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HALL COEFFICIENT
AND RESISTIVITY OF α - AND
 β -BRASS FROM 20-600° C

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The Hall coefficients and resistivities of $Cu-Zn$ alloys in the α - and β -range have been determined by an A.C. method. The observed resistivities are in agreement with earlier results. The sign of the Hall coefficient is normal for all specimens investigated; in the α -range, R_H decreases with increasing Zn content more rapidly than predicted by free electron theory and shows a strong temperature dependence for the Zn rich alloys. For β -brass, R_H is practically proportional to the resistivity for various temperatures including the temperature range of the order-disorder transition. Some implications of the results for the band structure of these alloys are suggested.

Introduction.

Measurements of the Hall coefficient have for a long time been extensively employed as a means of obtaining some insight into the band structure of pure metals and into the effect of alloying on this band structure. According to current theories, the Hall coefficient should, to a first approximation, be independent of temperature, at least at the higher temperatures where a time of relaxation can be defined. For this reason, and because of experimental difficulties, nearly all measurements have been made at room temperature only. Significant exceptions are the Hall coefficients of ferromagnetic materials, which have recently been studied in greater detail both experimentally and theoretically, and which exhibit strong temperature dependence and other anomalies.

For non-magnetic metals, and especially for alloys, the experimental evidence is scanty concerning the effect of temperature (including the effects of allotropic transformations and melting) on the Hall coefficient. The choice of α - and β -brass for the present investigation was dictated partly by the occurrence of an order-disorder transition in β -brass at moderate temperature, and partly by the availability of results of recent room temperature measurements on these alloys by conventional D.C. methods.

Our results show a pronounced temperature dependence, also for α -brasses, indicating that measurements at one temperature only may be of limited value also in other cases.

Experimental Method.

In order to make reliable determinations of the Hall coefficient at high temperatures we have chosen to use an A.C. apparatus, so that disturbing thermal and Ettinghausen e.m.f.'s are eliminated. Such a method is now in common use; the experimental set up employed in this work presents a modification which permits simultaneous determination both of the Hall coefficient (R_H) and the resistivity (ρ) with a minimum of probes attached to the sample.

Fig. 1 shows a schematic view of the equipment. The alternating current is taken from a push-pull amplifier (driven by an R - C oscillator) through a shielded transformer (T_1) with very low output impedance. When measuring R_H , the switches S_1 and S_2 are set in position a and the current is passed directly through the sample between A and B ; when measuring ρ , S_1 and S_2 are brought into position b and the current then flows through the series connection of the precision resistance R_1 and the sample. In principle, the Hall voltage, developed across the sample, might be measured directly between probe no. 3 and the sliding contact 4 of the potentiometer P (the ends of which are connected to the probes nos. 1 and 2) if P is first balanced against 3 with zero magnetic field. As the Hall voltage is of the order of micro-volts, this direct method necessitates the use of a stable oscillator and a stable high gain amplifier; a determination of the measuring current is also necessary. These difficulties can be avoided by compensating the Hall voltage, displacing the slide-contact 4 of P ; this potentiometer must therefore be calibrated very accurately. The actual construction, which is somewhat more complicated than indicated on Fig. 1, permits readings to one part in a million over a limited range.

The zero indicator connected between 3 and 4 consists of a well shielded input transformer T_3 , a battery driven amplifier

A_1 , and a selective feedback amplifier A_2 . The maximum total gain of this system amounts to 2×10^9 . The noise level referred to the input terminals 3 and 4 was about 3×10^{-9} volts when the indicator was tuned to 25 Hz (with a bandwidth of 1 Hz); this rest signal, usually observed on the oscilloscope, consisted mainly of 50 Hz pick-up from the mains.

In order to eliminate from the zero indicator any inductive or capacitive out-of-phase voltages existing between 3 and 4, the secondary of a variable air transformer T_2 , the primary of

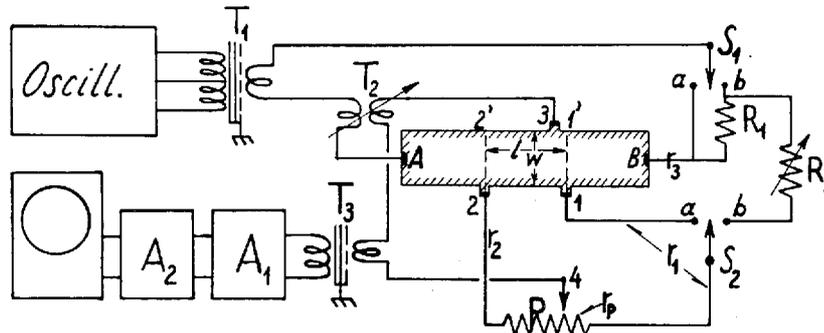


Fig. 1. Block diagram of the sample $A-B$ with the probes 1, 2, and 3 and associated electronic equipment.

which is connected in series with the measuring A.C. current, is inserted in series with the zero indicator.

The samples were rectangular, 45 mm \times 10 mm, with the probes 1 and 2 placed at a distance of 15 mm. The connecting conductors consisted of strips of copper foil, silver soldered to the sample by electrical heating with a spot welding apparatus. Insulation was provided by mica sheets, the whole assembly being firmly clamped between two thick copper plates. The outer faces of these plates were furnished with heating elements and thermal insulation; this furnace could be mounted in a box fitting into the air gap of the magnet. To prevent oxidation, carbon dioxide was passed through the box. The temperature was measured by a chromel-alumel couple, the junction being insulated from the sample by a thin mica sheet.

To measure ρ , P is first balanced with zero magnetic field, while the switches S_1 and S_2 are in position a ; S_1 and S_2 are then turned to position b , and the decade resistor R_2 is used

to balance the Wheatstone bridge formed by the resistances R_2 , $r_p + r_1 + r_2$, $R_1 + r_3$ and the sample resistance between 1—1' and 2—2'. As $R_2 \gg r_p$ we have, irrespective of the placing of probe no. 3,

$$\varrho = \frac{w}{l} t \frac{r_p R_1}{R_2} \left(1 + \frac{r_3}{R_1}\right) \left(1 + \frac{r_1 + r_2}{r_p}\right) \alpha, \quad (1)$$

where ϱ is the resistivity, t the thickness of the sample, and α is a numerical factor arising from the fact that the measuring current is fed to the sample through the point-like contacts A and B so that the current field in the regions between 1—1' and 2—2' is not quite homogeneous. By separate measurements on samples of different lengths, the value of α for the sample length normally used was determined to 1.010 ± 0.003 . The wiring resistances r_1 , r_2 , and r_3 were suppressed to such values that their effect on the determination of ϱ was less than 1 per cent. The switch S_2 was of the mercury type so that a small and reproducible contact resistance could be obtained.

To measure R_H , P is balanced with the magnetic field on (S_1 and S_2 are in position a); denoting the difference in potentiometer readings for the two field directions by Δx , we have

$$R_H/\varrho = \frac{l}{w} \frac{\Delta x \beta}{2 B \alpha} \left(1 + \frac{r_1 + r_2}{r_p}\right), \quad (2)$$

where B is the induction in the air gap of the magnet and α is the same correction factor as in (1). The correction factor β is different from unity owing to the finite length of the sample; from the published solutions of this problem ([1] [6]) we estimate β to 1.010 ± 0.004 .

From (1) and (2), R_H may be obtained.

The measurements were carried out with a current of 10—15 amps, a frequency of 25 Hz, and in a field of 0.55 Wb/m^2 . Experiments with other values revealed no dependence of ϱ and R_H on these factors.

The accuracy of the results is $\pm 0.5\%$ as regards the relative temperature dependence of ϱ and R_H . The absolute values of ϱ and R_H are, however, not better than ± 2 to 3% , owing to uncertainties in the dimensions of the samples. The temperature is considered correct within $\pm 2^\circ \text{C}$.

Results and Conclusions.

Fig. 2 shows the results of resistivity measurements. The copper sample was cut from commercial copper foil, the samples of α -brass were the same as those employed by O. GRAM JEPPESEN [7], and the sample of β -brass was prepared from a cast block with 52.3 atomic % of copper. The impurity contained in this block, consisting mainly of *Pb*, *Ag*, and *Cd*, was less than 0.03 %. The β -brass sample was milled down from the cast block and given some final rollings combined with a heat treatment at 600°C for a few seconds.

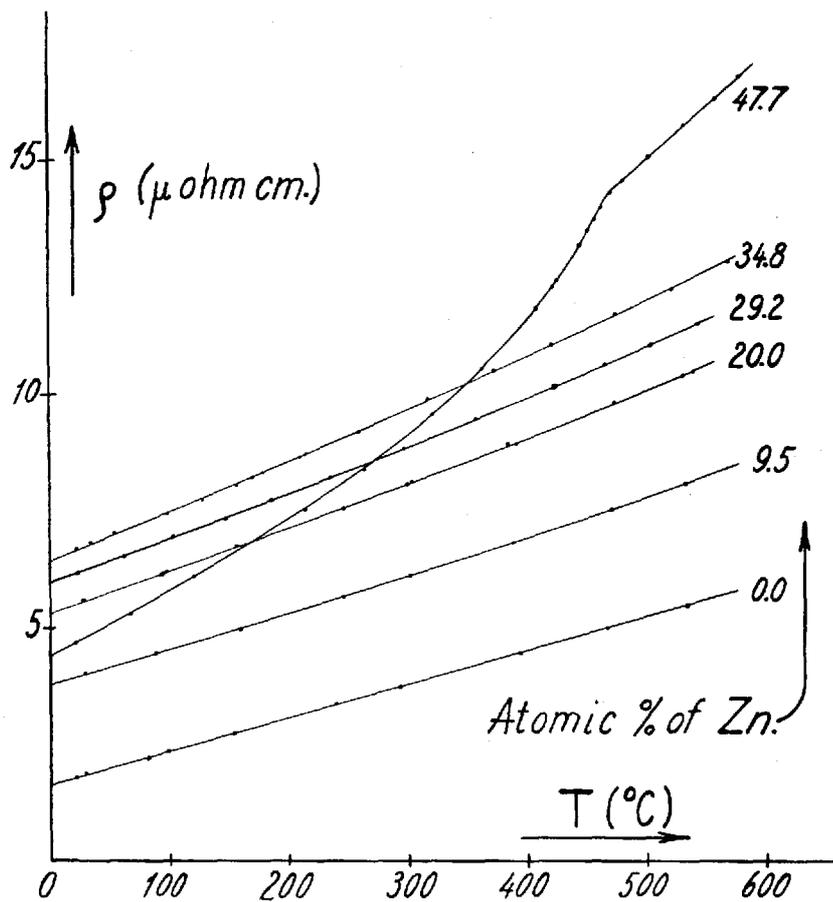


Fig. 2. Resistivity versus temperature for α - and β -brass.

The samples were not systematically annealed, but for each sample at least two measuring series, from 550°C to room temperature, were carried out; in general, the differences between the two measuring series were less than 1%. This fact and the data from the many annealing experiments on cold worked brasses (cf. the review article by T. BROOM [8]) make us believe that our values of ρ and R_H represent the true equilibrium values of these quantities. This applies also to β -brass, for which EGGLESTON and BOWMAN [9] have shown that disorder, induced by radiation with α -particles at -100°C, anneals in less than five minutes at 0°C.

The resistivities of the α -brasses are in agreement with earlier results [10]. The ρ - T curve for the β -brass is in agreement with those obtained by WEBB [11] for single crystals. Especially we observe, in accordance with WEBB, that the slope of the resistivity curve for the disordered state is greater than that for the totally ordered state, to such an extent that, if ρ_{disord} is extrapolated linearly to 0° K, we obtain a negative residual resistance. Moreover, WEBB states that this effect decreases on approaching the ideal 50:50 composition. The data of STEINWEHR and SCHULZE [12] for a single crystal with 50.9 atomic % Cu seem to extrapolate to a slightly positive residual resistance.

It is well known that the anomaly in the specific heat of β -brass extends 100°C above the transition temperature; this is usually attributed to the presence of short range order. Since the effect of this kind of order on the resistivity is not definitely established ([8] § 6.3) it might be of interest to extend the measurements of resistivity to higher temperatures.

R_H versus T is shown in Fig. 3, while Fig. 4 gives the quantity ρ/R_H (which in the free electron picture of metals is simply the reciprocal of the mobility of the electrons) versus T . The main features of these curves are:

- a) The sign of R_H is normal (negative) in the whole temperature range for both α - and β -brass.
- b) In the α -range, R_H is nearly a linear function of T , the slope increasing with increasing Zn-content, especially near the phase boundary. For the specimens near this boundary, R_H is almost proportional to ρ (Fig. 4).

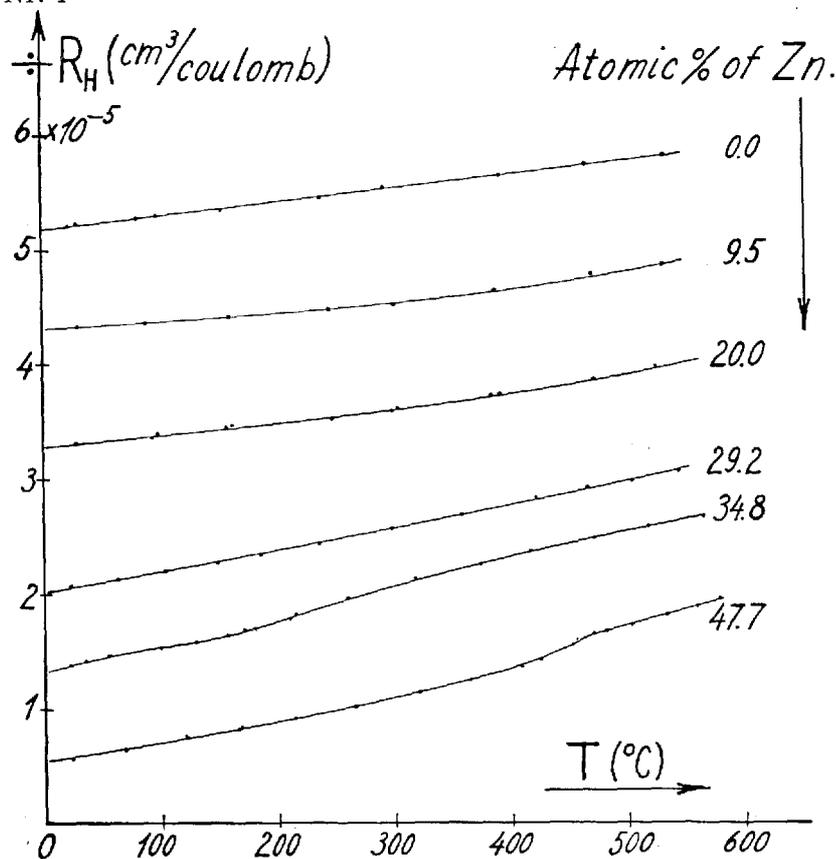


Fig. 3. Hall coefficient versus temperature for α - and β -brass.

- c) For β -brass, R_H is also nearly proportional to ρ , so that the anomaly in R_H is of the same type as that in ρ . Thus, the sign reversal of R_H observed in Cu_3Au [13] and in Ni_3Mn [14] is not revealed by the order-disorder transition in β -brass. In this connection, we note that the thermoelectric force, as determined by WEBB [11] for β -brass, behaves quite regularly from 0 to 600°C.
- d) The room temperature values of R_H for the α -brasses are a few per cent lower than those previously obtained by O. GRAM JEPPESEN [7] from D.C. measurements on the same specimens. The value of R_H for Cu at 20°C is in agreement with newer results ([7], [15]) which center on the value $-(5.25 \pm 0.1) \cdot 10^{-5} \text{ cm}^3/\text{Coulomb}$.

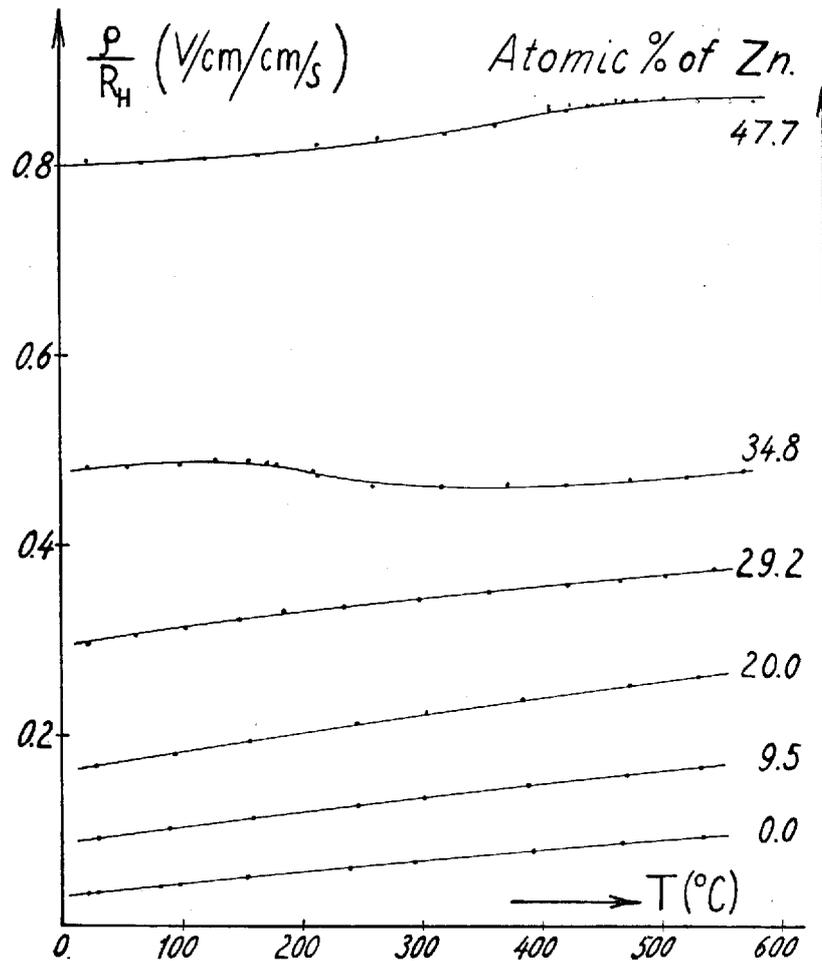


Fig. 4. q/R_H versus temperature for α - and β -brass.

In Fig. 5, R_H is plotted against the content of Zn for $T = 20^\circ\text{C}$ (curve C) and for $T = 600^\circ\text{C}$ (curve B); the values of R_H computed from the Sommerfeld formula (assuming that Cu contributes one and Zn two electrons per atom to the conduction band) have been plotted for comparison (curve A).

Concentrating first upon the low temperature values for the α -brasses, their deviations from the free electron values are easily understood in terms of the deformation of the Fermi surface from spherical symmetry when the Brillouin zone of

the alloys is gradually filled up. It is generally assumed (WILSON pp. 104 ff. [16]) that the instability of the α -phase in alloys like *Cu-Zn* occurs when the Fermi surface due to the filling up of electrons reaches the position corresponding to maximum electron level density. As this Fermi surface will be in contact with the boundaries of the Brillouin zone, it will be strongly deformed. It might therefore be expected that it contributes to the Hall effect an electron-like and a hole-like term which nearly cancel.

The temperature dependence of R_H might be explained by

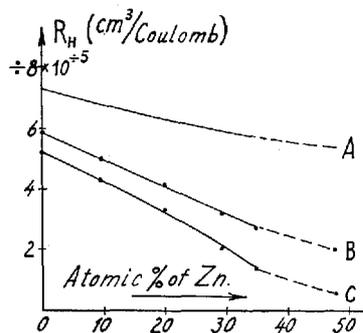


Fig. 5. Hall coefficient versus Zn content.

A: calculated according to free electron theory.

B: experimental values for $T = 600^\circ\text{C}$.

C: experimental values for $T = 20^\circ\text{C}$.

letting the division of the Fermi surface into an electron-like and a hole-like part depend on temperature, but a formal treatment along these lines seems to involve too many arbitrary assumptions to be really significant. Prof. B. L. AVERBACH (private communication) has tentatively suggested that this dependency is due to the thermal smearing of the Fermi surface at elevated temperatures, tending to restore its spherical form and thus reducing the deviation of R_H from the free electron value; this suggestion is supported by the shape of the curves in Fig. 5.

For the disordered state of β -brass, the above remarks on the α -phase may be applied literally, the only difference being that the Brillouin zone of the b.c.c. lattice can hold more electrons per atom than the Brillouin zone of the f.c.c. lattice before the point of maximum level density is reached.

Thus, the rather close agreement between the disordered β -brass and the Zn rich α -brasses does not seem fortuitous; unfortunately the disordered state cannot be quenched, and linear extrapolation to lower temperatures is unsafe, especially because linear extrapolation of the resistivity leads to a negative residual resistivity.

When β -brass is brought into the totally ordered state, i.e. below 200°C , the original Brillouin zone is divided into two equal parts by the formation of interior boundaries (corresponding to the superlattice lines observed in X-ray diffraction). If there is no overlap between the subzones, the energetically lower zone will be full and the higher one will be about half full, as the electron-atom ratio of the β -phase is near $3/2$. Thus, we should expect the ordered state to behave like a simple metal, i.e. with R_H close to the free electron value and only slightly temperature dependent, in disagreement with the actual behaviour. If the subzones do overlap to such an extent that both hole and electron conduction occur, a Hall coefficient of small magnitude at low temperatures and with a strong temperature dependence might result, in accordance with experiment.

In the intermediate temperature range from 200°C — 470°C , where the long range order is gradually destroyed, the band structure proposed for the ordered state changes continuously into that of the disordered state; we do not, however, suggest any explanation of the fact that R_H/ρ is nearly constant during this transition.

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