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Magnetic Susceptibility of Dilute Alloys of Nickel in Copper between 2.5°K and 295°K*

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The magnetic susceptibilities of pure Cu and dilute Cu–Ni alloys containing 0.59, 1.16, and 2.48 atomic percent Ni have been measured by a Gouy method at temperatures between 295°K and 2.5°K. At room temperature all the alloys were found to be diamagnetic, the numerical value of the susceptibility decreasing with increasing nickel content, as found by earlier workers. The paramagnetic contributions found at low temperatures were, however, considerably smaller than those previously reported, although the 2.48% alloy was paramagnetic at temperatures below 16°K. The resultant susceptibility of each alloy is given with reasonable accuracy by an expression of the form $aT+b+(c/T)$, and the significance of each of these terms is discussed. A theoretical model, in which the number of nickel atoms possessing resultant magnetic moments is temperature-dependent and which fitted the earlier high-temperature data reasonably well, has been found inadequate for the new low-temperature results.

INTRODUCTION

In early theories of alloy formation,[1] the outer electrons were considered to occupy energy states properly described by Bloch functions which are a property of the crystal as a whole and are not modified by the presence of the solute or "impurity" atom. Where the constituent elements differ in the number of electrons contributed to the Fermi distribution, it must be assumed that the screening of the nuclear charge that is necessary to avoid a catastrophe in the electrical resistance[2] is accomplished by a pile up of the Fermi electrons in the neighborhood of the atom contributing the greater number of electrons. More recently, an alternative possibility has been considered by Friedel[3] and others,[4] in which some or all of the outer electrons of the solute atoms are considered to occupy localized "bound" states which may or may not overlap the Fermi distribution of quasi-free electrons of the matrix metal. The importance of a proper description of states due to the solute constituents in dilute alloys is emphasized by the appearance of anomalous transport properties in dilute alloys of noble metals at low temperatures.

Magnetic susceptibility measurements provide a powerful tool for determining electronic configurations. Such measurements have been instrumental in revealing the electronic configurations of certain transition metals dissolved in noble metals. For example, the magnetic contribution of small amounts of iron dissolved in either copper or gold[5] or of small amounts of manganese dissolved in copper[6] exhibits a simple Curie-Weiss behavior indicating that the dissolved ions in these systems are well described by a bound electron picture, while the silver-palladium and nickel-rich copper-nickel alloys are best described by a band model assuming that the outer electrons of the alloying elements fill up states in the Fermi distribution. However, in the case of the copper-rich copper-nickel alloys, neither model appears to describe the experimental results.[7] Small additions of nickel to copper give a paramagnetic contribution which is not expected on the basis of the simple Mott band model[8] or the more detailed collective electron treatment given by Wohlfarth.[9] In this model it is assumed that with the addition of copper to nickel the "valence" electrons contributed by the copper atoms fill up holes in the unmodified nickel 3*d* band as well as available states at the top of the Fermi distribution of 4*s* electrons such that at 60 atomic percent copper all the available *d*-states are occupied. A similar description obtains in the case of silver-palladium alloys and is well verified by experiment.[7] That the situation is not so simple in the case of copper-nickel alloys was indicated by the results of measurements of specific heat[10] and magnetic susceptibility, both in the neighborhood of 60 percent copper[11] and at the copper-rich end of the system.[12] In particular, the susceptibility measurements on dilute alloys of nickel in copper by Kaufmann and Starr[12] down to the temperatures of liquid hydrogen showed peculiarities in

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magnitude and temperature dependence that are not readily described by the simple theories.

A model recently advanced by one of the authors[13] and worked out in detail using a form of Fermi-Dirac statistics shows rather good agreement with the Kaufmann and Starr copper-nickel susceptibility data for room temperature and above.[14] However, these early results, especially those for the lower temperatures, could not be discussed with confidence since the contribution of nickel has to be found by subtracting a copper susceptibility which exhibits rather questionable peculiarities. In view of the considerable interest attaching to these alloys, it was felt that remeasurement of the alloys and an extension of these measurements to helium temperatures was desirable.

METHOD OF MEASUREMENT

Susceptibility measurements were made by the Gouy method using a commercially made semimicrobalance completely enclosed in a vacuum-tight aluminum box, glass windows in which permit observation of the weighing process. Rotary controls passing through vacuum seals in the vacuum box permit the balance to be operated from without. The sample is suspended from the balance beam in a long hollow tube which forms part of the same vacuum system as the balance case and which extends downward into a Dewar located between the poles of an ADL electromagnet.

Before each low-temperature run, the vacuum box was evacuated by an oil diffusion pump and then sufficient helium gas was added to assure thermal equilibrium between the sample and the cooling bath. The helium pressure required for adequate heat transfer (about 1 mm Hg) was determined by a thermometry run in which a carbon resistance thermometer was attached to a copper sample suspended in the tube from the balance in the same manner as for susceptibility measurements.

Field measurements for each reading were made with a Rawson Rotating Coil Fluxmeter calibrated against a nuclear resonance meter. This instrument gives the only significant error in these measurements since its relative accuracy during one run is only $\pm\frac{1}{2}\%$. The resultant error in susceptibility is about twice the error in the field determination.

SAMPLE PREPARATION

The pure copper sample was made from American Smelting and Refining Company copper rated at 99.999% pure and probably containing less than one part per million iron or nickel. The copper rod was swaged and drawn in ferrous dies, heavily pickled to remove surface ferromagnetic contamination, and then drawn through diamond dies to its final diameter of 0.0157 inch. A six-inch-long bundle of 250 of these wires constituted the sample. A bundle of wires was used instead of a single rod in order to reduce overdamping of the sample (an effect due to eddy currents which is very pronounced in pure copper at low temperatures).

After susceptibility measurements were completed at all temperatures on the unannealed bundle of copper wires, it was sealed in an evacuated quartz tube and annealed at 900°C for 120 hours.

The three copper-nickel alloys were fabricated from the same pure copper and electrolytic nickel containing about 0.01% iron. The copper and nickel were sealed in an evacuated quartz tube and held in the molten state for 30 minutes at 1140°C while the quartz tube was rocked back and forth to assure good mixing. The melt was then quenched into a water bath to provide the equivalent of a chill-cast ingot in which long-range segregation is minimized. These ingots were then swaged into 0.256 inch diameter rods. Six-inch samples were cut from each rod and pickled in a 50% solution of HNO_3 to a diameter of 0.250 inch to remove surface ferromagnetic contamination. Finally, the samples were sealed individually in evacuated quartz tubes and homogenized at 950°C for 100 hours. Chemical analyses made on pieces of the rods taken from positions immediately adjacent to the top and bottom of each 6-in. sample indicate a nickel content for the samples of 0.59, 1.16, and 2.48 atomic percent.

RESULTS OF SUSCEPTIBILITY MEASUREMENTS

Susceptibility measurements were made on each sample at temperatures extending from room temperature to helium temperatures. At each temperature, readings were made at field strengths ranging from 5000 gauss to 22 000 gauss. These results were plotted in the Honda manner[15] and showed no ferromagnetic contamination except in the case of the pure copper wires before annealing. These wires indicated a ferromagnetic content equivalent to 1.1 parts per million of iron in its normal ferromagnetic state. The accuracy of the data is such that a zero slope for the Honda plot (observed for all other samples) indicates an equivalent iron content of less than 5 parts in 10^8. The loss of the ferromagnetic contribution to the moment in copper after annealing is in agreement with similar observations of Constant *et al.*[16]

Since uncertainties as large as 2% were anticipated between susceptibility measurements made on different days, a special room-temperature comparison run was made. All the samples were measured without changing the fluxmeter location or its calibration. Thus the relative accuracy of these room-temperature susceptibility values was better than 1%. The susceptibility

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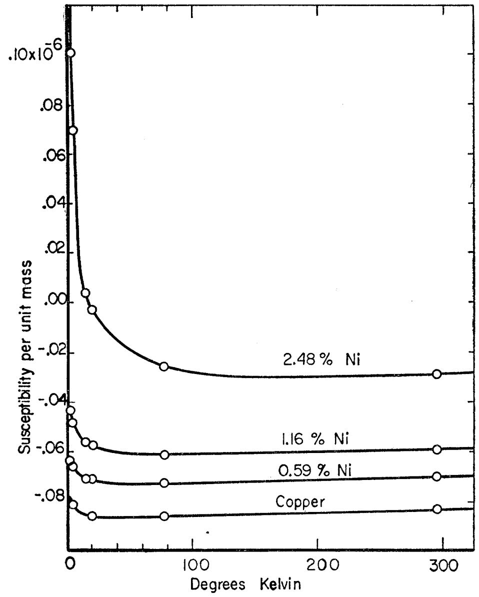

FIG. 1. The magnetic susceptibility per unit mass of copper and the copper-nickel alloys in cgs units.

values obtained at various temperatures were then adjusted to conform with the room-temperature results obtained in the room temperature comparison run. This adjustment was never greater than 1.6%. The relative accuracy at all temperatures for all samples is therefore about ±1%. These susceptibility values are shown in Fig. 1 and Table I. The present values are compared with those of previous investigators in Fig. 2.

INTERPRETATION OF RESULTS

The greater tendency toward paramagnetism exhibited at low temperatures by the Kaufmann and Starr[12] and the Bitter, Kaufmann, Starr, and Pan[17] data is probably due to the lower purity of the samples used by them. Also, their samples were apparently not annealed after cold working and the authors have observed in pure copper a temperature-dependent paramagnetism before annealing which is just twice that observed after annealing.

It should be pointed out that there is excellent agreement in slope and absolute value at room temperature between the present data and those of reference 17 as well as those of reference 12. This agreement gives grounds for confidence in both the low-temperature results of the present work and the high-temperature results of the previous work. Recent low-temperature susceptibility measurements on pure copper by Bowers[18] are in good agreement with the present data except for the disturbing discrepancy at 77°K as indicated in Fig. 2.

TABLE I. Magnetic susceptibility of copper and copper-nickel alloys for various temperatures, in cgs mass units.

Annealed Cu		Cu+0.59% Ni		Cu+1.16% Ni		Cu+2.48% Ni	
°K	$\chi\times10^6$	°K	$\chi\times10^6$	°K	$\chi\times10^6$	°K	$\chi\times10^6$
295	−0.0839	295	−0.0703	295	−0.0596	295	−0.0289
77	−0.0865	77	−0.0728	77	−0.0616	77	−0.0257
20.4	−0.0865	20.4	−0.0714	20.4	−0.0576	20.4	−0.0029
4.2	−0.0812	14.9	−0.0714	14.6	−0.0561	15.7	+0.0035
		4.2	−0.0661	4.2	−0.0481	4.2	+0.0696
		2.5	−0.0641	2.6	−0.0438	2.5	+0.1077

The paramagnetic contribution of the nickel atoms, which is large in terms of a band model and yet fails to exhibit the Curie-Weiss temperature dependence associated with bound states, led to the suggestion of an excitation theory in which the proportion of nickel atoms with a resultant moment increases with temperature. (This is the localized-state analog of the transfer effect discussed for the band model by Wohlfarth.[9]) This theory uses the standard band model for copper, but superposes for each nickel atom a narrow impurity level at an energy ϵ_0, $k\theta$ below the Fermi level at absolute zero, ζ_0. This level can be regarded as representing the least tightly bound electron of a nickel atom in the configuration $3d$.[10] At temperatures above absolute zero, a small number of these electrons will be thermally excited into vacant states at the Fermi level, thereby creating $3d^9$ nickel ions.

Assuming that the energy required to doubly ionize the nickel atom is prohibitive, then (thinking in terms of holes) each state in the impurity level may have one hole with spin up, or one hole with spin down, but never both. This leads to a modified form of the Fermi-Dirac electron distribution function, as discussed by Wilson:[19]

$$f=\frac{1}{1+2e^{(\epsilon_0-\zeta)/kT}}.$$

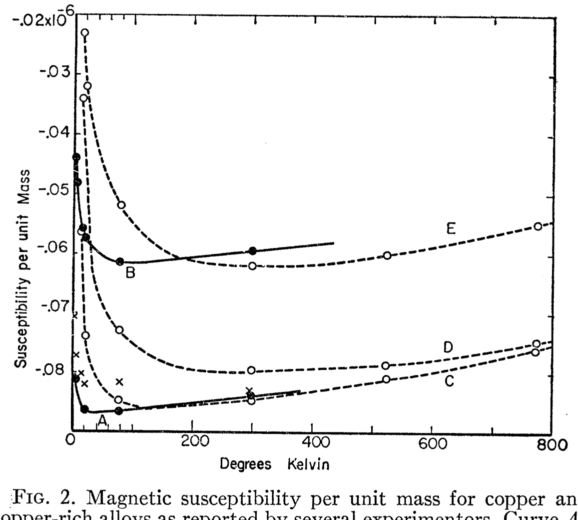

FIG. 2. Magnetic susceptibility per unit mass for copper and copper-rich alloys as reported by several experimentors. Curve A: pure annealed copper (present work); Curve B: copper plus 1.16% nickel (present work); Curve C: very pure copper by Bitter *et al.*[17]; Curve D: copper plus 0.0025% iron by Bitter *et al.*[17]; Curve E: copper plus 1.02% nickel by Kaufmann and Starr[12]; ×'s: pure copper by Bowers.[18]

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[17] Bitter, Kaufmann, Starr, and Pan, Phys. Rev. **60**, 134 (1941).

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By using this distribution function, the susceptibility contribution per nickel atom can be shown to be

$$\chi_a = \frac{1}{1+\frac{1}{2}e^{(\zeta-\epsilon_0)/kT}}\frac{\mu^2}{kT}, \tag{1}$$

where μ is the magnetic moment associated with each electron. This equation can be rewritten in the form

$$\chi_a = (n/n_0)(\mu^2/kT),$$

where n/n_0 is the number of vacant impurity levels divided by the number of available impurity levels, that is, the fraction of nickel atoms in the excited state.

The quantity n/n_0 for a given alloy at various temperatures can be obtained theoretically from the distribution function, while experimental values for n/n_0 at various temperatures can be found by requiring Eq. (1) to describe the susceptibility contribution of solute nickel atoms at each temperature. The agreement between the experimentally and theoretically determined values for n/n_0 can be made fairly good above room temperature by proper selection of the parameter θ, where $k\theta$ is the energy of the impurity level below the Fermi level at absolute zero.

A plot of n/n_0 obtained from susceptibility measurements below room temperature on the 1.16% nickel in copper sample is given in Fig. 3. Two theoretical curves for n/n_0 are shown in the same figure. One uses $\theta = 106°$K and passes through the experimental hydrogen-temperature point while the other uses $\theta = 800°$K and passes through the experimental nitrogen-temperature point.

It is clear from these curves that the excitation theory cannot satisfactorily describe the experimental results at low temperatures. Even a modification of the model in which the impurity levels are assumed to be spread out over a range of energies is unsatisfactorily since no combination of the family of curves for n/n_0 would fit the experimental curve for n/n_0 in Fig. 3.

An alternative picture which gives better agreement with the experimental results has been considered, in which the presence of the nickel atoms modifies the density of states at the top of the Fermi distribution in such a way as to produce an increase in the Pauli paramagnetism and changes in other properties which depend upon the density of states. The assumption of such a modification is justifiable on the basis of considerations either of lattice distortion or of fluctuations in the periodic potential of the lattice due to individual nickel atoms or clusters. The latter possibility has, in fact, been considered on a qualitative basis by Smoluchowski,[20] and by Goldman.[21]

TABLE II. Constants of the empirical equation $\chi = aT + b + (c/T)$ as determined for copper and copper-nickel alloys by using experimental data obtained at temperatures 295, 77, and 4.2°K.

	Annealed Cu	Cu+0.59% Ni	Cu+1.16% Ni	Cu+2.48% Ni
a	$+0.12\times10^{-10}$	$+0.12\times10^{-10}$	$+0.12\times10^{-10}$	$+0.045\times10^{-10}$
b	-0.0877×10^{-6}	-0.0742×10^{-6}	-0.0633×10^{-6}	-0.0317×10^{-6}
c	$+0.027\times10^{-6}$	$+0.034\times10^{-6}$	$+0.064\times10^{-6}$	$+0.425\times10^{-6}$

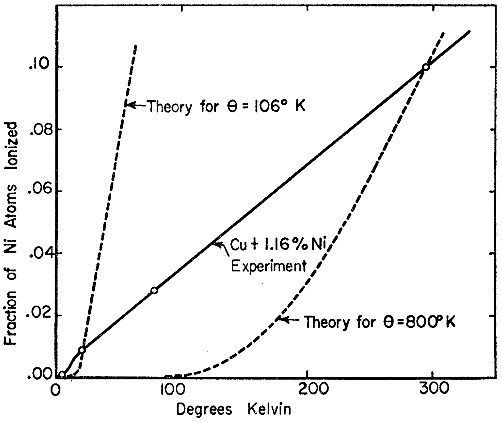

FIG. 3. Fraction of nickel atoms excited into $3d^9$ state at various temperatures as indicated by susceptibility measurements of sample containing 1.16% nickel in copper. Dashed curves give theoretically predicted values for the fraction for two choices of the parameter θ.

In order to facilitate the discussion of this model the experimental susceptibilities have been expressed by equations of the form

$$\chi = aT + b + (c/T).$$

Kaufmann and Starr[12] attempted to fit their susceptibility results with such equations, but were successful only for nickel concentrations between 10% and 35% and temperatures above 14°K. The present data for dilute alloys and pure copper can be expressed in this form with fair accuracy for all experimental points. The constants of this equation, recorded for each sample in Table II, are determined from experimental points at 295°K, 77°K, and 4.2°K.

For these low nickel concentrations, the constant b appears to depend nearly linearly on composition with a slope of 0.023×10^{-6} cgs units per atomic percent nickel. This increase could be due to an increasing Pauli paramagnetism associated with the increased density of states near the Fermi level. Such an increase in density of states is indicated by the electronic specific heat data shown in Fig. 4. However, the increase in density of states indicated by the conduction electron contribution to susceptibility also shown in Fig. 4 is considerably larger than that indicated by specific heat data. A portion of this larger fractional increase in susceptibility could be attributed to an increase in effective mass as indicated by the specific heat data; the remainder, on this model, would have to be attributed to possible changes in exchange and correlation energies. The conduction electron suscepti-

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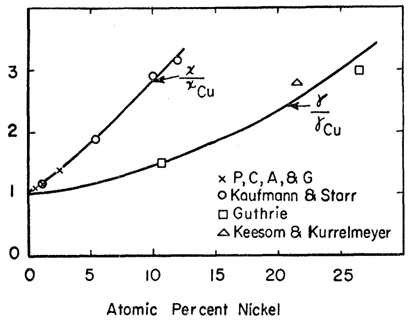

FIG. 4. Apparent increase in the density of states at the Fermi level as indicated by susceptibility and specific heat measurements. χ/χ_{Cu} is the room-temperature mass susceptibility of the copper-nickel alloy (minus a core susceptibility of -0.23×10^{-6}) divided by a like term for pure copper. γ/γ_{Cu} is the linear specific heat term for the copper-nickel alloy divided by the same term for pure copper. χ_{Cu} was taken to be $(-0.0839+0.23)\times10^{-6}$ from the present work, while γ_{Cu} was taken to be 0.688 millijoule mole^{-1} deg^{-2} in accordance with the work of Corak, Garfunkel, Satterthwaite, and Wexler [Phys. Rev. **98**, 1699 (1955)].

bilities in Fig. 4 have been obtained by subtracting a core diamagnetism of -0.23×10^{-6} from the total room temperature susceptibilities. The specific heat and susceptibility curves have been normalized by dividing the experimental values for the alloys by the experimental values for pure copper.

The rather small values for c in all but the 2.48% nickel in copper sample could be accounted for by small amounts of iron impurity in a paramagnetic state. For example, a fractional iron content of 5×10^{-7} in an electronic configuration with four unpaired spins could account for the magnitude of c observed in pure copper. The nuclear moment is very small, contributing only 12% of the observed c in copper. The huge increase in c from the 1.16% to the 2.48% sample suggests that this is an intrinsic property of the alloy. The possibility that this effect was caused by poor mixing or homogenizing was considered, but the chemical analyses indicate that the 2.48% nickel in copper sample was, if anything, better mixed than the other two and the homogenization process was identical.

An interesting relationship is produced if we make the *ad hoc* assumption that nickel atoms dilutely alloyed in copper contribute no magnetic moment unless they have three or more nearest neighbors of nickel, in which case they contribute one Bohr magneton per atom. Applying the binomial expansion to the alloys, one finds that the fraction of nickel atoms with three or more nearest neighbors of nickel is 4.34×10^{-5}, 3.17×10^{-4}, and 2.84×10^{-3} for the 0.59, 1.16, and 2.48 atomic percent nickel in copper samples respectively. The fraction of nickel atoms contributing a moment of one Bohr magneton required to produce the observed increase in c over the value of c recorded for pure copper is 19.4×10^{-5}, 5.43×10^{-4}, and 2.72×10^{-3}, respectively.

Table II shows the values for a to be 0.12×10^{-10} for all except the 2.48% nickel sample. This apparent change in a may not be real since the large value of c for this sample makes accurate determination of a difficult. A similar increasing paramagnetic contribution with increasing temperature in the alkali metals has been attributed by Stoner[22] to an increasing density of states per electron caused by thermal expansion of the crystal lattice. Using a simple free-electron model and assuming the conduction electron susceptibility contribution to be proportional to the density of states at the Fermi level, the Stoner theory predicts a value for a which is $\frac{1}{3}$ the observed value for these samples. This failure to predict the correct value for a should not preclude association of a with thermal expansion since this simple model assumes a parabolic band for copper and neglects possible variations in effective mass and exchange and correlation energies.

SUMMARY

A Gouy balance has been used to measure the magnetic susceptibilities of dilute alloys of nickel in copper down to the temperatures of liquid helium. At the higher temperatures, agreement is obtained with the earlier work of Kaufmann and Starr and the anomalous temperature dependence of the susceptibility in all these alloys has been confirmed. At the lower temperatures, however, this temperature dependence is not as pronounced as suggested in the earlier work. An excitation mechanism postulated to explain the earlier results has been more thoroughly investigated and found to be inadequate to explain the newer results of this investigation. A qualitative understanding of the effects observed is possible but a quantitative description of all the anomalous effects observed in this alloy system must await a better theoretical description of impurity states in alloys.

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[22] E. C. Stoner, *Magnetism and Matter* (Methuen & Co., Ltd., London, 1934), first edition, p. 509.