For the sake of simplicity the NaCl, CsCl and ZnS lattices only will be explicitly considered, but the CaF_2 lattice can be considered in a similar though more complicated manner.

Owing to the action of the alternating electric field, the ions are forced into vibrations; besides this 'forced' vibration we must also consider the 'free' vibration which in fact constitutes the thermal motion of the ions. There is one principal difference between this forced vibration and the thermal motion, which is not encountered in the simple case of forced and free vibration of one single particle. The thermal motion is disorderly, i. e. the single ions are vibrating independently in every direction, whereas the forced vibration is orderly, because it is regulated by the external field. The ions must move in the direction of the field and with the same frequency. The wave-length of the residual ray is of the order 10^{-3} cm., whereas the distance between neighbouring ions is of the order 10^{-8} cm., it will thus be realized that the force and thereby the displacements of the ions is uniform in large sections of the crystal. This means in fact that by the 'forced' vibration the entire lattice of positive ions vibrates with regard to the entire lattice of negative ions. The disorderly thermal motion has a much larger probability or entropy than has the the orderly forced vibration, consequently the radiant energy causing the forced vibration will steadily be transformed into heat energy. The rate at which this transformation proceeds determines the damping or absorption coefficient of the crystalline substance. In classical theory the damping is described by introducing, in the equation of motion of the ion, a dissipative force proportional to the velocity of the ion; but on the quantum theory the energy transfer must take place in quanta, and as far as I know an adequate mechanism of the damping process has not been described. It is realized, that further assumptions and unknown quantities must be introduced should the damping be considered. Therefore in accordance with Dehlinger, Born and Heckmann, we have introduced the assumption 7) to the effect that "dissipative forces are disregarded, i. e. the damping of the ionic motion is neglected" and also assumption 3) that "the ions shall be devoid of thermal motion". I am not sure to what extent this latter assumption is necessary for the present, but if it is introduced now the problem becomes very simple; we are in fact left with the forced vibration of the lattice of positive ions with regard to the lattice of negative ions. It is found convenient to consider the simple-harmonic vibration of the ions as the primary motion, and afterwards to discuss the forces acting on the ions.

Consider an ion of charge $+\nu e$ and mass m_1 performing a simple-harmonic vibration of frequency ω. The displacement at time t is:

$$s_1 = a_1 \cos(\omega t); \tag{21}$$

where a_1 is the amplitude. An ion of opposite charge $-\nu e$ with mass m_2 will perform a similar vibration with the same frequency, the opposite phase and with the amplitude a_2. The restoring force necessary for maintaining the vibration is equal to the acceleration multiplied by the mass.

$$m_1 \frac{d^2 s_1}{dt^2} = -m_1 a_1 \omega^2 \cos(\omega t); \tag{22}$$

This force must result from the other forces acting on the ion. These may be separated into: a) the intrinsic repulsive force which according to assumption (5) is a central force depending solely on the distance between the (nuclei of the) ions. The change in this force we will for the present assume to be proportional to the relative displacement of the ions, this assumption is proved later on page (110). The proportionality factor we term K.

$$K(s_1 - s_2) = K(a_1 + a_2)\cos(\omega t); \tag{23}$$

b) the total electrostatic force due to the action of the inner field of force on the ion. As considered on page (75) this force is composed by external and internal forces. Since the restoring force and the intrinsic repulsive force both vary with $\cos(\omega t)$ the electrostatic force must also vary with $\cos(\omega t)$ i. e., it must be in phase with the motion of the ion; if damping be present this will no longer be the case.

It is to be remarked that the calculation on page (76) of the strength of the inner field of force is only valid when the damping is negligible. U being the moment of one cubic centimeter of the dielectric, is necessarily in phase with the motion of the charged particles (ions or electrons) composing the dielectric, but if damping be present it is not in phase with Q which expresses the external force.

As a consequence of what has been said, the electrostatic force on the ion can be written:

$$\nu e I \cos(\omega t); \tag{24}$$

where I stands for the amplitude value of the strength of the inner field. The factor $\cos(\omega t)$ which appears in all terms can be omitted and hence the total balance of forces becomes:

$$-m_1 a_1 \omega^2 = \nu e I - K(a_1 + a_2) \tag{25}$$

The expression for the oppositely charged ion is similar. Only $m_1 a_1$ has to be replaced by $m_2 a_2$. It is seen that the right hand side of the equation is unaltered, consequently $m_1 a_1$ must be equal to $m_2 a_2$. This means that the centre of gravity is not moved during the vibration. It follows that:

$$a_1 = \frac{m_2}{m_1+m_2}(a_1+a_2); \qquad (26)$$

Introducing this in equation (25) and rearranging:

$$(a_1+a_2)\left[K-\frac{m_1 m_2}{m_1+m_2}\,\omega^2\right] = \nu e I; \qquad (27)$$

According to equation (3) the moment μ_A, obtained by displacing the ions in a molecule, is equal to the charge νe multiplied by the relative displacement of the ions. Furthermore it follows from equation (5) that this induced moment is proportional to the strength of the inner field of force, the constant proportionality factor being α_A. Hence:

$$\frac{a_1+a_2}{I} = \frac{\nu e(a_1+a_2)}{\nu e I} = \frac{\mu_A}{\nu e I} = \frac{\alpha_A}{\nu e}; \qquad (28)$$

Introducing this in equation (27);

$$K - \frac{m_1 m_2 \omega^2}{m_1+m_2} = \frac{\nu^2 e^2}{\alpha_A}; \qquad (29)$$

K can be evaluated by extrapolating to low frequencies. (Not always zero frequency as the complication due to acoustic vibrations may then arise.) The term containing ω^2 rapidly becomes negligible and we have:

$$K = \frac{\nu^2 e^2}{\alpha_{A_0}}; \qquad (30)$$

where α_{A_0} is the constant value of the ionic polarizability holding at low frequency. This value of K is introduced:

$$\omega^2 = \frac{(m_1+m_2)\,\nu^2 e^2}{m_1 m_2}\left[\frac{1}{\alpha_{A_0}} - \frac{1}{\alpha_A}\right]; \qquad (31)$$

Here the frequency ω is expressed by the atomic polarizabilities α_{A_0} and α_A. These are not directly measurable quantities, but by means of equation (18) they can be expressed in terms of dielectric constants and refractive indices. It will be convenient first to reduce the difference:

$$\frac{1}{\alpha_{A_0}} - \frac{1}{\alpha_A} = \frac{4\pi N\delta}{M}\left[1+\frac{\beta}{3}(n^2-1)\right]\left[\frac{1+\frac{\beta}{3}(\varepsilon_0-1)}{\varepsilon_0-n^2} - \frac{1+\frac{\beta}{3}(\varepsilon-1)}{\varepsilon-n^2}\right];$$

to:

$$\frac{1}{\alpha_{A_0}} - \frac{1}{\alpha_A} = \frac{4\pi N\delta}{M}\,\frac{\left[1+\frac{\beta}{3}(n^2-1)\right]^2\left[\varepsilon-\varepsilon_0\right]}{[\varepsilon_0-n^2]\,[\varepsilon-n^2]}; \qquad (32)$$

This is introduced into equation (31).

$$\omega^2 = \frac{(m_1+m_2)\,\nu^2 e^2}{m_1 m_2}\cdot\frac{4\pi N\delta}{M}\cdot\frac{\left[1+\frac{\beta}{3}(n^2-1)\right]^2\left[\varepsilon-\varepsilon_0\right]}{[\varepsilon_0-n^2]\,[\varepsilon-n^2]}; \qquad (33)$$

Certain reductions are made. $\frac{M}{N}$ is the mass of one molecule which is also expressed by m_1+m_2, these terms therefore cancel out. Furthermore $\frac{e}{m_1}$ is equal to $\frac{F}{M_1}$ where F is one Faraday, and M_1 the atomic weight (gram-atom) of the ion. It is also found expedient to replace the frequency by the wave-length $\lambda = \frac{2\pi c}{\omega}$ where c is the velocity of light.

As a result of these changes the following general expression is obtained:

$$\lambda^2 = \frac{\pi c^2 M_1 M_2 [\varepsilon_0 - n^2] [\varepsilon - n^2]}{\nu^2 F^2 \delta \left[1 + \frac{\beta}{3}(n^2 - 1)\right]^2 [\varepsilon - \varepsilon_0]}; \tag{34}$$

It will be convenient to recall the symbols not stated above: ν is the valency: δ the density; n the constant refractive index (in the near infra-red); ε_0 the constant dielectric constant for long waves (not always infinitely long waves); ε the variable dielectric 'constant' at the wave-length λ. β is a parameter (see page 76). The above expression (34) is a very general one, dependent as it is on two independent variables namely ε and β.

Certain characteristic wave-lengths will now be deduced by ascribing characteristic values to ε and β. In the first place the wave-length corresponding to ε equals infinity and β equals zero is determined:

$$\lambda_B^2 = \frac{\pi c^2 M_1 M_2}{\nu^2 F^2 \delta} [\varepsilon_0 - n^2]; \tag{35}$$

This is the same relation as derived by BORN[1]. This BORN wave-length will be used for reference.

If ε is equal to infinity and β equal to unity an expression similar to that of DEHLINGER[2] is obtained:

$$\lambda_D^2 = \lambda_B^2 \frac{9}{(n^2 + 2)^2}; \tag{36}$$

The more general case of ε equal to infinity and β arbitrary leads to the same relation as derived by HECKMANN[3]:

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[1] BORN M. and BOLLNOW O. F.: Handbuch d. Physik. **24**, 390 (1927) Eq. 43'.

[2] DEHLINGER W.: Physik. ZS. **15**, 276 (1914).

[3] HECKMANN G.: ZS. Kristall. **61**, 265 (1925).

$$\lambda_H^2 = \lambda_B^2 \frac{1}{\left[1 + \frac{\beta}{3}(n^2 - 1)\right]^2}; \tag{37}$$

In the second place the wave-lengths corresponding to ε equals zero are considered. Again we have one characteristic wave-length for β equals zero;

$$\lambda_I^2 = \lambda_B^2 \frac{n^2}{\varepsilon_0}; \tag{38}$$

and another for β equals unity:

$$\lambda_E^2 = \lambda_B^2 \frac{n^2}{\varepsilon_0} \cdot \frac{9}{(n^2 + 2)^2}; \tag{39}$$

In the third place we will consider the wave-lengths corresponding to ε equal to unity. This means that the dielectric constant and the refractive index are equal to those of the vacuum and practically to those of air. At such a wave-length the radiation therefore passes unrefracted, and, as will be seen shortly, unreflected through the powder in air. Hence, this corresponds to the CHRISTIANSEN[1] wave-length λ_C which for a number of compounds has been measured by BOWLING BARNES and BONNER[2]. As before we have one theoretical wave-length for β equals zero:

$$\lambda_J^2 = \lambda_B^2 \frac{n^2 - 1}{\varepsilon_0 - 1}; \tag{40}$$

and another for β equals unity:

$$\lambda_K^2 = \lambda_B^2 \frac{n^2 - 1}{\varepsilon_0 - 1} \cdot \frac{9}{(n^2 + 2)^2}; \tag{41}$$

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[1] CHRISTIANSEN C.: Ann. d. Physik. **23**, 298 (1884).

[2] BOWLING BARNES R. and BONNER L. G.: Physical Rev. **49**, 732 (1936).

Absorption and Reflection in the Infra-Red Region.

In principle the dielectric constant is a measurable quantity, still measurements in the infra-red region are not practicable. Of related properties the coefficient of absorption and the reflection ratio are those more frequently measured.

In our assumption (7) we have neglected the damping and thereby also the absorption. The occurrence of sensible absorption shows that this assumption can only be approximately correct. In the cases of slight damping the absorption maximum is situated close to the wave-length at which ε becomes infinite, which means that λ_A has to be compared with λ_B or λ_D.

The relation between the reflection ratio R, and the dielectric constant ε or the corresponding refractive index n is, in the case of perpendicular incidense and no damping, given by FRESNEL's[1] formula:

$$R = \left[\frac{n \pm 1}{n + 1}\right]^2 = \left[\frac{\sqrt{\varepsilon} \pm 1}{\sqrt{\varepsilon} + 1}\right]^2 \qquad (42)$$

Generally the negative sign has to be used, but if ε is negative and consequently n imaginary the positive sign must be employed in order that a real value of R, namely unity, may be obtained. This means that the reflection is total for all negative values of ε. Now ε has negative values within a certain region of wave-length; the wave-lengths corresponding to values of ε of zero and minus infinity are the border values of the region inside which reflection is total.

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[1] This formula was derived by FRESNEL: Œuvres, tom **1**, pp 441. on the basis of the undulatory theory. It has since been derived on the basis of Maxwell's electromagnetic wave theory, see for instance: KÖNIG W. in Handbuch d. Physik. Bd. **20**, p 200 and 214. It is found as the solution of a second order equation, whence the sign ± appears.

The variation of the reflection ratio with wave-length is probably demonstrated better if a special case, for instance NaCl, is considered in a diagram. In Fig. 4 the circles and the unbroken curve represent the experimental reflection curve determined by RUBENS[1]. The triangles give the reflection measured by CZERNY[2] and CARTWRIGHT and CZERNY[3]. The Christiansen wave-length as determined by BOWLING BARNES and BONNER l. c. is also shown in the diagram. Two theoretical reflection curves are drawn. The dotted curve is obtained when β is put equal to zero and

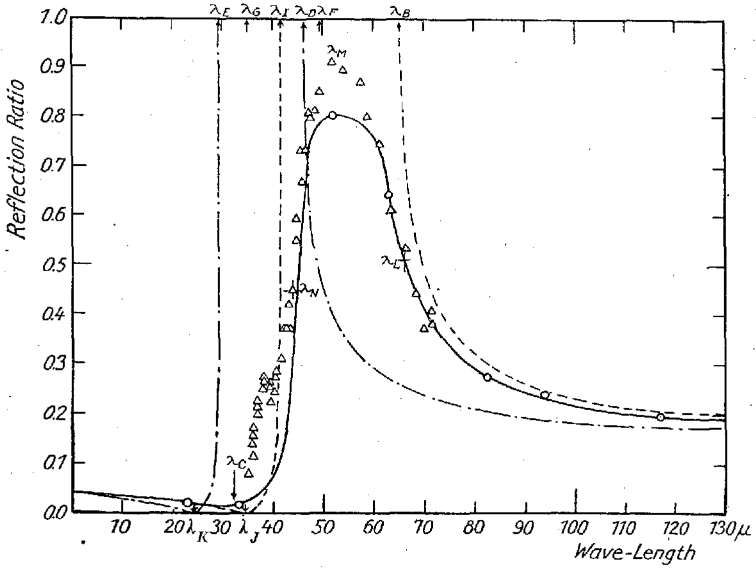

Fig. 4.

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[1] RUBENS H.: Sitzber. Preuss. Akad. d. Wiss. II (1915).

[2] CZERNY M.: ZS. f. Physik. **65**, 600 (1930).

[3] CARTWRIGHT C. H. and CZERNY M.: ZS. f. Physik. **85**, 269 (1933). CARTWRIGHT C. H. and CZERNY M.: ZS. f. Physik. **90**, 457 (1934).

the dot and dash curve is obtained when β is equal to unity. The curves are obtained using ε as a parameter. From FRESNEL's relation (42) the reflection ratio R corresponding to a selected value of ε is calculated, and from equation (34) the wave-length corresponding to the same value of ε is determined. HECKMANN described the theoretical reflection curve as resembling the profile of a table mountain. Outside the region of total reflection the reflection ratio decreases steeply.

The experimental data agree far better with the dotted curve than with the dot and dash curve. This shows that β must be close to zero. The experimental curve in so far as such can be drawn, has no 'edges' and lies altogether below the theoretical curve for β equals zero. This may be due to many causes: In the first place the measurements were performed necessarily using a rather inhomogeneous radiation (wide slit). In the second place the theoretical curve must vary from the experimental because the theoretical treatment does not take into account higher harmonic vibrations. And in the third place, if damping be considered the theoretical curve will be still further altered.

Reflection curves similar to the above have been determined for more compounds, but since the representation by curves takes too much space, characteristic wave-lengths are quoted in table (3). As there are no distinguishable 'edges' on the experimental curves some other characteristic points must be chosen for representation. The values taken are the wave-length λ_M corresponding to maximum of reflection and those corresponding to the half height of the reflection mountain. The latter are those at which the reflection ratio is the mean of the maximum value and the value representing the level to the same side of the mountain. It will be seen from Fig. 4 that the 'half height' wave-lengths are well defined, and furthermore that each of these is close to an 'edge' on the theoretical curve. λ_L being close to λ_B, and λ_N close to λ_I. The breadth of the experimental mountain as measured between the 'half height' wave-lengths is thus equal to the breadth of the theoretical mountain as measured between the 'edges'.

From the present theory, which neglects the influence of damping, it follows that the reflection is total in a region, and consequently no single maximum value is obtained. In order to derive a theoretical maximum value one must introduce a slight damping, i. e. a dissipative force. This means a great complication, because the simple expression of FRESNEL (42) and even the generalized equations of CLAUSIUS-MOSOTTI and LORENZ-LORENTZ (12) and (16) are only valid in so far as the damping may be neglected.

The wave-length of the reflection maximum has been computed by FÖRSTERLING[1], whose expression, using our symbols, can be written:

$$\frac{1}{\lambda_F^2} = \frac{1}{\lambda_B^2} + \frac{F^2 \delta^2}{2\, n^2 \pi\, c^2 M_1 M_2};$$

which can be reduced to:

$$\lambda_F^2 = \lambda_B^2 \frac{2\, n^2}{\varepsilon_0 + n^2} \tag{43}$$

This holds for $\beta = 0$; the corresponding expression for $\beta = 1$ is:

$$\lambda_G^2 = \lambda_B^2 \frac{2\, n^2}{\varepsilon_0 + n^2} \cdot \frac{9}{(n^2+2)^2}; \tag{44}$$

Values of λ_F and λ_G are quoted in table 3.

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[1] FÖRSTERLING K.: Ann. d. Physik. **61**, 577 (1920).

HAVELOCK[1] derived an expression different from that of FÖRSTERLING. According to O. FUCHS and K. L. WOLF[2] Havelock's expression is the more accurate one. The calculations of FÖRSTERLING and HAVELOCK were carried out on the classical theory of absorption; but as remarked on page (79) the very basis of this theory is invalid, and therefore neither of the two expressions are considered safe. Our only purpose in quoting FÖRSTERLING wave-lengths is to obtain a comparison with HECKMANN's data.

It is found that the equations (34) to (44) may also be applied to the CaF_2 lattice if ν^2 is replaced by the product $\nu_1 \nu_2$ of the valencies of the ions. Hence for CaF_2 ν^2 is put equal to 2.

Experimental Test.

Experimental data used in the formulae are given in table 1 in which M_1 and M_2 are the atomic weights of the ions; ε_0 is the dielectric constant for long waves. The density δ is quoted, and the refractive index n is extrapolated to the near infra-red, using data from LANDOLT-BÖRNSTEINS tables[3]. In a few cases n^2 is quoted from the paper of EUCKEN and BÜCHNER (cited next page) all data applies to room temperature.

In table 2 theoretical wave-lengths as given by the expressions (35) and (36) are compared to the wave-length of the absorption maximum; note that the experimental wave-length in all cases but one is situated between the two

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[1] HAVELOCK T. H.: Proc. Roy. Soc. London. A. **105**, 488 (1924).

[2] FUCHS O. and WOLF K. L.: ZS. f. Physik. **46**, 506 (1928).

[3] LANDOLT-BÖRNSTEIN: Tabellen. Tables 81 and 170 in the Erg. Bd. I, II and III in particular.

Table 1. Experimental Data used in the Formulae.

	M_1	M_2	ν	δ	ε_0	n	n^2
LiF	6.94	19.0	1	2.64	9.27 E. B.	1.39	1.92 E. B.
NaF	23.0	19.0	1	2.80	6.0 K.	1.32	1.74
NaCl ...	23.0	35.46	1	2.16	5.62 E. B.	1.50	2.25
NaBr ...	23.0	79.9	1	3.20	5.99 E.	1.62	2.62
NaI	23.0	126.9	1	3.67	6.60 E.	1.71	2.91
KCl	39.1	35.46	1	1.99	4.68 E. B.	1.46	2.13
KBr	39.1	79.9	1	2.74	4.78 E.	1.53	2.33
KI	39.1	126.9	1	3.12	4.94 E.	1.64	2.69
RbCl ...	85.4	35.46	1	2.76	5.0 A.	1.48	2.19
RbBr ...	85.4	79.9	1	3.36	5.0 A.	1.53	2.33
RbI	85.4	126.9	1	3.55	5.0 A.	1.62	2.63
CsCl	132.8	35.46	1	3.98	7.20 H_1	1.61	2.60
CsBr ...	132.8	79.9	1	4.45	6.51 H_1	1.67	2.78
CsI	132.8	126.9	1	4.51	5.65 H_1	1.74	3.03
NH_4Cl ..	18.04	35.46	1	1.53	6.96 J.	1.62	2.63
TlCl	204.4	35.46	1	7.02	31.9 E. B.	2.26	5.10 E. B.
TlBr	204.4	79.9	1	7.54	29.8 E. B.	2.33	5.41 E. B.
AgCl	107.9	35.46	1	5.56	12.3 E. B.	2.02	4.04 E. B.
AgBr ...	107.9	79.9	1	6.4	13.1 E. B.	2.15	4.62 E. B.
BeO	9.02	16.0	2	3.00	7.35 H_2	1.72	2.95
MgO	24.32	16.0	2	3.65	9.8 H_2	1.72	2.95
CaO	40.08	16.0	2	3.4	11.8 H_2	1.81	3.28
SrO	87.63	16.0	2	5.0	13.3 H_2	1.82	3.31
ZnS	65.38	32.06	2	4.06	8.3 L. R.	2.25	5.07
CaF_2 ...	40.08	19.0	2—1	3.18	8.43 E. K.	1.411	1.99
SrF_2 ...	87.63	19.0	2—1	4.28	7.69 E. K.	1.441	2.08
BaF_2 ...	137.36	19.0	2—1	4.89	7.33 E. K.	1.444	2.09

The dielectric constants were measured by:

E. ERRERA J.: ZS. Elektrochemie. **36**, 818 (1930).
E. K. ERRERA J. and KETELAAR H.: J. Phys. et Radium. (7) **3**, 240 (1932).
E. B. EUCKEN A. and BÜCHNER A.: ZS. physik. Ch. B. **27**, 321 (1935).
H_1 HØJENDAHL K.: ZS. physik. Ch. B. **20**, 63 (1933).
H_2 „ „ This work.
J. JAEGER R.: Ann. d. Physik. (4) **53**, 409 (1917).
L. R. LIEBISCH TH. and RUBENS H.: Sitzber. Preuss. Akad. Wiss. XLVIII (1919).
K. KYROPOULOS S.: ZS. f. Physik. **63**, 849 (1930).
A. Average of measurements by ERRERA, KYROPOULOS and myself.

Table 2. Test on Infra-Red Transmission Data.

	Absorption maximum				Christiansen wave-length			
	theoretical		experimental		theoretical		experimental	
	λ_B	λ_D	λ_A	β_A	λ_J	λ_K	λ_C	β_C
LiF ...	35.2	27.0	32.6 B_1	0.26	11.7	9.0	11.2 B_2	0.15
NaF ..	47.4	38.0	40.6 B_1	0.68				
NaCl .	65.6	46.3	61.1 B.C.	0.18	34.2	24.1	32.0 B_2	0.16
NaBr .	80.8	52.5	74.7 B_1	0.15	46.1	29.9	37 B_2	0.45
NaI ...	99.3	60.7	85.5 B_1	0.25	58.0	35.4	49 B_2	0.29
KCl ...	77.6	56.3	70.7 B.C.	0.26	43.0	31.2	37 B_2	0.43
KBr ..	97.2	67.4	88.3 B_1	0.23	57.7	40.0	52 B_2	0.25
KI	110.0	70.4	102.0 B_1	0.13	72.0	46.1	64 B_2	0.22
RbCl .	102.1	73.2	84.8 B_1	0.52	55.7	39.9	45 B_2	0.60
RbBr .	135.3	93.7	114.0 B_1	0.42	78.1	54.1	65 B_2	0.45
RbI ...	156.0	101.1	129.5 B_1	0.38	99.4	64.4	73 B_2	0.67
CsCl ..	136	89	102.0 B_1	0.63	69.2	45.1	50 B_2	0.72
CsBr ..	173	109	134.0 B_1	0.49	98.2	61.6	60 B_2	1.07
TlCl ..					111	47	45 B_2	1.07
TlBr ..					165	67	64 B_2	1.07
BeO ..	13.2	8.0	13.5 T.	— 0.03	7.3	4.5	8 T.	— 0.13
MgO ..	24.8	15.1	14.2 T.	1.14	11.6	7.1	12.2 B_2	— 0.06
CaO ..	36.8	20.9	22.1 T.	0.87	17.0	9.6	16 T.	0.08

Transmission in infra-red was measured by:

B. C. Bowling Barnes R. and Czerny M.: ZS. f. Physik. **72,** 447 (1931).
B_1 Bowling Barnes R.: ZS. f. Physik. **75,** 723 (1932).
B_2 Bowling Barnes R. and Bonner L. G.: Physical Rev. **49,** 732 (1936).
T. Tolksdorf S.: ZS. f. physik. Ch. **132,** 161 (1928).

corresponding theoretical wave-lengths. MgO and BeO are exceptions, but the discrepancy is not larger than what may be due to experimental error. Hence the two theoretical values define a region within which the experimental absorption maximum is found.

The above theoretical wave-lengths λ_B and λ_D are those obtained for β equals unity and zero. It is of interest to see what value shall be ascribed to β in order that relation (37) shall hold with accuracy. For this purpose the wave-length of the absorption maximum λ_A is introduced in place of λ_H, hence:

$$1 + \frac{\beta}{3}(n^2 - 1) = \frac{\lambda_B}{\lambda_A};$$

from which β can be determined:

$$\beta = \frac{3\left(\frac{\lambda_B}{\lambda_A} - 1\right)}{n^2 - 1}; \tag{45}$$

By means of this expressions the β_A values in column (5) are calculated. Considering the alkali-halides it will be realized that the variation of β_A with the inner polarizability of the anion, so marked in the case of the β determined from the relation between compressibility and dielectric constant and refractive index, is far less pronounced in the present case. (Compare p. 122).

In the second section of table 2 theoretical wave-lengths as given by the expressions (40) and (41) are compared to the experimental Christiansen wave-length measured by Bowling Barnes. This Christiansen wave-length constitutes the transmission maximum in the case of a powder, hence, such transmission maxima measured by Tolksdorf are also quoted. For MgO Bowling Barnes found the same maximum as Tolksdorf. Values of the parameter β_C are calculated by means of the above formula (45), replacing λ_B/λ_A by λ_J/λ_C. For the alkali-halides the agreement in most cases is fair; note that the absorption curves determined by Bowling Barnes and Czerny are measured on plates or films. For the oxides the agreement between the two different values of β is bad. The explanation is presumably the following. Tolksdorf actually measured the transmission minimum, but because the radiation may be scattered owing to reflection on the surfaces of the single particles in the powder, the transmission minimum and the true absorption maximum are not identical.

The characteristic wave-lengths of each reflection curve are quoted in table 3. In the cases of NaCl, KCl, KBr, KI, ZnS and CaF_2 it will be noticed that the half height — maximum — half height' wave-lengths of the experimental reflection curve agree well with the corresponding 'edge — maximum — edge' wave-lengths of that theoretical curve which is obtained using the value β equals zero (expressions (35) (43) and (38)). This also shows that the breadth of the experimental reflection mountain is equal to the theoretical breadth, which is considered a verification of the theory. If the theory is correct the absorption maximum should be situated close to the larger of the 'half height wave-lengths'. This holds fairly well for NaCl, KCl, KBr and KI but not at all for LiF.

An empirical value of β can be evaluated from reflection data by a method similar to that applied to transmission data. Such a calculation was in fact first undertaken by Heckmann[1], and his values of β are quoted in the last column. Our calculation is performed using equation (45). In place of the ratio λ_B/λ_A the ratio λ_F/λ_M is introduced. According to theory these ratios should be equal, granted of course that the Försterling expression is sufficiently accurate. Values of β_R evaluated from reflection data are quoted in the column next to the last. That the experimental error is considerable is appreciated if the β values from reflection data are compared with those found from transmission data. Especially in the cases of LiF and NaF the error must be large. In the case of other alkali-halides,

Table 3. Test on Reflection Data.

	Theoretical						Experimental Reflection				Heckmann
	$\beta = 0$			$\beta = 1$							
	Edge (35)	Max (43)	Edge (38)	Edge (36)	Max (44)	Edge (39)	half height	Max	half height		
	λ_B	λ_F	λ_I	λ_D	λ_G	λ_E	λ_L	λ_M	λ_N	β_R	β_H
LiF	35.2	20.6	16.1	27.0	15.8	12.3	20.0	17.1	14.6 Re.	0.67	
NaF	47.4	31.9		38.0	25.5			35.8	Re. B.	−0.40	
NaCl . . .	65.6	49.6	41.5	46.3	35.0	29.3	66.5	51.7	43.5 C.	−0.10	−0.15
KCl	77.6	62.0	52.4	56.3	44.5	38.0	78	62	53 C.	0.00	−0.16
KBr	97.2	78.6	68.0	67.4	55.0	47.2	95	83	68 R.	−0.12	−0.28
KI	110.0	92.0	81.2	70.4	59.1	52.0	104	94	85 R.	−0.03	+0.09
RbCl . . .	102	80	68	73	57	48		74	Re.	0.19	
NH_4Cl . .	78	58	48	51	37	32	64	52	45 R.	0.21	
TlCl	306	160	122	129	68	52	150	100	65 R.	0.44	0.69
TlBr	422	234	180	171	95	73	200	117	95 R.	0.68	0.75
AgCl	139	98	80	69	49	40	120	90	58 R.	0.09	0.14
AgBr . . .	197	142	117	89	65	53	200	110	83 R.	0.24	0.17
ZnS	37.7	32.8	29.4	16.0	13.9	12.5	40.5	31.8	27.5 L.R.	0.02	0.13
CaF_2	51.0	31.5	24.8	38.4	23.7	18.4	40	32.8	21 K.S.	−0.11	
SrF_2	61.5	39.7	31.6	45.2	29.2	23.2		40.7	Re. B.	−0.07	
BaF_2	68.7	45.8	36.7	50.4	33.6	26.9		50.7	Re. B.	−0.27	

Reflection data were measured by:

C.	Czerny M.: ZS. f. Physik. **65**, 600 (1930).
K. S.	Kellner L.: ZS. f. Physik. **56**, 231 (1929).
R.	Rubens H.: Sitzber. Preuss. Akad. Wiss. II (1915).
L. R.	Liebisch T. and Rubens H.: Sitzber. Preuss. Akad. Wiss. XLVIII (1919).
Re.	Reinkober O.: ZS. f. Physik. **39**, 439 (1926).
Re. B.	Reinkober O. and Bluth M.: Ann. d. Physik. (5) **6**, 785 (1930).

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[1] Heckmann G.: ZS. Kristall. **61**, 266 (1925).

besides a large experimental error there can also be distinguished a systematic deviation, in that the β values found from transmission are as a rule larger than those found from reflection. This systematic deviation is an indication of the limitation of the theory.

Although data, more extensive and in some respects more accurate than those employed by Heckmann have here been considered, we are not able to derive further conclusions than he did. This, however, will be possible by means of our second relation, namely that between dielectric constant, refractive index and compressibility. Further discussion will therefore be postponed till this relation has been derived and tested.

The Interionic Forces.

The forces between the ions have hitherto been treated in a very general manner, the only assumption being, that for small displacements the force arising shall be proportional to the relative displacements of the ions (strictly the nuclei). In order to carry out a theoretical calculation of the compressibility, the mathematical form of the potential between two ions must be considered more specifically. The calculation is based upon assumptions 4, 5, and 6 on page 65. According to assumption 4) the forces between the ions can be separated into two types: a) the electrostatic force which follows Coulomb's law, and b) a short range intrinsic repulsive force which keeps the ions apart. The nature of and mathematical form of the latter is not quite settled.

Born and Lande[1], who first encountered the problem, considered the potential of intrinsic repulsive force between two ions to be given by the expression $b \times r^{-n}$, where r is

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[1] Born M. and Lande A.: Verh. D. physik. Ges. **20**, 210 (1918).

the distance between the ions and b and n are constants for the same combination of ions. According to modern theory the intrinsic force arises from a certain quantum-mechanical interaction (antisymmetric coupling) of the electrons in the two ions[1,2], and as a consequence an exponential relation is to be expected. Born and Mayer[3] write this:

$$\varphi_{(B)} = b e^{\frac{r_1 + r_2 - r}{\varrho}}$$

where r_1 and r_2 are the ionic radii; r the distance; ϱ equals 0.345×10^{-8} cm. the same constant for all alkali-halides, and b a constant for the same salt. According to Pauling[4] b has to be replaced by a polynomial. In recent papers which have been obtained since the major part of the present paper was written, Wasastjerna[5,6,7] makes efforts to evaluate this polynomial from experimental data. He finds that the dominant terms are those containing r to the sixth or eigth power.

All investigators agree in considering the intrinsic repulsive force as a short range central force. In the present exposition it is attempted to make this the only assumption regarding this force, therefore the potential of the intrinsic repulsive force between two ions is considered to be given by the Taylor series:

$$\varphi_{(L \pm l)} = \varphi_L \pm \varphi' l + \frac{\varphi''}{2} l^2 \pm \ldots . \tag{46}$$

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[1] Heitler W. and London F.: ZS. f. Physik. **44**, 455 (1927).
[2] London F.: Naturwissenschaften. **17**, 516 (1929).
[3] Born M. and Mayer J. E.: ZS. f. Physik. **75**, 1 (1932).
[4] Pauling L.: ZS. f. Krist. **67**, 377 (1928).
[5] Wasastjerna J. A.: S. Sc. Fennica. C. Phys. Mat. VI. **22** (1932).
[6] Wasastjerna J. A.: S. Sc. Fennica. C. Phys. Mat. VIII. **20** (1935).
[7] Wasastjerna J. A.: S. Sc. Fennica. C. Phys. Mat. VIII. **21** (1935).

where L is the mutual distance, l the change in it, and φ_L, φ' and φ'' are constants. The TAYLOR series is practicable because l as a rule is very small compared to L, whence only the first few (three) members of the series need consideration.

If now the ionic lattice be deformed, the forces mentioned come into play. There are two types of deformation of special interest, which will be discussed in the following. The first type of deformation is the homogeneous contraction resulting from a compression of the crystal. The second type of deformation is the relative displacement of the lattices of oppositely charged ions contemplated on page 66.

The Compressibility of Regular Crystals.

According to restriction 6) on page 65 not only the forces between neighbours, but also the forces between next neighbours are to be considered. The above TAYLOR series (46) with the constants φ_L, φ' and φ'' is considered to represent the potential between neighbour ions. The potential of intrinsic repulsive forces between next neighbours is considered to be given by another TAYLOR series:

$$\psi_{(L_1 \pm l_1)} = \psi_{L_1} \pm \psi' o l + \frac{\psi''}{2} o^2 l^2 \pm \dots \qquad (47)$$

where ψ_{L_1}, ψ' and ψ'' are new constants. The normal distance L_1 between next neighbours is different from L, it is actually equal to oL where o is a constant factor. Hence the change in distance is equal to ol. There are two different combinations of next neighbours present namely $(+\,+)$ and $(-\,-)$, but as a rule the intrinsic repulsive force between cations is negligible and only that between anions needs consideration.

The total potential energy due to intrinsic repulsive forces between one ion and its neighbours is obtained by multiplying expression (46) by the coordination number k, i. e. the number of neighbours of any one ion. Similarly the potential energy between one ion and its next neighbours is obtained by multiplying expression (47) by k_1 which is the number of next neighbours of an ion.

Besides the intrinsic repulsive forces considered, electrostatic forces between ions are also present. The electrostatic potential energy of two ions of charges νe and $\nu_1 e$ at a distance L is:

$$\varphi_E = \frac{\nu \nu_1 e^2}{L};$$

The electrostatic potential energy of one ion with respect to all other ions in the lattice is obtained by multiplying the above expression by a constant j which is:

$$j = \sum{}' \frac{L_0}{L_1}; \qquad (48)$$

where L_1 is the distance between the ion considered and any other ion, and L_0 that between neighbour ions. The summation shall be extended over all ions, counting each ion once and considering the sign of the ion.[1]

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[1] MADELUNG E.: Physik. ZS. 19, 524 (1918), applied a mathematical artifice in order to determine the constant j, because a direct summation was not found feasible. — The writer should like to point out that a direct summation still may be practicable if only it proceeds on a definite plan: Consider for instance a crystal growing by the successive addition of neutral ionic layers. If now the potential energy of one ion in the crystal with respect to those in the layer is computed, it will be found that this increment of energy decreases rapidly as the crystal grows, and hence the total potential energy between one ion and all other ions can be evaluated. A profound treatment will be given later on pages 133—54.

Hence the total potential energy of one ion with respect to all other ions in the lattice is given by:

$$\phi_L = -\frac{j\nu\nu_1 e^2}{L} + k\varphi_L + k_1\psi_L; \qquad (49)$$

L is the normal i. e. the equilibrium distance between neighbour ions. This means that:

$$\frac{d\phi}{dL} = \frac{j\nu\nu_1 e^2}{L^2} + k\varphi' + k_1 o\psi' = 0; \qquad (50)$$

The change in distance between next neighbours dL_1 being odL. By compression the distance between neighbours is altered from L to $L-l$. By this change the potential energy is altered to:

$$\phi_L + \Delta\phi = -\frac{j\nu\nu_1 e^2}{L-l} + k\left[\varphi_L - \varphi' l + \frac{\varphi''}{2} l^2 \ldots.\right] +$$
$$+ k_1\left[\psi_{L_1} - \psi' ol + \frac{\psi''}{2} o^2 l^2 \ldots\right];$$

ϕ_L as given by expression (49) is subtracted. Furthermore by means of expression (50)

$$-j\nu\nu_1 e_2 \text{ is replaced by } (k\varphi' + k_1 o\psi')\,L^2;$$

Hence an expression for the energy change is obtained:

$$\Delta\phi = (k\varphi' + k_1 o\psi')\,L^2\left[\frac{1}{L-l} - \frac{1}{L}\right] - k\varphi' l + \frac{k\varphi''}{2} l^2 -$$
$$- k_1 o\psi' l + \frac{k_1 o^2\psi''}{2} l^2 \ldots.$$

Neglecting the third power terms of l the expression:

$$L^2\left[\frac{1}{L-l} - \frac{1}{L}\right] \text{ reduces to } l + \frac{l^2}{L};$$

This is introduced:

$$\Delta\phi = k\varphi' l + k_1 o\psi' l + k\varphi'\frac{l^2}{L} + k_1 o\psi'\frac{l^2}{L}$$
$$- k\varphi' l - k_1 o\psi' l + k\varphi''\frac{l^2}{2} + k_1 o^2\psi''\frac{l^2}{2};$$

It is seen that first power terms cancel.

$$\Delta\phi = \left[k\left(\frac{\varphi'}{L} + \frac{\varphi''}{2}\right) + k_1\left(\frac{o\psi'}{L} + \frac{o^2\psi''}{2}\right)\right] l^2 = Dl^2; \qquad (51)$$

The change in energy is thus proportional to the square of the change in distance between the ions, this means that HOOKE's law is valid. In case l is so large that third power terms become significant, HOOKE's law will no longer be valid. In the following treatment it is found practical to make use of the proportionality factor D as a parameter. $\Delta\phi$ is the change in potential energy due to changes, arising from compression, in forces between one ion and all other ions. The energy of N ions is not N times but only $\frac{N}{2}$ times as great, for in our summation we count each distance twice, i. e. count both ba and ab. Hence the energy change to be ascribed to any one ion is only half of $\Delta\phi$. As the molecule (in the cases of the NaCl, CsCl and ZnS lattices) contains two ions, $\Delta\phi$ represents the energy change per molecule.

Owing to the change in distance from L to $L-l$ the volume occupied by a molecule is diminished. In the normal state this volume is $V = BL^3$ where the constant B is 2 for the NaCl lattice, $\frac{8}{3\sqrt{3}}$ for the CsCl lattice and $\frac{16}{3\sqrt{3}}$ for the ZnS lattice. (52)

The change due to compression in the volume occupied by a molecule is:

$$\Delta V = BL^3 - B(L-l)^3 = B\left[3L^2 l - 3Ll^2 + l^3\right] \backsim 3BL^2 l; \quad (53)$$

the two latter terms being negligible compared to the first one.

The external pressure p necessary to perform the compression is equal to $-\frac{\delta(\Delta\Phi)}{\delta(\Delta V)}$. Thus combining (51) and (53):

$$p = -\frac{\delta(\Delta\Phi)}{\delta(\Delta V)} = -\frac{\frac{\delta(\Delta\Phi)}{\delta l}}{\frac{\delta(\Delta V)}{\delta l}} = -\frac{2Dl}{3BL^2}; \quad (54)$$

from which:

$$\frac{\delta p}{\delta(\Delta V)} = \frac{\frac{\delta p}{\delta l}}{\frac{\delta(\Delta V)}{\delta l}} = -\frac{2D}{9B^2L^4};$$

The compressibility is defined as:

$$\varkappa = -\frac{1}{V}\frac{\delta(\Delta V)}{\delta p};$$

introducing the values of V and $\frac{\delta p}{\delta(\Delta V)}$, this becomes:

$$\varkappa = \frac{1}{BL^3}\cdot\frac{9B^2L^4}{2D} = \frac{9BL}{2D}; \quad (55)$$

Putting in the value of D, the following general expression for the compressibility is obtained:

$$\varkappa = \frac{9B}{k\left(\frac{2\varphi'}{L^2} + \frac{\varphi''}{L}\right) + k_1\left(\frac{2o\psi'}{L^2} + \frac{o^2\psi''}{L}\right)}; \quad (56)$$

where B is a constant characteristic of the lattice type; k is the number of neighbours of any one ion; k_1 the number of next neighbours; L the distance between neighbours; o the ratio of the distances between neighbours and next neighbours. φ', φ'' and ψ', ψ'' are constants in the TAYLOR series (46) and (47).

The second term containing k_1 in the denominator is due to forces between next neighbours. As a rule it is considerably smaller than the first one. If it be neglected the expression reduces to:

$$\varkappa = \frac{9BL}{k\left(\frac{2\varphi'}{L} + \varphi''\right)}; \quad (57)$$

This expression will be used in the following discourse. The error introduced by disregarding the intrinsic repulsive force between next neighbours will be discussed later.

Relative Displacement of Positive and negative Ions.

Although the problem of the interaction of a crystal lattice with an electric field has been shown on pages 70—72 to depend on assumptions concerning the Lorentz force; nevertheless, the problem can be treated on the same general lines as the compressibility was in the last section. In addition the problems of dielectric polarization and compressibility may be linked together.

Consider a regular ionic crystal, and suppose the lattice of positive ions as an entirety is displaced with regard to the lattice of negative ions. The relative displacement of the force-centres (not necessarily the nuclei) is s. Next neighbours, always having the same sign, are not displaced relative to each other. The forces between next neighbours therefore are not altered, whence, according to restriction 6), the total change in the potential energy of the intrinsic repulsive forces is due to changes in distances between neighbours. The neighbours of any one ion in a regular diagonal lattice form either a regular tetrahedron, a regular octahedron or a cube.

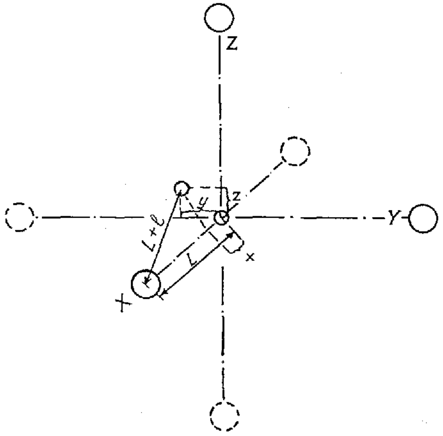

Fig. 5.

The octahedric arrangement which is found in the NaCl lattice is considered first. In figure 5 the central ion is placed at the origin of Cartesian coordinates, and the neighbour ions are placed on the coordinate axes at the distances L. The potential energy of the intrinsic repulsive force between the central ion and one of its neighbours is given by the Taylor series (46). We shall now determine the change in this potential energy and the force which will arise when the central ion is displaced the distance s with the components x, y and z.

It is found that the first power terms of x, y, z cancel one another, therefore terms containing x, y, z to the second power are significant. Terms to the third and fourth power are neglected.

First consider the change l in L the distance between the central ion and one of its neighbours situated on the X axis. This change is:

$$l = \sqrt{(\pm L - x)^2 + y^2 + z^2} - L; \tag{58}$$

or

$$l = (L \pm x)\sqrt{1 + \frac{y^2 + z^2}{(L \pm x)^2}} - L;$$

The numerator contains y and z to the second power, hence third power terms will only be neglected if x in the denominator is discarded. Furthermore the reduction $\sqrt{1+\varDelta} = 1 + \frac{\varDelta}{2}$ is used, the error introduced thereby is in the fourth power of y and z, and we get:

$$l = (L \pm x)\left[1 + \frac{y^2 + z^2}{2L^2}\right] - L;$$

In the multiplication the third power term is neglected. Hence:

$$l = \pm x + \frac{y^2 + z^2}{2L}; \tag{59}$$

and neglecting terms to the third and fourth power we obtain:

$$l^2 = x^2. \tag{60}$$

These values are introduced into the Taylor series (46), whence the potential energy due to one neighbour ion on the X axis is found to be:

$$\varphi_{L+l} = \varphi_L + \varphi'\left[\pm x + \frac{y^2 + z^2}{2L}\right] + \frac{\varphi''}{2}x^2;$$

When we consider both neighbour ions on the X axis, the first power terms (having opposite sign) cancel, and we have the change in potential energy due to the displacement:

$$\varDelta\varphi_x = \varphi'\frac{y^2 + z^2}{L} + \varphi'' x^2.$$

Similar expressions are found for the ions on the y and z axes. By summation the potential energy change due to all six neighbours is:

$$\Delta\phi = \varphi' \frac{2(x^2+y^2+z^2)}{L} + \varphi''(x^2+y^2+z^2);$$

$x^2+y^2+z^2$ is equal to s^2, hence the above expression reduces to:

$$\Delta\phi = \left[\frac{2\varphi'}{L} + \varphi''\right] s^2. \qquad (61)$$

It is seen that the change in energy $\Delta\phi$ is proportional to the square of the displacement, and furthermore that the proportionality factor is independent of the direction of the displacement. These results are only valid for small displacements. If the displacement is so large that third power terms become significant, the elastic energy will no longer be proportional to the square of the displacement, and the proportionality factor no longer the same in all directions. Just as was the case for compression, HOOKE's law will no longer be valid.

The tetrahedric and cubic arrangements.

In the ZnS lattice the neighbours of any one ion form a regular tetrahedron, in the CsCl lattice they form a cube, and in the CaF_2 lattice the F^- ions form a cube round the Ca^{++} ion, and the Ca^{++} ions form a tetrahedron round any F^- ion. As shown in figure 6 a regular tetrahedron is formed from ions placed at every second corner of a cube. Hence the cases of the regular tetrahedron and the cube can be treated together. Cartesian coordinate axes are placed in the lattice as shown in the figure. The coordinates of the neighbour ions are $X = \pm g$; $Y = \pm g$ and $Z = \pm g$. In the case of the cubic arrangement all combinations of + and — have to be considered, in the case of the tetrahedric arrangement the

combinations (— — —), (— + +), (+ — +) and (+ + —) only. The distance L between one corner of the cube and the centre, i. e. that between one neighbour ion and the central ion in its initial position is $L = \sqrt{3}\,g$.

Consider as before the central ion to be displaced the small distance s. The general case of the ion being displaced in any direction has been considered by the writer. The calculations are similar to those regarding the octahedron. Just as was found for the octahedron, the change in potential energy is proportional to the square of the displacement and the proportionality factor is independent of the direction of the displacement in the crystal. The calculations for the general case, however, are lengthy, but they are simplified if the displacement considered takes place in the direction of one of the axes. This therefore is considered here. The coordinates of the displaced central ion are x, o, o. The change in distance between the central ion and any one of its neighbour ions is:

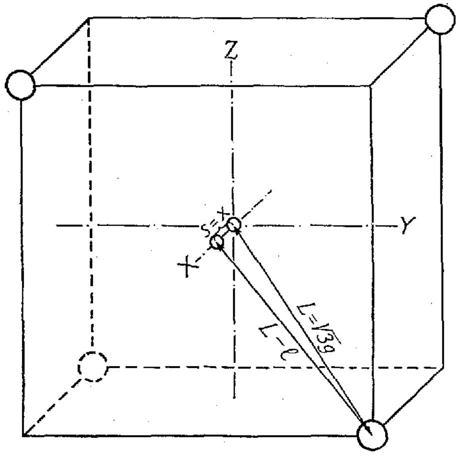

Fig. 6.

$$l = \sqrt{(\pm g - x)^2 + g^2 + g^2} - \sqrt{3}\,g; \qquad (62)$$

which can also be written:

$$l = \left(\sqrt{3}\,g \pm \frac{x}{\sqrt{3}}\right) \sqrt{1 + \frac{\frac{2}{3}x^2}{\left(\sqrt{3}\,g \pm \frac{x}{\sqrt{3}}\right)^2}} - \sqrt{3}\,g;$$

This is reduced, firstly by omitting the second term in the denominator, secondly by the familiar reduction $\sqrt{1+\Delta} = 1 + \frac{\Delta}{2}$, and thirdly by neglecting third power terms in the multiplication. As a result we obtain:

$$l = \pm \frac{x}{\sqrt{3}} + \frac{x^2}{3\sqrt{3}\,g}; \tag{63}$$

and neglecting third power terms:

$$l = \frac{x^2}{3}; \tag{64}$$

These values are introduced in the TAYLOR series (46) representing the potential energy of intrinsic repulsive forces between the central ion and one of its neighbours; hence:

$$\Delta\varphi_1 = \varphi_{L+l} - \varphi_L = \varphi' \left[\pm \frac{x}{\sqrt{3}} + \frac{x^2}{3\sqrt{3}\,g}\right] + \varphi'' \frac{x^2}{6};$$

By the summation over all neighbour ions the terms containing x to the first power cancel, and for the tetrahedric arrangement it is found:

$$\Delta\phi = \varphi' \frac{4x^2}{3\sqrt{3}\,g} + \varphi'' \frac{2x^2}{3};$$

It is advantageous to introduce L in place of $\sqrt{3}$g, furthermore $x = s$.

$$\Delta\phi = \frac{2}{3}\left[\frac{2\varphi'}{L} + \varphi''\right] s^2; \tag{65}$$

Similarly for the cubic arrangement:

$$\Delta\phi = \frac{4}{3}\left[\frac{2\varphi'}{L} + \varphi''\right] s^2; \tag{66}$$

Regular arrangements in general.

If we compare these equations with (61) it will be seen that the different equations can be replaced by:

$$\Delta\phi = \frac{k}{6}\left[\frac{2\varphi'}{L} + \varphi''\right] s^2; \tag{67}$$

where k is the coordination number, i. e. the number of neighbours surrounding an ion.

$\Delta\phi$ is the energy required in order to displace the central ion the distance s. In displacing the ion we have to work against an elastic force f. This force can be evaluated by differentiation:

$$f = \frac{d(\Delta\phi)}{ds} = \frac{k}{3}\left[\frac{2\varphi'}{L} + \varphi''\right] s; \tag{68}$$

At the present stage it is found expedient to include the proof of a statement given earlier. On page (71) it was stated that the electrostatic force, close to the centre of a regular configuration of ions placed on a spherical surface, is negligibly small. The electrostatic potential energy between two ions of charges νe and $\nu_1 e$ and distance L apart is:

$$\varphi_E = \frac{\nu\nu_1 e^2}{L};$$

$$\text{Hence:}\quad \varphi' = \frac{d\varphi_E}{dL} = -\frac{\nu\nu_1 e^2}{L^2} \text{ and } \varphi'' = \frac{2\nu\nu_1 e^2}{L^3};$$

$$\text{Thus:}\quad \frac{2\varphi'}{L} + \varphi'' = 0; \tag{69}$$

If this is introduced in equation (68), it is seen that the force near the centre of the configuration becomes zero independent of direction of displacement. This of course only holds for small displacements, since it is subject to the same restriction, as the entire calculation above, namely that the cube of the displacement shall be small compared to the square of it. We have demonstrated the correctness of our assumption in the cases of the octahedron, tetrahedron and cube, but in all probability it will hold for other regular configurations. (Regular is to be taken in the crystallographic sense of the word.) For the limiting case of the evenly charged spherical surface our assumption is valid for all displacements smaller than the radius.

A Relation between Compressibility and Atomic Polarizability.

Equation (68) as derived considers elastic forces between neighbour ions only. In the case considered on page 103 where the lattices of positive and negative ions are relatively displaced, the contribution of force due to ions at greater distances than L is negligible, and f can be considered the total elastic force exerted on one ion by the entire lattice.

This force was also considered on page 81; there it was assumed that the force was proportional to the relative displacement of the ions. Now we have actually found, that this assumption holds good, and furthermore that the proportionality factor, which was then termed K, has the value:

$$K = \frac{k}{3}\left[\frac{2\,\varphi'}{L} + \varphi''\right]. \qquad (70)$$

There is one objection to be made: the relative displacement considered in defining K was that of the nuclei, whereas the displacement s in the above calculations is that of the force-centres of intrinsic repulsive forces. By action of the field

the electrons in the ion are shifted with regard to the nucleus. The intrinsic repulsive force between two ions, however, is dependent not only on the relative distances of the nuclei, but also and probably more on the location and motion of the electronic systems in the two ions. Hence it will be realized that the above equation (70) is not absolutely exact, still we will use it for the present. A modified expression will be derived later on pages 124—28,

The constant K can be determined by means of equation (30). In this way the field constants φ' and φ'' may be expressed in terms of the atomic polarizability α_{A_0}. Hence:

$$K = \frac{k}{3}\left[\frac{2\,\varphi'}{L} + \varphi''\right] = \frac{\nu^2 e^2}{\alpha_{A_0}}; \qquad (71)$$

The same function of φ' and φ'' also appears in the equations (56) and (57). At present we will consider equation (57). It may be rearranged as follows:

$$K = \frac{k}{3}\left[\frac{2\,\varphi'}{L} + \varphi''\right] = \frac{3\,BL}{\varkappa}; \qquad (72)$$

Putting the two values of K equal it is seen that a simple relation between the compressibility $\varkappa$ and the atomic polarizability α_{A_0} can be derived. Hence:

$$\varkappa = \frac{3\,BL\,\alpha_{A_0}}{\nu^2 e^2}. \qquad (73)$$

Experimental Test.

With a view to numerical calculation, the value of α_{A_0} from expression (18) is introduced:

$$\varkappa = \frac{3\,BL}{\nu^2 e^2} \cdot \frac{M}{4\,\pi N \delta} \cdot \frac{\varepsilon_0 - n^2}{\left[1 + \frac{\beta}{3}(\varepsilon_0 - 1)\right]\left[1 + \frac{\beta}{3}(n^2 - 1)\right]}; \quad (74)$$

It is not necessary to consider both L and δ as these are related. The volume occupied by a molecule can be expressed both by $\frac{M}{N\delta}$ and by BL^3 (this is the definition of B). Either L or δ, N and M can be eliminated, the latter is found the more advantageous. Hence:

$$\varkappa = \frac{3\,B^2 L^4}{4\,\pi \nu^2 e^2} \cdot \frac{\varepsilon_0 - n^2}{\left[1 + \frac{\beta}{3}(\varepsilon_0 - 1)\right]\left[1 + \frac{\beta}{3}(n^2 - 1)\right]}; \quad (75)$$

It is convenient to unite such magnitudes as are constant for the same valency and lattice type into one numerical constant.

$$C = \frac{9\,B^2}{4\,\pi \nu^2 e^2};$$

(why the number 3 is replaced by the number 9 will appear later).

Two limiting values of β in particular are to be considered. First β equals unity which gives:

$$\varkappa_1 = \frac{CL^4}{3} \cdot \frac{[\varepsilon_0 - n^2]}{\left[1 + \frac{1}{3}(\varepsilon_0 - 1)\right]\left[1 + \frac{1}{3}(n^2 - 1)\right]} = \frac{3\,CL^4[\varepsilon_0 - n^2]}{[\varepsilon_0 + 2]\,[n^2 + 2]}$$

$$\varkappa_1 = CL^4 \left[\frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} - \frac{n^2 - 1}{n^2 + 2}\right] = CL^4 p_A. \quad (77)$$

The latter transformation is convenient because in the thesis on dipole moment[1], there was calculated a table of the familiar polarization and refraction functions:

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[1] HØJENDAHL K.: Studies of Dipole-Moment. Copenhagen (1928) p. 152.

$$p_A = p - p_E;\ p = \frac{\varepsilon - 1}{\varepsilon + 2};\ \text{and}\ p_E = \frac{n^2 - 1}{n^2 + 2};$$

The last calculation also explains why the particular value of C was chosen.

The second limiting value of the compressibility obtained for β equals zero is:

$$\varkappa_2 = \frac{1}{3}\,CL^4[\varepsilon_0 - n^2]; \quad (78)$$

In table 5 columns 4 and 5 such limiting values of the compressibility are compared with the experimental compressibility quoted in column 6. The data are mainly recent ones by BRIDGMAN (marked B.) and by SLATER (marked S.); in a few cases earlier data of RICHARDS and JONES (marked R. J.) are employed. As the different investigators used different units, the data from LANDOLT-BÖRNSTEIN's tables are quoted, and further references are also given there[1].

Experimental data used in the formulae are collected in table 4. ν is the valency; L the distance between neighbour ions, the values quoted are taken for the most part from a survey by EWALD[2] supplemented by recent data from LANDOLT-BÖRNSTEIN's tables[3]. The dielectric constant ε_0, and the square of the refractive index n^2 are transferred from table 1. The few values not given there, if marked by E. were measured by ERRERA[4], and if marked by E. B. were measured by EUCKEN and BÜCHNER[5].

The above theoretical values of $\varkappa$ (77) and (78) are the

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[1] LANDOLT-BÖRNSTEIN: Tabellen. Ergbd. I and III; table 26 p.

[2] Handbuch d. Physik. Bd. 24., 334—5 and 339, by P. P. EWALD.

[3] LANDOLT-BÖRNSTEIN: Tabellen. Ergbd. I, II, III; table 155 d.

[4] ERRERA J.: ZS. Elektrochemie **36**, 818 (1930).

[5] EUCKEN A. and BÜCHNER A.: ZS. physik. Ch. (B) **27**, 321 (1934).

limiting values corresponding to β equals unity or zero. It is also of interest to see what value must be ascribed to β in order that equation (75) shall hold with accuracy. To derive this value, $\varkappa$ in equation (75) is put equal to the experimental value $\varkappa_3$. Dividing equation (78) by equation (75) the constant C, the distance L and the term $\varepsilon_0 - n^2$ cancel, and we have:

$$\left[1+\frac{\beta}{3}(\varepsilon_0-1)\right]\left[1+\frac{\beta}{3}(n^2-1)\right]=\frac{\varkappa_2}{\varkappa_3}; \tag{79}$$

This is a quadratic equation the solution of which is:

$$\beta = -\frac{3(\varepsilon_0+n^2-2)}{2(\varepsilon_0-1)(n^2-1)}\left[1 \pm \sqrt{1+\frac{4(\varepsilon_0-1)(n^2-1)\left(\frac{\varvarkappa_2}{\varkappa_3}-1\right)}{(\varepsilon_0+n^2-2)^2}}\right] \tag{80}$$

The positive sign in front of the surd always leads to numerically large negative values of β. In tables 2 and 3 we found from transmission and reflection data that β as a rule is positive or eventually has a small negative value. Therefore the negative sign in front of the surd is the only one considered, and values of β obtained in this manner are quoted in table 5 column 7.

The variation in β is compared with the variation in some other properties; for instance with d, in column 8, which is the distance of free space between the anions. If these are considered as spheres of radius r and the distance between the centres of the anions is oL where o is a factor, which is constant to the lattice type (see p. 98) we have:

$$d = oL - 2r \tag{81}$$

In the case of the NaCl lattice o is $\sqrt{2}$; in the case of the CsCl lattice it is $\frac{2}{\sqrt{3}}$. Values of the ionic radii are given later in table 7.

Table 4. Experimental Data used in the Formulae.

	Lattice	ν	$L \cdot 10^8$ cm	ε_0	n^2	p_E	p_A	$\frac{\varepsilon_0-n^2}{3}$
LiF	NaCl	1	2.07	9.27	1.92	0.235	0.500	2.45
LiCl	,,	1	2.57	11.05 E.	2.75	0.368	0.401	2.77
LiBr	,,	1	2.74	12.1 E.	3.16	0.419	0.369	2.98
LiI	,,	1	3.03	11.03 E.	3.80	0.483	0.288	2.41
NaF	,,	1	2.31	6.0	1.74	0.198	0.427	1.42
NaCl ...	,,	1	2.81	5.62	2.25	0.294	0.313	1.12
NaBr ...	,,	1	2.97	5.99	2.62	0.351	0.274	1.12
NaI	,,	1	3.23	6.60	2.91	0.389	0.260	1.23
KF	,,	1	2.66	6.05 E.	1.85	0.221	0.407	1.40
KCl	,,	1	3.14	4.68	2.13	0.274	0.277	0.85
KBr	,,	1	3.29	4.78	2.33	0.307	0.249	0.82
KI	,,	1	3.53	4.94	2.69	0.360	0.208	0.75
RbF	,,	1	2.82	5.91 E.	1.93	0.237	0.383	1.33
RbCl ...	,,	1	3.27	5.0	2.19	0.284	0.287	0.93
RbBr ...	,,	1	3.42	5.0	2.33	0.307	0.274	0.89
RbI	,,	1	3.66	5.0	2.63	0.352	0.219	0.79
AgCl	,,	1	2.77	12.3	4.04	0.503	0.288	2.75
AgBr ...	,,	1	2.88	13.1	4.62	0.547	0.254	2.83
MgO	,,	2	2.10	9.8	2.95	0.394	0.352	2.28
CaO	,,	2	2.40	11.8	3.28	0.432	0.353	2.86
SrO	,,	2	2.57	13.3	3.31	0.435	0.366	3.33
CsCl	CsCl	1	3.56	7.20	2.60	0.348	0.327	1.53
CsBr	,,	1	3.71	6.51	2.78	0.372	0.275	1.24
CsI	,,	1	3.95	5.65	3.03	0.404	0.204	0.87
NH_4Cl ..	,,	1	3.34	6.96	2.62	0.351	0.314	1.45
TlCl	,,	1	3.33	31.9	5.10	0.578	0.334	8.90
TlBr	,,	1	3.44	29.8	5.41	0.595	0.311	8.13
CuCl	ZnS	1	2.34	10.0 E. B.	3.57	0.461	0.289	2.14
CuBr ...	,,	1	2.46	8.0 E. B.	4.08	0.507	0.193	1.31
ZnS	,,	2	2.33	8.3	5.07	0.576	0.133	1.08
BeO	ZnO	2	1.65	7.35	2.95	0.394	0.285	1.47
CaF_2	CaF_2	2—1	2.36	8.43	1.99	0.248	0.465	2.15
SrF_2	,,	2—1	2.50	7.69	2.08	0.265	0.426	1.87
BaF_2	,,	2—1	2.69	7.33	2.09	0.266	0.412	1.75

Table 5. Comparison between Theoretical and Experimental Compressibility.

			theoretical		experimental			
	B	C	$\varkappa_1$	$\varkappa_2$	$\varkappa_3$		β	d
			all × 10^6		$cm^2/kg.$			× 10^8 cm.
LiF	2	12.3	1.13	5.5	1.50	S.	0.73	0.27
LiCl	,,	,,	2.16	14.9	3.34	S.	0.66	0.01
LiBr	,,	,,	2.56	20.7	4.23	S.	0.64	— 0.04
LiI	,,	,,	2.99	25.0	5.889	B.	0.54	— 0.11
NaF	,,	,,	1.50	5.0	2.07	B.	0.65	0.61
NaCl	,,	,,	2.40	8.6	4.182	B.	0.47	0.37
NaBr ...	,,	,,	2.63	10.7	4.98	S.	0.44	0.28
NaI	,,	,,	3.48	16.5	6.936	B.	0.45	0.17
KF	,,	,,	2.51	8.6	3.25	S.	0.71	1.10
KCl	,,	,,	3.32	10.2	5.53	S.	0.46	0.82
KBr	,,	,,	3.60	11.9	6.56	S.	0.42	0.73
KI	,,	,,	3.98	14.4	8.37	S.	0.34	0.59
RbF	,,	,,	2.99	10.4				
RbCl	,,	,,	4.04	13.1	6.52	B.	0.51	1.00
RbBr ...	,,	,,	4.61	15.0	7.78	S.	0.45	0.92
RbI	,,	,,	4.83	17.4	9.39	S.	0.39	0.78
AgCl	,,	,,	2.09	19.9	2.4	R. J.	0.89	0.30
AgBr	,,	,,	2.16	24.0	2.7	R. J.	0.85	0.15
MgO	,,	3.08	0.211	1.37	0.5904	B.	0.32	0.33
CaO	,,	,,	0.360	2.93	4.57	B.	— 0.09	0.76
SrO	,,	,,	0.492	4.47				
CsCl	$\frac{8}{3\sqrt{3}}$	7.30	3.84	18.0	5.829	B.	0.63	0.49
CsBr ...	,,	,,	3.81	17.2	6.918	B.	0.50	0.36
CsI	,,	,,	3.63	15.5	8.403	B.	0.33	0.16
NH_4Cl ..	,,	,,	2.86	13.1	5.9	B.	0.41	0.24
TlCl	,,	,,	3.00	80.0	4.8	R. J.	0.74	0.23
TlBr	,,	,,	3.18	83.1	5.2	R. J.	0.71	0.05
CuCl ...	$\frac{16}{3\sqrt{3}}$	29.21	2.53	18.7	2.463	B.	1.02	0.20
CuBr ...	,,	,,	2:06	14.0	2.87	B.	0.75	0.10
ZnS	,,	7.30	0.286	2.32	1.281	B.	0.18	0.32
BeO	,,	,,	0.154	0.79				
CaF_2	$\frac{16}{3\sqrt{3}}$	7.30	1.05	4.87	1.206	B.	0.87	0.07
SrF_2	,,	,,	1.21	5.33	1.58	B.	0.75	0.23
BaF			1.58	6.68	2.07	B.	0.74	0.45

Discussion.

It will be seen that the experimental compressibility has a value which in nearly all cases lies between the two corresponding theoretical values. The only exceptions are CuCl and CaO.

In the case of CuCl the experimental value is so close to the region of the theoretical values, that it is safe to say that here the experimental value is equal to the theoretical value obtained when β is equal to unity, i. e. when the entire Lorentz force is taken to be present.

The value found for CaO is far outside the region of the theoretical values. It is very hard at first sight to understand why CaO alone should show this large discrepancy. An explanation however, is found when the original paper of Bridgman is consulted[1]. Some parts of interest are quoted verbatim: About MgO Bridgman writes:

> "*I was most fortunate to obtain a water-clear transparent crystal of artificial origin*". . . . For this the compressibility at 30° and pressure zero was found to be 5.904×10^{-7}.

(This is the experimental compressibility quoted in table 5 column 6.)

> "*Before the sample of clear crystal MgO was obtained, measurements had been carried through in the regular way on a compressed slug of powdered MgO, made from Kahlbaum's MgO, zur Analyse. . . . The absolute value of the compressibility was of the order of twice that of the crystal, however.*"

It was now found by Bridgman that although the slug had been compressed by an immense pressure it was still porous.

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[1] Bridgmann P. W.: Proc. Amer. Acad. **67**, 345 (1932).

Due to the pores and to the irregular "amorphous" arrangement of the ions in the slug, the compressibility is considerably larger in the slug than in the crystal. About CaO Bridgman writes:

> "*The compressibility of CaO appears not to have been determined previously. The enormously greater value than for MgO is noteworthy and would seem to demand explanation. The crystal structure of MgO and CaO is the same and of the NaCl type. It is highly probable that if clear crystallized CaO could be obtained the same differences as compared with the compressed slug would be found as were shown by MgO.*"

The quotation leaves little to be added. The experimental compressibility of CaO quoted in table 5 column 6 is that of the slug. This is probably more than twice as large as that of crystalline CaO. It is to the crystalline state however, that our relations should be applied. Hence, if the true compressibility be only 2.78×10^{-6}, namely half the compressibility of the slug, it enters into the region of the theoretical values, and the discrepancy of CaO has disappeared.

The above quotation indicates what is the greatest difficulty at present attached to the measurements of compressibility of oxides. It is not in the experimental procedure, although the difficulties overcome by Bridgman undoubtedly are numerous, but it is in the provision of large and perfect crystals, where the difficulty lies.

The same remarks can also be applied to the dielectric constants of oxides. Here the experimental difficulties are admittedly smaller, and discrepancies of the above magnitude are not found. Still the discrepancies of dielectric constants are considerable and hardly due to experimental error. In the cases of three different samples of MgO powder of different origins I found the dielectric constants to be: 9.9; 9.3 and 9.8 respectively, whereas Güntherschulze and Keller[1] found the value 8.2. This means a discrepancy of about 20 per cent. To elucidate the problem of relative errors in dielectric constants of oxides, it would be valuable if the dielectric constant of clear crystalline MgO were measured using Eucken and Büchner's method, which presumably would be the most accurate one in this case.

If the theories of Clausius-Mosotti and Lorenz-Lorentz were absolutely true, and the other assumptions we have introduced were also strictly permissible, the experimental compressibility should be given by equation (77), i. e. it should be equal to $\varkappa_1$. Actually a deviation is found. As a measure of this deviation the factor β was introduced. This factor which represents the virtual fraction of the Lorentz force has been calculated by means of equation (80) and is given in table 5 column 7.

It is interesting to compare the present values of β_K as obtained from compressibility with those earlier values obtained from infra-red data. This comparison is made in table 6.

The values of β_A from absorption agree well with the corresponding values of β_K from compressibility in the cases of the Rb and Cs-halides, whilst β_A is somewhat smaller than β_K in the cases of the Li, Na and K-halides. The values of β_C from the Christiansen wave-length on the average agree with the corresponding values of β_K from compressibility; still large values of β_C are often larger, and small values smaller, than the corresponding values of β_K; but this may well be due to experimental error. It appears on the whole that the haphazard error on the β values from

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[1] Güntherschulze A. and Keller F.: ZS. f. Physik. **75**, 82 (1932).

Table 6. Comparison between β values of different origin.

	Compressibility β_K	Absorption β_A	Christiansen β_C	Reflection β_R
LiF	0.73	0.26	0.15	0.67
NaF	0.65	0.68		— 0.40
NaCl	0.47	0.18	0.16	— 0.10
NaBr	0.44	0.15	0.45	
NaI	0.45	0.25	0.29	
KCl	0.46	0.26	0.43	0.00
KBr	0.42	0.23	0.25	— 0.12
KI	0.34	0.13	0.22	— 0.03
RbCl	0.51	0.52	0.60	0.19
RbBr	0.45	0.42	0.45	
RbI	0.39	0.38	0.67	
CsCl	0.63	0.63	0.72	
CsBr	0.50	0.49	1.07	
NH_4Cl	0.41			0.21
TlCl	0.74		1.07	0.44
TlBr	0.71		1.07	0.68
AgCl	0.89			0.09
AgBr	0.85			0.24
MgO	0.32	1.14	— 0.06	0.02
ZnS	0.18			
CaF_2	0.87			— 0.11
SrF_2	0.75			— 0.07
BaF_2	0.74			— 0.27

infra-red measurements is considerable and larger than the error on the β_K values from compressibility. The values of β_R from reflection are definitely smaller than the other values of β; this deviation, however, may well be due to assumptions involved in FÖRSTERLING's relation.

On the whole we may conclude, that the values of β_K, β_A and β_C agree inside the experimental error, and hence the deviation from a simple relationship may solely be ascribed to the uncertainty of the LORENTZ force. Whether the deviation actually is due to this one cause is another question.

A question of interest is, whether it is possible to find regularity in the variation of β with the periodical system of elements, and whether this variation can be related to other properties of the ions or of the lattice. Important properties of the ions are: the charge; the size as expressed by the ionic radius, and the inner polarisability as expressed by the molar refraction of the ion. In order that properties other than those considered shall not complicate the matter, it is desirable that the ions all should have similar electronic structures. This is achieved in the case of the alkali-halides, because then all component ions have similar noble gas structures with two s. and six p. electrons in the outer electron shell. In this case the charge on the ions is always the same, namely plus or minus one electronic charge. Furthermore the ionic radius and the inner polarizability are related, because they are both dependent on the dimensions of the outer electronic orbit, or in modern language on the distribution of electrons in the outer shell.

In table 7 values of β, as found from compressibility and dielectric constant, are compared with the ionic radii given by GOLDSCHMIDT[1], and with the "molar" refraction of the ion as given by FAJANS and JOOS[2]. A twofold variation is of course to be considered, one with the cation, and one with the anion. It is perceived that the variation of β_K is not

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[1] GOLDSCHMIDT V. M.: Ber. D. chem. Ges. **60**, 1270 (1927).

[2] FAJANS K. and JOOS G.: ZS. f. Physik. **23**, 20 (1924).

completely haphazard, but a regular variation is found. The variation with size and polarizability of the anion (the cation being maintained constant) is the larger and is one way only, i. e. β_K always decreases with increasing size and refraction of the anion. The variation with the cation is not so large, apparently β_K is a minimum for the sodium or potassium ion.

In the β values obtained from absorption, transmission or reflection measurements, similar regularities can only just be traced, but no more than that. The experimental error is probably so large that any regularities are masked.

Table 7. Variation of β_K in the System of Alkali-Halides.

		F	Cl	Br	I	
	Radius → ↓	1.33	1.81	1.96	2.20	P_E^+ ↓
Li	0.78	0.73	0.66	0.64	0.54	0.20
Na ...	0.98	0.65	0.47	0.44	0.45	0.50
K	1.33	0.71	0.46	0.42	0.34	2.23
Rb	1.49		0.51	0.45	0.39	3.58
Cs	1.65		0.63	0.50	0.33	6.24
	P_E^- →	2.50	9.00	12.67	19.24←Refraction	↑

Besides the influence of these ionic properties, influences due to the nature of the lattice must also be considered. One of these is important. By the reduction of expression (56) to give (57) the intrinsic repulsive forces between next-neighbours were neglected. In doing this a systematic error is introduced in the calculation which followed, and this also affects β_K. The repulsion between next-neighbours depends largely on the degree of contact between them. We have introduced the free distance d quoted in the last column of table 5 as a measure of the degree of contact between anions. Contact between cations is not found. If there is no contact, i. e. if the free distance is large, the repulsion between next-neighbours is presumably negligible. This will be seen if the values of β_K found for RbCl, RbBr and RbI are compared with those found for CsCl, CsBr and CsI. These salts crystallize in two different lattice-structures, having largely different distances between anions, which distances however, are all so large that no contact occurs. As will be seen from table 7 this sudden change in distances between anions is not followed by any large change in β_K. The closest contact is found for LiCl, LiBr and LiI, it seems likely that the remarkable increase in β_K found for these compounds is probably caused by the effect of anions in contact. The effect of repulsion between anions will be such that the compressibility is diminished. According to equation (75) a decrease in $\varkappa$ all other things being equal will manifest itself as an increase in β.

This probably explains the peculiar variation of β_K with size and polarizability of the cation. It is likely that β always decreases with decreasing size and polarizability of the cation; in the case of the lithium salts, however, this decrease is more than compensated by the increase due to anion contact.

The effect of other changes in the nature of the ions can be estimated if salts other than the alkali-halides are compared with them. The effect of valency for instance, is estimated if values of β_K for the oxides of the metals of the second group are compared with those of the alkali-halides.

Now it must be borne in mind that in the calculation of β_K the valency has already been taken into account, and so the present estimation is to some extent a proof of the relationship. The value of β_K for MgO is 0.31, which is somewhat smaller than that for NaCl namely 0.47, with which it is reasonable to compare it, since the O^{--} ion has a refraction similar to that of the Cl^- ion. The experimental error in the value of β_K for CaO is too large for a test. The small value of β_K for ZnS is probably caused by the large polarizability of the S^{--} ion, furthermore the Zn^{++} ion has not noble gas structure. Otherwise it is found that salts whose cations have not noble gas structure, exhibit comparatively large values of β_K. Such for instance is the case of the Cu^+, Ag^+ and Tl^+ chlorides and bromides. The ionic radii of these cations are comparable with those of the alkali ions, whereas the refractions are considerably larger. Hence it is argued, that the internal polarizability rather than the ionic radius has the principal influence on β. This influence can be generalized as follows: "β increases with increasing internal polarizability or refraction of the cation, and decreases with increasing refraction of the anion!" So far the relationship is empirical. In this respect and in others, it is similar to the relationship holding for the variation of the molar refraction of salts as dealt with by Fajans and Joos[1].

The Force-Centre of the Intrinsic Repulsive Force.

The deviation from equation (77) is not to be ascribed to the uncertainty of the Lorentz force alone, the irrelevance

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[1] Fajans K. and Joos G.: ZS. f. Physik. **23**, 1 (1924).

of some other assumption involved in the treatment may also contribute.

A possible cause of discrepancy has been introduced by the assumption that the nucleus is the force-centre of the polarized ion. This assumption was introduced in order to derive expression (70), but an objection was made then. In view of the theory of Heitler and London[1] it is evident that the above assumption cannot be correct. The intrinsic repulsive force is caused by an interaction of the electrons rather than of the nuclei, it must therefore depend on the relative location of the electrons rather than on that of the nuclei. Now it is a question whether the intrinsic repulsive force can be in any way regarded as a central force. But as calculation will be rendered much more difficult without this assumption, we will try to retain it. The force-centre cannot always be situated at the nucleus, it must be shifted in the same direction as are the electrons. As a reasonable conception we will now assume the force-centre to be represented by the mass- or charge-centre of the outer electron shell.

The separation into outer and inner electrons is arbitrary, especially as it is not granted that the number of outer electrons is an integer, because the electron cannot be considered 'outer' in all parts of its orbit. Since the number of outer electrons is thus unsettled, it is suggestive to consider this as the unknown magnitude which is to be determined on the assumption that the present cause of discrepancy is the preponderant one. It is assumed that only the outer electrons contribute to the internal polarizability α_E of the ion. If now the strength of the inner field of force is unity the displacement of the outer electron shell with regard to the nucleus becomes:

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[1] London F.: Naturwissenschaften. **17**, 516 (1929).

$$s_1 = \frac{\alpha_E^+}{\gamma_1 e} \text{ for the cation, and } s_2 = \frac{\alpha_E^-}{\gamma_2 e} \text{ for the anion} \quad (82)$$

The numbers of outer electrons γ_1 and γ_2 are assumed to be equal in the following, and the suffixes are therefore omitted.

By action of the field the ions as such are also displaced. According to equations (3—5) the relative displacement of the nuclei is given by:

$$s_3 = \frac{\alpha_A}{\nu e};$$

The electrons of both anion and cation are displaced in the same direction as the anion as such, whereas the cation as such is displaced in the opposite direction. It follows that the relative displacement of the two outer electron shells is given by:

$$s_4 = s_3 + s_2 - s_1 = \frac{\alpha_A}{\nu e} + \frac{\alpha_E^- - \alpha_E^+}{\gamma e}; \quad (83)$$

As argued above the intrinsic repulsive force depends on the relative displacement s_4 of the electron shells, and not on that of the nuclei, namely s_3; hence it will be realized that s_4 and not s_3 ought to be introduced in equation (68). In order to correct equation (70) and the equations which followed we may introduce the correction factor:

$$\frac{s_4}{s_3} = 1 + \frac{\nu}{\gamma} \cdot \frac{\alpha_E^- - \alpha_E^+}{\alpha_A}; \quad (84)$$

This correction factor can be applied to the theoretical compressibility $\varkappa_1$ obtained from equation (77). If the present cause of discrepancy is the preponderant one the experimental compressibility $\varkappa_3$ should be obtained thereby. This means that the ratio s_4/s_3 should be equal to the ratio $\varkappa_3/\varkappa_1$. With a view to numerical calculation the following transformations are performed.

$$\frac{\varkappa_3}{\varkappa_1} - 1 = \frac{\nu}{\gamma} \cdot \frac{P_E^- - P_E^+}{P_A} = \frac{\nu}{\gamma} \cdot \frac{P_E}{P_A} \cdot \frac{P_E^- - P_E^+}{P_E} = \frac{\nu}{\gamma} \cdot \frac{p_E}{p_A} \cdot \frac{P_E^- - P_E^+}{P_E^- + P_E^+};$$

From this again γ can be calculated.

$$\gamma = \frac{\nu}{\frac{\varkappa_3}{\varkappa_1} - 1} \cdot \frac{p_E}{p_A} \cdot \frac{P_E^- - P_E^+}{P_E^- + P_E^+}; \quad (85)$$

The reason why the transformation was made in the above manner is that ν, p_E and p_A have already been quoted in table 4; $\varkappa_1$ and $\varkappa_3$ in table 5; and P_E^+ and P_E^- in table 7. The values of γ calculated for the alkali-halides by means of the above equation are tabulated in table 8. The arrangement is similar to that of table 7.

Table 8. Number of Effective Outer Electrons γ.

	F	Cl	Br	I
Li	1.21	1.61	1.69	1.69
Na	0.82	1.13	1.33	1.47
K	0.10	0.90	1.06	1.25
Rb		0.66	0.91	1.17
Cs		0.37	0.56	0.77

As will be seen from the table 8, γ is not found to be the same for all salts. It is furthermore considerably smaller than six, the number of electrons in the loosely held *p*-subgroup. Thus it is likely that the present cause of discrepancy is not the only one. On the other hand it cannot be neglected as being inconsiderable. As argued above, all six p electrons cannot be considered 'outer' electrons at the same time. They presumably describe orbits round the nucleus. The deflection caused by an external field is considerably larger at an outer, than at an inner loop of an orbit. Hence electrons in inner loops do not contribute nearly as much as those in outer loops. We may express this by asserting that the electrons in inner loops do not count at all. As a consequence of this the number of effective outer electrons may be considerably smaller than six; still one can hardly expect it to be as small as unity.

Too small values for the number of outer electrons are also found from the relation of Drude and Voigt, concerning the dispersion in ultra-violet. By means of this relation, the number of outer electrons in the noble gases were determined by Cuthbertson and Quarder. The resultant numbers quoted from Handbuch der Physik are[1]:

He 1.11; Ne 2.37; A 4.58; Kr 4.90; Xe 5.61.

It will be seen that these numbers are also smaller than the number of electrons usually taken to be in the outer shell. The explanation is similar to that given above.

Note on the Effect of Thermal Motion.

Professor J. A. Wasastjerna (in a discussion following his reading of the present manuscript) commented on assumption 3) on page 64 i. e.:

The lattice shall be perfect and the ions devoid of thermal motion. Actually the latter is not even the case at the absolute zero of temperature, but the amplitudes are generally small.

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[1] Handbuch der Physik: **20**, 490—91. Wolf K. L. and Herzfeld K. F.

Wasastjerna remarked that the amplitudes are not small under any circumstances. At room temperature the amplitudes are of the order ten per cent of the distance between the ions, and at the absolute zero of temperature they are of the order five per cent. of the distance. He pointed out that the neglect of thermal motion is an important cause of discrepancy.

It is admitted that the neglect of thermal motion contributes to the discrepancy; but it is another question how great this contribution would be and how it may be evaluated. In the writers opinion the proper procedure would be, to measure the property in view at a variety of temperatures, to plot in a diagram the measured values against the corresponding amplitudes, and to extrapolate to zero amplitude. (Not to the absolute zero of temperature.) The present experimental data, however, are too scant and inexact for performing such an extrapolation with any degree of accuracy. Possibly the compressibility can be extrapolated by means of the procedure proposed by Hildebrand[1], Born and Mayer[2] and Wasastjerna[3,4]; but as regards the dielectric constant and the residual ray, new experiments must be undertaken at various temperatures, before the effect of thermal motion can be evaluated.

Summary.

1) The entire treatment is restricted to regular ionic lattices, and is subject to certain assumptions which are stated in the preliminary pages.

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[1] Hildebrand J. H.: ZS. f. Physik. **67**, 127 (1931).
[2] Born M. and Mayer J. E.: ZS. f. Physik. **75**, 1 (1932).
[3] Wasastjerna J. A.: Soc. Sc. Fennica. Com. Phys. Mat. VIII. **20** (1935).
[4] Wasastjerna J. A.: Soc. Sc. Fennica. Com. Phys. Mat. VIII. **21** (1935).

2) The theory of the "LORENTZ" force is put forward in a simple manner mainly following DEBYE, but emphasizing the inherent uncertainty pointed out by HECKMANN. As a measure of the uncertainty the parameter β is introduced which denotes the virtual fraction of the classical LORENTZ force.

3) By means of a simple statement, regarding the inertia of a vibrating ion and the forces acting on it, an expression for the dispersion of the dielectric constant in the far infra-red is derived. The influence of damping being neglected, the dielectric constant becomes infinite at the natural frequency of the ionic motion. The corresponding wave-length is found to be given by HECKMANN's relation, which includes BORN's relation as a special case.

4) The natural frequency is approximately equal to the frequency of the absorption maximum, but not to that of the reflection maximum. (The residual ray.) The shape of the reflection curve is discussed.

5) The various relations are tested on the experimental data available. The discrepansies may be ascribed solely to the uncertainty of the LORENTZ force, whence reasonable values of β have been determined.

6) The intrinsic repulsive force between two ions is assumed to be a short range central force. It is found convenient to expand it into a TAYLOR series.

7) The compressibility can be expressed as a function of the second and the third coefficient of this TAYLOR series.

8) The change in potential energy of intrinsic repulsive forces arising from a relative displacement of the lattices of positive and negative ions respectively is computed. For small displacements the resultant elastic force is proportional to the displacement and independent of the direction in the crystal. The proportionality factor is expressed by the same function of the second and the third coefficient of the TAYLOR series as is the compressibility.

9) Both coefficients therefore can simultaneously be eliminated whereby a relation connecting measurable quantities is derived. These are: the compressibility, the lattice dimensions, the dielectric constant and the refractive index.

10) The parameter β is the only arbitrary magnitude involved. It can therefore be determined by means of the experimental data. Values between unity and zero are found in nearly all cases. The values of β found from compressibility data are similar to those found from the absorption maximum in the far infra-red, and to those found from the CHRISTIANSEN wave-lengths (measured by BOWLING BARNES and BONNER), but somewhat larger than those found from reflection data.

11) The compressibility as a rule is measured with greater accuracy and for more compounds than is the absorption, transmission or reflection in the far infra-red. As a consequence the values of β found from compressibility data are employed in an empirical manner to elucidate the relationship between the deviation of the LORENTZ force and various properties of the ionic lattice.

12) Thus it is found that β increases with increasing internal polarizability of the cation, and decreases with increasing internal polarisability of the anion.

13) Intrinsic repulsive forces between next-neighbours are

found to be insignificant except in the case of anion contact which causes an increase in β.

14) The deviation expressed by β may also be ascribed partly to an irrelevance of some of the other assumptions involved. For instance it is likely that the intrinsic repulsive force is not a central force, and if it has to be described as such, then the force-centre of the polarized ion cannot be situated at the nucleus. The alternate conception of the force-centre as situated at the charge-centre of the outer electron shell is considered. It is likely that part of the deviation has to be explained in some such way.

15) The neglect of thermal motion may also contribute to the deviation.

III.

ON AN ELEMENTARY METHOD OF CALCULATING MADELUNG'S CONSTANT

WITH A DETERMINATION OF THE ELECTROSTATIC LATTICE ENERGY OF THE IDEALIZED CALCITE LATTICE

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The lattice energy of a salt is defined as the energy necessary to form free gas ions from one grammolecule of the crystal; it is not to be confused with the heat of vaporisation of the salt crystal; salt vapours, at attainable temperatures at all events, do not consist of separate ions, but of clusters of associated ions, these being the molecules in the ordinary sense. The difference between the heat of vaporization and the lattice energy, which is the energy gained by the association and mutual polarization of the ions in forming the cluster, has been calculated by BORN and HEISENBERG[1] who, computing also the lattice energy, were able to evaluate the heat of vaporization of the alkali-halides in fair agreement with experimental data.

The lattice energy is also of great importance as regards the solubility of salts in various solvents. According to FAJANS[2] the heat of solution of a salt in a solvent is equal to the difference between the heat of solvation of the gas ions, and the lattice energy of the salt crystal. This has been emphasized by BJERRUM[3]. In a more qualitative manner the lattice energy is related to the hardness, the melting point, and several other properties of the salt crystal.

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[1] BORN M. and HEISENBERG W.: ZS. f. Physik. **23**, 388 (1924).
[2] FAJANS K.: Naturwissenschaften. Heft **37**, 1 (1921).
[3] BJERRUM N.: Ber. D. chem. Ges. **62**, 1091 (1929).

The lattice energy can be determined by means of Born's cycle[1], this method, however, has the disadvantage that the electron affinity of the anion is implied, and as a rule this energy term is badly known. The lattice energy can also be calculated directly on the basis of certain assumptions regarding the forces between the ions. These forces can be separated into two types; a) the electrostatic force which follows Coulomb's law, and b) a short range repulsive force which keeps the ions apart; and the lattice energy can accordingly be separated into a major electrostatic part, and a minor repulsive part. A calculation of the repulsive part was first carried out by Born and Landé[2], and afterwards refined by Born and Mayer[3] and Wasastjerna[4]; this part amounts to about one tenth of the electrostatic part; it cannot be determined with any great accuracy, since an accurate expression for the relation between repulsive force and distance of ions is not known.

The calculation of the electrostatic part of the lattice energy is the theme of the present investigation, and in what follows we will restrict ourselves to that item: The electrostatic potential energy of two ions of charges νe and $\nu_1 e$ at a distance L is:

$$\varphi = \frac{\nu\nu_1 e^2}{L}; \tag{1}$$

To obtain the potential energy ϕ of an ion with respect to all other ions in the lattice we must sum up over all distances with due regard to the signs of the ions. It is convenient to introduce a standard distance L_0.

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[1] Born M.: Verh. d. D. Physik. Ges. **21**, 679 (1919).

[2] Born M. and Landé A.: Verh. d. D. Physik. Ges. **20**, 210 (1918).

[3] Born M. and Mayer J. E.: ZS. f. Physik. **75**, 1 (1932).

[4] Wasastjerna J. A.: S. Sc. Fennica. C. Phys. Mat. VI. **22**; VIII. **20**; VIII. **21**.

$$\phi = \frac{\nu\nu_1 e^2}{L_0} \sum{}' \frac{L_0}{L} = \frac{\nu\nu_1 e^2}{L_0} j; \tag{2}$$

The factor j is termed Madelung's constant, the numerical value of it is proportional to the particular value chosen for L_0, but for a given standard distance it is a constant number characteristic of the lattice. The electrostatic lattice energy of a grammolecule Φ is only half the sum of the ϕ values of the constituent ions, for in our summation we count each distance twice, counting both a—b and b—a.

$$\Phi = \frac{N}{2}(\phi_1 u + \phi_2 v + \ldots.); \tag{3}$$

N is Avogadro's constant, and u and v are the numbers of ions of different types in the molecule. The constant j cannot be evaluated by an uncritical summation, because the ratio $\frac{L_0}{L}$ decreases only slowly, and the number of ions increases rapidly with the distance; it is therefore necessary to proceed on a definite plan.

Madelung[1], who first calculated the value of j for the NaCl lattice, considered at the first instance the potential of an ion with respect to a linear, equidistant row of alternately charged ions. If the reference ion is one of the row, the summation gives a well known series, namely:

$$2\left(1-\frac{1}{2}+\frac{1}{3}-\frac{1}{4}\ \ldots\ldots\right) = 2\ ln.\ 2. = 1.3863 \tag{4}$$

If, however, the ion is outside the row, the summation is by no means so simple. Madelung evolved the distribution of electric charge along the line of the row into a Fourier

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[1] Madelung E.: Physik. ZS. **19**, 524 (1918).

series, which means that he replaced the discrete charges by a number of superimposed continuous charges, having charge densities varying as cosine functions. In practice only two members of the FOURIER series need consideration, namely that having the ionic distance as period, and that having one third of this distance as period. The problem is now reduced to the determination of the potential energy of an ion with respect to a linear charge the density of which varies as a cosine function. This problem can be solved by means of high mathematics, the solution involving a cylinder function, namely HANKEL's function that is tabulated in JAHNKE and EMDE's Funktionentafel[1]. The potential energy was found to decrease considerably with the distance between the ion and the row, and hence the summing up of the contributions of comparatively few rows sufficed to give a reasonably accurate value of MADELUNG's constant for the entire lattice. EWALD[2] has proposed another method which, however, is still less understandable to persons not acquainted with the highest of mathematics.

Now it is not my opinion that the use of high mathematics to physical chemical problems should be abandoned, since in many cases there is no other way, still if a more elementary way can be found this is worth while, because a considerably greater number of persons will then be able to understand the derivation. That an elementary method of calculating MADELUNG's constant can be derived, which is even less cumbersome as regards the numerical calculation than the above methods, I should like to show:

It is a familiar fact that crystals, growing from a solution, as a rule acquire a nearly perfect external shape. This is not accidental, on the contrary, we must infer that the perfect crystal is more probable, and this again can only be explained by the internal energy or the lattice energy of the perfect crystal attaining a maximum value. This value depends on the size of the crystal, but only slightly, as will be seen later; this is in agreement with the fact that the solubility of small crystals is only slightly greater than that of large crystals, granted of course that the crystals are perfect. In order that the lattice energy of even a small crystal shall approach closely to that of an infinite crystal, the crystal must not only be perfect in every way, but it must presumably also be electro-neutral, i. e. it must contain equal numbers of positive and negative charges. The fact that a maximum of lattice energy has been attained, means that the forces on the outside charge neutralize each other, which can only be the case if the crystal is electro-neutral.

The new method of calculating electrostatic lattice energy is the following: In the case of the smallest possible perfect and electro-neutral crystal we sum up the reciprocals of the relative distances between one reference ion and all other ions in the crystal whereby a value j_1 of the MADELUNG constant for the minute crystal is obtained. Afterwards the crystal is allowed to grow equally in all directions by deposit of a mono-ionic layer or a layer of crystal units, and in this way a larger perfect and electro-neutral crystal is built. Now the reciprocals of the distances between the above reference ion and the ions of the newly deposited layer are summed up as before, and a value j_2 is obtained which is termed the contribution of the second division. In a similar manner we determine the contributions of the subsequent divisions. Now it will be observed that these contributions diminish exceedingly with the distance from the reference ion, and as a

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[1] JAHNKE F. and EMDE E.: Funktionentafel. Leipzig (1909) p. 135.

[2] EWALD P. P.; Ann. d. Physik. **64**, 253 (1921).

rule only few contributions need be summed up to give practically the entire electrostatic lattice energy of the infinite lattice.

In order to demonstrate the method by the simplest example we will consider a two-dimensional lattice, for instance, an ion bearing (1, 0, 0) plane of the NaCl lattice, see Fig. 1. In this the reference ion is marked *R*, and the relative distances from the reference ion are written in the circles representing the other ions. This relative distance can always be expressed by $\sqrt{n}$ where n is a whole number, which facilitates the calculus, as $^1/\sqrt{n}$ is tabulated in Barlow's tables of squares and cubes. The ions are classified into divisions as will be seen from the figure, each new division forming a frame around the former one. The summation was carried out on a calculating machine, and the following contributions were found.

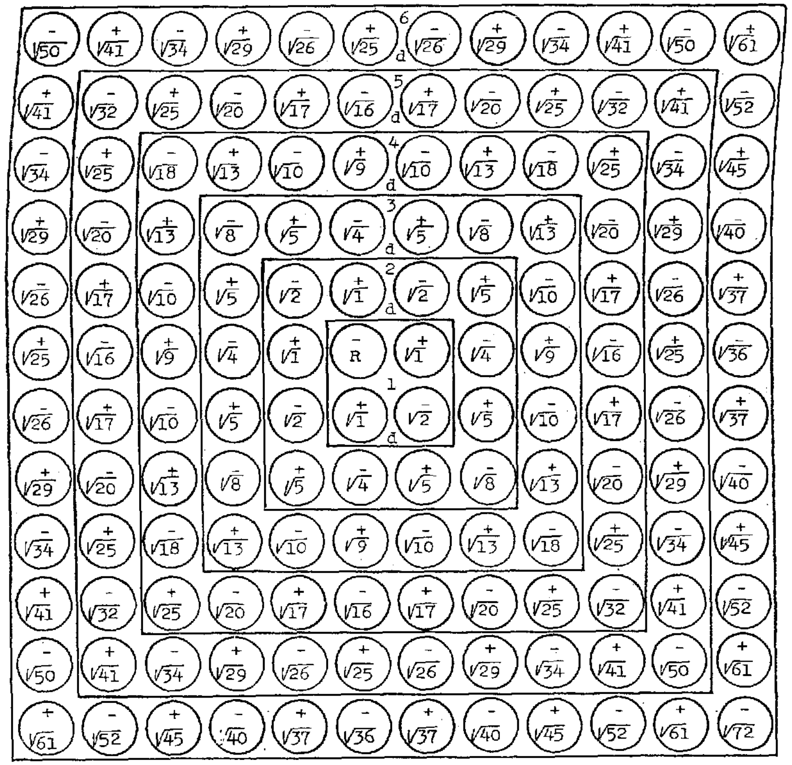

Fig. 1.

1 division: $\frac{2}{1}-\frac{1}{\sqrt{2}}$ $= 1.29289$

2 division: $\frac{2}{1}-\frac{3}{\sqrt{2}}-\frac{2}{\sqrt{4}}+\frac{4}{\sqrt{5}}-\frac{1}{\sqrt{8}}$ $= 0.31398$

3 division: $= 0.00365$

4 division: $= 0.00299$

5 division: $= 0.00098$

6 division: $= 0.00044$

Total 1.61493 ± 0.001

The electrostatic lattice energy of the entire NaCl lattice is more important. The smallest possible crystal of NaCl consists of eight ions forming a cube. The reference ion is one corner of this cube. The subsequent divisions form something similar to a system of Chinese boxes. The calculation was carried out as above using Barlow's tables and the calculating machine. The following contributions were obtained:

1 division: $\frac{3}{1}-\frac{3}{\sqrt{2}}+\frac{1}{\sqrt{3}}$ $= 1.456030$

2 division: $\frac{3}{1}-\frac{9}{\sqrt{2}}+\frac{7}{\sqrt{3}}-\frac{3}{\sqrt{4}}+\frac{12}{\sqrt{5}}-$

$-\frac{12}{\sqrt{6}}-\frac{3}{\sqrt{8}}+\frac{6}{\sqrt{9}}-\frac{1}{\sqrt{12}}$ $= 0.295739$

3 division: $= -0.004729$

4 division: $= 0.000679$

5 division: $= -0.000221$

Total 1.747498 ± 0.0005

Note! that a value of 1.7518, which is only 3 per mille in error, can be obtained from the first two divisions. This will suffice to demonstrate for students how Madelung's constant may be determined. In order to approximate Madelung's constant as closely as possible from the above data, the contributions of the subsequent divisions have been evaluated by extrapolation. In diagram 2 the logaritms of the numerical values of the above contributions are plotted against the numbers of the divisions, and the logaritms of the subsequent contributions are graphically extrapolated. In this manner we found:

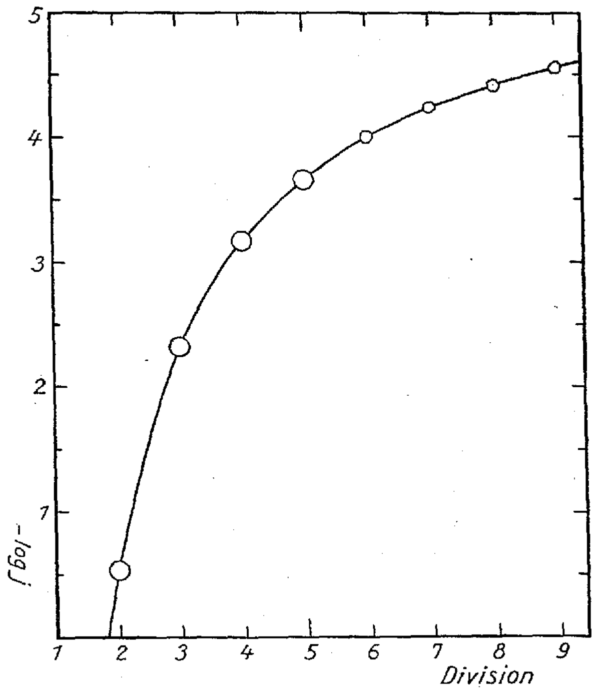

Fig. 2.

6 division: = 0.000100
7 division: = −0.000059
8 division: = 0.000040
9 division: = −0.000028
estimated for further divisions = 0.000007

Total 0.000060
added to the above 1.747498

we obtain as our most accurate value 1.747558

This is very close to the values found by Madelung l. c. and by Emersleben[1] who found: 1.747557.

Kossel[2] has calculated the energy involved in placing an ion anywhere at the surface of a NaCl crystal. He found that this energy depends, in a large measure, on the position of the ion, and thus explains why crystals grow in a definite habit. The different energy terms determined by Kossel can easily be derived from the above values of the electrostatic energy of an ion with respect to a row, a plane layer, or a three-dimensional lattice of ions. We can, for instance, determine the energy gained by placing an ion in the proper position outside a plane (1, 0, 0) surface of a large NaCl crystal. In order to do that we will consider an ion inside a large NaCl crystal, its electrostatic energy with respect to all other ions being expressed by Madelung's constant 1.7476. We are now removing all ions except the reference ion in a (1, 0, 0) layer. The energy required for removing these ions from the reference ion was determined above to be 1.6149. The energy left, i. e. 1.7476 − 1.6149 = 0.1327 is the energy of the reference ion placed properly outside

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[1] Emersleben O.: Physik. ZS. **24**, 104 (1923).

[2] Kossel W. in a monograph edited by Falkenhagen: Quantentheorie und Chemie.

the (1, 0, 0) surfaces of two crystals, hence this energy is just twice the energy to be determined. We find 0.0663, whereas Kossel found 0.0662. In a similar manner we find the energy gained by placing an ion properly outside the edge of a (1, 0, 0) layer to be equal to: $^1/_2(1.6149 - 1.3863) = 0.1143$, whilst Kossel found 0.1144. We are thus able to confirm Kossel's data.

The Electrostatic Lattice Energy of the Calcite and the Sodium Hydrofluoride Lattices.

The electrostatic lattice energy has, as far as I know, only been calculated for the NaCl lattice, the CsCl lattice, the ZnS lattices (both blende and wurtzite), the CaF_2 lattice, the Cu_2O lattice and the two TiO_2 lattices (rutile and anatase)[1]. The calcite lattice is one of the simplest and most important among the lattices which, as I believed, had not been considered earlier; afterwards, however, I perceived that Evjen[2] had already considered the idealized calcite lattice. Later on Evjens data will be compared with mine. As we do not know how the electric charge of the carbonate ion is distributed, the lattice will be idealized in such a way that the total charge becomes located at the centre of the ion, i. e. on the carbon atom. It is not likely that the distribution of electricity inside the carbonate ion will affect the lattice energy to any great extent. By this idealization the calcite lattice becomes equivalent to a NaCl lattice, compressed along a trigonal axis. In a similar manner the $NaHF_2$ lattice corresponds to a NaCl lattice, expanded along a trigonal axis. The ions in the planes perpendicular to the trigonal axis are all alike, and form a net-work of equilateral triangles; the distances between ions in such a plane are not altered by compression or expansion, but so are the distances between the ionic layers. The distance between neighbouring layers, which is the smallest intercept on the principal axis, will be employed for a standard distance L_0. The distances within the layer can be expressed by $L_1 \sqrt{m}$, where m is a whole number, and L_1 the radius of a circle circumscribing the equilateral triangle. The ratio $p = \frac{L_1}{L_0}$ is used for the parameter of the lattice. We are going to calculate the values of Madelung's factor j for a number of parameters, and in order to facilitate the calculation the parameters chosen are square roots of whole numbers; the distance between any two ions may then be expressed by $L_0 \sqrt{n}$ where n is a whole number, whence Barlow's tables can be employed as before.

The ions in the lattice are classified into divisions as before, but now these divisions are rhombohedral shells, and as a rule not cubical. A model of the NaCl lattice, and drawings of its (1, 1, 1) planes, were of great use in classifying and calculating relative distances. These drawings, however, are not reproduced, as they would occupy too much space, it is considered sufficient to give the (squares of) the relative distances between the reference ion and the other ions in the inner rhombohedron (Table 1) and those between the reference ion and the ions in the second division (Table 2).

The squares of the distances from the principal axis through the reference ion is given in the first column, and the square of the distance from the layer containing the reference ion is given in the second column. The last column gives the

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[1] For references see: Born M. and Bollnow O. F.: Hdb. d. Physik. **24**, 438 (1927).

[2] Evjen H. M.: Physical Review. **39**, 680 (1932).

Table 1. Inner Rhombohedron or 1st Division.

dist. from axis	dist. from layer	parameter						number
		1	$\sqrt{2}$	$\sqrt{3}$	$\sqrt{4}$	$\sqrt{5}$	$\sqrt{8}$	
		square of distance						
1	1	2	3	4	5	6	9	+ 3
1	4	5	6	7	8	9	12	− 3
0	9	9	9	9	9	9	9	+ 1

Table 2. 1st Rhombohedral Shell or 2d Division.

dist. from axis	dist. from layer	parameter						number
		1	$\sqrt{2}$	$\sqrt{3}$	$\sqrt{4}$	$\sqrt{5}$	$\sqrt{8}$	
		square of distance						
1	1	2	3	4	5	6	9	+ 3
1	4	5	6	7	8	9	12	− 3
0	9	9	9	9	9	9	9	+ 1
4	1	5	9	13	17	21	33	+ 3
3	0	3	6	9	12	15	24	− 6
9	0	9	18	27	36	45	72	− 3
4	1	5	9	13	17	21	33	+ 3
7	1	8	15	22	29	36	57	+ 6
4	4	8	12	16	20	24	36	− 3
7	4	11	18	25	32	39	60	− 6
3	9	12	15	18	21	24	33	+ 6
9	9	18	27	36	45	54	81	+ 3
1	16	17	18	19	20	21	24	− 3
4	16	20	24	28	32	36	48	− 3
1	25	26	27	28	29	30	33	+ 3
0	36	36	36	36	36	36	36	− 1

number of ions having the same distance, the sign plus indicating attraction, and the sign minus repulsion.

The cases considered above were those in which the parameter p is the square root of a whole number. A calculation has, however, also been carried out in some cases where the number under the surd was a simple fraction $\sqrt{\frac{k}{l}}$. In order to make use of BARLOW's tables, we were here obliged to choose another standard distance, namely one which is a $\sqrt{l}$ part of the distance between the layers. In this way the relative distances between the ions become expressed by square roots of whole numbers. Afterwards when the reciprocals have been summed up to give the contribution of the division, we may transfer to the usual value of L_0 by multiplying the total by $\sqrt{l}$. Such transferred values for the contributions are quoted in the following table 3 together with the values obtained by means of the above tables 1 and 2.

Table 3. MADELUNG's Factor for the Idealized Calcite Lattice.

Parameter	$\sqrt{\frac{1}{2}}$	$\sqrt{\frac{2}{3}}$	1	$\sqrt{\frac{3}{2}}$
1 division........	+ 1.3686	+ 1.2684	+ 1.1130	+ 0.9515
2 division........	− 0.4178	− 0.1651	+ 0.0462	+ 0.1441
3 division........	+ 0.0761	+ 0.0505	+ 0.0211	+ 0.0040
4 division........	− 0.0284	− 0.0198	− 0.0098	− 0.0029
Total	+ 0.9985	+ 1.1340	+ 1.1705	+ 1.0967

Parameter	$\sqrt{2}$	$\sqrt{3}$	$\sqrt{4}$	$\sqrt{5}$	$\sqrt{8}$
1 division........	+ 0.8406	+ 0.6994	+ 0.6143	+ 0.5581	+ 0.4673
2 division........	+ 0.1707	+ 0.1747	+ 0.1660	+ 0.1572	+ 0.1416
3 division........	− 0.0027	− 0.0092	− 0.0137	− 0.0175	− 0.0264
4 division........	+ 0.0004	+ 0.0035	+ 0.0049	+ 0.0058	+ 0.0075
Total	+ 1.0090	+ 0.8684	+ 0.7715	+ 0.7036	+ 0.5900

The parameter value $\sqrt{2}$ corresponds to the undeformed NaCl lattice considered page 141; hence it is an important check on the calculation to compare the present values of the contributions, division by division, with those found before. The earlier standard distance is $\sqrt{3}$ times as large as the present one, and hence each of the former contributions should be $\sqrt{3}$ times as large as the present one. For the total we find: $1.0090 \times \sqrt{3} = 1.74764$, whereas the first four divisions on page 141 gave a total of 1.74772. The discrepancy of 0.05 per mille gives a measure of the inaccuracy of the calculation itself. In the case of the NaCl lattice, i. e. for the parameter value $\sqrt{2}$, the electrostatic potential energy of an inner ion in a minute crystal consisting of 512 ions is practically equal to that of an ion in an infinite crystal, for other values of the parameter this will not be the case. A measure of the error, due to the neglection of outside ions, can be obtained in the case of the parameter value $\sqrt{8}$. For this value the deformed NaCl lattice becomes a CsCl lattice, as will be observed when the values of relative distances in tables 1 and 2 are examined. An accurate value of MADELUNG's constant for the infinite CsCl lattice has been calculated by EMERSLEBEN l. c. who (on EWALD's method) found a value of 2.035356 using the lattice spacing for a standard distance; transferring this to our standard distance by dividing by $\sqrt{12}$ we obtain a value of 0.587557. The difference of 4.1 per mille between this value and our corresponding value of 0.5900 is a measure of the error arising from our neglection of the outside ions. This is the case with the parameter value $\sqrt{8}$, for the value $\sqrt{2}$ the error is insignificant, hence we expect this error not to exceed, at any rate, one per cent, not only in the interval between the parameter values of $\sqrt{2}$ and $\sqrt{8}$, but also between those of $\sqrt{2}$ and $\sqrt{\frac{1}{2}}$. In the case of the CsCl lattice we have not approached the accuracy of EMERSLEBEN's calculations, as we did in the case of the NaCl lattice, still it is of pedagogical interest that a reasonably accurate value of MADELUNG's constant can be calculated by the elementary method also in the case of the CsCl lattice.

The following empirical formula was derived using the values of the totals from table 3 corresponding to the parameters $\sqrt{\frac{1}{2}}$, $\sqrt{\frac{2}{3}}$, 1, $\sqrt{2}$ and $\sqrt{5}$:

$$j = +0.3573 + 2.085\frac{1}{p^2} - 1.9185\frac{1}{p^4} + 0.7754\frac{1}{p^6} - 0.1286\frac{1}{p^8}; \quad (5)$$

The parameters not employed in the adjustment of the formula showed the following deviations: for $p = \sqrt{\frac{3}{2}}$, -2.2 per mille; for $p = \sqrt{3}$, $+2.5$ per mille; for $p = \sqrt{4}$, $+1.5$ per mille, and for $p = \sqrt{8}$, $+1.8$ per mille. To this must be added the more significant error due to the neglection of outside ions, whence the total error becomes of the order of one per cent.

The electrostatic part of the lattice energy of one gram-molecule can be calculated by means of the equations (2) and (3). In the present case ν and ν_1 are equal, and Φ_1 and Φ_2 are equal, whereas u and v are both equal to unity, and hence these equations may be reduced to:

$$\Phi = Ne^2\frac{\nu^2 j}{L_0} = 3.300 \times 10^{-6}\frac{\nu^2 j}{L_0}\,\text{k cal}. \quad (6)$$

The numerical factor is computed, using the value of 6.061×10^{23} for AVOGADRO's number N, and 4.774×10^{-10} e. s. u. for the electronic charge e; furthermore, the conversion factor 4.185×10^{10} is employed in order to express the energy in kcal. Experimental and calculated data are given in table 4.

Table 4. The Electrostatic Lattice Energy pro Grammolecule

of compounds crystallizing in the calcite or the $NaHF_2$ lattice.

	ν	a_h Å	c_h Å	L_0 Å	p	j	Φ kcal.
$NaNO_3$	1	4.98	16.56	1.380	2.05	0.756	180
$MgCO_3$	2	4.60[1]	15.21[1]	1.268	2.10	0.741	772
$CaCO_3$	2	4.98[1]	17.04[1]	1.421	2.01	0.769	714
$ZnCO_3$	2	4.65[1]	14.98[1]	1.249	2.14	0.729	771
$CdCO_3$	2	4.91[1]	16.25[1]	1.355	2.09	0.743	724
$MnCO_3$	2	4.85[1]	15.52[1]	1.294	2.16	0.724	739
$FeCO_3$	2	4.67[1]	15.25[1]	1.272	2.12	0.735	762
$ScBO_3$	3	4.75[1]	15.27[1]	1.274	2.15	0.727	1690
$InBO_3$	3	4.77[1]	15.46[1]	1.289	2.13	0.724	1670
YBO_3	3	5.06[1]	17.21[1]	1.435	2.03	0.762	1580
$NaHF_2$	1		13.84[3]	2.305	0.855	1.155	165
NaN_3	1	3.64[2]	15.20[2]	2.533	0.830	1.145	149

[1] GOLDSCHMIDT V. M. and HAUPTMANN H.: Nachr. Göttingen. III. 16. (1932).
[2] HENDRICKS S. B. and PAULING L.: Journ. Amer. Chem. Soc. 47, 2906 (1925).
[3] ANDERSEN C. C. and HASSEL O.: Z. physik. Chem. 123, 151 (1926).

ν is the valency; a_h is the translation in the direction of the secondary axis, and c_h the translation in the direction of the principal axis (the hexagonal axes). The standard distance L_0 is the distance between ionic layers perpendicular to the principal axis, hence in the case of the calcite lattice it is ${}^{c_h}\!/_{12}$ and in the case of the $NaHF_2$ lattice it is ${}^{c_h}\!/_{6}$. The parameter p was defined as $\frac{L_1}{L_0}$ where L_1 is equal to ${}^{a_h}\!/_{\sqrt{3}}$.

The electrostatic lattice energies of the above carbonates and borates are considerable and these compounds are consequently insoluble in water. GOLDSCHMIDT and HAUPTMANN were aware of this and remarked furthermore that $ScBO_3$ and $InBO_3$ are resistant even against strong acids. It is likely that future methods of isolating scandium will be based on the stability of scandium borate. GOLDSCHMIDT and HAUPTMANN also determined the hardness which increases in the sequence $LiNO_3$, $MgCO_3$ and $ScBO_3$.

After the above paper had been written I perceived that EVJEN[1] had already proposed a similar method of determining MADELUNG's constant. In order to demonstrate the similarity and the difference between EVJEN's method and the present one it is found appropriate, verbatim, to quote the following sentences from EVJEN's paper:

"This immediately suggests a simple method of calculating the MADELUNG constant: Sum directly the potentials of the ions over a cube of side *nd* around the origin. The potentials of the ions inside the cube are summed in the ordinary manner each being given unit weight; the potentials of the ions forming the surface of the cube, however, are given the weights $^1/_2$, $^1/_4$ or $^1/_8$ according as they are situated on a face, an edge or a corner of the cube. This procedure, of course, is equivalent to summing by cells rather than by ions."

The last sentence quoted expresses the essential difference between EVJEN's method and the present one.

EVJEN has furthermore calculated MADELUNG's constant for the idealized calcite lattice. He used MADELUNG's method, and gives his results as a curve in a diagram on rather too small a scale. In order to compare his results with mine I have transferred my data to his standard distance, which is always the smallest distance between neighbour ions; and to his parameter, an angle φ the tan of which is $\frac{p}{4}$. The data thus transformed have been plotted as points (crosses)

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[1] EVJEN H. M.: Physical Review. 39, 680 (1932).

into the diagram, Fig. 3. It will be observed that, especially in a region about $\varphi = 25^\circ$, the agreement is not particularly good, the deviation amounting to about 1.3 per cent. Now one might raise the objection to my calculation that perhaps this deviation arises from the neglection of ions outside the rhombohedron of 512 ions. In view of this I have calculated the contribution of one more shell of ions, i. e. a 5th division, for the case of $p = \sqrt{4}$ or $\varphi = 26.56^\circ$. I found a value of $-0{,}0028$ for this contribution. Using this, together with the other contributions for the case of the parameter $\sqrt{4}$ in table 3, for an extrapolation similar to that shown in Fig. 2, I found a value of 0.7699 for Madelung's factor. This is all on the basis of the old standard distance; transferring that to the present standard distance, i. e. the smallest distance between neighbour ions, I got a value of 1.722.

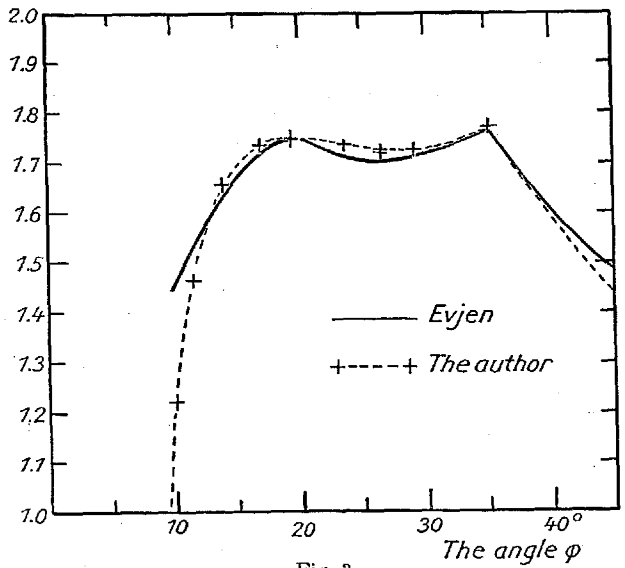

Fig. 3.

This most accurate value, which is probably no more than 1 per mille in error, is 2 per mille below my former value, but more than 10 per mille above Evjen's curve. Hence we are probably allowed to conclude that our calculations are the more accurate.

Summary.

The electrostatic lattice energy of a salt crystal cannot be evaluated by an uncritical summation, because the electrostatic force is a long range force, and the number of ions increases considerably with the distance. Madelung therefore applied a mathematical artifice in order to carry out the calculation. It is, however, found that a direct summation is feasible provided that it proceeds on a definite plan; this plan being founded on the experience that crystals of a nearly perfect shape can be obtained by crystallization. Perfect electro-neutral crystals were therefore used as stages in the calculation, and it was found that the lattice energy of even a small but perfect crystal comes close to that of an infinite crystal. Thus the electrostatic energy of an inner ion in a NaCl cube of 64 ions is no more than three per mille different from the lattice energy of an infinite NaCl lattice. By means of crystal cubes containing up to 1000 ions a value of 1.747558 has been extrapolated for Madelung's constant of the NaCl lattice in perfect agreement with Emersleben.

If the electric charge of the anion is assumed to be located at the centre, the calcite and NaHF$_2$ lattices may be described as a NaCl lattice deformed by being compressed or expanded along a trigonal axis. By the deformation a cube becomes a rhombohedron, and the lattice acquires a parameter determining the relative dimensions of the rhombohedron. The electrostatic energy of an inner ion with respect to all other ions in a rhombohedric crystal of 512 ions has been calculated in the case of nine values of the parameter, and an empiric formula for the variation of Madelung's factor with the parameter has been derived. The value of the electrostatic part of the lattice energy has been calculated in kcal, for $NaNO_3$, $MgCO_3$, $CaCO_3$, $ZnCO_3$, $CdCO_3$, $MnCO_3$, $FeCO_3$, $ScBO_3$, $InBO_3$, YBO_3, $NaHF_2$ and NaN_3. Evjen has earlier calculated Madelung's factor for the idealized calcite lattice, and in a diagram his data are compared with mine.

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MENGENFUNKTIONEN UND KONVEXE KÖRPER

VON

W. FENCHEL UND B. JESSEN

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