Neutron-Diffraction Observations on the Cu(Fe) Kondo System*

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Polarized-neutron diffraction studies are reported on a series of dilute Cu(Fe) alloys in which the 3*d*-electron magnetization induced by an applied magnetic field is sensed in the (111) Bragg reflection. Utilizing the concentration dependence, the isolated-Fe-center magnetization is found to be considerably larger than the total magnetization at temperatures below 10 K. The observations lend support to the development of a Kondo spin-compensated singlet state at low temperature.

The characterization of the magnetic state resulting from the addition of magnetic solute atoms into nonmagnetic metallic host lattices (generally referred to as Kondo alloys) has continued to be elusive in spite of formidable attack both experimentally and theoretically.[1] Theoretical approaches accounting for the anomalous Curie-Weiss dependence of the magnetic susceptibility at "low" temperature have centered around two models: (1) the formation of a low-temperature singlet state for the impurity ion as coupled to the conduction electrons, the Kondo compensation-cloud model, and (2) the collapse of the impurity-ion magnetization at low temperature by spin-fluctuation processes, the localized-spin-fluctuation (LSF) model. Various microscopic examination tools (NMR, Mössbauer absorption, nuclear orientation, slow-neutron scattering) have been applied in attempts at identifying the proper theoretical picture pertinent to various alloy systems and it is fair to say that acceptable clarity has not been obtained. Earlier neutron-scattering studies in Bragg diffraction of Cu(Fe) by Stassis and Shull[2] and in diffuse scattering of Al(Mn) by Kroo and Szentirmay[3] and Bauer and Seitz[4] have not been entirely conclusive because of relatively high impurity concentration.

The present neutron experiments are of elastic-Bragg-reflection nature on crystals of Cu(Fe) with Fe concentration 387, 709, and 1007 ppm (atomic) and on pure Cu (< 2 ppm Fe). An applied magnetic field of 53.8 kG induces a sample magnetization and this is sensed in the Bragg-reflection intensity of polarized neutrons yielding the residual polarization ratio r, defined as the deviation from unity of the intensity ratio obtained upon neutron polarization inversion. This experimental quantity is very small and in sufficient approximation is given by $r = 4\langle p\rangle/\langle b\rangle$, where $\langle p\rangle$ and $\langle b\rangle$ are the mean magnetic and nuclear scattering amplitudes of an average lattice site. The magnetic-scattering amplitude is related to the impurity-center magnetic moment μ (in units of μ_B) and its form factor for scattering f according to $p(\mathrm{cm}) = 0.270\times 10^{-12}\mu f$.

In their classic paper, Tholence and Tournier[5] have shown that the iron impurity centers added to a copper lattice are of two types: (1) those which are truly isolated with minimum interaction between each other and (2) those which happen to fall within a certain interaction volume containing Z lattice sites and which interact with each other. These authors showed that a proper extrapolation of the concentration dependence could yield the isolated-center magnetization which we are primarily interested in. Thus with an impurity concentration c (atom fraction), the fraction of lattice sites occupied by isolated centers becomes $c(1-c)^Z$ and the fractional number of paired centers becomes $c(1-c)^{Z-1}Zc/2$ so that

$$r = (4/\langle b\rangle)\left[c(1-c)^Z p_1 + c(1-c)^{Z-1}\tfrac{1}{2}Zcp_2\right]. \quad (1)$$

Here, p_1 represents the magnetic-scattering amplitude of an isolated center and p_2 the amplitude of a pair of interacting centers. Thus a display of the normalized quantity $r/c(1-c)^Z$ should be closely linear with c, yielding both p_1 and p_2.

After single-crystal growth, the specimen ingots were homogenized in evacuated quartz ampoules for 3 days at 1000°C followed by rapid quenching. Chemical analysis was performed on specimens taken from different parts of the ingots and showed the Fe concentration to agree with the nominal values within the analytical ac-

TABLE I. Residual polarization ratio values obtained in the (111) Bragg reflection for Cu(Fe) alloys and pure Cu specimens. All polarization ratio values are extinction corrected, expressed as parts per 10^5, and correspond to an applied field strength of 53.8 kG. Standard errors of quantities are given in parentheses.

	Temperature (Kelvin)	Cu <2 ppm	Cu(Fe)-A 387 ppm	Cu(Fe)-B 709 ppm	Cu(Fe)-C 1007 ppm
MITR	1.23		101.6(7.8)	113.0(6.2)	
Data	1.50		89.8(7.8)	115.0(8.1)	118.1(5.8)
	1.76		74.4(10.2)	107.0(6.7)	100.0(5.5)
(λ=1.050 Å)	2.30		63.8(7.9)	76.3(7.7)	103.0(5.0)
	3.00		37.9(7.0)	75.0(7.8)	83.7(6.9)
	4.18		37.7(5.4)	77.4(8.1)	86.4(5.3)
	24				25.3(4.9)
HFIR	1.64	47.4(3.5)	75.5(4.8)	102.3(5.6)	
Data	1.83	35.3(5.3)			100.9(4.9)
	4.2	10.9(3.6)	32.3(5.3)	56.7(5.1)	79.7(5.1)
(λ=1.026 Å)	25	-7.1(5.4)			
Extinction Correction Factor		1.235(8)	1.319(6)	1.243(9)	1.060(3)

curacy of 10% with no detectable variation within the individual ingots. Oriented slices from the ingots were then studied for extinction analysis in symmetric Laue transmission over a wide range of neutron wavelengths. Cold pressing of the slices was pursued until the degree of extinction in the (111) Bragg reflection was capable of quantitative assessment. A modified Zachariasen extinction theory[6] pertinent to the case of symmetric Laue transmission was used in this with excellent fitting yielding accurate values for the extinction correction factor. In both the extinction analysis and the later polarized-neutron study, window wavelengths were used for which no simultaneous Bragg-reflection contamination is permitted in the primary (111) reflection.

Polarization-ratio measurements were made in the fast-flipping mode and periodic checks on the reality of the small-signal effect showed that statistical accuracy in the ratio could be achieved. The extinction-corrected values of r for the various specimens are given in Table I and displayed in Fig. 1 as a function of T^{-1} with data being obtained at both the Massachusetts Institute of Technology Research Reactor (MITR) and the Oak Ridge high-flux isotope reactor (HFIR). The standard errors (in parentheses) arise from the statistical accuracy as adjusted slightly for the uncertainty in the extinction correction.

Within the accuracy of the data points, the variation with T^{-1} is linear; the solid lines in Fig. 1 are the linear least-squares fits; the dashed lines are the 68%-confidence error bands. The pronounced T^{-1} effect for pure Cu arises because of nuclear-spin-dependent scattering associated with nuclear polarization induced by the applied field at these temperatures. The least-squares fit to the pure-Cu data points reflects both our measurements and those obtained by Abragam *et al.*[7] using a different spin-precession technique. It is to be noted that the Cu data also show a high-temperature intercept in agreement with

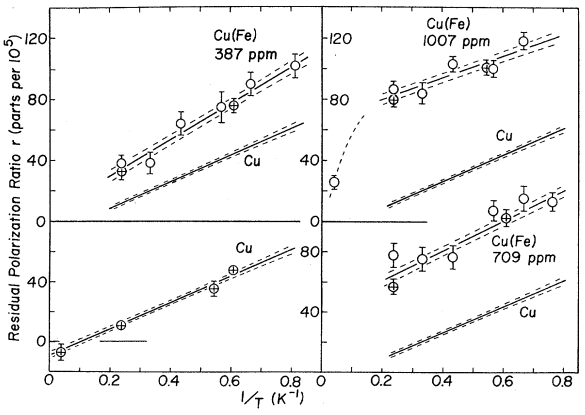

FIG. 1. Residual polarization ratio of (111) Bragg reflection in Cu(Fe) alloys and in pure Cu as a function of T^{-1}. $r_{diam}+r_{so}=-11.3\times10^{-5}$ for pure Cu. Open circles are data taken with MITR; circled pluses are data taken at HFIR.

the calculated temperature-independent diamagnetic scattering (−12.6) and Schwinger spin-orbit scattering (+1.3 units).

The difference between the alloy and pure-Cu values represents the magnetic scattering associated with the Fe centers and this has the two components contained in Eq. (1). Figure 2 shows the normalized values for the magnetic residual polarization ratio as a function of the concentration for selected temperature values. Values shown are those from the confidence error bands of Fig. 1 with appropriate standard error. A value 200 has been used in this analysis for the pair interaction parameter Z as suggested by magnetization studies[5,8] and we may note that our results are insensitive to this selection. A least-squares fit to the data points is shown with intercept values at zero concentration. It is to be noted that the slope of the concentration dependence (a measure of the pair scattering amplitude) changes sign through this temperature range unlike the magnetization results which are always of positive slope. This does not necessarily represent a discrepancy between the two types of experiments because the neutron scattering depends upon the pair magnetization structure as well as its magnitude.

The intercept values of Fig. 2 can be converted into magnetization per isolated center through use of the (111) form factor, 0.579 as determined in Ref. 2, and a value for $\langle b \rangle$ representative of Cu, 0.76×10^{-12} cm. This magnetization is displayed in Fig. 3 as a function of temperature. For comparison there is shown also the bulk or total magnetization as summarized by Steiner, Hüfner, and Zrodjewski[9] based on four independent magnetization studies yielding excellent Curie-Weiss fitting, and that to be expected for a free spin in our applied field.

It is seen that the magnetization visible in neutron diffraction, namely that associated[2] with the $3d$-electron group of mean radius about 0.5 Å, is noticeably larger than the total magnetization at low temperature with the two quantities coalescing in the region of 10 K. This would suggest *the presence of a compensating contribution to the magnetization that develops at low temperature,* one not seen in neutron Bragg diffraction if its spatial extent were appreciably larger than 0.5 Å, in agreement with the Kondo model of a compensating cloud of conduction-electron polarization. These observations would disagree with those expected from a single-entity magnetization source decreasing in magnitude at low temperature as in an LSF model.

The conclusions just arrived at are seemingly contradictory to those which have developed from Knight-shift studies of the hyperfine-field distribution by both (a) NMR measurement at near-neighbor Cu sites by Boyce and Slichter[10] and (b) Mössbauer Fe absorption by Steiner, Hüfner, and Zdrojewski[9] and others[11] in which the same temperature dependence as the total magnetization is found. From the different perspective views of the nuclear studies, it is concluded that a single-entity, localized source of the magnetization must be present, as in an LSF model. We may note however that a relaxation of the generally held view that the Kondo compensation cloud is of long-range character might allow the construction of a model compatible with all of the experiments. A shrinkage of the polarizable part

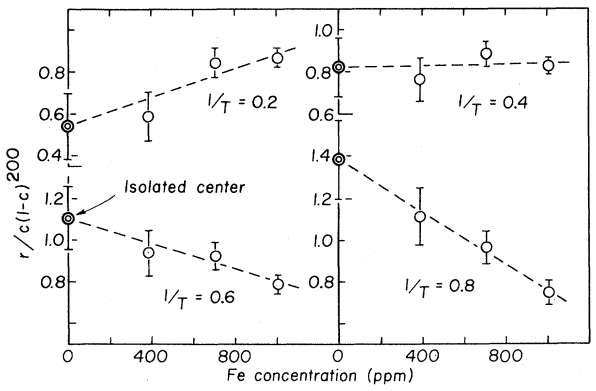

FIG. 2. Normalized r values as a function of concentration at selected temperatures. Intercept values are shown which lead to isolated-center magnetization.

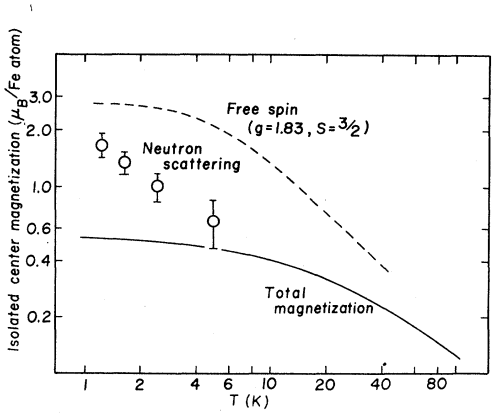

FIG. 3. Isolated-Fe-center magnetization in Cu(Fe) as a function of temperature.

of the compensating cloud to 4s-electron-shell dimensions would still be undetectable in Bragg neutron diffraction. Moreover it is to be recognized that the "viewing" time scale associated with neutron passage is less than the intrinsic fluctuation time of the magnetic center in contrast to the much longer time associated with the other techniques.

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Effect of the Electron-Electron Interaction on the Excitation Energies of an *n*-Inversion Layer on Si

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The influence of the electron-electron interaction on the energy of electrons in the lowest and first-excited sub-bands of an inversion layer has been evaluated. When these corrections are included very good agreement with experimental results is obtained. A bound inter–sub-band exciton is predicted.

The exchange energy of electrons in the lowest sub-band of an inversion layer formed near the SiO_2-Si[001] interface in a metal-insulator-semiconductor structure was calculated by Chaplik[1] and by Stern[2,3] and is of the order of -10 meV. In a previous paper[4] I calculated the correlation energy and found that it further lowers the energy of electrons in the lowest sub-band by about 5 meV. Since the separation in energy between the two lowest sub-bands is of the order of 10 meV,[5] many-body effects strongly affect the energy of transition from the lowest to the first-excited sub-band.

For *p*-type inversion layers Ohkawa, Ando, and Uemura[6] have calculated the self-energy of a hole in the lowest sub-band. They found that the energy separation between the lowest and first-excited sub-bands is in much better agreement with measurements[7] when exchange and correlation in the lowest sub-band is taken into account.

In *n*-inversion layers, however, I have found that the calculated inter–sub-band splitting is much larger than measured if only the self-energy of the lowest sub-band is considered.

In this Letter I present results of a calculation of the correlation energy of an electron in the first-excited sub-band. It is also of the order of -10 meV and the energy separation as a function of inversion-layer density is found to agree very well with optical measurements.[8,9]

The bare Coulomb interaction between two electrons Fourier analyzed in the two dimensions