Specific Heats of Some Copper-Rich Copper-Nickel Alloys at Liquid Helium Temperatures*†

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(Received September 15, 1958)

Helium-temperature heat capacity measurements have been made using samples containing 60, 65, 75, and 90 weight percent of copper in nickel. The results are in approximate agreement with the previous work of Keesom and Kurrelmeyer. The more copper-rich samples have been found to obey a law of the type $c_v=\gamma T+\beta T^3$, but anomalies have been noted in the results of measurements on some of the samples containing 35 and 40 weight percent of nickel. These anomalies are attributed to a magnetic effect. Analysis of the results shows that the usual collective electron interpretation of the intrinsic magnetization of Cu-Ni alloys is oversimplified.

I. INTRODUCTION

THE Cu-Ni alloys have often been used as an example of a system whose behavior is readily explained by simple rigid-band arguments. Calculations of density of states by Krutter[1] and also by Fletcher[2] and others[3,4] have shown that copper or nickel may be expected to have a dense band of states made up of wave functions which are similar to $3d$ atomic wave functions, as well as another band of states of much lower density but covering a wider energy range. This second group of states is presumed to possess wave functions which are similar to $4s$ atomic wave functions. According to collective electron arguments,[5,6] the spontaneous magnetization of nickel or of nickel-rich copper-nickel alloys is due to unpaired spins of electrons occupying states with $3d$-type wave functions. This is supported by measurements which show that the gyromagnetic ratio of nickel is 1.92. This leads one to believe that the magnetic moment of nickel is almost entirely of spin origin.

A direct extension of this line of thought has been used[5] to explain the linear relation between copper concentration and low-temperature spontaneous magnetization in copper-nickel alloys. It has been observed that the low-temperature spontaneous magnetization appears to decrease by one Bohr magneton for every copper atom which replaces a nickel atom in a copper-nickel alloy. This spontaneous magnetization is 0.6 Bohr magneton/atom in pure nickel, and goes to zero at approximately 60% copper. The simple explanation states that copper and nickel share a common set of bands, and each substituted copper atom adds an extra electron which is contributed almost exclusively to the common "d" bands. In pure nickel all of the unfilled "d" holes are presumed to be of one spin orientation. As electrons are added, unoccupied states in the "d" band are populated, so that previously unpaired spins become paired. By this reasoning, both halves of the d band will be filled at a concentration of approximately 60% copper in nickel. This simple filling effect would lead to the observed[7–10] linear relation between copper concentration and low-temperature saturation magnetization. It implies also that a Cu-Ni alloy containing 60 atomic percent or more of copper should have a low density of states at the Fermi surface, since the density of states is then only that contributed by the $4s$-type band.

The atomic heat of simple metals is found to obey the law $c_v=\gamma T+\beta T^3$ at sufficiently low temperatures. The simple theoretical treatments show[11,12] that in this region the constants gamma and beta have the values

$$\gamma=(\pi^2k^2/3)N(E_F), \quad (1)$$

$$\beta=464.3/\theta^3 \text{ cal/mole } (^\circ\text{K})^4, \quad (2)$$

where $N(E_F)$ is the density of electronic energy states at the Fermi surface, and θ is the Debye characteristic temperature.

If we assume that these relations have validity in the copper-nickel alloys, then gamma is a measure of the density of states at the Fermi surface, for these alloys, just as it is for simple metals.

Keesom and Kurrelmeyer[13] have measured the low-temperature heat capacities of samples containing 20,

* Work supported by the U. S. Atomic Energy Commission, the Office of Naval Research, and the Allegheny-Ludlum Steel Corporation.

† Submitted (by G.L.G.) in partial fulfillment of the requirements for the Ph.D. degree at the Carnegie Institute of Technology.

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TABLE I. Copper-nickel alloy specimen characteristics.

Sample No.	Ingot No.	Analysis, in weight percent Cu	Ni	Co	Fe	Mn	Al	C	Si	Pb	P	Sample form	Heat treatment	Sample size in moles
1	6852-W	89.86	10.05	0.05	0.02	<0.01	tr	<0.01	0.02	tr	tr	Solid block	Swaged and homogenized	4.004
2	6888-W	74.97	24.9	0.09	0.02	<0.01	tr	<0.01	0.01	tr	tr	Solid bar	Swaged and homogenized	3.2
3	6888-W	No analysis										Chips in capsule	Swaged and homogenized, then cold-worked	1.88
4	6887-W	64.68	35.1	0.14	0.02	<0.01	tr	<0.01	0.01	tr	tr	Chips in capsule	Swaged and homogenized, then cold-worked	1.70
5	6887-W	64.65	34.9	0.14	0.02	<0.01	tr	<0.01	0.01	tr	tr	Solid bar	Swaged and homogenized	3.3
6	3-Ford	64.8	35.2	0.02	0.02	<0.01	tr	<0.01	0.01	tr	tr	Solid bar	Swaged and homogenized	3.05
7	6587-W	59.52	39.9	no anal.	0.05	tr	tr	no analysis				Chips in capsule	Swaged and homogenized, then cold-worked	1.89

40, 60, and 80 weight percent of Cu in Ni. They found an anomalous relationship between c_v and T for the sample containing 60 weight percent of Cu in Ni and also noted a much smaller anomaly in the results of their measurements on the 80% Cu sample. Both of these measurements indicated values of $N(E_F)$ which were much too high to be accounted for by the simple theory outlined above. Keesom and Kurrelmeyer cited the desirability of further measurements in the composition range from 60 to 80% Cu, but no such additional data have been reported prior to the present paper.

II. METHODS OF MEASUREMENT

The technique employed in the present work is a fairly standard one which has been used previously by others.[13–16] A sample, in the form of a solid block, or in the form of chips contained in a helium-filled capsule, was supplied with an electrical resistance thermometer and an electrical heater. This composite specimen was suspended on nylon threads in an enclosure which could be continuously evacuated. The resistance thermometer, a carbon resistor, was calibrated against the vapor pressure of a surrounding helium bath, using helium gas as a heat transfer medium. This transfer gas was then removed by a diffusion pump and a series of heating periods begun. The resistance *versus* time drift curves before and after the heating periods were nearly always straight lines. The resistance values obtained by extrapolating these curves into the middle of the heating periods were converted into temperatures. The difference between two such temperatures associated with one heating period was assumed to be caused solely by the measured electrical energy input. The heat capacity was calculated and assigned to a temperature equal to the average of the two temperatures obtained by the above extrapolations.

The experimental arrangement differed slightly from that which is commonly used. The electrical heater and thermometer circuits were joined at a common point at the sample and superconducting leads were used to provide electrical connections between the sample and the Stupakoff seals on the calorimeter can. As a result, three electrical leads were attached to the sample instead of the usual eight.

Five separate radiation baffles were inserted in the vacuum pumping line, and an aluminum foil shield was used on the sample. The low number (3) of Stupakoff seals, a VMF 100 diffusion pump, and extensive use of a bath manipulation technique[17] produced pressures which could not be read at an externally located 1949 RCA ionization gauge. These pressures were less than 10^{-6} mm of Hg at the gauge, and this is believed[17] to correspond to a pressure of the order of 10^{-8} mm of Hg at the sample. As a result, the resistance *versus* time drift curves were straight and nearly flat.

The calculations were programmed for the Carnegie Institute of Technology Computation Laboratory's IBM-Model 650 computer. This made it feasible to use a least squares procedure to fit a parametric $f(R,T)=0$ relation to the thermometer calibration data. This was done, using Clement's T_E vapor pressure table[18] in conjunction with the relation

$$[(\log_{10}R)/T]^{\frac{1}{2}}=A+B\log_{10}R+C(\log_{10}R)^2,$$

where the parameters A, B, and C were adjusted in such a way as to minimize the quantity $\sum_i(T_m-T_{\text{calc}})_i^2$. The fitting process commonly produced rms temperature deviations of 0.002°K or 0.003°K, and occasionally resulted in rms deviations of less than 0.001°K.

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III. EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

A tabulation of sample characteristics appears in Table I. The experimental results appear in Fig. 1, plotted as c_v/T *vs* T^2.

Figure 1 shows that there is little difficulty in obtaining a value for γ for the samples containing 75 and 90 weight percent Cu. Samples No. 1 and No. 2 rather clearly give $\gamma=(2.50\pm0.05)\times10^{-4}$ cal/mole (°K)^2, $\theta=343$°K; and $\gamma=(4.85\pm0.1)\times10^{-4}$ cal/mole (°K)^2, $\theta=385$°K for the 90–10 and 75–25 compositions, respectively. However, some of the samples containing 60 or 65 weight percent Cu show definite signs of deviations from the usual linear plus cubic temperature dependence of the specific heat. This makes both "γ" and "θ" nebulous quantities. It is assumed that the curvature of the c/T *vs* T^2 plots for these compositions is due to a magnetic contribution to the specific heat. Speculation concerning the details of this phenomenon based on the information now available is not regarded as profitable. If, however, this magnetic contribution is small at 4°K, one may attempt to extract a value for γ from the values of c/T at 4°K for these samples by subtracting a reasonable value for the amount contributed by the T^2 or lattice vibration term. Such a process leads one to assign γ values of $(9.6\pm1)\times10^{-4}$ cal/mole (°K)^2 and $(14.8\pm1.5)\times10^{-4}$ cal/mole (°K)^2 for the 65–35 and 60–40 Cu-Ni compositions, respectively. We shall refer to these quantities as "effective γ" values.

The high values for these "effective γ's," as well as the relatively high value of the γ for the 75–25 Cu-Ni alloy samples, are in conflict with the usual interpretation of the intrinsic magnetization data. The present data indicate a high density of states at compositions which are usually associated with a "filled *d*-band."

A simple collective-electron approach[6] to ferromagnetism may be used to calculate the density of states for a material which is almost but not quite ferromagnetic, provided the average value of the exchange integral for the electron pairs is known. Such a calculation is carried out in an appendix, using a value

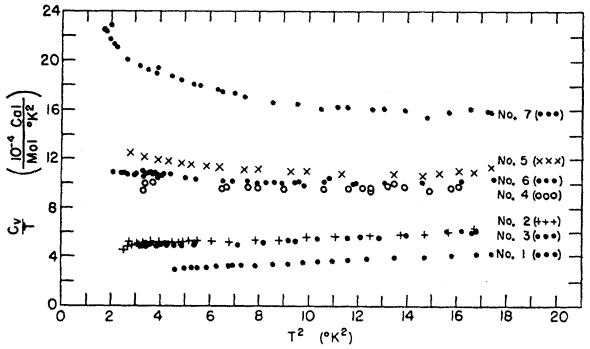

FIG. 1. c_v/T *vs* T^2 for several Cu-Ni alloy samples. The form and composition of the samples are listed in Table I.

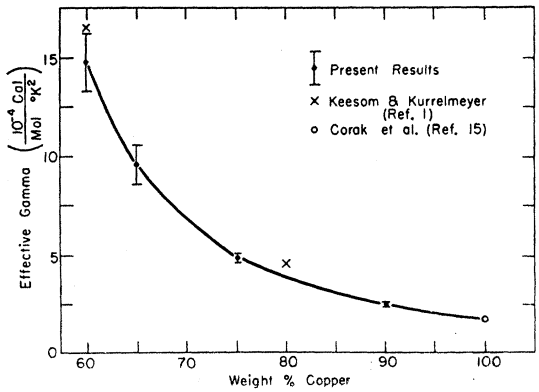

FIG. 2. γ or "effective γ" *vs* weight percent of copper for Cu-Ni alloys. Estimates of the uncertainty of the γ's are indicated only for the present results.

derived by Slater[19] for the average value for the exchange integral for pairs of 3*d* electrons in nickel. This calculation gives 10×10^{-4} cal/mole (°K)^2 for the value of γ for a nickel-like material which is not quite ferromagnetic.

Measurements of the low-temperature magnetic moment as a function of temperature and applied field have been performed by Arrott and Goldman,[10,20] using samples cut from the same ingots as were the samples used in the present specific heat measurements. These workers have concluded that the specimens containing 60 weight percent of copper are barely ferromagnetic, while those containing 65 weight percent of copper are paramagnetic. This suggests that the values of c/T for the 65 weight percent sample should be compared with the value of γ calculated in the appendix. The agreement is better than might be expected and is regarded as fortuitous. However, it is apparent that on no grounds may it be said that there is any reason to speak of "filled *d*-bands" for 60–40 Cu-Ni alloys.

If the gammas and effective gammas suggested by the data as plotted in Fig. 2 are viewed as being indicative of the shape of a density of states curve for Cu or for Ni, the indicated shape fails to agree with that calculated by Fletcher,[2] Krutter,[1] Howarth,[21] *et al.*

Possible causes of difficulties in simple theoretical interpretations of Cu-Ni alloy data are obvious. There is reason to doubt that density of states calculations for Cu or Ni have application to Cu-Ni alloys, since the alloys present a nonperiodic potential problem. If one argues that a virtual lattice[22] is applicable, it must be remembered that investigations[23–25] of effects of perturbations have shown that the perturbations caused by the nonperiodicity of the potential bring about the

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greatest changes in $N(E)$ near the ends of bands. This complication is presumably present in a 60–40 Cu-Ni alloy.

ACKNOWLEDGMENTS

We wish to acknowledge numerous helpful discussions with Drs. A. Arrott, D. L. Burk, and P. M. Marcus. We are grateful to the Westinghouse Electric Corporation and the Ford Motor Company who provided the specimen materials used in this work.

APPENDIX. MINIMUM GAMMA FOR FERROMAGNETISM IN CU-NI ALLOYS

When a determinantal wave function is used, a term of the type

$$E_{ex}=\sum_{\parallel \text{ spins};\, i\neq j}\int u_i^*(1)u_j^*(2)\frac{e^2}{r_{12}}u_j(1)u_i(2)dv_{12} \quad (3)$$

appears in the total energy. This is called the exchange energy.

If there is a total of N electrons, there are approximately $N^2/2$ contributions to the exchange energy, each of these $N^2/2$ contributions being one of the individual terms in the sum given above. If, however, $n/2$ electrons change spin direction, there are now

$$(N/2+n/2)^2+(N/2-n/2)^2 \quad (4)$$

terms in the sum, or

$$N^2/2+n^2/2 \quad (5)$$

such terms. If I is an assumed average value for integrals of the type

$$\int u_i^*(1)u_j^*(2)\frac{e^2}{r_{12}}u_i(2)u_j(1)dv_{12}, \quad (6)$$

then

$$dE_{ex}/dn\cong nI. \quad (7)$$

For small shifts of electrons from one spin direction to another, we may assume that $N_{\frac{1}{2}}(E_F)$ is a constant. Then for cases where only a few spins have changed sign, the difference in Fermi energies between the two half-bands is

$$\Delta E_F\cong n/N_{\frac{1}{2}}(E_F), \quad (8)$$

where $N_{\frac{1}{2}}(E_F)$ is the density of states in one half-band.

The increased total Fermi energy due to a further shift of $dn/2$ electrons will be $[n/N_{\frac{1}{2}}(E_F)]dn/2$. If this increase is less in absolute value than the decrease in energy due to exchange, the alignment process will continue for a system at 0°K. Therefore, we have

$$\frac{n}{N_{\frac{1}{2}}(E_F)}\frac{dn}{2}<Indn \quad (9)$$

as a criterion for ferromagnetism at 0°K. Or,

$$N_{\frac{1}{2}}(E_F)=1/2I \quad (10)$$

for the critical situation.

Since

$$\gamma=\tfrac{2}{3}\pi^2k^2N_{\frac{1}{2}}(E_F) \quad (11)$$

for both half-bands, we are able to estimate a value for γ for the Cu-Ni alloy of critical composition for which ferromagnetism is almost but not quite an actuality at 0°K.

It has been shown by Slater[19] that a reasonable average value for the exchange integral

$$I=\int u_i^*(1)u_j^*(2)\frac{e^2}{r_{12}}u_i(2)u_j(1)dv_{12} \quad (6)$$

for two arbitrarily chosen d-band Bloch-type wave functions for nickel is 4629 cm^{-1}/N, where N is the number of atoms. For a mole of the material, this gives $I=1.61\times10^{-36}$ erg. Using

$$\gamma_{\text{crit},\,d}=2\pi^2k^2/6I \quad (12)$$

from (10) and (11), we obtain

$$\gamma_{\text{crit},\,d}\cong10^{-3}\text{ cal/mole (°K)}^2. \quad (13)$$

This shows clearly that the value of γ for a 60–40 or 65–35 Cu-Ni alloy cannot be expected to approximate the γ of pure copper. It also shows that a collective electron treatment would suggest the presence of d-band holes in both half-bands of some nonferromagnetic alloys near the 60–40 composition.