

Specific Heats of Dilute Cu-Co Alloys between 1.5° and 4.5°K

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Specific heats of eight specimens of dilute copper-cobalt alloys were measured in the range of 1.5° to 4.5°K. Cobalt concentration of these samples lay between $\frac{1}{4}$ and $2\frac{1}{2}$ weight percent. At all concentrations the specific heat is greater than that of pure copper, with the excess linear in temperature and quadratic in concentration for the lower concentrations at the higher temperatures. Near the lower end of this temperature range, samples of greater than 1 $\frac{1}{4}$ % cobalt also exhibit an additional anomaly which appears to have a characteristic temperature proportional to cobalt concentration. A comparison to the specific heats of dilute Cu-Mn alloys shows that the magnetic interactions in Cu-Co and Cu-Mn must differ greatly in character.

INTRODUCTION

AT absolute zero the resistivity of a so-called pure metal is determined by the residual impurities of the specimen, and as the temperature is increased the scattering by thermal vibrations of the lattice causes the resistivity to increase monotonically. However, the addition of dilute amounts of paramagnetic ions to a high-conductivity metal causes a resistivity which undergoes either a maximum followed by a minimum, or simply a minimum, as the temperature is increased from absolute zero.¹⁻⁶ The fact that there are two types of anomaly, one possessing and the other lacking a maximum in resistivity, indicates that these alloys constitute two different groups. The alloys having a maximum and a minimum are characterized by Cu-Mn, which also displays an anomalous magnetoresistance⁶ and an antiferromagnetic transition at low temperatures.^{7,8} The alloys having only a minimum in resistivity are represented by Cu-Co, which has a normal magnetoresistance at low temperatures.⁹ However, the inverse susceptibility of these alloys is not a linear function of temperature below about 50°K and seems to indicate the initiation of some ordering, even though no magnetic transition is observed in the range of measurement.

Brailsford and Overhauser¹⁰ have investigated the effect upon resistivity of the addition of paramagnetic ions to high-conductivity metals, and have found that ferromagnetically coupled nearest-neighbor ion pairs produce a scattering cross section which increases with diminishing temperature. At sufficiently low temperatures the ion pair scattering will predominate over the

phonon scattering to produce an increase in resistivity with further reduction in temperature, giving rise to a resistivity minimum. If a ferromagnetic or an antiferromagnetic transition occurs, then the spin disorder scattering must decrease as the magnetic ordering increases, thereby causing a reduction in the resistivity. In the case of Cu-Mn, the resistivity maximum is undoubtedly explained by the antiferromagnetic ordering, and at sufficiently low temperatures this ordering decreases the resistivity by an amount greater than the increase in resistivity due to pair scattering per degree reduction in temperature. The exact convolution of the resistivity curve is thus determined by the relative magnitudes of the ion pair, spin disorder, and phonon scattering as the temperature proceeds toward absolute zero. These temperature-dependent components are superposed upon the temperature-independent resistivity of the single cobalt ion scattering, which constitutes the major component of the resistance at low temperatures.

The recent measurements of the specific heats of dilute copper-manganese alloys by Zimmerman and Hoare¹¹ have shown: (1) that below the Néel temperature the specific heat of the alloy in excess of that of pure copper is independent of manganese concentration; (2) that this excess is a linear function of temperature; (3) that the Néel temperature is a linear function of the manganese concentration; and (4) that the excess entropy indicates a spin of about 2 for the manganese ions. The first three of these are accounted for in semi-quantitative fashion by the electron spin-density wave ordering proposed by Overhauser.¹² A more qualitative explanation has been suggested by Marshall¹³ in terms of the well-known Yoside interaction. The measurements presented in this paper were undertaken to provide both a comparison to the Cu-Mn data in a case lacking the antiferromagnetic ordering and further information about the interactions causing the anomalies in resistivity and susceptibility.

¹ A. N. Gerritsen and J. O. Linde, *Physica* **18**, 877 (1952).

² A. N. Gerritsen, *Physica* **25**, 489 (1959).

³ A. N. Gerritsen and J. O. Linde, *Physica* **17**, 573 (1951).

⁴ G. J. Los and A. N. Gerritsen, *Physica* **23**, 633 (1957).

⁵ A. N. Gerritsen, *Physica* **23**, 1087 (1957).

⁶ R. W. Schmitt and I. S. Jacobs, *J. Phys. Chem. Solids* **3**, 324 (1957).

⁷ J. Owen, M. Browne, W. D. Knight, and C. Kittel, *Phys. Rev.* **102**, 1501 (1956).

⁸ J. Owen, M. Browne, V. Arp, and A. F. Kip, *J. Phys. Chem. Solids* **2**, 85 (1957).

⁹ I. S. Jacobs and R. W. Schmitt, *Phys. Rev.* **113**, 459 (1959).

¹⁰ A. D. Brailsford and A. W. Overhauser, *Phys. Rev. Letters* **3**, 331 (1959); and *J. Phys. Chem. Solids* **15**, 140 (1960).

¹¹ J. E. Zimmerman and F. E. Hoare, *J. Phys. Chem. Solids* **17**, 52 (1960).

¹² A. W. Overhauser, *Phys. Rev. Letters* **3**, 414 (1959); and *J. Phys. Chem. Solids* **13**, 71 (1959).

¹³ W. Marshall, *Phys. Rev.* **118**, 1519 (1960).

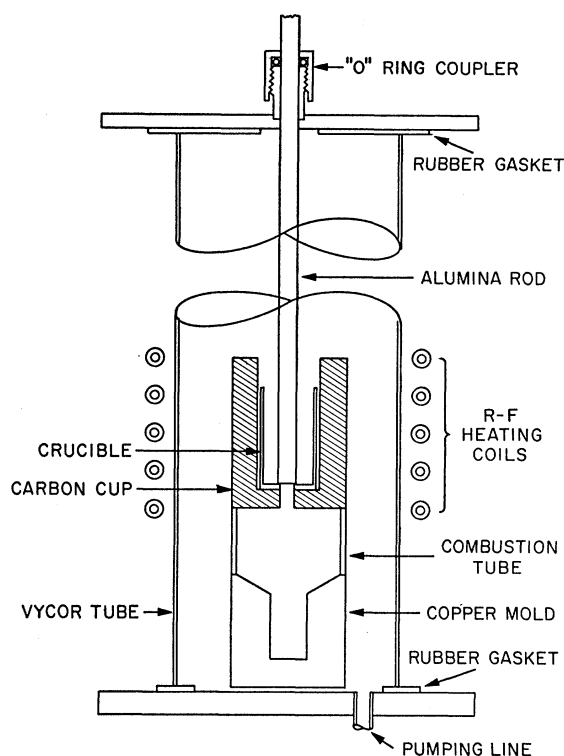


FIG. 1. Vacuum melting furnace for chill casting of samples having small mass.

EXPERIMENTAL METHOD

Samples were prepared from spectroscopically pure copper rods and cobalt sponge obtained from Johnson-Matthey and Company. To avoid any possible contamination by iron, the 3-mm diam copper rods were never sawed but were broken by hand when necessary. Alloying and chill casting were performed in a simple vacuum melting furnace shown in Fig. 1. An effective valve was made by ultrasonically drilling a $\frac{1}{4}$ -in. hole in the bottom of the recrystallized alumina crucible and covering the hole with the $\frac{3}{8}$ -in. alumina rod held in place by the O ring seal at the top of the Vycor melting tube. After the induction heating of the sample was complete, the rf furnace was stopped and the valve was opened by lifting the rod up out of the crucible. The surface tension of the molten alloys was found to be great enough that a tight fit of the rod over the hole was not necessary, for with the small samples used the molten copper would not even flow through a $\frac{1}{8}$ -in. hole unless the walls of the hole had first been coated with oxide. Therefore the crucibles were cleaned in nitric acid before each melt.

Samples were alloyed in 60-g sizes and chill cast in the copper mold into samples $\frac{9}{16}$ in. in diameter and about $1\frac{1}{2}$ in. long. These were vacuum annealed at 1000°C for 24 hr and then fast quenched in a water bath. Finally they were machined into samples $\frac{1}{2}$ in. in diameter and 1 in. long, weighing about 28 g. The magnetic studies on copper-cobalt alloys by Schmitt

and Jacobs⁶ and by Becker¹⁴ establish that these alloying procedures are more than sufficient to prevent the formation of cobalt atom clusters up to a concentration of 2% cobalt, beyond which there are no data. As a further test, the $2\frac{1}{4}$ and $2\frac{1}{2}$ % concentration samples were examined microscopically and showed no signs of cobalt precipitation.

The calorimeter, shown in Fig. 2, employed a mechanical thermal switch to make contact between the sample and bath. The switching mechanism was simply a $\frac{1}{8}$ -in. Monel tube actuated by a thumb screw, with a bellows to provide a vacuum seal. The tube was thermally shunted along its length and at the bottom as shown. The lower end of the tube was terminated with a Micarta rod $\frac{1}{2}$ in. in diameter and 1 in. long. Three wires of Brown and Sharpe No. 36 manganin wire were clamped equidistantly about the circumference of this rod by a strap of 0.005-in. copper shim held by a screw and nut in the manner of a hose clamp. The wires extended beyond the lower end of the Micarta rod and were attached at their lower ends to another clamp of copper shim by threading them through small holes in the shim and knotting. The sample was then clamped in this device and thereby suspended coaxially about $\frac{1}{16}$ in. below the end of the Micarta rod. The clamping screw also served to attach a heater-carbon resistance thermometer assembly of the type described by Zimmerman and Hoare.¹¹ With the sample thus suspended, thermal switching was achieved by lowering the sample to press against the innermost shielding can. The Micarta rod, with which the upper end of the sample made contact when the switch was closed, assured that thermal

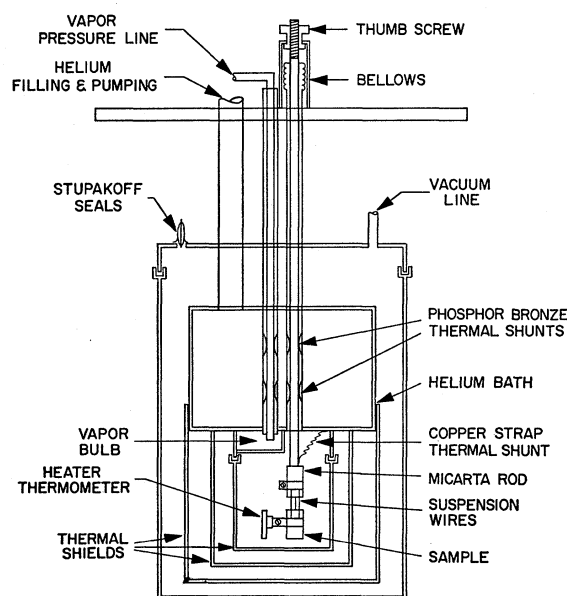


FIG. 2. Thermal switch calorimeter.

¹⁴ J. J. Becker, *Report of A.I.E.E. Conference on Magnetism and Magnetic Materials*, 1957, p. 288 [Suppl. J. Appl. Phys. **29**, 317 (1958)].

contact was only effective at the bottom of the sample and prevented any possible heat leaks through the switching rod. Thermal contact with the shielding can was optimized by depositing a film of indium solder on the bottom of the can, thus assuring a broad area of contact for the sample because of the high conformability of the soft indium.

The thermometer was calibrated by taking between 20 and 25 simultaneous measurements of resistance and helium vapor pressure at points approximately equally spaced in temperature from 4.4° to 1.4°K. A least-squares fit was made to the equation

$$(\log R/T)^{\frac{1}{2}} = A + B \log R + C(\log R)^2,$$

where R is the resistance and T the absolute temperature. Maximum deviations from this function of about 3 mdeg were obtained.

Specific heat measurements were made in the usual manner, with a series of temperature readings being taken at equal time intervals (usually a half-minute, but sometimes longer) to determine drift rate followed by a metered heat input, and then another drift rate determination. The small drift rates of the thermal switch calorimeter allowed measurements to be taken with heat inputs that caused changes of 2% of the absolute temperature of the sample. At the higher temperature, fluctuations in the potentiometer became equal to and greater than the drift rate, and careful drift rate determinations had to be made so that this effect would average from the data.

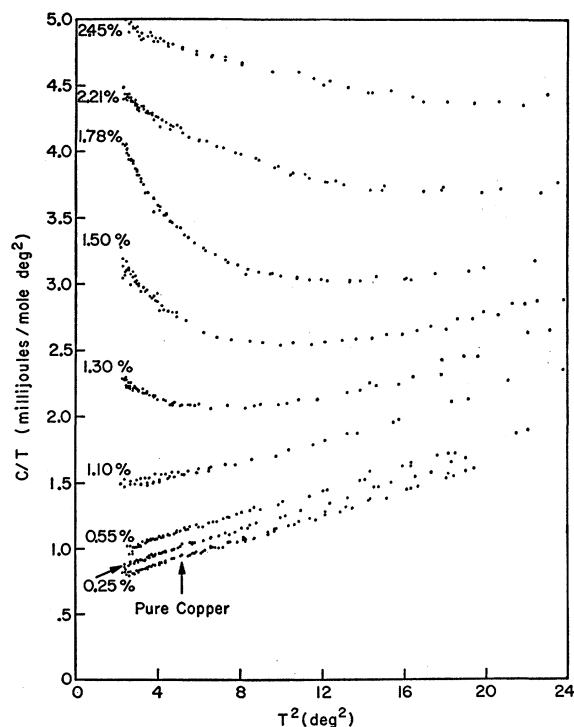


FIG. 3. Specific heats of dilute Cu-Co alloys.

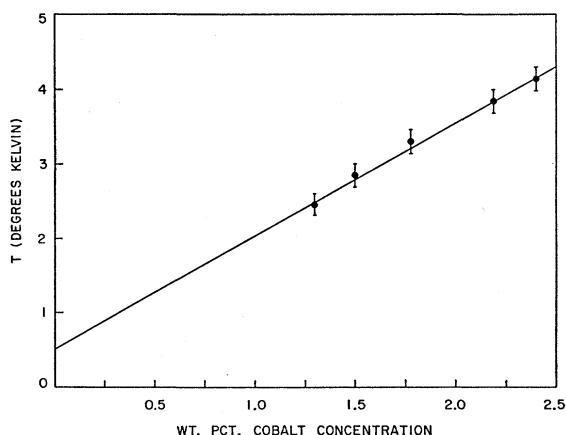


FIG. 4. Temperature of initiation of low-temperature anomaly vs temperature.

The specific heat of the heater-thermometer assembly and sample support was determined by measurements of the specific heats of three samples of spectroscopically pure copper varying in mass from 15 to 30 g. This also served to measure the accuracy of the thermometer calibration obtained using the thermal switch and calorimeter. The results agreed with the determination of the specific heat of pure copper by Corak *et al.*¹⁵ to within $\frac{1}{3}\%$ and had a root-mean-square deviation of 0.6% over some 70 measurements made on each sample.

RESULTS

Measurements were made on samples having concentrations of roughly $\frac{1}{4}$, $\frac{1}{2}$, 1, $1\frac{1}{4}$, $1\frac{1}{2}$, $1\frac{3}{4}$, $2\frac{1}{4}$, and $2\frac{1}{2}$ weight percent of cobalt in copper. This spans the range of alloys able to be made with real assurance that segregation of the cobalt ions does not occur to some extent. The results are shown on a graph of C/T vs T^2 in Fig. 3 together with the data of the specific heat of pure copper.

Several trends are apparent in these measurements. The first is that the position of the strong upswing in specific heat at the low-temperature end of the curves moves upward in temperature with an increase in the cobalt-ion concentration. Because none of the measurements reveal the full extent of this anomaly, the variation of its onset temperature with concentration has been estimated from the positions of the minima in the specific heat curves. The result is plotted in Fig. 4, which shows that the temperature at which this anomaly occurs is a linear function of cobalt concentration.

A second observation is that the specific heat curves are all parallel to that of pure copper on the C/T vs T^2 plot at temperatures above the large low-temperature anomaly. Therefore the specific heat excess is linear in temperature in this range.

Finally, the excess specific heat in the linear region

¹⁵ W. S. Corak, M. P. Garfunkel, C. B. Satterthwaite, and A. Wexler, Phys. Rev. **98**, 1699 (1955).

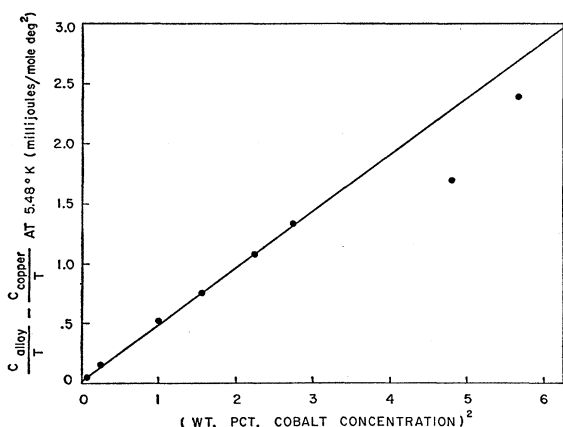


Fig. 5. C_p/T excess vs the square of cobalt concentration.

is a quadratic function of the concentration of the cobalt ions as shown by Fig. 5. The measurements for the two highest concentrations are probably not correct because the linear region does not begin within the temperature range investigated. However, the fact that these higher concentration alloys ($>2\%$) do not produce a great enough specific heat excess below the linear region indicates that they will be even more deficient when finally in that region. Therefore the quadratic dependence upon concentration must not hold above 2% .

It is interesting to compare these results with those of Zimmerman and Hoare on copper-manganese alloys to see if there might be some similarity in the interactions causing the two specific heat anomalies. The $2\frac{1}{4}\%$ and $2\frac{1}{2}\%$ concentration samples do not have as steep a rise in C/T as do the lower concentration samples at the lower temperatures, and therefore might be exhibiting the beginning of a Cu-Mn ordering in which the specific heats are linear in temperature and constant in concentration below the transition temperature. However, it is not typical of this type of ordering to maintain the large differences in specific heat above the transition temperature as occurs in Cu-Co. Finally, the concentration dependence of the transition temperature as shown in Fig. 4 is only $1.5^\circ\text{K}/\text{wt.}\%$, which is more than an order of magnitude less than the $26^\circ\text{K}/\text{wt.}\%$ found in the Cu-Mn alloys. Therefore the interactions in Cu-Co and Cu-Mn must be quite different in character.

The information which these data provide concerning the theories of Overhauser¹² and Marshall¹³ is hard to

evaluate. However, if the local field probability distribution described by Marshall is generally applicable to dilute alloys of paramagnetic ions in high-conductivity metals, then Cu-Co and Cu-Mn should have similar specific heats. On the other hand, if the Overhauser theory is correct in maintaining that the antiferromagnetic ordering in Cu-Mn is necessary to produce the specific heat anomaly, the Cu-Co and Cu-Mn should have different types of specific heat anomalies, as has been found.

Assuming spin $\frac{3}{2}$, a calculation of entropy in the 1.5° to 4.5°K temperature range shows that the linear part of the specific heat accounts for an ordering of less than 4% of the available cobalt spins for any of the samples measured. If these moments are to be completely ordered at 0°K , considerable entropy must lie above and below the range measured. The curvature of the inverse susceptibility below 50°K indicates that some part of the specific heat anomaly must exist throughout the range below that temperature. The resistivity minimum also lies at temperatures above 20°K (and probably below 50°K),⁹ which would seem to corroborate a relatively high temperature for the termination of the low-temperature specific heat anomaly, even though it is difficult to specifically associate this anomaly with the establishment of the ferromagnetic ion pair coupling.

On the other hand, the magneto-resistance data⁹ show a non-concentration-dependent linear relationship between the change in resistivity and the square of the magnetization per gram. This indicates that the paramagnetic ions are not yet strongly coupled and are still able to freely align themselves in a small applied magnetic field for temperatures above 1.2°K . Calculations¹⁶ of the magnitude of the reduction in resistance as a function of magnetization would seem to confirm that the majority of the ions exist in isolation rather than in magnetically coupled clusters above 1.2°K . Therefore the majority of the internal spin alignment must occur below 1.2°K , and so the specific heat must also have a very large anomaly below that temperature.

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¹⁶ A. D. Brailsford (private communication).