PHYSICAL REVIEW VOLUME 76, NUMBER 5 SEPTEMBER 1, 1949

Temperature Dependence of Susceptibility of Zinc, Cadmium, and Gamma-Brass*

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(Received May 9, 1949)

The temperature dependence (14°K–373°K) of the diamagnetic susceptibility of zinc and cadmium single crystals and several polycrystalline gamma-brasses has been investigated. For zinc, pronounced maxima occur in the susceptibility parallel to the hexagonal axis ($\chi_{\parallel}$) at 40°K and 105°K, and minima occur at 60°K and 180°K. The susceptibility perpendicular to the hexagonal axis ($\chi_{\perp}$) is independent of temperature from 14°K to 100°K and then decreases linearly as the temperature is increased. For cadmium, $\chi_{\parallel}$ decreases by a factor of three between 14°K and 373°K while $\chi_{\perp}$ increases by 7 percent in the same temperature interval. Measurements on polycrystals of copper-zinc alloys in the gamma-phase show that the temperature coefficient of susceptibility changes from positive to negative as copper content is increased, in agreement with previously reported measurements above room temperature. At the copper rich end of the phase, the susceptibility increases by 10 percent between 14°K and 293°K; at the zinc rich end of the phase, the susceptibility decreases by 3 percent in the same temperature interval.

WHILE the temperature dependence of the susceptibility of weakly paramagnetic and diamagnetic metallic elements has been extensively investigated for polycrystalline specimens,[1] data for single crystals and alloys is meager, particularly at low temperatures. Measurements which have been made on single crystals and alloys are however of considerable interest: the temperature dependence of susceptibility of bismuth,[2] antimony,[3] and graphite[4] single crystals, exhibits a marked anisotropy which of course is not apparent from data on polycrystals; for bismuth[2] and antimony alloys,[5] a slight change in composition produces a reversal in sign of the temperature coefficient of susceptibility and a similar effect has been observed at high temperatures for copper-zinc alloys in the gamma-phase.[6] As yet, these results have only been accounted for in a qualitative way. Further research along the same lines should yield information about the electronic structure of metals and prove useful in formulating a quantitative theory of the temperature dependence of susceptibility.

In the research reported here, the variation of susceptibility with temperature was investigated from 14°K to 300°K for single crystals of zinc and cadmium and for a series of polycrystalline copper-zinc alloys in the gamma-phase. The results for zinc were briefly reported in a previous communication.[7]

* Part of this work was included in a dissertation submitted in 1947 to the faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.

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*** Assisted by the ONR under contract N6ori-44.

[1] K. Honda, Ann. d. Physik **32**, 1027 (1910); M. Owen, Ann. d. Physik **37**, 657 (1912); W. J. de Haas and P. M. van Alphen, Comm. Phys. Lab. Leiden, No. 225b (1933).

[2] D. Shoenberg and Z. M. Uddin, Proc. Roy. Soc. **A156**, 687 (1936).

[3] D. Shoenberg and Z. M. Uddin, Proc. Roy. Soc. **32**, 499 (1936).

[4] N. Ganguli and K. S. Krishnan, Proc. Roy. Soc. **A177**, 168 (1941).

[5] S. H. Browne and C. T. Lane, Phys. Rev. **60**, 899 (1941).

[6] C. T. Lane, J. App. Phys. **8**, 693 (1937).

[7] J. A. Marcus, Phys. Rev. **71**, 559 (1947).

EXPERIMENTAL PROCEDURE

Single crystals of zinc and cadmium were grown by the Bridgman[8] method of slowly lowering a Pyrex tube containing the molten, outgassed metal through an electric furnace having a large temperature gradient. The resulting crystal was roughly 0.5 cm in diameter and 5 cm long. To obtain small cylindrical specimens suitable for measurements by the Faraday method, the rods were cut into sections 0.5 cm long by coating with paraffin, circumscribing notches in the paraffin at appropriate intervals and etching with acid. Where, as in some of the zinc rods, the cleavage plane was almost perpendicular to the axis of the rod, specimens of the desired dimensions were obtained by cleavage. While cutting with acid undoubtedly involved less deformation than cleavage, measurements on specimens prepared in the two ways differed by less than the experimental error. The cadmium and zinc used were Johnson, Matthey & Company H. S. metals for which the supplier's analysis indicated 99.999 percent purity.

Small polycrystalline specimens of copper-zinc alloys in the gamma-phase were synthesized and annealed by the method fully described by Lane.[6] Having obtained five alloys with compositions fairly well distributed

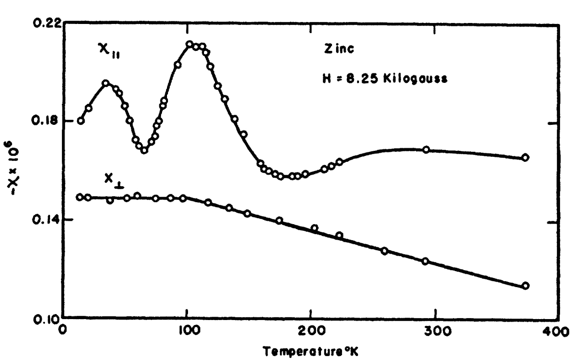

FIG. 1. Temperature dependence of the principal susceptibilities of zinc at a constant field strength of 8.25 kilogauss.

[8] P. W. Bridgman, Proc. Am. Acad. **60**, 305 (1925).

across the phase, it was intended that measurements be made on both polycrystals and single crystals. However, attempts to grow single crystals failed and measurements were confined to polycrystalline specimens. The composition of the alloys was determined from the initial weight of the constituents and final weight of the castings, any loss in weight during the alloying process being ascribed to vaporization of zinc. No further chemical analysis was deemed necessary since at room temperature, the variation of susceptibility with composition was in sufficiently good agreement with the results

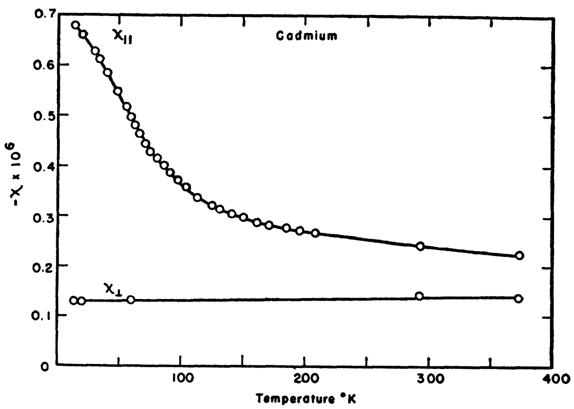

FIG. 2. Temperature dependence of the principal susceptibilities of cadmium.

of Smith[9] and Lane.[6] The materials used were Johnson, Matthey & Company H. S. brand copper (99.999 percent purity) and New Jersey Zinc Company S. P. zinc (99.999 percent purity). Mass susceptibilities were determined by the Faraday method employing a Sucksmith ring balance as described in a previous paper.[10]

Fixed temperatures were obtained by the use of liquid hydrogen, oxygen, nitrogen, air, methane, and ethylene, and were determined from vapor pressure measurements. Data at intermediate temperatures were obtained by allowing the specimen to warm up after the evaporation of the refrigerant, three and one-half hours being required for the specimen to reach room temperature after the evaporation of liquid hydrogen. During the warm-up, temperatures were measured with a calibrated copper-constantin thermocouple soldered to the copper tube surrounding the specimen. Readings agreed with those at fixed temperatures to within ±1°K in the range where both methods were employed.

RESULTS AND DISCUSSION

A. Zinc

The temperature variation of the principal susceptibilities was measured from 14°K to 373°K in a magnetic field of 8.25 kilogauss, and the curves of Fig. 1 obtained.[11] For the susceptibility parallel to the hexagonal axis ($\chi_{\parallel}$), pronounced maxima occur at temperatures of 40°K and 105°K and minima at 65°K and 180°K. Below 64°K, $\chi_{\parallel}$ is field dependent[10] with the result that this part of the curve is of little significance for the present discussion.

TABLE I. Principal susceptibilities of cadmium at room temperature.

	$-\chi_{\parallel}\times10^6$	$-\chi_{\perp}\times10^6$	$\chi_{\parallel}/\chi_{\perp}$
McLennan, Ruedy, and Cohen[a]	0.261	0.160	1.63
Rao[b]	0.223	0.163	1.34
Present work	0.243	0.142	1.71

[a] McLennan, Ruedy, and Cohen, Proc. Roy. Soc. **A121**, 9 (1928).
[b] S. R. Rao and S. Sriraman, Proc. Roy. Soc. **A166**, 325 (1938).

In contrast, the temperature dependence of the susceptibility perpendicular to the hexagonal axis ($\chi_{\perp}$) is normal, having a constant value of -0.150×10^{-6} from 14°K to 100°K and then decreasing linearly to -0.114×10^{-6} at 373°K.

The peculiar temperature dependence of $\chi_{\parallel}$ does not seem to have been observed in other metals although Shoenberg[2] has found a single maximum or minimum in some bismuth alloys. For bismuth alloyed with 0.4 percent to 4 percent lead, a maximum occurs in $\chi_{\perp}$ at a temperature which increases from 100°K to 300°K as the lead content is increased, and a similar maximum occurs for bismuth-tin alloys. Where bismuth is alloyed with 0.11 percent tellurium, $\chi_{\perp}$ has a minimum in the neighborhood of 200°K. While the diamagnetism of these alloys is from five to fifteen times greater than that of free bismuth ions, the diamagnetism of zinc is less than that of free zinc ions (-0.23×10^{-6}) for temperatures down to 14°K and the net effect of the valence electrons must be paramagnetic. It therefore seems likely that the temperature dependence of the electron paramagnetism is of relatively greater importance for

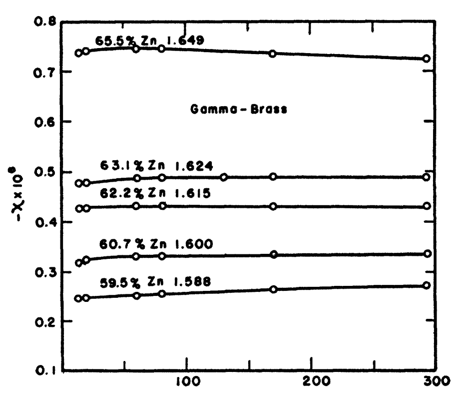

FIG. 3. Temperature dependence of the susceptibility of several gamma-brasses. The parameters are zinc content by weight and the electron ratio.

[9] C. S. Smith, Physics **6**, 47 (1935).
[10] J. A. Marcus, Phys. Rev. **76**, 413 (1949).
[11] For a comparison of our room temperature values of the principal susceptibilities with the results of other investigators, see Table I of reference 10.

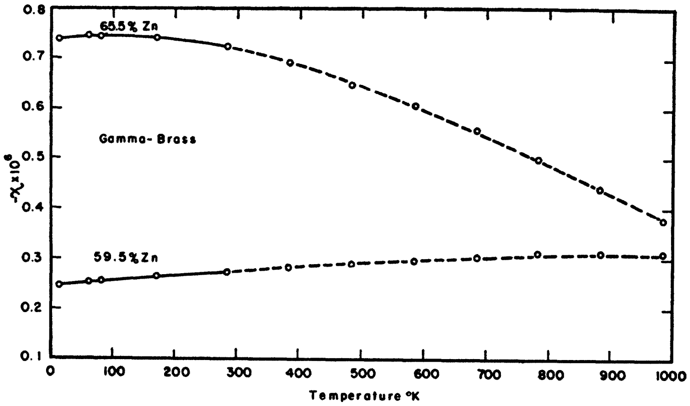

FIG. 4. Temperature dependence of the susceptibility of two gamma-brasses. The dashed part of the curves is taken from Lane's measurements.

zinc and may account for the more complicated susceptibility-temperature curves of Fig. 1.

B. Cadmium

The principal susceptibilities were measured at room temperature and 14°K in fields ranging from 3 to 9 kilogauss. No field dependence was observed at either temperature, indicating the absence of ferromagnetic impurities. Results at room temperature together with those of other investigators are given in Table I. The discrepancies are larger than can be accounted for by calibration errors and are most probably due to a difference in purity. Figure 2 shows the variation of the principal susceptibilities with temperature. The susceptibility parallel to the hexagonal axis ($\chi_{\parallel}$) increases by a factor of three from -0.225×10^{-6} at 373°K to -0.679×10^{-6} at 14°K and the increase apparently continues to lower temperatures. In the same temperature range, the susceptibility perpendicular to the hexagonal axis ($\chi_{\perp}$) decreases linearly to -0.130×10^{-6} at 14°K. The average susceptibility as calculated from these results using the formula $\bar{\chi}=\frac{1}{3}(\chi_{\parallel}+2\chi_{\perp})$, is 76 percent greater at 14°K than at room temperature which is in good agreement with the 78 percent increase observed in measurements on a polycrystal by de Haas and van Alphen.[1]

The striking difference in the susceptibility-temperature curves for cadmium and zinc indicates that the electronic structure of the two metals is significantly different despite a similarity in crystal structure. This is further borne out by the observation of an anomalous field dependence of susceptibility[10] and resistance[12] at low temperatures for zinc but not for cadmium. Bismuth[2] and antimony[3, 13] parallel zinc and cadmium with respect to these phenomena and the combined results should prove useful in determining the detailed electronic structures of these metals.

C. Gamma-Brass

The susceptibility of five polycrystalline specimens of copper-zinc alloys in the gamma-phase was measured at room temperature and 14°K in fields ranging from 3 to 9 kilogauss. No field dependence of susceptibility was observed and the room temperature values were in good agreement with those of Smith[9] and Lane.[6] Figure 3 shows the variation of susceptibility with temperature from 14°K to 293°K for the alloys where the curve for each specimen is identified by the weight percent of zinc and the electron ratio. At the copper rich end of the phase, the susceptibility decreases with decrease in temperature, the total change being 10 percent; at the zinc rich end of the phase, the susceptibility increases with decrease in temperature showing a total change of 3 percent.

Results for the most diamagnetic and least diamagnetic alloys are shown in Fig. 4 together with Lane's measurements on specimens of the same composition taken above room temperature. For the 65.5 percent Zn alloy, the temperature coefficient decreases considerably at low temperatures while for the 59.9 percent Zn alloy, very little change is observed.

Since no significantly new features were observed at low temperatures, Lane's[6] discussion of the thermomagnetic properties of gamma-phase alloys at high temperatures appears to be applicable over the extended temperature range.

The author wishes to thank Professor C. T. Lane and Dr. Henry Fairbank for their generous advice and assistance.

[12] Lazarev, Nachimovich, and Parfenova, C. R. Acad. Sci. U.R.S.S. **24**, 855 (1939).

[13] L. Schubnikov and W. J. de Haas, Comm. Phys. Lab. Leiden Nos. 207a, 207d (1930).