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Magnetic Susceptibility of Copper-Nickel and Silver-Palladium Alloys at Low Temperatures*

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The magnetic susceptibilities of copper-nickel alloys with up to 39 atomic percent nickel and silver-palladium alloys with up to 10 atomic percent palladium have been measured by the Gouy method at temperatures between 295°K and 2.1°K. Measurements are reported on samples with an impurity content of less than 10 parts per million and on samples with greater impurity content. The susceptibility is nearly temperature-independent for all the silver-palladium alloys and for the copper-nickel alloys with up to 27% nickel. Higher nickel concentrations give rise to a $1/T$ susceptibility term which is too large to be accounted for by impurity content. The simple band model of Mott adequately describes the susceptibility of the silver-palladium alloys but fails to predict the large temperature-independent paramagnetic contribution of nickel in copper. Exchange energies calculated by the Stoner collective electron method for the copper-nickel alloys, using specific heat and susceptibility data, are somewhat unsatisfactory and suggest the presence of another mechanism.

INTRODUCTION

THE copper-nickel and silver-palladium alloy systems have received considerable attention from solid-state physicists because of the similar electronic structure of copper and silver and of nickel and palladium, and because both alloy systems are solid solutions with a face-centered-cubic structure over the entire range from pure noble metal to pure transition metal. Despite these obvious similarities, these alloy systems exhibit rather different optical, thermal, electric, and magnetic properties.[1] Many of these differences have been resolved by qualitative arguments based on the simple band model of Mott[2] and Stoner[3] and the more detailed collective electron treatment of Wohlfarth[4]; however, the properties observed in the copper-rich copper-nickel alloys are not easily explained by these models. In particular, the anomalously large paramagnetic contribution of nickel in copper reported by Kaufmann and Starr,[5] which can be divided somewhat crudely into a temperature-independent term and a $1/T$ term, has remained unexplained. Recent measurements by one of us[6] on very pure Cu-Ni alloys containing up to 2.5% nickel confirm the temperature-independent portion of the contribution but show considerably less $1/T$ dependence, thus suggesting that much of the previously reported temperature dependence was due to ferromagnetic impurities. While the large temperature-independent contribution cannot be explained by the simple band model, the elimination of the anomalous temperature dependence should greatly aid in finding a suitable model.

In order to further verify the temperature-independent nature of the nickel contribution, new measurements are here reported on samples containing up to 39% nickel, in which even greater purity was maintained. Measurements have also been made on silver-palladium alloys containing up to 10% palladium to determine whether they exhibit the temperature-independent susceptibility predicted by the simple band model. All susceptibility measurements were made with a Gouy balance which has been described previously.[6]

SAMPLE PREPARATION

All copper-nickel samples except for the 38.8% nickel sample were prepared by us from American Smelting and Refining Company, copper rated at 99.999% pure, and Johnson Matthey spectroscopic grade nickel, rated at better than 99.997% pure, with transition metal impurities of ten parts per million iron, two parts per million manganese, and less than one part per million cobalt. The pure metals were sealed together in evacuated quartz tubes and agitated in the molten state for over half an hour to assure good mixing. The melt was then quenched in water to minimize long-range segregation and the ingots were swaged into cylindrical rods from which specimens six inches in length were cut. Finally, these specimens were heavily pickled in nitric acid to remove surface ferromagnetic contamination and homogenized at a temperature about 70° below the solidus for 100 hours. Having been made in sealed containers, the composition of the samples should be determined accurately by the weights of the initial ingredients, and these are the compositions listed. However, a chemical analysis was made on every sample, and in each case it checked the magnitude and uniformity of the composition to the accuracy of the chemical analysis. The melting temperature of the 38.8% nickel sample is sufficiently high that it could not be alloyed in quartz. It was supplied to us in sample form by F. A. Badia of

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† Now with International Business Machines Research Laboratories, Poughkeepsie, New York.

[1] B. R. Coles, Proc. Phys. Soc. (London) **B65**, 221 (1952).

[2] N. F. Mott, Proc. Phys. Soc. (London) **A47**, 571 (1936).

[3] E. C. Stoner, Phil. Mag. **15**, 1018 (1933).

[4] E. P. Wohlfarth, Proc. Roy. Soc. (London) **A195**, 434 (1949).

[5] A. R. Kaufmann and C. Starr, Phys. Rev. **63**, 445 (1943). Similar results have also been reported on a 37% Ni in Cu sample down to 2°K by A. Arrott, thesis, Carnegie Institute of Technology, Pittsburgh, Pennsylvania, 1954 (unpublished).

[6] Pugh, Coles, Arrott, and Goldman, Phys. Rev. **105**, 814 (1957).

the International Nickel Company and was produced by standard high-purity methods in a vacuum furnace using a graphite crucible. A spectrographic analysis of the alloy indicates that it should be as pure as or purer than our own alloys, since it contains less than one part per million of iron, cobalt, or manganese. After we received it, it was heavily pickled and homogenized at 1150°C for 120 hours. The data reported here for pure copper are the same data as previously reported[6] for 99.999% pure copper.

The first four silver-palladium samples were prepared for us by Johnson Matthey Company using silver rated at 99.995% pure and palladium rated at 99.9% pure with traces of copper, silver, the platinum group metals, iron, silicon, and gold. The last four samples were made by us using Johnson Matthey silver of purity greater than 99.999% and palladium sponge rated at 99.995% pure. Our fabrication technique was similar to that used for copper-nickel. The metals were sealed in an evacuated quartz tube, agitated for 45 minutes in the molten state at 1140°C, and then quenched in water. Six-inch rods swaged from the ingots were then heavily pickled and homogenized at 900°C for 120 hours. The compositions given for the samples fabricated by Johnson Matthey are as stated by them and are supposed to be good to 0.2% of the total weight. The listed compositions of the samples fabricated by us were obtained from the weights of the initial ingredients and checked by chemical analysis.

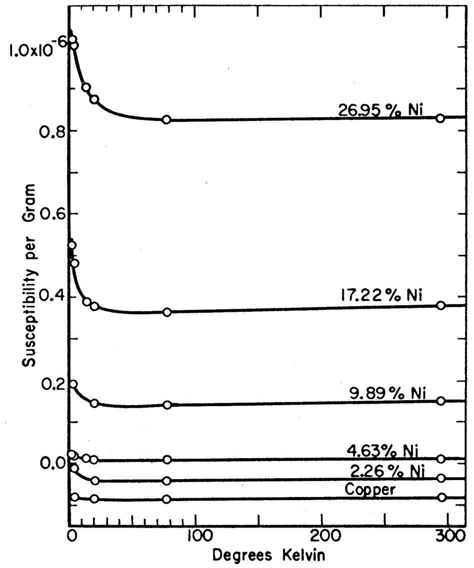

FIG. 1. The magnetic susceptibility per unit mass of copper and the copper-nickel alloys in cgs units.

EXPERIMENTAL RESULTS

Results of the susceptibility measurements on the copper-nickel alloys are shown in Table I and Fig. 1, while those for silver-palladium are shown in Table II. Each susceptibility point listed is the result of force measurements taken at fields ranging from 5000 oersteds to 22 000 oersteds and extrapolated to infinite fields by the Honda method. No measurements were made on the 38.8% nickel sample below 14.0°K because the forces would have been beyond the range of our balance. All copper-nickel samples exhibited a field-independent susceptibility, which, to our accuracy, requires a ferromagnetic content of less than three Bohr magnetons in 10^8 atoms. In contrast to this, the silver-palladium alloys exhibited a temperature-independent ferromagnetism of 0.33, 1.00, 0.73, and 0.53 Bohr magnetons in 10^6 atoms for increasing palladium content in the first four alloys and 0.51, 1.13, 0.07, and 0.11 Bohr magnetons in 10^6 atoms for increasing palladium content in the second four alloys. It is a bit surprising that so little decrease in ferromagnetism was brought about by the increased purity of the second group of silver-palladium alloys, and also that ferromagnetism does not increase monotonically with palladium content since the palladium had a lower purity than the silver in each case. The expected error in the copper-nickel data is less than $\frac{1}{2}$%; but due to the slope in the Honda plot for the silver-palladium alloys, the relative values of susceptibility between samples may be in error by more than 1%. The temperature dependences of the silver-palladium alloys are, however, just as accurate as for the copper-nickel alloys.

TABLE I. Magnetic susceptibility of Cu-Ni alloys for various temperatures in cgs mass units times 10^6.

	295°	77°	20.4°	14.0°	4.2°	2.1°
Cu	−0.0839	−0.0865	−0.0865		−0.0812	
Cu+2.26% Ni	−0.0358	−0.0392	−0.0395		−0.0087	
Cu+4.63% Ni	0.0134	0.0097	0.0116	0.0125	0.0170	0.0221
Cu+9.89% Ni	0.150	0.140	0.144		0.197	
Cu+17.22% Ni	0.381	0.362	0.373	0.383	0.482	0.528
Cu+26.95% Ni	0.832	0.828	0.874	0.903	1.022	1.132
Cu+38.8% Ni	2.93	7.16	23.1	32.1		

DISCUSSION OF SILVER-PALLADIUM ALLOYS

The susceptibility of the silver-palladium alloys seems to be well described in terms of the simple band model originally proposed by Mott.[2] The density-of-states curve, illustrated schematically in Fig. 2 for the copper-nickel alloys, may be applied directly to the silver-

TABLE II. Magnetic susceptibility of Ag-Pd alloys for various temperatures in cgs mass units times 10^6.

	295°	77°	20.4°	4.2°	2.1°
Ag	−0.181	−0.182	−0.183	−0.183	
Ag+2.02% Pd	−0.177	−0.181	−0.179	−0.180	−0.178
Ag+6.07% Pd	−0.173	−0.177	−0.176	−0.171	−0.169
Ag+10.15% Pd	−0.172	−0.176	−0.170	−0.140	−0.132
Ag	−0.180				
Ag+2.03% Pd	−0.182				
Ag+6.04% Pd	−0.183				
Ag+10.12% Pd	−0.181	−0.183	−0.183	−0.182	−0.180

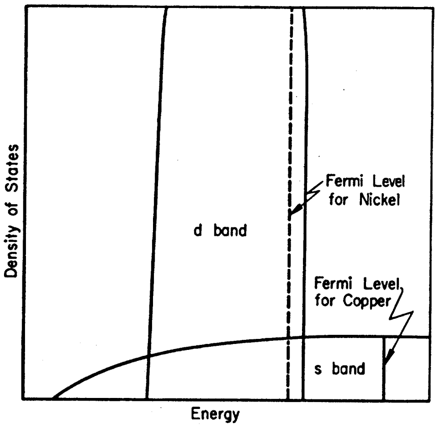

FIG. 2. The density-of-states curve for the two alloy systems as a function of energy.

palladium alloys. For pure silver, as for pure copper, the ten *d* states per atom are fully occupied while the conduction band (or *s* band, since it consists predominately of *s* states) is half full with one electron per atom. Additions of palladium to silver are thought to make no change in the density-of-states curve, but result in a lowering of the Fermi level since palladium has one fewer electron per atom than silver. At a concentration of about 40% palladium, the Fermi level is presumed to have dropped down to the *d* band and further additions of palladium result in the emptying of the *d* band and a large increase in the density of states at the Fermi level. The dashed line in Fig. 2 illustrates the location of the Fermi level for pure palladium. This model is moderately well supported by low-temperature specific heat measurements of Hoare and Yates[7] which show only a small increase below a content of 40% palladium in silver, after which a pronounced increase occurs. It is even more convincingly verified by Svensson's susceptibility measurements[8] which show little change at room temperature for alloys containing up to 40% palladium, while further additions of palladium result in a rapid increase in paramagnetism. The present measurements on alloys containing up to 10% palladium verify these results and further demonstrate that the susceptibility is temperature-independent as should be expected of a diamagnetic or Pauli paramagnetic material.

The present data can be expressed by an empirical equation of the form

$$\chi = aT + b + (c/T), \tag{1}$$

and the constants of this equation as determined for each alloy are given in Table III. The fact that b is approximately independent of palladium content is predicted by the simple band model, and the very slight increase in diamagnetism in the very pure samples is in agreement with Svensson.[8] The slight tendency toward paramagnetism with increasing palladium content in the first four samples is probably associated with impurities added to the alloy along with the palladium. The small $1/T$ dependence of the less pure samples has been virtually eliminated in the very pure 10.12% palladium sample, thus indicating that all $1/T$ dependence in these alloys is due to impurities. Even in the less pure 10.15% palladium sample, three parts in 10^7 of impurity with four unpaired spins per atom could give the $1/T$ dependence observed. The very small increase in paramagnetism with increasing temperature as indicated by the values for a can be accounted for to within a factor of two for pure silver by an increasing density of states caused by thermal expansion of the crystal lattice, but the variation of a with impurity content as indicated by the first four samples is not so readily explained.

DISCUSSION OF COPPER-NICKEL ALLOYS

The temperature dependence of the susceptibility of the copper-nickel alloys cannot be expressed accurately by Eq. (1). An approximate fit can be obtained, however, and the constants of this equation are listed in Table IV, as determined for each alloy using points at 295°, 77°, and 4.2°, except for the 38.8% nickel sample for which b and c were determined using points at 295°, 77°, and 20.4°. As in the case of the silver-palladium alloys, there is a very small but definitely measurable a coefficient; and there seems to be no satisfactory explanation for its variation, either with nickel content or impurity content. The $1/T$ dependence is practically negligible for all but the 38.8% nickel sample, and the c coefficient could be accounted for even in the 26.95% nickel sample by as little as two parts in 10^6 of an impurity having four localized unpaired spins per atom. This is well within the estimated purity of the samples so that it is possible to attribute all of the $1/T$ dependence to impurities. This point of view is well supported by the fact that values reported for c have rapidly decreased as sample purity has increased. Values of c reported by Kaufmann and Starr[5] are 20 to 150 times larger than those reported here for similar compositions,

TABLE III. Constants of the empirical equation $\chi = aT + b + (c/T)$ for the Ag-Pd alloys.

Sample composition in atomic percent	$a \times 10^{10}$	$b \times 10^6$	$c \times 10^6$
Ag	+0.07	−0.183	+0.000
Ag+2.02% Pd	+0.18	−0.182	+0.008
Ag+6.07% Pd	+0.19	−0.178	+0.040
Ag+10.15% Pd	+0.23	−0.179	+0.099
Ag	(+0.07)[a]	−0.182	
Ag+2.03% Pd	(+0.08)[a]	−0.184	
Ag+6.04% Pd	(+0.08)[a]	−0.185	
Ag+10.12% Pd	+0.09	−0.183	+0.003

[a] Assumed values of a used to calculate b.

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[7] F. E. Hoare and B. Yates, Proc. Roy. Soc. (London) **A240**, 42 (1957).

[8] B. Svensson, Ann. Physik **14**, 669 (1933).

while the value of c previously reported by one of us[6] for a 2.5% nickel sample is more than ten times larger than now reported for a 4.63% nickel sample. The fact that c does not increase monotonically with nickel content in the present data is further reason to suspect impurities. The evidence thus suggests very strongly that additions of up to 27% nickel to copper contribute no susceptibility term with a $1/T$ dependence, but the data for the 38.8% nickel sample indicate a pronounced $1/T$ dependence that cannot be accounted for by impurities since it corresponds to one atom per ten thousand having four unpaired spins, and the spectrographic analysis indicates a content of less than one impurity atom per million. It should be noted that the method of preparation was slightly different for this sample, but it is hard to see how this could account for the large value of c. Actually a large temperature dependence should be expected in alloys containing almost enough nickel to be ferromagnetic.

An interesting feature of all these alloys is that the turn up at low temperatures is not nearly as sharp as predicted by a $1/T$ term. This is indicated by the fact that values for c obtained using points at 2.1° instead of 4.2° are 20 to 40% lower. This effect can be accounted for if the unpaired spins are described by Fermi-Dirac statistics and have a Fermi temperature of only a few degrees Kelvin as would be true in a very narrow band.

The properties of the copper-nickel system are most often described in terms of the same simple band model already applied to silver-palladium, using the density-of-states curve illustrated in Fig. 2. However, because this model predicts little, if any, change in the density of states at the Fermi level with up to 40% nickel, it is unable to describe the large increase in the b term which accompanies additions of nickel to copper. It also fails to describe the apparent increase in the density of states indicated by low-temperature specific heat measurements. By use of a more general collective electron treatment, the apparent increase in the density of states at the Fermi level, g_F, can be determined from either specific heat or susceptibility data. In calculating g_F from susceptibility data, b is assumed to be equal to a core susceptibility of -0.23×10^{-6} for all alloys plus a conduction electron contribution of $\mu^2 g_F[1-\frac{1}{3}(m/m^*)^2]$, where m^* is assumed to be 1.5 in accordance with specific heat data. The values obtained for g_F are indicated in Fig. 3 with all values normalized to $g_F=1$ for pure copper as determined from the specific heat data of Guthrie, Friedberg, and Goldman.[9] The discrepancy between the two curves can be resolved by the introduction of an exchange parameter in accordance with the parabolic band method of Stoner.[10] Values for the parameter $\theta'\times10^{-3}$ of 4.0, 9.2, 10.9, 11.9, 9.1, 6.3, and 2.6 have been obtained for our copper-nickel samples beginning with the pure copper sample and taking the samples in order of increasing nickel content. A plot of θ' *versus* composition rises rapidly to a peak at 10% nickel and then drops slowly with increasing nickel content until 40% nickel is reached. While this model does fit the data, it is hard to justify the decreasing value of θ' between 10 and 40% nickel.

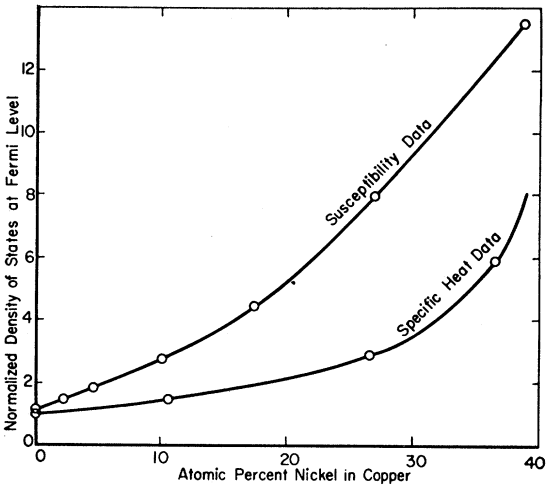

FIG. 3. Comparison of the density of states at the Fermi level of the copper-nickel system, indicated by magnetic susceptibility and specific heat measurements. Densities are normalized to a density of states at the Fermi level equal to unity for pure copper, obtained from specific heat measurements.

TABLE IV. Constants of the empirical equation $\chi=aT+b+(c/T)$ for the Cu-Ni alloys.

Sample composition in atomic percent	$a\times10^{10}$	$b\times10^{6}$	$c\times10^{6}$
Cu	+0.12	−0.0877	+0.027
Cu+2.26% Ni	+0.22	−0.0427	+0.142
Cu+4.63% Ni	+0.19	+0.0078	+0.038
Cu+9.89% Ni	+0.60	+0.1316	+0.275
Cu+17.22% Ni	+1.10	+0.347	+0.567
Cu+26.95% Ni	+0.37	+0.817	+0.865
Cu+38.8% Ni		+1.48	+435

Because considerable evidence points toward the possible existence of holes in the d band even with small amounts of nickel in copper, a more complicated model has been tried in which each nickel atom contributes 9.4 electrons to the d band and 0.6 electrons to the conduction band, and the density of states and exchange parameter for the s band are assumed to be changed only slightly by the addition of nickel. In this model g_F and θ_d' for the d band can be obtained from specific heat and susceptibility data, respectively. The results for $\theta_d'\times10^{-3}$ given in order of increasing nickel content beginning with the 2.26% nickel sample are 6.3, 5.0, 3.6, 3.1, 2.1, and 0.4. Again, an exchange temperature which decreases with nickel content is obtained. This will occur for any reasonable band model assumed, since g_F obtained from specific heat data increases more rapidly than g_F obtained from susceptibility data in the concentration range above 10 to 20% nickel.

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[9] Guthrie, Friedberg, and Goldman, Bull. Am. Phys. Soc. Ser. II, 1, 147 (1956).

[10] E. C. Stoner, Acta Met. **2**, 259 (1954).

The rather unreasonable decrease in θ' with nickel content predicted by all such exchange calculations strongly suggests the presence of some other mechanism. Large admixtures of p and d states to the conduction band with additions of nickel to copper could give rise to an appreciable Van Vleck temperature-independent paramagnetism as discussed by Kubo and Obata,[11] and such admixtures do not seem unreasonable in view of the rapid changes in optical, thermal, electric, and magnetic properties of these alloys as the nickel content is increased.

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[11] R. Kubo and Y. Obata, J. Phys. Soc. Japan 11, 547 (1956).

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Energy Loss of Fast Charged Particles in LiH

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The quantum theory of the electromagnetic interaction of particles and fields in dense matter predicts that fast charged particles lose their kinetic energy to longitudinal electronic excitations influenced by one-electron and collective effects. Both effects are to be expected in metals and insulators, but to varying degrees. A clear identification of collective excitations in insulators is still lacking.

LiH is the best-suited crystal for predicting the one-electron and collective effects on the longitudinal electronic excitations in an insulator, and for verifying such prediction experimentally. The characteristic energy loss spectrum and the mean excitation potential of the LiH crystal are estimated. One finds that the longitudinal excitations in this insulator crystal are of predominantly collective character. The results are so significantly different from those obtained by neglecting collective effects that stopping experiments in single as well as in multiple scattering can clearly identify the collective effects and confirm the theoretical predictions.

1. STATEMENT OF PROBLEM

CHARACTERISTIC energy losses of singly scattered electrons are observed in metals and insulators.[1] The quantum theory of electromagnetic interactions of particles and fields in dense substances attributes these energy losses to the excitation of longitudinal oscillations with both one-electron and collective ("plasma") components.[2,3] However, it has been argued that electrons in filled bands cannot oscillate collectively,[4,5] and that, in any event, characteristic energy losses can be explained entirely by one-electron band transitions.[5–7] A clear-cut experimental identification of collective oscillations in insulators is still lacking and would be desirable.

LiH is the insulator with the fewest electrons per atom and with the highest ratio of valence- to core-electrons, to which Bragg's additivity rule for stopping powers is least applicable. It is best suited for estimating theoretically the one-electron and collective effects on the longitudinal excitations of the valence electrons, and for giving decisive experimental confirmation of the importance of collective effects in an insulator, as predicted by theory. In the following, the characteristic energy-loss spectrum and the mean excitation potential of the LiH crystal are estimated. One finds that fast charged particles should excite the valence electrons to energy levels of predominantly collective character. The results differ so significantly from those one obtains by considering only one-electron band transitions (which is not justified by theory) that stopping experiments in single scattering and multiple scattering can demonstrate clearly the excitation of collective polarization oscillations in this insulator crystal.

2. EXCITATION LEVELS

Suppose the response of a substance to an electrodynamic disturbance can be described by the excitation of coupled one-electron and field oscillators. One may then separate these oscillators into their transverse and longitudinal normal modes by a suitable transformation of the total Hamiltonian.[3] The transverse normal modes do not contain collective components. They correspond to just the one-electron oscillators (f_n,ω_n) of oscillator strength f_n and frequency ω_n in the semiempirical Drude-formulation of the dielectric constant $\epsilon(\omega)$. The eigenfrequencies of the longitudinal normal modes are given by the solutions $\omega=\Omega_{n'}$ of the equation $\epsilon(\omega)=0$.

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[2] D. Pines, Revs. Modern Phys. 28, 184 (1956).

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[4] P. A. Wolff, Phys. Rev. 92, 18 (1953); however, see H. Kanazawa, Progr. Theoret. Phys. Japan 13, 227 (1955).

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