

Θ with increasing T to a minimum which occurred at values of T ranging from 6°K for potassium to over 100°K for Mo; the increase in Θ with increasing T beyond the minimum tends to be more rapid for those substances having lower values of β ; at T much greater than that for minimum Θ , the value of Θ becomes practically constant (little different from the minimum Θ for the substances having large β).

ACKNOWLEDGMENTS

The author would like to express his gratitude to the many people who have aided him in this work, particularly to Ronnie Long who wrote the program for the specific heat calculations, and to Dewaine Heller who wrote the program for obtaining the Debye Θ from the specific heat.

Specific Heats of Dilute Au-Co Alloys between 1.2° and 5°K

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(Received November 6, 1961)

The specific heats of six specimens of dilute Au-Co alloys were measured between 1.2° and 5°K. Cobalt concentration of these samples lay between $\frac{1}{2}$ and $3\frac{1}{2}$ at.%. The specific heat is greater than that of pure gold at all alloy concentrations, with the excess at the higher temperatures being linear in temperature and proportional to the $\frac{3}{2}$ power of concentration for samples containing less than 2 at.% of cobalt. At the lower temperatures the specific heat excess is no longer linear in temperature, but diminishes less rapidly with decreasing temperature. The character of the specific heats of these Au-Co alloys is found to be very similar to the specific heats of dilute Cu-Co alloys.

INTRODUCTION

THESE measurements of the low-temperature specific heats of dilute gold-cobalt alloys constitute one of a series of investigations of the specific heats of dilute alloys of paramagnetic ions in noble metals.^{1,2} It is expected that such data will be of value in providing the basis for a clearer insight into the mechanism of magnetic interactions in metals.

At present, quite complete resistance and magneto-resistance data exist for the entire set of dilute alloys of paramagnetic ions in noble metals.^{3,4} Resistivities are found to have a maximum followed by a minimum, or just a minimum, as the temperature increases from absolute zero. In both cases, existence of the minima can be accounted for by the ferromagnetically coupled ion pair scattering proposed by Brailsford and Overhauser,⁵ while the maxima seem to be associated with the reduction of spin-disorder scattering accompanying a large-scale magnetic ordering.

Susceptibility measurements,³ on the other hand, are only available for a few members of this class of alloys, and are unreliable in some cases because of the high impurity content of the specimens used. However, recent

susceptibility measurements using high purity materials do show obvious correlation with the resistivity data. Cu-Mn⁶⁻⁹ and Ag-Mn^{7,10} both possess resistivity maxima and are antiferromagnetically ordered at low temperatures with susceptibilities that are similar to each other in character. Cu-Co¹¹ exhibits only a resistivity minimum and yet has a negative Curie temperature as measured from the high-temperature data. However, its susceptibility increases very rapidly near absolute zero, indicating that a cooperative antiferromagnetic ordering is not taking place. Susceptibility measurements for Cu-Fe^{12,13} have been made from 300°K down to liquid hydrogen temperatures and appear to be quite similar in character to measurements for Cu-Co, with no indication of long-range ordering above 14°K. And as might be expected, Cu-Fe exhibits only a resistivity minimum.⁴

Specific heat data are now available for dilute alloys of Cu-Mn,¹ Ag-Mn,¹⁴ Cu-Co,² and Cu-Fe,⁴ in addition to the present measurements on Au-Co. The data on

⁶ J. Owen, M. Browne, W. D. Knight, and C. Kittel, *Phys. Rev.* **102**, 1501 (1956).

⁷ J. Owen, M. Browne, V. Arp, and A. F. Kip, *J. Phys. Chem. Solids* **2**, 85 (1957).

⁸ A. N. Gerritsen and J. O. Linde, *Physica* **18**, 877 (1952).

⁹ R. W. Schmitt and I. S. Jacobs, *J. Phys. Chem. Solids* **3**, 324 (1957).

¹⁰ A. N. Gerritsen and J. O. Linde, *Physica* **17**, 573 (1951).

¹¹ I. S. Jacobs and R. W. Schmitt, *Phys. Rev.* **113**, 459 (1959).

¹² C. Berghorst, *Z. Metallk.* **52**, 179 (1961).

¹³ F. Bitter, A. R. Kaufmann, C. Starr, and S. T. Pan, *Phys. Rev.* **60**, 134 (1941).

¹⁴ J. De Nobel and F. J. Du Chatenier, *Physica* **25**, 969 (1959).

¹ J. E. Zimmerman and F. E. Hoare, *J. Phys. Chem. Solids* **17**, 52 (1960).

² L. T. Crane and J. E. Zimmerman, *Phys. Rev.* **123**, 113 (1961).

³ See A. N. Gerritsen, *Physica* **25**, 489 (1959) for a compilation of references concerning alloys of paramagnetic ions in noble metals.

⁴ J. P. Franck, F. D. Manchester, and D. L. Martin, *Proc. Roy. Soc. (London)* **A263**, 494 (1961).

⁵ A. D. Brailsford and A. W. Overhauser, *Phys. Rev. Letters* **3**, 331 (1959); and *J. Phys. Chem. Solids* **15**, 140 (1960).

Cu-Mn and Cu-Co have shown a basic dissimilarity between the magnetic interactions in the antiferromagnetically ordered alloys and those which lack such an ordering. The antiferromagnetically ordered Cu-Mn alloys have an anomaly that is linear in temperature and roughly independent of concentration below the transition temperature, with a transition temperature that is a linear function of Mn ion concentration. On the other hand, measurements of the specific heats of dilute Cu-Co alloys between 1.5° and 5°K reveal an anomaly that is linear in temperature and a quadratic function of ion concentration at the higher temperatures, and rises rapidly on a C/T plot at lower temperatures as the temperature is reduced toward absolute zero. Although the antiferromagnetic Ag-Mn and the non-magnetically-ordered Cu-Fe data are only available over an extremely dilute concentration range, their specific heats have the same character as Cu-Mn and Cu-Co, respectively. These measurements on Au-Co were undertaken to more firmly establish the similarity of the specific heats of the non-antiferromagnetically-ordered alloys, and to provide further data for the study of the magnetic interactions in these alloys as a function of paramagnetic ion concentration. Since the gold-cobalt alloys also afford larger lattice parameters than exist in Cu-Co, it was further hoped that these measurements would provide information concerning the variation in magnetic interaction with distance.

EXPERIMENTAL METHOD

The gold and cobalt were obtained in spectroscopic purity from the American Smelting and Refining Company and Johnson-Matthey and Company, respectively. Samples were melted and chill cast in a high vacuum in the rf furnace used in making the Cu-Co samples.² A 24-hour anneal at 1000°C was followed by a rapid quench in an iced brine bath. Cobalt concentration was determined by a chemical quantitative analysis of the alloyed samples. Although no studies have been made on Au-Co to assure the efficiency of the annealing technique in preventing precipitation of cobalt, similar alloy systems have been examined and strongly indicate that this technique is valid for Au-Co. The solubility of both cobalt and iron in copper is much less than the solubility of cobalt in gold at the annealing temperature and yet neither a magnetic study of Cu-Co^{11,15} nor an x-ray diffraction study of Cu-Fe¹⁶ showed evidence of precipitation after a 1000°C anneal and quench. As a crude test for precipitation, the 3% Au-Co sample was reannealed and quenched in a water bath, which affords somewhat slower cooling than iced brine, and subsequent specific heat measurements were identical with those made after the iced brine quench. The calorimeter was the same

¹⁵ 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)].

¹⁶ J. B. Newkirk, *Trans. Am. Inst. Mining, Met. Petrol. Engrs.* **209**, 1214 (1957).

as that used in the Cu-Co measurements and has previously been described in detail.²

RESULTS

Measurements were made using samples of 0.6, 1, 1.8, 2.6, 3, and 3.5 at.% cobalt concentration as well as pure gold, and are shown in Fig. 1 on a plot of C/T versus T^2 . The specific heat in excess of that of pure gold is identical in character with that of the Cu-Co alloys. In both cases, the excess C/T maintains a constant value at the high temperature end of the range for any given cobalt concentration, and rises strongly at the lower temperature.

The constant value of the excess C/T at the high-temperature portion of these measurements establishes that the excess specific heat is linear in temperature in that region and varies in magnitude with concentration. A measurement of the concentration dependence of the linear specific heat excess is more difficult than in the case of Cu-Co because the total value of the specific heat and the accompanying magnitude of error is more than four times larger at the higher temperatures for the Au-Co alloys, while the specific heat excess is less than twice as great at any given value of cobalt concentration. Figure 2 shows the change in excess specific heat in the linear region as a function of cobalt ion concentration. A plot of these points on a log-log graph shows that the magnitude of the excess specific heat in this region is proportional to the $\frac{3}{2}$ power of the cobalt concentration, with a proportionality constant of roughly

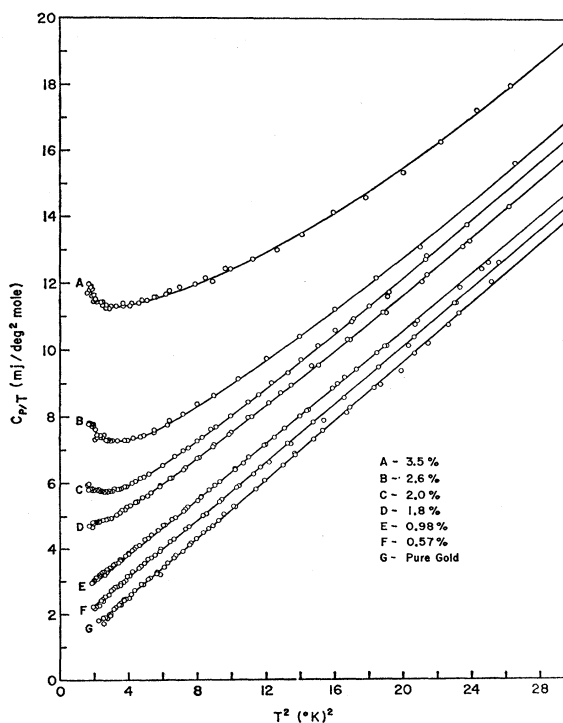


FIG. 1. The specific heats of dilute Au-Co alloys.

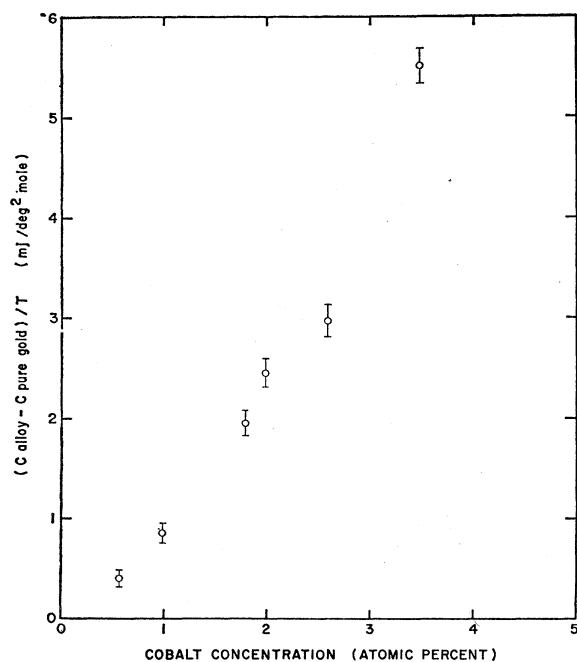


FIG. 2. C_p/T excess vs cobalt concentration.

0.8 mJ/deg² mole/(at.%)³. A similar plot for Cu-Co reveals a specific heat excess that is proportional to the square of the concentration, with a proportionality constant of 0.5 mJ/deg² mole/(at.%)². In both cases the proportionalities only pertain to specimens of less than 2 at.% cobalt concentration, for further increments in cobalt cause the the excess specific heat to increase less rapidly than is necessary to be in agreement with the respective concentration dependences.

The large upswing in C/T at low temperatures is not as much in evidence in Au-Co as in Cu-Co, and only the three highest concentration samples show definite evidence of its existence. If the minimal values of C/T are taken to be the initiation points of the rise in C/T as the temperature is reduced, and if the temperature dependence of the positions of these minima are assumed to be linear as occurs in Cu-Co, then the 2.0 and 2.6 at.% samples indicate a value of 0.75°K/at.% for the temperature dependence of the initiation of the upswing. The corresponding measurement in Cu-Co yields a value of 1.5°K/at.%.

Since the magnetic ordering of the cobalt ions must be complete at absolute zero, the total entropy associated with the excess specific heat must equal $Nk \ln(2S+1)$, where S is the electron spin of the ions, N is the number of ions present, and k is Boltzmann's constant. However, a measurement of the excess entropy between 1.2° and 5°K. shows that less than 4% of the magnetic moments are disordered within this temperature range if a spin of $\frac{3}{2}$ is assigned to the ions. The same value was also found for the excess entropy of Cu-Co alloys in this temperature range. Since no magnetic data are available for Au-Co, it is impossible to specify the temperature at which the magnetic ordering takes place, but the great similarity of the Au-Co specific heats to those of the Cu-Co alloys indicates that the magnetic ordering processes of the two systems should be similar. Since the magnetoresistance data establish that no long-range magnetic ordering occurs above 1.6°K in Cu-Co, the same is probably true for the Au-Co alloys. Therefore, the major part of the magnetic entropy for Au-Co would seem to be below 1.2°K.

Very little can be said as yet concerning the magnetic interactions which cause the anomaly in these non-antiferromagnetically-ordered alloys. However, the anomalies of Cu-Co, Cu-Fe, and Au-Co exhibited in the 1.2°-5°K temperature range are not similar to any part of the Cu-Mn and Ag-Mn anomalies that result from cooperative phenomena, and thus the magnetic interactions are expected to be different for the two cases. It is also interesting that the measurements of Guthrie *et al.*¹⁷ on Cu-Ni reveal a specific heat excess that is linear in temperature in the 1.5°-5°K range and which is very similar to the linear region of specific heat excess in Cu-Co, Au-Co, and Cu-Fe. Since the major part of this linear specific heat excess would seem to result from the magnetic interactions common to these non-cooperatively-ordered alloys, this would account for the anomalous changes in electron density at the Fermi surface calculated by Guthrie *et al.* for Cu-Ni.

ACKNOWLEDGMENT

The author wishes to thank Dr. H. Sato for many helpful discussions concerning this work.

¹⁷ G. L. Guthrie, S. A. Friedberg, and J. E. Goldman, Phys. Rev. 113, 45 (1959).