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Temperature dependence of the resistivity of CuFe thin films with Fe concentrations above 0.1 at.%*

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The resistivity of low-temperature condensed CuFe thin films was measured in the range $1.5 \lesssim T \lesssim 17$ K. Fe concentrations ranged from ~ 0.04 to ~ 0.9 at.%. The resistivity exhibited an approximately logarithmic rise down to ~ 10 K and a less rapid rise below 10 K. The logarithmic slope per at.% Fe of the resistivity curve decreased with increasing Fe concentration. The change in $(1/c)(d\rho/d\ln T)$ is interpreted as resulting from interactions between the Fe atoms.

I. INTRODUCTION

The interaction of the conduction electrons of a nonmagnetic metal with isolated magnetic impurities gives rise to the resistivity minimum or Kondo effect.[1,2] Dilute CuFe alloys are usually considered to be the prototypical Kondo system.[3] In such alloys it has been assumed that the Fe impurities independently scatter the Cu conduction electrons; however, a number of recent experiments have shown that this assumption is often not valid. For example, Tholence and Tournier[4] have found that the magnetization of CuFe contains terms both linear and quadratic in the Fe concentration; the quadratic terms are attributed to the presence of interacting Fe atoms. Similar effects have been found by Franz and Sellmeyer,[5] and Hirschkoff *et al.*[6] In addition, measurements of the resistivity of extremely dilute CuFe alloys by Star *et al.*[7] have shown a small resistivity increase occurring below 0.1 K which they attribute to Fe-Fe interactions.

The measurements described above have demonstrated that interactions between impurities occur even in very dilute CuFe alloys. It is thus of interest to study less-dilute ("finite concentration") alloys, in which the scattering of conduction electrons may be dominated by mechanisms involving interactions between the Fe atoms. The primary difficulty in making such measurements is the low solubility of Fe in Cu. Because of the low solubility, CuFe alloys with a finite Fe concentration may not be random alloys, i.e., the Fe may cluster or precipitate; consequently, such alloys have properties that depend strongly on their annealing history and the amount of cold working to which they have been subjected.[8,9] In order to circumvent this problem, the CuFe samples used in the present work were prepared by depositing a CuFe thin film onto a substrate held at cryogenic temperatures. This method, known as "quench condensation," should produce a uniform CuFe thin film which is free of problems due to Fe clustering that occur in bulk samples. One difficulty with the present method is that the sample thickness cannot be determined as accurately as for a bulk sample; this introduces a fairly large systematic error in the magnitude of the resistivity. In addition, the quench condensed films have a high degree of lattice disorder.[10] While the lattice disorder does not change the temperature dependence of the resistivity above ~5 K,[11] it does make it impossible to determine the magnitude of the resistivity due to scattering from the magnetic impurities.

The purpose of the present work was to determine the temperature dependence of the resistivity of quench-condensed CuFe films with an Fe concentration high enough so that effects due to interactions between the Fe impurities dominate the measured resistivity. The measurements covered the temperature interval $1.5 \lesssim T \lesssim 17$ K; Fe concentrations ranged from 0.038- to 0.91-at.% Fe. Previous measurements on quench-condensed CuFe films have been reported by Korn[12]; however, Korn's films were deposited at 77 K and annealed at 190 K before the measurements were made.

II. EXPERIMENTAL DETAILS

A CuFe master alloy (~1-at.% Fe) was prepared by melting together Cu (99.999% pure) and Fe (99.9% pure) in a covered graphite crucible in a vacuum furnace. Samples with lower Fe concentration were made by remelting pieces of the master alloy with additional Cu. The CuFe ingots were cut into ~0.1-g pellets and then etched in HNO_3 to remove surface contamination. One CuFe pellet from each batch was sent to Johnson-Matthey[13] for analysis of the Fe concentration.

The CuFe films were prepared by flash evaporating a single CuFe pellet from a tungsten boat[14] onto a z-cut natural quartz substrate held at ~7 K in a liquid-He cryostat evaporator (Fig. 1). The

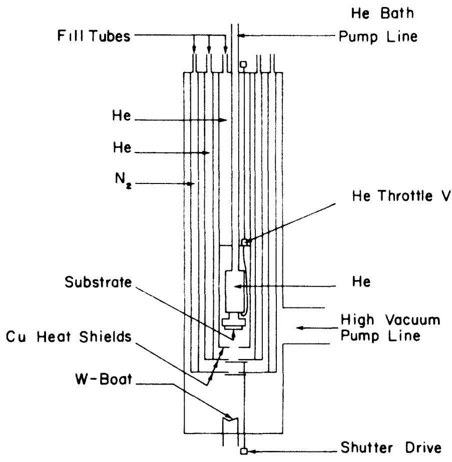

FIG. 1. Liquid-helium cryostat evaporator.

films were deposited at a rate of ~100 Å/sec, and ranged from 300 to 600 Å thick. This method of film preparation, often called "quench condensation," produces CuFe films composed of small crystallites (~25–35 Å).[10] The structure of quench-condensed CuFe films is not stable; therefore, before making any measurements the films were annealed at a temperature above the highest point at which measurements were to be made (usually ~17 K). Annealing to 17 K produced an irreversible decrease of ~2% in the resistivity. Several pure Cu films were prepared in the same way as the alloy films. These films had residual resistivities ranging from 13 to 20 $\mu\Omega$ cm. The reason for the large variation is not known. After annealing, the resistivity of the pure Cu films was independent of temperature within the resolution of the measurements, demonstrating that the phonon contribution to the resistivity was negligibly small in the range of interest.

The film resistances were measured with a four-terminal ac bridge having a relative accuracy of ±0.007%. The data were taken on an X-Y recorder and digitized at 0.5-K intervals. The length-to-width ratio of the films was $L/W = 29.87 \pm 0.40$. The film thickness was determined interferometrically with an accuracy of ±15%. The probable error in the Fe concentration is ±5%; however, the concentration values may be systematically low.[15] Temperature was monitored with a germanium-resistance thermometer.

III. RESULTS

The resistivity of the CuFe films exhibited an approximately logarithmic rise beginning just below the temperature of the resistivity minimum (Fig. 2). The logarithmic slope per at.% Fe of the resistivity curve

$$\Gamma = -\frac{1}{c}\frac{d\rho}{d\ln T}\bigg|_{T=16\,\mathrm{K}} \tag{1}$$

was dependent on the Fe concentration c, decreasing as c increased (Fig. 3). A similar effect has been observed by Laborde and Radhakrishna[16] for CuMn alloys and by Ford *et al.*[17] for AuFe alloys. At sufficiently low temperatures the increase in resistivity was less rapid than logarithmic. The deviations from logarithmic behavior became significant at ~8 K in the lowest concentration film (0.038-at.% Fe) and at ~16 K in the highest concentration film (0.91-at.% Fe), with the highest-concentration film showing the largest departure from logarithmic behavior. Had the measurements extended below 1 K it is probable that the 0.91-at.% film would have shown a resistivity *maximum* at $T \sim 1$ K. Korn[12] found a resistivity maximum at $T \simeq 1.8$ K in a CuFe film with the same nominal Fe concentration.

The measurements made on quench-condensed pure Cu films show that phonon scattering makes a negligible contribution to the resistivity in the range of the measurements. Thus the resistivity is given by

$$\rho(T) = \rho_0 + \rho_{\mathrm{spin}}(T)\,, \tag{2}$$

where ρ_{spin} is the temperature-dependent resistivity due to magnetic scattering by the Fe, and ρ_0 is the temperature-independent resistivity due to scattering from defects in the Cu lattice. Since ρ_0 varied from run to run, and since ρ_0 and ρ_{spin} were of the same order of magnitude, only the temperature dependence and not the magnitude of ρ_{spin} can

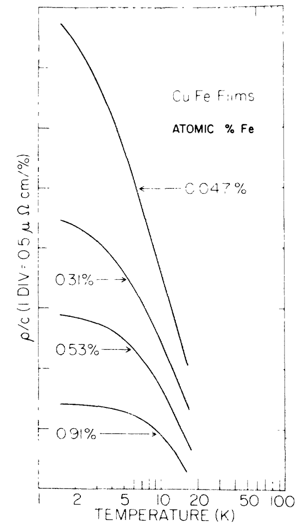

FIG. 2. Resistivity per at.% Fe of four of the low-temperature-deposited CuFe thin films. The curves have been given arbitrary vertical displacements.

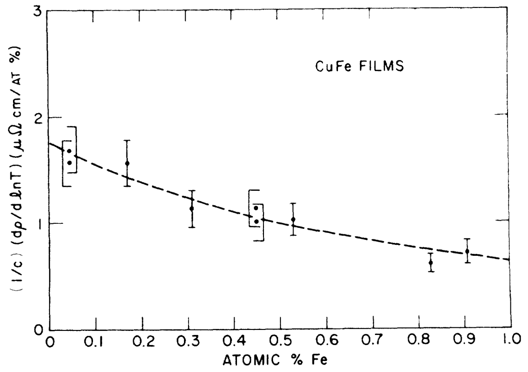

FIG. 3. Logarithmic slope per at.% Fe of the resistivity curve at 16 K. The large error bars are due to the error in the measurement of film thickness. The dashed line is $L_{ex}(\bar{n})$ as given by Matho and Béal-Monod (Ref. 25) with n chosen so as to agree with the low-concentration data.

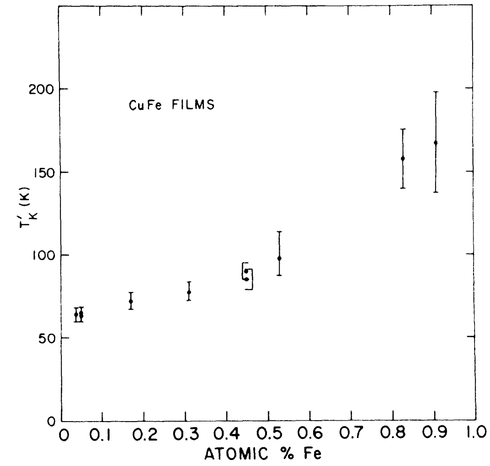

FIG. 4. Characteristic temperature T'_K determined from the least-squares fit of the data to the Applebaum-Kondo formula [Eq. (3)].

be determined from the data. In particular, $\rho_{\text{spin}}(0)$, the spin-dependent resistivity in the unitarity limit, cannot be estimated from the data.

In order to compare the various runs and analyze the way in which the resistivity curve depends on Fe concentration, it is convenient to have an empirical formula for $\rho(T)$. Although the resistivity formula derived by Applebaum and Kondo[18] (AK) is not theoretically appropriate to the present data, Summers, Lipham, and Roberts[19] have found the AK temperature dependence to be quite useful as an empirical aid in measuring changes in the resistivity curve of CuFe. Therefore, the data were analyzed by a least-squares fit to the formula

$$\rho(T) = c\{\rho(0) - B[(T/T'_K)\ln(T/T'_K)]^2\}, \qquad (3)$$

which has the AK temperature dependence. Equation (3) is not capable of fitting the data over the entire range of the measurements, but it does give an excellent fit over the restricted range $8 \le T \le 16$ K. The parameters $\rho(0)$, B, and T'_K determined by the fit, as well as the film thickness D, concentration c, and the logarithmic slope per at.% Fe are given in Table I. T'_K is plotted vs c in Fig. 4. Note that $\rho(0)$ is the sum of ρ_0 and $\rho_{\text{spin}}(0)$ and is *not* the resistivity in the unitarity limit. In Fig. 5 the resistance of three of the films is plotted as a function of $\ln T/T'_K$. The solid curve in Fig. 5 is calculated from Eq. (3) using the values of c, $\rho(0)$, B, and T'_K given in Table I. Below ~8 K the calculated curves deviate systematically from the data, falling below the data for $c \lesssim 0.5$ at.% and above the data for $c \gtrsim 0.5$ at.%. Similar deviations were found for all the films.

As shown by Summers, Lipham, and Roberts[19] the value of T'_K provides a convenient measure of changes in the shape of the $\rho(T)$ curve. In the present measurements T'_K increased with Fe concentration from $T'_K \simeq 60$ K in the low-concentration limit to $T'_K \simeq 90$ K for $c \simeq 0.5$-at.% Fe (Fig. 4).

TABLE I. Film thickness, Fe concentration, resistance at 4 K, and values of the experimental parameters T'_K, B, $\rho(0)$, and Γ for the CuFe films.

Film No.	Thickness D (Å)	Fe concentration (at.%)	R (4 K) (Ω)	T'_K (K)	B (μΩ cm/at.%)	$\rho(0)$[a] (μΩ cm)	Γ[b] (μΩ cm/at.%)
1204	...	0.038	169.12	64	...	...	...
311	440	0.047	134.46	65	21.9	19.8	1.69
408	300	0.047	192.38	65	20.2	19.3	1.57
220	380	0.17	192.08	73	20.2	24.5	1.57
206	630	0.31	117.46	79	13.8	24.9	1.12
215	350	0.45	338.52	87	14.7	39.8	1.14
301	295	0.45	353.48	91	13.1	35.0	1.01
211	480	0.53	235.86	97	12.6	38.0	1.01
225	285	0.83	419.11	157	9.7	40.0	0.57
123	340	0.91	534.50	168	13.3	69.0	0.71

[a] $\rho(0) = \rho_0 + \rho_{\text{spin}}(0)$.

[b] $\Gamma = -(1/c)(d\rho/d\ln T)|_{T=16\,\text{K}}$.

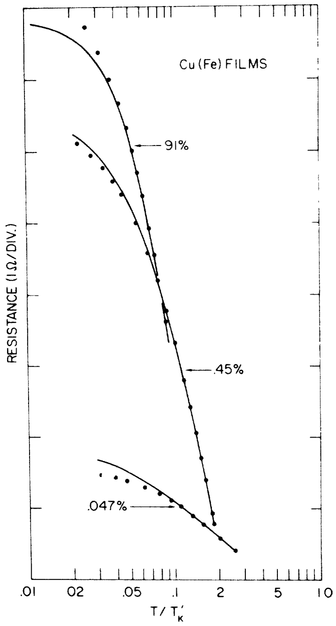

FIG. 5. Resistance of three of the CuFe films plotted as a function of T/T_K'. The dots give the resistance as calculated from Eq. (3) using the values of c, $\rho(0)$, B, and T_K' given in Table I.

The value found in the low-concentration limit agrees with the results of Summers, Lipham, and Roberts[19] and Loram, Whall, and Ford.[20]

IV. DISCUSSION

A number of recent experiments have given information about interactions between impurity atoms in dilute magnetic alloys. For example, Mössbauer spectra obtained for CuFe show line splittings which have been interpreted as arising from interactions between pairs of Fe atoms.[21] Secondly, the magnetization of dilute CuFe alloys has been found to contain both a term proportional to the impurity concentration c and a term proportional to c^2 which was attributed to interacting pairs of Fe atoms.[4-6,22,23] Finally, Star *et al.*[7] have observed a small logarithmic increase in the resistivity of extremely dilute CuFe alloys at temperatures below 0.1 K which they suggest is due to pairs of Fe atoms. It is not yet clear whether the interacting Fe atoms are nearest-neighbor pairs, resulting from the possible nonrandom nature of bulk CuFe alloys, or whether the interacting atoms are separated by some distance and are coupled by the Ruderman-Kittel-Kasuya-Yosida interaction.[24] It is quite probable that both situations exist in bulk alloys. However, quench condensed CuFe films should have a random distribution of Fe atoms and thus few nearest-neighbor impurity pairs are expected to be present.

Although there does not seem to be a theoretical treatment of interaction effects in CuFe that is directly relevant to the present measurements, Matho and Béal-Monod[25,26] have given a theoretical treatment which describes interaction effects in AuMn and AgMn.[27] Their theory considers the effects of interactions between pairs of impurity atoms coupled via the Ruderman-Kittel-Kasuya-Yosida interaction. The essential result is that "the effect of interactions is contained in a function that multiplies the isolated spin resistivity"[25]

$$\rho(c, T) = c[R_v - \overline{R} \ln(T/T_1) L(\overline{n})] , \qquad (4)$$

where c is the impurity concentration; R_v, $\overline{R}$, and T_1 are constants independent of c; and $L(\overline{n})$ is the function that accounts for the effects of impurity interactions. The function $L(\overline{n})$ depends both on c and temperature, however the temperature dependence should be small above ~10 K and will be neglected in the present case.[28] When the temperature dependence of $L(\overline{n})$ is negligible, Eq. (4) predicts a resistivity which depends logarithmically on temperature, with a slope which decreases with increasing Fe concentration in agreement with the present measurements at temperatures above ~10 K. The solid curve shown in Fig. 3 is $L_{ex}(\overline{n})$ as taken from the paper by Matho and Béal-Monod[25]; it is in qualitative agreement with the data. The large error bars on $(1/c)(d\rho/d\ln T)$ are primarily due to inaccuracy in determination of the film thickness.

In the preceding discussion it was assumed that the interacting Fe atoms were not nearest-neighbor pairs. However, another interpretation of the data is also plausible; namely, that the quench-condensed CuFe films are not random alloys but instead contain clusters of two or more Fe atoms. Since the clustering would reduce the effective impurity concentration, the calculated value of the logarithmic slope per at.% Fe would decrease with increasing Fe concentration, giving a result that appeared to agree with the theory of Matho and Béal-Monod, but in fact was due to an entirely different mechanism. The present results are not sufficient to determine whether the interacting Fe atoms are clustered or separated by some distance.

In the future it is planned to study CuFe films with Fe concentrations above 1% so that resistivity maxima are present and to extend the measurements to lower temperatures.

V. SUMMARY

The temperature dependence of the resistivity of low-temperature-deposited CuFe films was measured in the range $1.5 \lesssim T \lesssim 17$ K. The Fe concentration ranged from 0.038 to 0.91 at.%, and thus was high enough so that effects due to interactions between the Fe impurities were evident.

The resistivity of the CuFe films showed an approximately logarithmic rise with decreasing temperature. The logarithmic slope per at.% Fe $(1/c)(d\rho/d\ln T)$ decreased with increasing Fe concentration. At sufficiently low temperatures the resistivity increased at a less than logarithmic rate. In the range $8 \leq T \leq 16$ K the resistivity of the CuFe films could be fit to the Applebaum-Kondo formula[18] [Eq. (3)]. The characteristic temperature T'_K determined from the fit to Eq. (3) was in agreement with measurements made on dilute bulk CuFe alloys.[19,20] For the higher concentration films T'_K was found to increase with Fe concentration.

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[1] J. Kondo, Prog. Theor. Phys. 32, 37 (1964).

[2] J. Kondo, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1969), Vol. 23, p. 183.

[3] A. J. Heeger, in Ref. 2, p. 283.

[4] J. L. Tholence and R. Tournier, Phys. Rev. Lett. 25, 867 (1970).

[5] J. M. Franz and D. J. Sellmeyer, Phys. Rev. B 8, 2083 (1973).

[6] E. C. Hirschkoff, M. R. Shanabarger, O. G. Symko, and J. C. Wheatley, J. Low Temp. Phys. 5, 545 (1971).

[7] W. M. Star, F. B. Basters, G. M. Nap, E. DeVroede, and C. Van Baarle, Physica (Utr.) 58, 585 (1972).

[8] K. Svensson, Fifth International Conference on Low Temperature Physics, Moscow, 1966 (unpublished).

[9] S. G. Humble, K. Svensson, and H. Astrom, Phys. Scrip. 1, 151 (1970).

[10] E. Feldtkeller, Z. Phys. 157, 65 (1959).

[11] P. J. Silverman and C. V. Briscoe, Solid State Commun. 16, 367 (1975).

[12] D. Korn, Z. Phys. 238, 275 (1970).

[13] Johnson, Mathey Chemicals Ltd., Orchard Rd., Royston, Herts, SG8 5HE, England.

[14] P. J. Silverman and J. W. Baker, Rev. Sci. Instrum. 46, 1121 (1975).

[15] The analyzed Fe concentrations were ~30% less than the nominal concentrations. It is possible that this was due to the small size (~0.15 g) of the samples sent for analysis. Since the conclusions reached in this paper are of a qualitative nature, they are not affected by this possible systematic error.

[16] O. Laborde and P. Radhakrishna, Solid State Commun. 9, 701 (1971).

[17] P. J. Ford, T. E. Whall, and J. W. Loram, Phys. Rev. B 2, 1547 (1970).

[18] J. A. Applebaum and J. Kondo, Phys. Rev. Lett. 19, 906 (1967).

[19] G. P. Summers, J. G. Lipham, and L. D. Roberts, Phys. Rev. B 8, 2106 (1973).

[20] J. W. Loram, T. E. Whall, and P. J. Ford, Phys. Rev. B 2, 857 (1970).

[21] S. J. Campbell, P. E. Clarke, and P. R. Liddell, J. Phys. F 2, L114 (1972).

[22] H. E. Ekström and H. P. Meyers, Phys. Kondens. Materie 14, 265 (1972).

[23] S. Mishra and P. B. Beck, Phys. Status Solidi 19, 267 (1973).

[24] M. A. Ruderman and C. Kittel, Phys. Rev. 96, 99 (1954); R. Kasuya, Prog. Theor. Phys. 16, 45 (1956); K. Yosida, Phys. Rev. 106, 893 (1957).

[25] K. Matho and M. T. Béal-Monod, Phys. Rev. B 5, 1899 (1972).

[26] K. Matho and M. T. Béal-Monod, J. Phys. F 3, 136 (1973).

[27] As presented, the results of Matho and Béal-Monod (Ref. 25) cannot be applied to CuFe; in particular they give the wrong prediction for the concentration dependence of the resistivity *maximum* in CuFe (Ref. 12). However, the result contained in [Eq. (4)], i.e., that the effect of the interactions is contained in the function $L(\bar{n})$, is statistical in nature and does not depend on the details of the calculation. Thus, it should be at least qualitatively correct when applied to CuFe.

[28] The temperature dependence of $L(\bar{n})$ arises from the fact that only those impurities with a coupling energy exceeding k_BT will interact; thus as *T decreases n*, the mean number of impurities that interact with each other, will *increase* (Ref. 25). However, in disordered CuFe films, n is probably limited by the small size of the Cu grains; consequently, the temperature dependence of $L(\bar{n})$ should be less than would be the case for a crystalline sample.