

Magnetic Interactions and High-Field Magnetization in Dilute Magnetic Alloys*

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Magnetic interactions have been investigated in Cu(Mn) and Cu(Fe) alloys with concentrations ranging from several hundred to several thousand ppm. In each system two sets of alloys were prepared in different ways to test for sensitivity to structural modifications. In the Cu(Mn) alloys there was very little difference in magnetic properties of the two sets of alloys which is consistent with the expectation that the Cu(Mn) alloys form good random solid solutions. The magnetic properties were compared with the recent mean-random-field theory of Klein in the low-temperature limit. It was found that the theory is able to explain the concentration dependence of the initial susceptibility and also gives a semiquantitatively correct description of the magnetization to 100 kOe. In the Cu(Fe) alloys the results confirm in part recent work of Tholence and Tournier who, working with much more dilute samples, showed that there exist isolated Fe atoms and ferromagnetically coupled Fe-Fe pairs. The pair magnetization saturates at ≈ 60 kOe for $T \lesssim 4$ °K and each pair has associated with it a spin of ≈ 3 . The pair concentration was determined from magnetization and recent Mössbauer experiments in several different sets of alloys. It was shown that this pair density depends sensitively on sample-preparation techniques and cold work, i.e., on modifications of the structure of these supersaturated alloys. It is therefore argued that the pairs are not coupled by long-range Ruderman-Kittel-type interactions but rather they should be regarded as near-neighbor pairs acting as a diatomic molecule dissolved in the copper matrix. The most concentrated alloys in each set of samples (0.6 at.%) exhibited remanence below 3.5 °K. The magnitude of the remanence was proportional to the pair densities in the respective sample sets, suggesting that the ordering was a cooperative effect between the pairs through a mechanism that is not clearly defined. It was shown how the spin-glass transitions recently observed by Svensson in cold-worked alloys could be understood in terms of the breaking up of pairs and other clusters—with a subsequent return to a more random alloy. Finally, the 1.6 °K spin polarization associated with an isolated Fe impurity to ≈ 100 kOe is compared to two Brillouin functions; one corresponding to $T = 1.6$ °K and the second to $T = 30.6$ °K ($\approx 1.6 + T_K$). The second function fits the data fairly well but there is no theoretical justification for this agreement.

I. INTRODUCTION

The understanding of magnetism in metals involves two fundamental concepts. The first of these concerns the formation of a magnetic moment on the atom in the presence of the conduction electrons of the metal. The second involves the long-range interactions between moments, which lead to ferromagnetism or antiferromagnetism. By studying the properties of small amounts of magnetic impurity in a nonmagnetic host, one might hope to eliminate the impurity-impurity interactions and concentrate on the properties of the single impurity. Theoretical work by Friedel and by Anderson¹ has led to an understanding of the conditions under which moments form on impurity atoms in metals. By considering the scattering of conduction electrons by well-defined moments on impurities, Kondo² explained the resistance minimum observed in these alloys. This led to the present understanding of the single-impurity problem (Kondo effect), which is extensively reviewed theoretically and experimentally by Kondo³ and Heeger.⁴

In the single-impurity limit it is found that an alloy may be characterized by a parameter T_K , the Kondo temperature, which is independent of impurity concentration. As impurity concentration is increased, interactions between moments via the conduction electrons become important and it is these interactions that are of interest in the present work.

Both Cu(Fe) and Cu(Mn) have been studied⁴ in the dilute limit with Cu(Fe) being a classical example of a Kondo system with $T_K \approx 10$ °K.⁴ Cu(Mn), on the other hand, has $T_K \approx 0.002$ °K⁵ and exhibits resistivity and susceptibility maxima at higher concentrations. It is expected that the magnetic properties of the two systems in the concentration range where impurity-impurity interactions become important, will reflect these differences.

The purpose of this work was to study the magnetic properties of both Cu(Mn) and Cu(Fe) over a range of concentrations extending from the region dominated by single-impurity effects to a region dominated by impurity-impurity interaction effects. The magnetic properties of Cu(Mn) have been

studied⁵⁻⁹ over a wide range of concentrations and temperatures, with most effort on low-field susceptibility in the concentration range where interaction effects dominate the magnetic properties. On the other hand, the magnetic properties of Cu(Fe) have been studied^{4,10-13} with emphasis on the single-impurity problem. Recent studies of Cu(Fe) by Tholence and Tournier¹³ indicate that interactions may exist for impurity concentrations below 300 ppm, a concentration region previously expected to be in the single-impurity limit.¹⁴ Thus studies involving interactions have shed new light on the "single"-impurity problem in Cu(Fe).

In the present investigation the approach was to obtain more information on interacting moments by studying the way they magnetize in high magnetic fields. To do this we have measured the magnetization of the alloys in magnetic fields to approximately 100 kOe at liquid-helium temperatures, and the initial susceptibility to temperatures of approximately 50 °K.

Recent calculations by Klein¹⁵ give expressions for low-temperature initial susceptibility and field-dependent magnetization for interacting moments. Attempts to apply this theory to the magnetization of Cu(Fe) and Cu(Mn) alloys will be discussed, and a comment will be made on the high-field magnetization of a single spin for temperatures much below the Kondo temperature. Preliminary accounts of this work have been given elsewhere.¹⁶

II. EXPERIMENTAL PROCEDURE

A. Sample Preparation

Cu(Fe) and Cu(Mn) alloys were prepared using 99.9999% Cu (supplied by Cominco American, Inc.). The solute metals were Ferrovac-E Fe of approximately 99.99% (supplied by Crucible Steel Co. of America) and 99.9% Mn (supplied by Johnson Matthey). As explained more fully below, two sets of each alloy system were prepared in order to test the magnetic properties for sensitivity to structural differences produced by varying sample-preparation procedures. This is particularly important for the Cu(Fe) alloys, *which are supersaturated*, and we shall return to considerations of this nature in the following sections. The constituents were melted in zirconium oxide crucibles in a vacuum induction furnace and held approximately 100 °C above the melting temperature¹⁷ for 1 h. The melt was chill cast under positive pressure of helium into a split copper mold cooled with liquid nitrogen. All samples were made from master alloys of approximately 1-at. % solute content. Two samples in the shape of cylinders (0.190×0.190 in.) were machined from the ingot of about 0.250-in. diameter. The cylinders were heavily chemically etched, and one was annealed. Cu(Mn) sam-

TABLE I. Analyzed sample concentration.

Sample	Impurity concentration	
	(ppm)	at. %
Cu(Fe) - 1	447	4.47×10^{-2}
- 2	842	8.42×10^{-2}
- 3	1370	1.37×10^{-1}
- 4	1750	1.75×10^{-1}
- 5	2300	2.30×10^{-1}
- 6	6140	6.14×10^{-1}
Cu(Fe) - 1A	447	4.47×10^{-2}
- 2A	842	8.42×10^{-2}
- 3A	1270	1.27×10^{-1}
- 4A	1750	1.75×10^{-1}
- 5A	2410	2.41×10^{-1}
- 6A	5960	5.96×10^{-1}
Cu(Mn) - 2A	430	4.30×10^{-2}
- 3A	848	8.48×10^{-2}
- 4A	1310	1.31×10^{-1}
- 5A	3430	3.43×10^{-1}

ples were annealed in sealed Vycor tubes evacuated to 1×10^{-6} Torr for 40 h at 500 °C and allowed to oven cool to room temperature. Cu(Fe) samples were sealed in Vycor tubes containing high-purity argon (less than 1-ppm O₂) and held at 900 °C for 48 h before being quenched rapidly in ice water in a process that broke the Vycor tube. Impurity concentrations *c* determined by atomic-absorption spectroscopy are given in Table I. Although it is difficult to determine the absolute accuracy of this analysis, it is estimated to be $\pm 3.0\%$. Low-field measurements of Cu(Mn) alloys showed no measurable differences between annealed and unannealed samples. In order to improve the accuracy of the impurity concentrations, the unannealed Cu(Mn) samples were actually used (i. e., dissolved) for a spectroscopic analysis and these samples are not listed in Table I.

B. Measurement Techniques

A Princeton Applied Research vibrating-sample magnetometer was used to measure bulk magnetization of the Cu(Fe) and Cu(Mn) alloys. Magnetization measurements were made between 1.6 and approximately 50 °K in fields up to 10 kOe using a conventional electromagnet.

High-field measurements to 95 kOe at 1.6 and 4.4 °K were made using an RCA Nb₃Sn superconducting solenoid. A Janis Vari-Temp Dewar was employed in both magnets. Temperature was regulated electronically for low-field measurements above 4.2 °K. Regulated temperatures below 4.2 °K were achieved by pumping—with a Walker regulator—on liquid helium introduced into the sample chamber. Sample temperature was determined using a calibrated GaAs diode (Lake Shore Cryo-

tronics, Inc.) periodically introduced into the sample area. It is estimated that the temperature is known to about $\pm 3.0\%$ over the entire range. The magnetic field is known to approximately $\pm 1.5\%$ for the low-field measurement, and to $\pm 2.0\%$ for high-field data. The magnitude of the magnetization was calibrated with respect to the moment of pure nickel¹⁸ (57.5 emu at 4.4 °K). Details of the apparatus, temperature control, and calibration are given elsewhere.¹⁶ All measurements of alloy magnetization were corrected for the diamagnetism of pure copper given by Hurd¹⁹ as $\chi_{\text{Cu}} = -88.11 \times 10^{-9}$ emu/g. Initial susceptibility is defined as $\chi_i = (dM/dH)_{H \leq 500 \text{ Oe}}$ and high-field susceptibility is given by $\chi_{\text{HF}} = (dM/dH)_{\text{HF}}$, where M is the impurity magnetization and H is the magnetic field.

Most data for each sample were taken several times to determine repeatability. Estimates of the uncertainties in magnetization and susceptibility measurements are shown by error bars on the figures.

III. EXPERIMENTAL RESULTS

A. Low-field Susceptibility

Figure 1 is a plot of inverse susceptibility versus T for the set of Cu(Mn) alloys. For temperatures above 10 °K all samples show approximately linear behavior indicative of a Curie-Weiss (C-W) susceptibility. Although a C-W analysis is not rigorously applicable,²⁰ it serves as a comparison to measurements on more dilute noninteracting moments. The C-W law gives

$$\chi_i = (n \mu_{\text{eff}}^2 / 3k_B)(T - \Theta)^{-1}, \quad (3.1)$$

where χ_i is the initial impurity susceptibility per unit mass, n is the number of impurity atoms per unit mass of alloy, Θ is the Weiss temperature, μ_{eff} is the effective moment per impurity, and the other symbols have their usual meanings. If we take $\mu_{\text{eff}} = g[S(S+1)]^{1/2} \mu_B$, where μ_B is the Bohr magneton, $g = 2.0$, and S is the spin on an impurity,

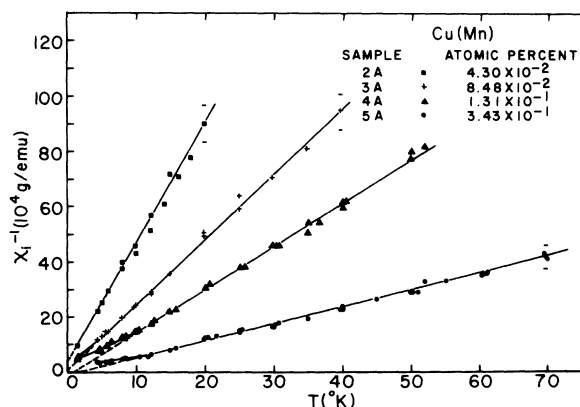


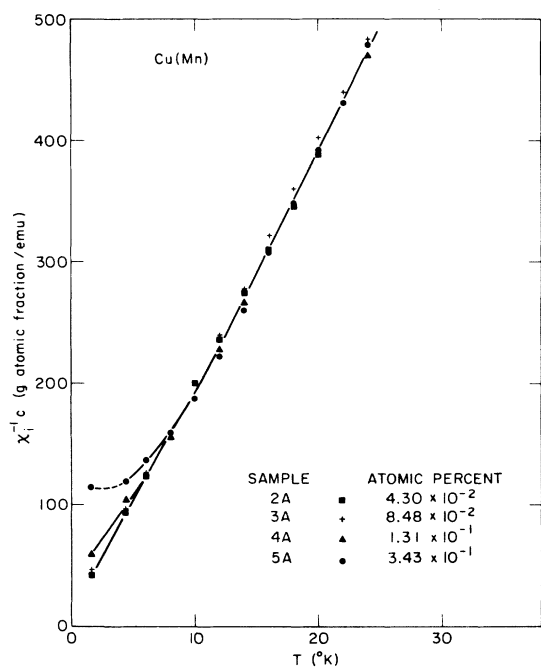
FIG. 1. Temperature dependence of inverse susceptibility for Cu(Mn) alloys.

we may calculate Θ , μ_{eff} , and S . The results of this calculation are given in Table II. These values can be compared to measurements by Hurd⁸ on Cu(Mn) for lower concentrations ($c < 200$ ppm), which give $\mu_{\text{eff}} = (4.93 \pm 0.025) \mu_B$ and an average Θ of $(-14 \pm 3)^\circ\text{K}$. More recent measurements⁵ at very low temperatures ($T \sim 200 \text{ m}^\circ\text{K}$) and concentrations ($c < 100$ ppm) give a concentration-independent $\Theta \approx 10 \text{ m}^\circ\text{K}$ and $\mu_{\text{eff}} = (4.5 \pm 0.4) \mu_B$. Measurements by others⁶ in concentration regions above 0.02 at. % generally indicate that Θ moves toward positive values with increasing impurity concentration. For temperatures below 10°K , deviations from the C-W law are associated with the apparent onset of antiferromagnetism observed in Cu(Mn).^{6,7} In Fig. 2 the smoothed data of Fig. 1 are normalized using sample concentration. This plot indicates clearly that χ_i above 10°K is approximately proportional to c and that significant deviations are observed for $T = 1.6^\circ\text{K}$.

A plot of c/χ_i vs T for the unannealed set of Cu(Fe) alloys is given in Fig. 3 and indicates that χ_i is not simply proportional to c . The down turn of c/χ_i at low temperatures observed for samples 1-5 has been recently observed¹³ for this system

TABLE II. Curie-Weiss analysis for Cu(Mn) and Cu(Fe) alloys.

Sample	Concentration (at. %)	μ_{eff}/μ_B	θ (°K)	S
Cu(Mn) - 2A	4.30×10^{-2}	5.2 ± 0.5	-0.8 ± 0.5	2.1 ± 0.2
- 3A	8.48×10^{-2}	5.0 ± 0.5	0.0 ± 0.5	2.0 ± 0.2
- 4A	1.31×10^{-1}	5.0 ± 0.5	$+1.0 \pm 0.5$	2.0 ± 0.2
- 5A	3.43×10^{-1}	4.9 ± 0.5	$+2.0 \pm 0.5$	2.0 ± 0.2
Cu(Fe) - 1	4.47×10^{-2}	3.3 ± 0.3	-10.4 ± 0.5	1.2 ± 0.2
- 2	8.42×10^{-2}	3.3 ± 0.3	-6.8 ± 0.5	1.2 ± 0.2
- 3	1.37×10^{-1}	3.5 ± 0.3	-4.6 ± 0.5	1.3 ± 0.2
- 4	1.75×10^{-1}	3.9 ± 0.4	-3.6 ± 0.5	1.5 ± 0.2
- 5	2.30×10^{-1}	4.0 ± 0.4	-1.6 ± 0.5	1.6 ± 0.2
- 6	6.14×10^{-1}	5.9 ± 0.5	$+0.6 \pm 0.5$	2.5 ± 0.2

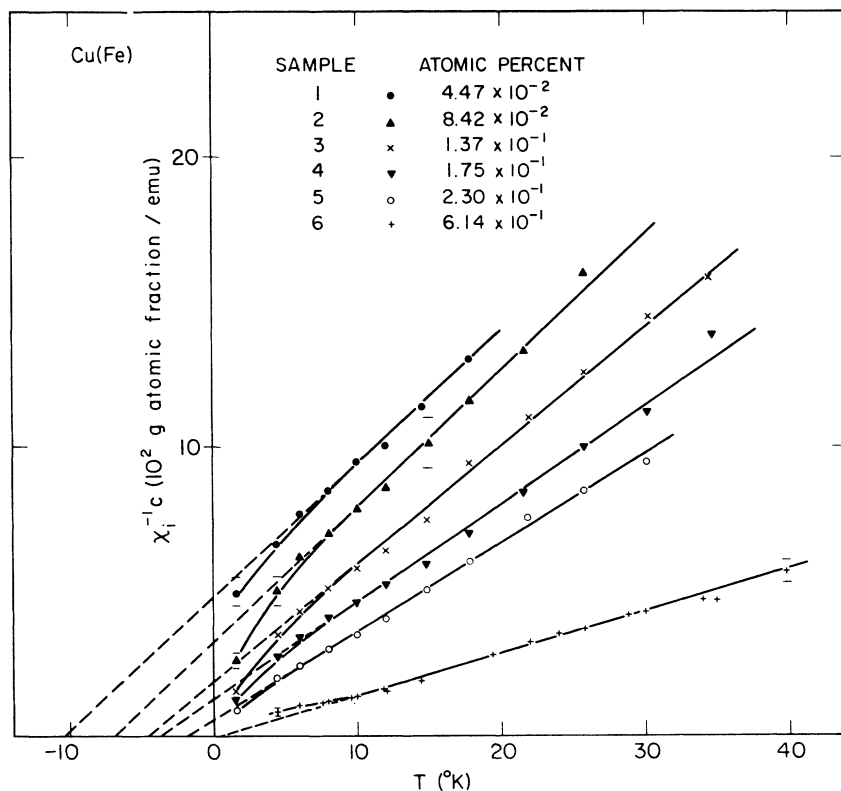
FIG. 2. c/χ_i vs T for Cu(Mn) alloys.

at concentrations below 600 ppm and is associated with a susceptibility containing both c and c^2 dependences. The change in character of c/χ_i , from

turning down at low T to nearly turning up (i. e., flattening) for Cu(Fe)-6, will be discussed in Sec. V. Similar data for annealed Cu(Fe) samples show the same characteristics while being less magnetic. Table II is given as a comparison with the Cu(Fe) data of Hurd¹¹ which give $\mu_{\text{eff}} = (3.68 \pm 0.20)\mu_B$, $\Theta = (-32 \pm 2)^\circ\text{K}$, and $S = 1.4$, for the single-impurity values.

B. Remanence

At $T = 1.6^\circ\text{K}$, Cu(Mn)-5 and Cu(Fe)-6 and -6A showed remanent magnetization as indicated in Figs. 4(a) and 4(b). These data were taken by cooling the samples in zero field to 1.6°K , taking data from the origin of Figs. 4(a) and 4(b) to 1.0 kOe or 300 Oe, respectively, increasing the field to 10 kOe and returning it to 1.0 kOe or 300 Oe, taking data again as the field was decreased to zero and then increased in the opposite direction, etc. At 1.6°K the remanent magnetization for the annealed sample [Cu(Fe)-6A] was smaller than for the unannealed one [Cu(Fe)-6]: $M_r^A = 81 \times 10^{-4}$ emu/g, whereas $M_r = 105 \times 10^{-4}$ emu/g. For both Cu(Fe) alloys, the remanence disappeared for $T > (3.5 \pm 0.2)^\circ\text{K}$. For Cu(Mn)-5, remanence was absent at $T = 4.4^\circ\text{K}$, though no measurements were made between 1.6 and 4.4°K to determine an ordering temperature.

FIG. 3. c/χ_i vs T for Cu(Fe) alloys (unannealed samples).

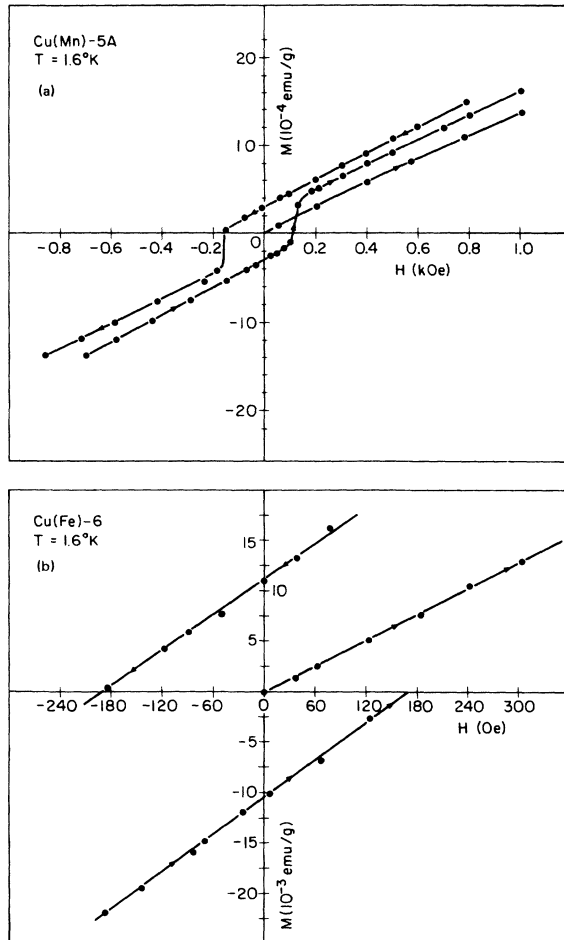


FIG. 4. Remanent magnetization at $T=1.6^\circ\text{K}$ for (a) Cu(Mn)-5A and (b) Cu(Fe)-6 (unannealed sample). Samples cooled in zero field.

C. High-Field Magnetization

High-field measurements to 95 kOe at 1.6 and 4.4 °K were made for all unannealed Cu(Fe) samples and at $T=1.6^\circ\text{K}$ for the annealed set. The results for the unannealed samples at 1.6 °K are shown in Fig. 5. Subsequent analysis has indicated uncertainty in the data at 1.6 °K for Cu(Fe)-1, and it has been deleted from Fig. 5. Similar measurements for the annealed Cu(Mn) alloys are shown for $T=1.6^\circ\text{K}$ in Fig. 6.

IV. THEORETICAL CONCEPTS

A. Random Molecular-Field Model

The method of random molecular fields has been used with some success to describe the magnetic^{15,21,22} and transport²³ properties of certain alloys, sometimes called "spin glasses," containing dilute concentrations of interacting magnetic im-

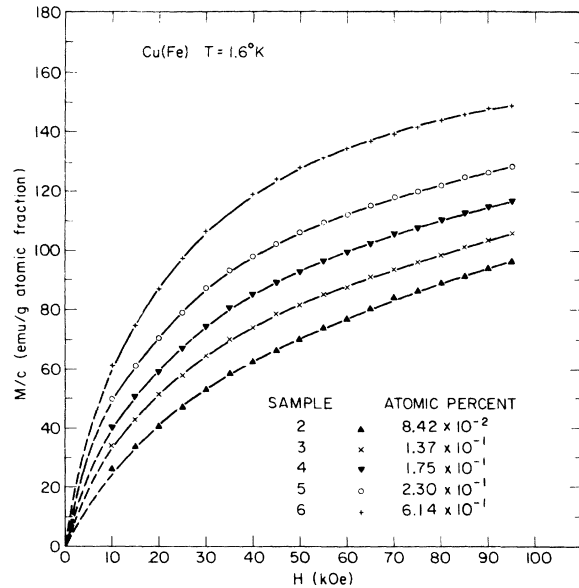


FIG. 5. High-field M/c vs field for Cu(Fe) alloys at $T=1.6^\circ\text{K}$ (unannealed samples).

purities in a nonmagnetic host. In this approximation an internal field is assumed to arise from an indirect exchange interaction via the conduction electrons, between magnetic impurities. Most attempts to treat the problem of interacting moments in metals assume the interaction given by Ruderman and Kittel,²⁴ Kasuya,²⁵ and Yosida²⁶ (RKKY) has the approximate form

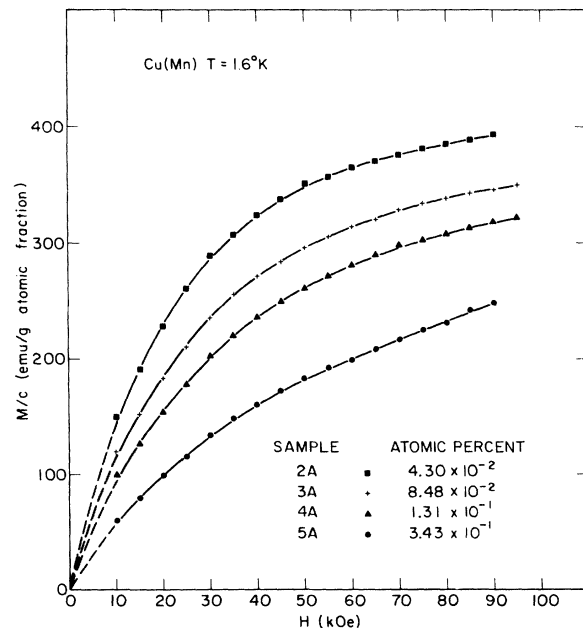


FIG. 6. High-field M/c vs H for Cu(Mn) alloys at $T=1.6^\circ\text{K}$.

$$E_{ij} = \alpha \bar{\mu}_i \cdot \bar{\mu}_j \frac{\cos(2k_F r_{ij})}{r_{ij}^3} \quad (4.1)$$

Here α is a constant, r_{ij} is the distance between moments $\bar{\mu}_i$ and $\bar{\mu}_j$, and k_F is the Fermi wave vector. The most recent works of Klein¹⁵ have relevance to the present work and will be described here briefly for future reference. It is assumed by Klein that the alloy may be considered as a random distribution of Ising-model spins in a non-magnetic host. Furthermore, the calculation considers only the limiting case as $c \rightarrow 0$ (introducing an error of order c^2), and that long-range magnetic order is absent in the solid. For such a system, the interaction Hamiltonian between magnetic moments μ_i has the form

$$H = \sum_{i < j} v_{ij} \mu_i \mu_j, \quad (4.2)$$

where the moments have values of ± 1 and the RKKY interaction potential is of the form

$$v_{ij} = a(\cos k_F r_{ij} / |\cos k_F r_{ij}|) r_{ij}^{-3}. \quad (4.3)$$

Here a is the interaction strength. The RKKY interaction is incorporated into the theory using the assumption that $k_F \bar{R} \gg 1$, where \bar{R} is the average distance between magnetic impurities. Under these conditions, Eq. (4.3) varies sufficiently rapidly that an impurity j is, on the average, just as likely to experience a positive as a negative potential from impurity i . Equation (4.3) is then approximated by

$$v_{ij} = +a/r_{ij}^3 \text{ or } -a/r_{ij}^3, \quad (4.4)$$

each with probability $\frac{1}{2}$.

Using a mean-random-field (MRF) approximation, a temperature- and concentration-dependent distribution $P(\bar{H})$ (probability distribution of the random molecular field \bar{H}) is determined. The thermodynamic variables of the system are obtained by integrating the expression for the thermodynamic variable of a single spin in a molecular field \bar{H} over the distribution for all fields. $P(\bar{H})$ is characterized by a temperature- and concentration-dependent width Δ . In the $T=0$ limit, $\Delta \rightarrow \Delta(\infty) = \gamma c$, where $\gamma = \frac{2}{3} \pi^2 |a| n_0$, a is the interaction strength between impurities at a distance of one lattice constant, and n_0 is the number of sites per unit cell ($n_0=4$ for an fcc lattice).

The results, when applied to the magnetic properties at very low temperatures, give a magnetic susceptibility which is independent of impurity concentration and a temperature-dependent susceptibility characterized by a maximum where the temperature of the maximum, T_{\max} , is proportional to impurity concentration. Similarly, the very-low-temperature specific heat is independent of impurity concentration and approximately

linear with T .

Recently, Klein¹⁵ has extended the above theory to include the presence of an external magnetic field H_{ext} . In this case Δ also depends on external magnetic field. In particular, the theory gives a low-temperature expression for the magnetization as a function of T , H_{ext} , and c . Low-temperature results relevant to this work, taken from Ref. 15, are given below:

$$\Delta = \gamma c \left[1 - \frac{\ln 4}{\pi} \frac{k_B T}{\gamma c} - \left(\frac{\ln 4}{\pi} \frac{k_B T}{\gamma c} \right)^2 \right], \quad (4.5)$$

$$\frac{\chi_i(T)}{N_0 \mu_B^2 / \pi} = \frac{2}{\gamma} \left[1 + \frac{\ln 4}{\pi} \frac{k_B T}{\gamma c} - \left(\frac{\pi^2}{12} - \frac{2 \ln^2 4}{\pi^2} \right) \left(\frac{k_B T}{\gamma c} \right)^2 \right] (\gamma c \gg k_B T). \quad (4.6)$$

$\chi_i(T)$ is the susceptibility per mole of alloy and N_0 is Avogadro's number. A useful relation for estimating γ is

$$k_B T_{\max} \approx 0.4 \Delta(\infty) = 0.4 \gamma c. \quad (4.7)$$

From Ref. 15, the low-temperature field-dependent magnetization is given by

$$M = \frac{2}{\pi} N c \mu_B \left\{ \tan^{-1} y_0 + \frac{2 y_0 \ln 2}{\pi (1 + y_0^2)^2} \left(\frac{kT}{\Delta(\infty)} \right) + \left(\frac{kT}{\Delta(\infty)} \right)^2 \left(\frac{y_0}{1 + y_0^2} \right) \left[\left(\frac{2 \ln 2}{\pi (1 + y_0^2)} \right)^2 \times \frac{4 + 3 y_0^2}{1 + y_0^2} - \frac{\pi^2}{12} \right] + O(T^3) \right\}, \quad (4.8)$$

where N is the number sites in the crystal and $y_0 = \mu_B H_{\text{ext}} / \Delta(\infty)$.

B. Experimental Evidence for a Molecular-Field Model

Low-temperature measurements at $T \sim 0.1 \text{ }^\circ\text{K}$ ⁹ indicate that for Cu(Mn) ($0.0186 < c < 0.196$ at. %) the susceptibility tends to a concentration-independent limit of $\chi_i = 1.0 \times 10^{-3}$ emu per mole of alloy. Specific-heat data²⁷ at liquid-helium temperatures for Cu(Mn) ($0.5 < c < 10.0$ at. %) indicate the specific heat due to impurities to be nearly linear in T and nearly independent of Mn concentration. Dreyfus *et al.*¹² compared the low-temperature specific heat and susceptibility for Cu(Mn), Au(Fe), and Cu(Fe) with theoretical relations between χ_i and heat capacity ΔC at $T \approx 0$. Excellent agreement was found for Cu(Mn) and Au(Fe).

In addition Klein and Shen²⁸ found good agreement with the MRF theory for $\chi_i(T)$ data for Au alloys [Au(Fe), Au(Cr), and Au(Mn)] in the temperature range $T_{\max} < T < 2T_{\max}$. In contrast, Cu(Fe) susceptibility measurements at $T \sim 0.5 \text{ }^\circ\text{K}$ ¹²

show a strong concentration dependence ($0.001 < c < 1.0$ at.%) with an abrupt change in this dependence at approximately 0.1 at.%. Specific-heat data for Cu(Fe)²⁹ also indicate a concentration dependence to $T \approx 0.4$ °K. This evidence lends support to the qualitative description of the random-molecular-field theory, at least for the Cu(Mn) and several Au-alloy systems.

C. Local-Environment Model and Impurity Magnetization

In a local-environment model of impurity magnetization, it is assumed that the magnetic properties of an impurity are, to a large extent, determined by the number and type of atoms in the immediate vicinity of the impurity. This approach was used by Jaccarino and Walker³⁰ to explain how Co atoms (nonmagnetic in Rh) form a moment in Rh(Pd) as the Pd concentration is increased. It was found that Co forms a moment only when it has two or more Pd atoms in its nearest-neighbor sites. The local conditions for moment formation have been studied in other systems, including Fe or Co in Al,³¹⁻³³ V in Au,³⁴⁻³⁷ Co in Au³⁸ or Cu,³⁹ and Ni in Cu.^{40,41}

Apart from the problem of forming impurity moments, the magnetization of a given moment may also depend on its local environment, as indicated by the recent study of Cu(Fe) by Tholence and Tournier.¹³ The relationship between their work and the present work will be discussed in detail in Sec. V.

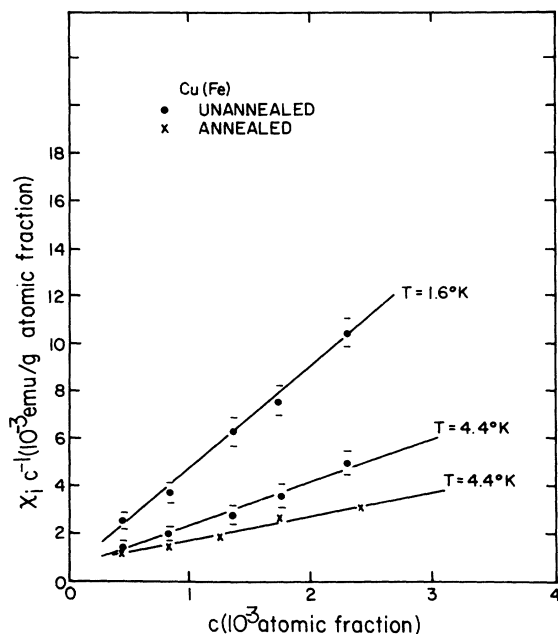


FIG. 7. χ_i/c vs c for lower concentration Cu(Fe) alloys at 1.6 and 4.4 °K.

The connection between bulk measurements of magnetization and local-environment model is made through the concentration dependence of the bulk magnetization. It is assumed that the N_i impurity atoms go into the N lattice sites randomly and that next-nearest-neighbor interactions are unimportant. Then the probability that a given impurity atom has η nearest-neighbor impurity atoms is given by

$$P_\eta(c) = Z! c^\eta (1-c)^{Z-\eta} / [(Z-\eta)! \eta!], \quad (4.9)$$

where Z is the number of nearest-neighbor sites for a given lattice ($Z=12$ for fcc) and $c = N_i/N$ is the impurity concentration. The number of "clusters" containing one, two, and three impurity atoms is given by $N_1 = NcP_0$, $N_2 = NcP_1/2$, and $N_3 = NcP_2/3$. If we associate a magnetization with each type of local environment, then the total impurity magnetization is given approximately by

$$M = N_1 M_1 + N_2 M_2 + N_3 M_3 + \dots \quad (4.10)$$

Here M_1 , M_2 , and M_3 are the magnetizations associated with a spin cluster containing one, two, and three impurity atoms, respectively.

V. Cu(Fe) DISCUSSION

A. General Features of the Magnetization

As discussed in Sec. IV, the experimental evidence indicates that Cu(Fe) has concentration dependences differing from those of Cu(Mn) and Au(Fe). For example, Fig. 2 shows that for Cu(Mn) $\chi_i \propto c$ above ~ 10 °K, while for Cu(Fe) this is *not* the case to 40 °K (or even to 300 °K⁴²), as seen in Fig. 3. The magnetic interactions in Cu(Fe) are therefore considerably stronger than those in Cu(Mn) in the sense that they cannot be broken up even by rather high-temperature thermal fluctuations. Furthermore these interactions are *ferromagnetic* in nature, since c/χ_i decreases as c increases. Figure 7 shows these interaction effects for the lower-concentration samples at 1.6 and 4.4 °K. At first glance this figure suggests that $\chi_i/c = a + bc$, which would suggest that the susceptibility contains two terms; one due to isolated iron atoms (ac) and one due to some type of iron clusters (bc^2). The figure then implies that there is very little temperature dependence between 1.6 and 4.2 °K for the isolated iron susceptibility ($a \approx \text{const}$) and that the cluster term (the slope of the lines) is considerably larger for the unannealed than for the annealed samples. It should be pointed out that the scatter in the χ_i data as well as the relatively narrow range of concentrations shown in Fig. 7 argue *against* saying that there is definitely simply a linear and quadratic concentration term in χ_i . However, we shall return in Sec. V C to a discussion of the concentration

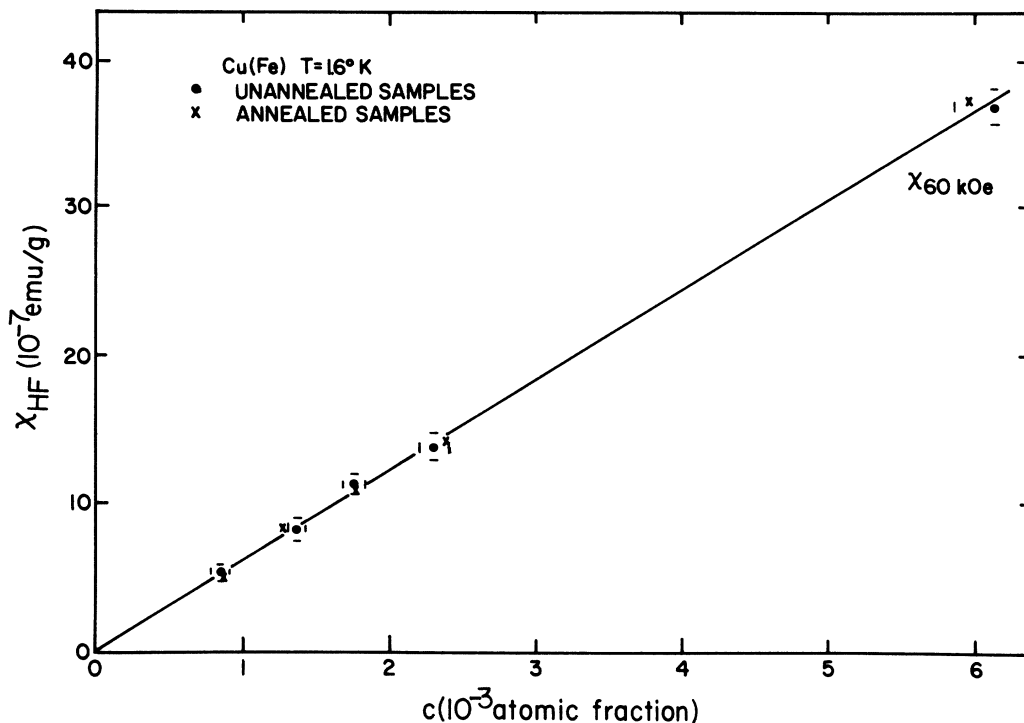


FIG. 8. High-field susceptibility vs c for the two sets of Cu(Fe) samples at 1.6°K.

dependence in connection with our more accurate high-field-magnetization data.

In contrast to the *differences* seen in the annealed and unannealed samples (Fig. 7), an interesting *similarity* between the two sets of samples is seen in Fig. 8. Namely, the high-field susceptibility $\chi_{HF} \equiv (dM/dH)_{HF}$ at 60 kOe is the same for both sets of samples. This indicates that χ_{HF} is dominated by the linear term in c and that annealing has little effect on the high-field behavior. Also of interest in Fig. 8 is the apparently negligible effect of the magnetic "ordering" (Fig. 4) on the value of χ_{HF} for the highest-concentration sample. That χ_{HF} for this sample below its ordering temperature lies on the same line as the lower-concentration samples, suggests either that the ordering involves only a small fraction of the spins, or else that at very high fields the interactions responsible for the ordering are overpowered by the interactions between the spins and the external field.

A final general feature of the results that should be mentioned is the low-temperature flattening of χ for the 6140-ppm sample. Thus, in Fig. 3, c/χ_t increases *above* the Curie-Weiss extrapolation below $\sim 10^\circ\text{K}$, behavior reminiscent of the higher-concentration Cu(Mn) samples as seen in Fig. 2. This indicates that there are some manifestations of the antiferromagnetic interactions which lead to typical spin-glass behavior, but, in addition,

there are ferromagnetic interactions present which complicate the normal situation.

In attempting to build a model to explain the above results it will be useful to consider in Secs. V B-D the magnetization in three different concentration regions: the extreme-dilution limit, the magnetic-interaction region, and the "spin-glass" region. It will be seen that the boundaries between these regions are not sharp, but it will facilitate the discussion to begin with the simplest situation (extreme dilution) and then proceed to the complex ("spin-glass") region.

B. Extreme Dilution Region

This is defined to be the $c \lesssim 300$ -ppm region, which corresponds to the region in which Tholence and Tournier (TT) were able to construct a model for these alloys.¹³ During the course of our experiments on higher-concentration alloys, TT showed that for $c \lesssim 300$ ppm the magnetization $M(H)$ to ~ 65 kOe contained terms linear and quadratic in c . They found that the susceptibility could be expressed as

$$\chi = C_1/(T + T_{K_1}) + C_2/(T + T_{K_2}),$$

where $C_1 \propto c$, $C_2 \propto c^2$, $T_{K_1} \approx 29^\circ\text{K}$, and $0 \lesssim T_{K_2} \lesssim 5^\circ\text{K}$. Since the c^2 magnetization term saturated at ~ 60 kOe, it was possible to measure both the saturation moment and density of the magnetic en-

ties associated with the c^2 term in $M(H)$. It was found that the spin associated with these entities was $S_2 \approx 2.7$, which is approximately $2S_1$, where $S_1 \approx \frac{5}{2}$ is the spin of an isolated iron impurity in copper. This, plus the c^2 dependence, led to the reasonable association of the c^2 term in $M(H)$ with *pairs* of Fe atoms which are ferromagnetically coupled. The density of pairs was found to be $130c^2$. Since this pair density is so much higher than that expected for random occupation of impurities on nearest-neighbor sites ($6c^2$), TT assumed that the pairs were coupled at long range via the RKKY interaction. In that case the total number of pairs (including the antiferromagnetically coupled atoms) would be $260c^2$ and the number of Fe atoms in pairs would be $520c^2$. This density then leads to an average volume per Fe atom in a pair from which TT suggested a critical radius ($\approx 11 \text{ \AA}$) for pair formation. This idea of pair formation by RKKY coupling has been adopted by several other workers who have observed interaction effects in Cu(Fe) alloys at low temperatures.^{10,14}

From the viewpoint of the Kondo effect, TT made an important contribution because they showed for the first time that interaction effects, which had confused much of the earlier experimental and theoretical work, were *not* negligible in Cu(Fe)—even down to the 10-ppm range. From the viewpoint of the present work, however, it is the magnetic interactions which are of major interest and we shall focus attention in the following on the nature of the interaction leading to pair formation and possibly to spin-glass transitions.

C. Magnetic Interaction Region

In the concentration region from ~ 500 to ~ 3000 ppm the magnetization cannot be analyzed simply in terms of c and c^2 contributions. This is seen already for the 600-ppm sample of TT, which deviates from the straight line M/c -vs- c plot for the lower- c samples. The reasons for this can be understood by referring to the local-environment model of Sec. IV C. Suppose that a given Fe atom has z sites in its neighborhood which, if occupied by another Fe atom, form a magnetic entity called a pair. Suppose also that the concentration is not so high that clusters of three or more have to be considered. Then, from Eqs. (4.9) and (4.10),

$$M = cN(1-c)^z M_1 + \frac{1}{2} z c^2 N(1-c)^{z-1} M_2,$$

where the coefficients of M_1 and M_2 are the number of isolated Fe atoms and the number of pairs of Fe atoms, respectively. Then

$$M = [Nc(1-c)^z] \left(M_1 + \frac{cz}{2(1-c)} M_2 \right).$$

Defining a new quantity μ and noting that $c \ll 1$, we

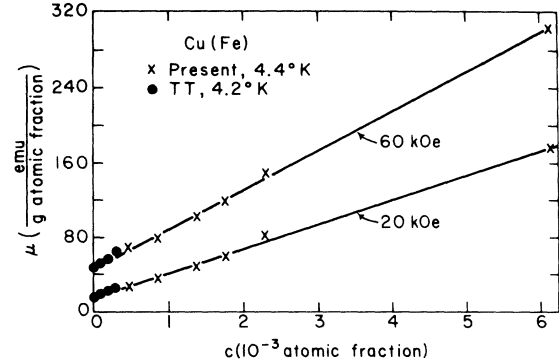


FIG. 9. Concentration dependence of μ (see text) at 20 and 60 kOe. Crosses are for unannealed alloys. The very low concentration data of TT are also shown.

have finally

$$\mu \equiv M/Nc(1-c)^z \approx M_1 + \frac{1}{2} z c M_2. \quad (5.1)$$

Since z is of order 10^2 , the $(1-c)^z$ factor becomes appreciable when $c \gtrsim 500$ ppm and it is this circumstance which destroys the straight-line plot of M/c vs c . In the $c \rightarrow 0$ limit this analysis clearly approaches that of TT. We have analyzed our low-temperature and high-field data with Eq. (5.1) in the following way. $\mu(H, c)$ was fitted to Eq. (5.1) with a computer program which determined the parameter z at each H and T . Fits were performed with our data alone *and* with those of TT to 60 kOe. This was done to test the two sets of data for consistency and for sensitivity to sample-preparation procedures. Figure 9 shows a typical example of such a fit. It is seen that our high- c data match approximately with the low- c data of TT, but that our slope, corresponding to the pair term, is somewhat smaller; this is true for both the Cu(Fe) and Cu(Fe)A alloys. An example of the field dependence to 90 kOe of M_1 and M_2 (derived from our data alone) is shown in Fig. 10, along with curves taken from TT. Again, there is semiquantitative agreement in both M_1 and M_2 and, in particular, the saturation value of M_2 (~ 500 emu/g) leads to a spin value $S_2 \approx 2.9$ per pair, which is similar to the value determined by TT. Fits with the Cu(Fe) (unannealed) alloys gave similar S_2 values, but both sets of samples showed smaller- z values than that suggested by TT ($z = 260$). For example, at 1.6°K the fits at 30 kOe for the Cu(Fe) and Cu(Fe)A samples gave $z = 170$ and 130, respectively. The accuracy of these z values is not better than 15–20%, but it is certainly true that the number of pairs in the Cu(Fe) samples is larger by a factor of $\sim \frac{3}{2}$ than in the Cu(Fe)A samples—as is seen explicitly also in Fig. 7.

To get further information on the nature of the magnetic pairs, we now consider recent Mössbauer

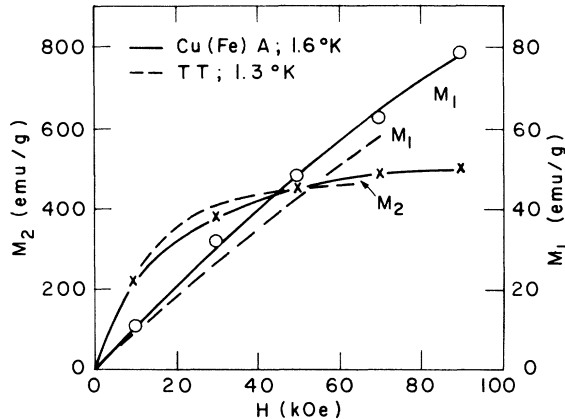


FIG. 10. Field dependence of the magnetization of isolated (M_1) and pairs (M_2) of Fe atoms. Data of TT to ~ 60 kOe are shown for comparison.

experiments on Cu(Fe) alloys in the range $c \lesssim 5000$ ppm. Although early work was done by Bennett and Swartzendruber,⁴³ Window,⁴⁴ and others, we shall consider here mainly the very recent work of Campbell *et al.*⁴⁵ and Knauer,⁴⁶ which covers more comprehensively the concentration region of interest. The main features of the results are as follows. At high temperatures (e.g., 300 °K) the Mössbauer spectra for dilute alloys consist of a single line with two smaller lines which are just resolvable on either side of the "central" line. As the concentration increases, the smaller lines increase in area relative to the central line. The interpretation given to these spectra is that the central line is due to isolated Fe atoms and the additional lines are due to Fe atoms in Fe clusters. Campbell *et al.*⁴⁵ analyzed their data by fitting them to a single Lorentzian line of relative area A_0 (the central line) and a number of doublets of relative area A_1 , A_2 , etc. In addition to the areas, the fit gave the isomer shifts and quadrupole splittings for the various doublets. The results showed that for the various doublets, the isomer shift and quadrupole splitting were approximately constant from sample to sample. This, along with the concentration dependence of the areas, suggested that the single line was due to isolated Fe atoms and succeeding doublets of decreasing intensity were due to the variation in electric field gradient at an iron site produced by the charge asymmetry of clusters of 2, 3, and 4 iron atoms. The isomer shift increased monotonically from ~ 0.0 mm/sec for the first doublet to ~ -0.14 mm/sec for the third doublet, and this is further reason for identifying each doublet with an increasing number of nearest-neighbor iron atoms; the isomer shift in pure iron is -0.22 mm/sec.

Additional information on local-environment

effects in these alloys was determined by the low-temperature work of Window.⁴⁴ He fitted the 1.4 °K data for several samples in the magnetically "ordered" state with a hyperfine-field distribution function $P(H)$, which showed peaks at ~ 80 , 150, 240 kOe, etc. The concentration dependence of the $P(H)$ curves indicated that there was a hyperfine field of 80 kOe for an isolated iron atom, ~ 150 kOe for an iron atom with one iron neighbor, etc., and this interpretation was quite consistent with the model discussed above.

It is now possible to make an informative connection between the above Mössbauer results and the present magnetization results. As determined by the Mössbauer effect, the ratio of the number of iron atoms in pairs to the number of isolated ones is A_1/A_0 , in the notation used above. Thus the Mössbauer ratio of iron pairs to isolated iron atoms is

$$R^M \equiv A_1/2A_0. \quad (5.2)$$

These areas are tabulated by Campbell *et al.*⁴⁵ and R^M is plotted in Fig. 11. Though Knauer did not analyze his data in the same manner as Campbell *et al.*, it is possible to derive values of R^M from his data⁴⁶ and these are also shown in Fig. 11. Knauer also showed that data obtained from single-crystal and polycrystalline samples were identical so that iron clustering at grain boundaries is insignificant for alloys with $c \lesssim 5000$ ppm. The magnetization analysis of Eq. (5.1) gives

$$R = \frac{1}{2}zc \quad (5.3)$$

for the ratio of pairs to singles, and Fig. 11 shows curves for $z = 260$, 170, and 130 relevant to various sets of samples as labeled on the figure. Since the slope of the curves is proportional to the pair concentration, Fig. 11 has the following implications: (i) All of the magnetization and Mössbauer samples have many more pairs than would be expected on the basis of a perfectly random nearest-neighbor occupation of iron atoms on the fcc lattice (for which $R = 6c$). (ii) All of the samples quenched either from the melt or from the high-temperature solid-solution phase have a higher pair density than the cold-rolled samples of Campbell *et al.* That is, the cold-rolled samples are much closer to random alloys than the quenched samples—a conclusion previously reached by Window and shown by the data in Table I of Campbell *et al.* The randomizing effect of cold rolling is greater for the higher-concentration alloys than for the lower-concentration ones in that the fractional deviation from the $R = 6c$ (random) curve is smaller at the higher concentrations. (iii) Among the quenched magnetization and Mössbauer samples there is a continual increase in the pair density as one goes from our solution-annealed samples to the solution-an-

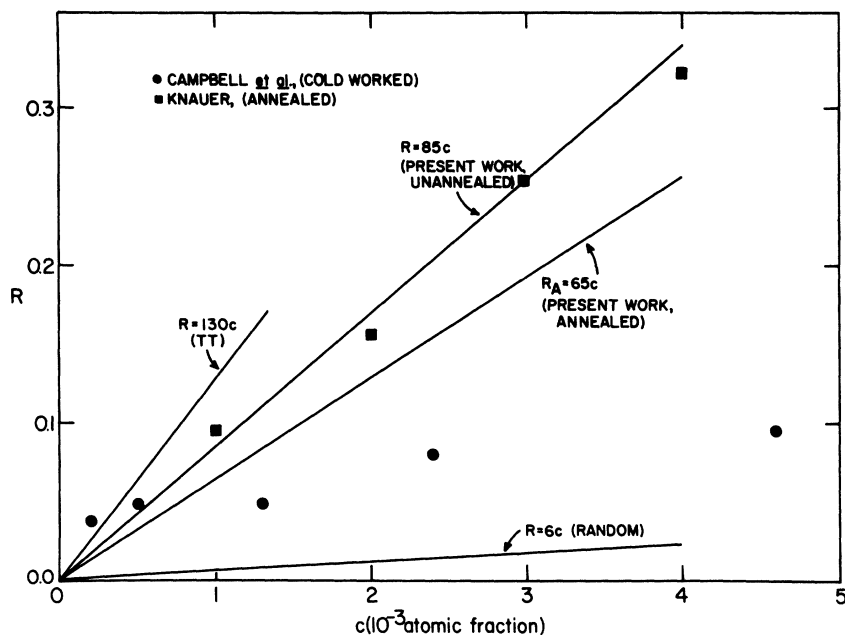


FIG. 11. Concentration dependence of the ratio of pair to isolated Fe atom concentration. The data are taken from the present work and various other sources as explained in text.

annealed Mössbauer samples and from our chill-cast samples to the chill-cast samples of TT.

Points (ii) and (iii) above indicate that the pair density is *not* an intrinsic property of atomic or electronic properties of the Cu(Fe) system, but rather is determined by structural effects which are strongly influenced by sample-preparation procedures. This ought not be too surprising when it is recalled that these alloys *are* supersaturated. The results generally are inconsistent with the supposition¹³ that the pairs result from long-range RKKY interactions between randomly placed spins. A critical coupling distance such as 11 Å, which is calculated directly from the pair density, clearly must be a function only of the parameters that enter the RKKY interaction—one of which is certainly not the structural state of the sample. A more reasonable explanation of the variation in pair density observed in the various sets of samples is that there is a strong tendency for *atomic* short-range ordering or clustering between the iron atoms, and that the degree of clustering is strongly influenced by quench rate, cold work, and other variables of the sample-preparation methods. Since the “collision probability” for two impurity atoms, which at high temperatures are mobile in the sample, would be expected to be proportional to c^2 , one would expect a c^2 term in the magnetization due to the magnetic properties of what might be called “diatomic Fe molecules” dissolved in the Cu matrix. Such nearest-neighbor magnetic pairs clearly should be treated from a self-consistent spin-polarized cluster model rather than from the RKKY viewpoint. In fact, Mössbauer and magnetization

studies of the type we have been discussing appear to have great promise for studying such impurity clusters dissolved in metals.

D. Spin-glass Transitions

One of the original motivations for the present work was to understand why Cu(Fe) apparently did not exhibit magnetic interactions and spin-glass transitions (susceptibility and resistivity maxima) similar to those seen in Cu(Mn), Au(Fe), and other alloys. There had been speculation by Klein,¹⁵ for example, that perhaps the spin correlations associated with the Kondo effect interfered with the RKKY coupling below the Kondo temperature ($\sim 10^\circ\text{K}$). Typically, the spin-glass transitions occur at a temperature $T_{\text{max}} \approx (20^\circ\text{K/at.}\%)c$. Thus for a 0.5-at. % alloy one would expect $T_{\text{max}} \approx 10^\circ\text{K}$. We have observed a type of magnetic “ordering” in our 0.6-at. % alloy, remanence below 3.5°K , as shown in Fig. 4. Our concentration and temperature ranges, however, made it impossible to determine the concentration dependence of the ordering temperature. An interesting clue concerning the nature of the ordering as manifested in the remanence is that the ratio of the annealed and unannealed remanence values is $M_r^A/M_r = 81/105 = 0.77$. This number is very close to the ratio P of the pair densities for the annealed and unannealed samples; from Eq. (5.3) $P = z^A/z \approx 130/170 = 0.76$, where z^A and z refer to annealed and unannealed values of the coupling parameter of Eq. (5.1). This correspondence rather strongly suggests that the remanence is due to the pairs which can be aligned by a field of order 10 kOe, but

which experience an interaction which keeps them aligned when the external field is reduced to zero. It is difficult to understand precisely the mechanism for this remanence but it may be due to long-range (RKKY-type) interactions between the pairs or perhaps interactions between the pairs and the "isolated" spins which, themselves, are unable to flip thermally at low temperatures.⁴⁷ Additional evidence on this point is contained in the work of Hirschhoff *et al.*,¹⁰ who found at very low temperatures (~ 0.01 – 0.4 °K) that there was an apparent ordering of the magnetic pairs at a temperature T_0 proportional to c^2 . At such low temperatures the magnetization contribution from the isolated spins is small. Since the typical spin-glass behavior in which $T_{\max} \propto c$ is explicable in terms of the RKKY coupling of single spins, it is reasonable to associate the observed ordering temperature T_0 with RKKY-type ordering between pairs whose concentration is proportional to c^2 .

Finally, it is possible to understand the spin-glass transition data of Svensson⁴⁸ in terms of the discussion of Sec. VA–C. Svensson found resistivity and susceptibility maxima in Cu(Fe) alloys but *only if* the samples were strongly cold worked. The temperatures of these transitions are shown in Fig. 12 along with other indications of transitions from magnetization and heat-capacity data. This behavior is quite reasonably explained in terms of our previous discussion. It was seen that cold work breaks up iron pairs and other larger clusters, leading to a much more random array of impurity spins. Such an array is probably similar to that which exists in the typical spin glasses Cu(Mn) and Au(Fe), which are good solid-solution alloys over a relatively wide concentration range. The reason for the absence of the suscepti-

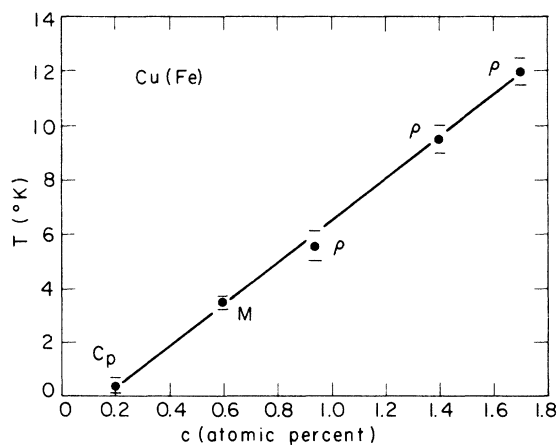


FIG. 12. Concentration dependence of the apparent "ordering" temperature as deduced from anomalies in heat capacity (Ref. 29), magnetization (present work), and resistivity (Ref. 48).

bility maxima in Svensson's alloys which were *not* cold worked is likely the fact that in these samples there is a much larger relative number of pairs and larger clusters, in comparison with the isolated spins, than in the cold-worked alloys. Since the pairs and probably the larger clusters have very low Kondo temperatures (Weiss temperatures), the total susceptibility, which is dominated by these pairs or clusters, continues to rise as T decreases—thus obliterating the more normal susceptibility maximum for which $T_{\max} \propto c$. At an extremely low temperature, the pairs order, leading to the transitions observed by Hirschhoff *et al.*¹⁰ for which $T_0 \propto c^2$. This description is no doubt an oversimplification because, as seen in Fig. 12, there may be a complex transition region between the low-concentration pair-pair ordering seen in the non-cold-worked samples and the predominantly Fe-Fe ordering seen in the cold-worked samples in which T_0 increases linearly with c . In this complex transition region it could well be the case that the ordering would have to be considered as due to a mixture of "isolated" and pair interimpurity interactions. An obvious experiment to test this would be to measure susceptibility of severely cold-worked samples to much lower concentrations and temperatures, to test the validity of the $T_{\max} \propto c$ relation for normal non-clustered spin glasses. One complicating feature of cold-worked alloys, however, is that the mean free path may be diminished somewhat, and this would be expected to decrease the coupling between spins.⁴ On the other hand, in Svensson's alloys, in which the Fe impurity scattering was already high, the presence of the additional scattering due to the working seems not to have interfered significantly with the spin coupling; the spin-glass transitions appear to be depending on concentration in the usual (mean-random-field) way, viz., $T_{\max} \propto c$.

E. Sub-Kondo Spin Polarization of a Magnetic Impurity at High Fields

Although it is somewhat peripheral to the main subject of this work, the data of Sec. V C contain information of interest for theoretical work on the Kondo problem. Namely, $M_1(H)$, the magnetization of an isolated Fe impurity, has been determined to 100 kOe for temperatures much below T_K . There have been several theoretical calculations^{49,50} of the magnetization of the impurity spin and its associated "spin-compensation" cloud, but there appears to be some doubt that any of these are valid for any real system.⁵¹ For example, a calculation of single-impurity magnetization for Cu(Fe) was made by Bloomfield *et al.*⁵⁰; but, unfortunately, they had to assume a spin value of $\frac{1}{2}$, which is known to be incorrect ($S \approx \frac{3}{2}$). It is there-

fore impossible even to compare on the same plot the experimental results with their calculation because clearly the saturation value they would obtain is $\sim \frac{1}{3}$ of the correct value; also the field axis would have to be scaled to account for the fact that the "effective field" ($\mu_B H$) is a function of the spin value assumed.

Figure 13 shows the experimental magnetization to high fields at 1.6°K. The data agree to within $\sim 10\%$ with those of TT in the region where they overlap ($H \lesssim 60$ kG). Simply for the sake of comparison we have shown also in Fig. 13 two curves based on Brillouin functions for $S_1 = \frac{3}{2}$ and $g = 2$. The upper one corresponds to the magnetization of a free spin- $\frac{3}{2}$ particle and clearly does not fit the experimental data. Also a plot of $B_{3/2}$ is shown with an "effective" temperature of $T+29 = 30.6^\circ\text{K}$. There is no *a priori* reason why this function should fit the data, but it at least has the virtue that as $H \rightarrow 0$, it leads to the experimentally observed susceptibility $(C_1/T+29)$.¹³ It is seen that this modified form of the Brillouin function does give a relatively good description of the data.

In conclusion, it would appear that further theoretical work on the magnetic polarization of a Kondo system in high fields is warranted.

VI. Cu(Mn) DISCUSSION

A. General Features of Cu(Mn) Magnetization

Figure 2 indicates that χ_i is approximately proportional to c for temperatures above 10°K and

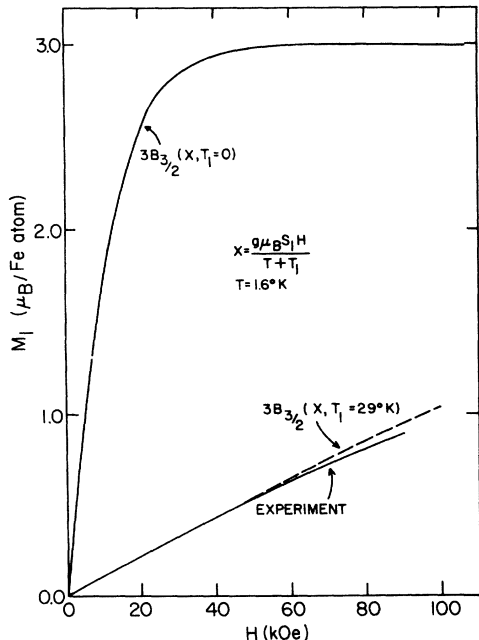


FIG. 13. Comparison of high-field magnetization of an isolated Fe spin at 1.6°K with free-spin and modified Brillouin functions, as explained in text.

that significant deviations from linearity are observed for $T = 1.6^\circ\text{K}$. A plot of χ_i/c vs c (Fig. 14) shows a decrease in the susceptibility per impurity as concentration is increased for T less than 8°K . A plot of M/c vs c for $T = 1.6^\circ\text{K}$ indicates similar behavior for fields up to 90 kOe. Figure 6 shows that for $T = 1.6^\circ\text{K}$ the impurity magnetization of the Cu(Mn) alloys studied is not saturated in a field of 95 kOe. The above results are all suggestive of antiferromagnetic interactions which have been observed^{6,7} in Cu(Mn) alloys containing greater than 1.0-at. % Mn at liquid-helium temperatures.

Kouvel⁷ found that Cu(Mn) alloys containing 5–30-at. % Mn exhibit a susceptibility maximum, and for $T < T_{\text{max}}$ remanent magnetization is observed. This was interpreted as a magnetic state in which ferromagnetism and antiferromagnetism coexist. A qualitative description⁵² has been given in terms of clusters of antiferromagnetically coupled Mn atoms having a nonzero net moment. The formation of the clusters as T approaches T_{max} accounts for the susceptibility maximum. At temperatures below T_{max} , ferromagnetic ordering occurs between clusters giving the remanence observed. The susceptibility maximum is similarly described in a statistical model given by Klein and Brout.²² Kouvel⁷ further suggests that nearest-neighbor Mn atoms coupled antiferromagnetically are responsible for the antiferromagnetic behavior.

B. Application of Mean-Random-Field Theory

As indicated in Sec. IV there is experimental evidence that Cu(Mn) at very low temperatures obeys the MRF model. Since Cu(Mn) exhibits a susceptibility maximum and has a concentration-independent low-temperature specific heat and susceptibility, it is possible to estimate the parameter $\Delta(\infty) = \gamma c$. Using this parameter, the initial susceptibility and field-dependent magnetization will be compared with theory.

Low-temperature susceptibility measurements by Dreyfus *et al.*¹² give $T_{\text{max}} = 2.2^\circ\text{K}$ for a 0.196-at. % Cu(Mn) alloy. Using Eq. (4.7),

$$k_B T_{\text{max}} \approx 0.4 \Delta(\infty) = 0.4 \gamma c,$$

one calculates $\gamma = 2.8 \times 10^3$ °K/at. fraction. The parameter γ may also be estimated using the limiting susceptibility $\chi_i = 1.0 \times 10^3$ emu per mole of alloy and the relation

$$\gamma = 2 N_0 \mu_B^2 S(S+1) / \chi(0) \pi. \quad (6.1)$$

Here we have used Eq. (4.6), corrected for the Ising-model approximation by including the spin factor $S(S+1)$. For $\chi_i \approx \chi(0)$ and $S = 2$ we find $\gamma = 1.42 \times 10^3$ °K/at. fraction. Since long-range order is not observed in Cu(Mn) for $T \geq T_{\text{max}}$ the estimate of γ , using Eq. (4.7), is suggested by Klein⁵³ and will be used here. Table III gives

TABLE III. Expansion parameter $k_B T/\Delta(\infty) = k_B T/\gamma c$ for Cu(Mn) alloys.

Cu(Mn)	c (at. %)	$k_B T/\Delta(\infty) = k_B T/\gamma c$	
		$T = 4.4^\circ\text{K}$	$T = 1.6^\circ\text{K}$
2A	4.30×10^{-2}	3.66	1.33
3A	8.48×10^{-2}	1.85	0.674
4A	1.31×10^{-1}	1.2	0.436
5A	3.43×10^{-1}	0.46	0.167

$k_B T/\Delta(\infty) = k_B T/\gamma c$ for the Cu(Mn) alloys measured at $T = 1.6$ and 4.4°K .

1. Initial susceptibility

Equation (4.6) in the limit $k_B T/\gamma c \ll 1$ gives

$$\chi_i(T) \approx \frac{2}{\gamma} \frac{N_0 \mu_B^2}{\pi} S(S+1) \left[1 + \frac{\ln 4}{\pi} \left(\frac{k_B T}{\gamma c} \right) \right], \quad (6.2)$$

which predicts the qualitative behavior of χ_i/c observed in Fig. 14. A plot of $\chi_i(T)$ vs $1/c$ for $T = 4.4$ and 1.6°K is given in Fig. 15. Clearly the conditions for Eq. (6.2) are not met for $T = 4.4^\circ\text{K}$ and severe deviations from a straight line are observed. At $T = 1.6^\circ\text{K}$, however, all samples except Cu(Mn)-2A meet the condition, and approximate qualitative agreement with Eq. (6.2) is found, except for the highest-concentration sample Cu(Mn)-5A, which exhibits remanence at this temperature. This raises a question concerning the range over which this theory may be applicable. At temperatures below 1.6°K one would expect samples with con-

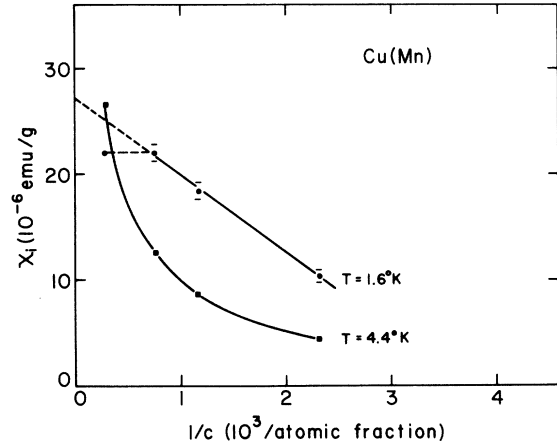


FIG. 15. χ_i vs $1/c$ for Cu(Mn) alloys at 4.4 and 1.6°K .

centration less than that of Cu(Mn)-5A (0.343 at. %) to show remanence and, hence, deviate from the susceptibility predicted by Eq. (6.2). Values for γ calculated from the slope and intercept of the fit shown in Fig. 15 give 1.47×10^3 ($^\circ\text{K}/\text{at. fraction}$) and 0.815×10^3 ($^\circ\text{K}/\text{at. fraction}$), respectively. This is an approximate agreement with γ as determined previously.

2. Field-dependent magnetization

The molecular-field theory discussed in Sec. IV gives a magnetization which depends on applied field, temperature, and impurity concentration. In the MRF approximation given by Klein,¹⁵ the

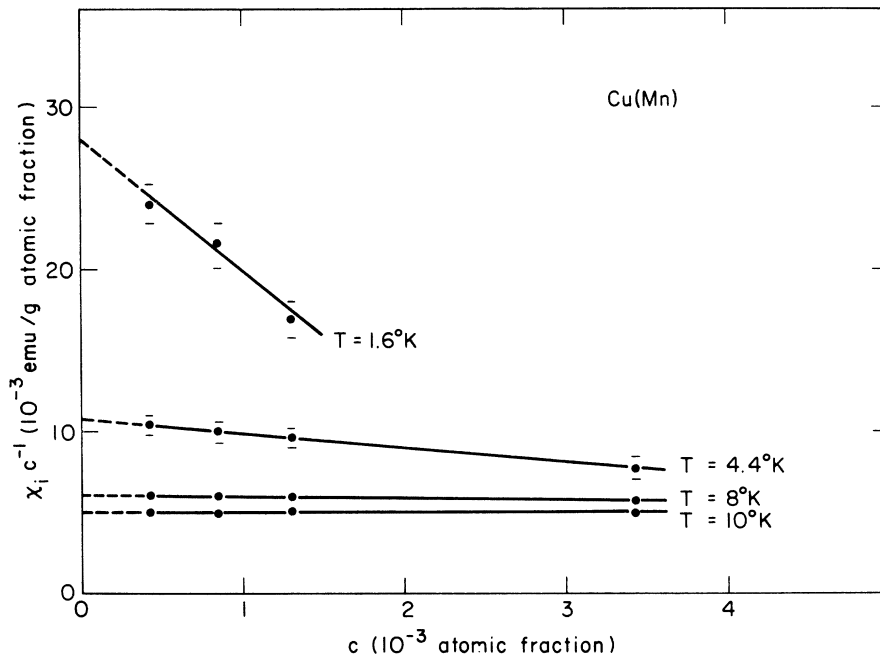


FIG. 14. χ_i/c vs c for Cu(Mn) alloys as a function of temperature. Cu(Mn)-5A shows remanence at 1.6°K , and is not shown.

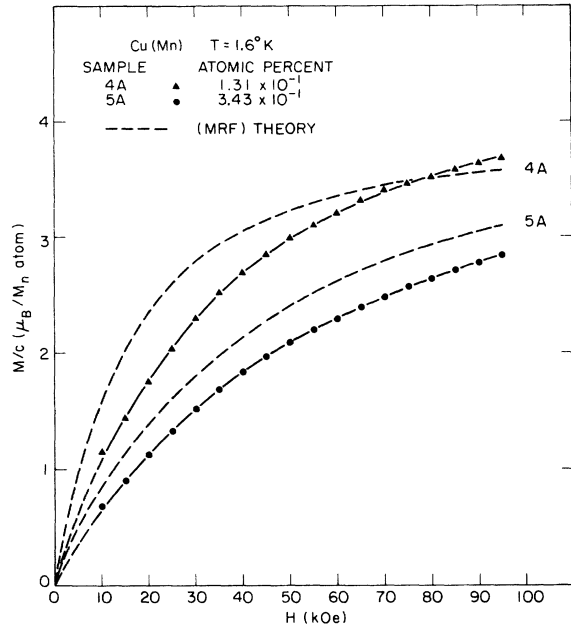


FIG. 16. Comparison of mean-random-field theory with M/c vs c for Cu(Mn)-4A and -5A at $T = 1.6^\circ\text{K}$.

expression for $M(H_{\text{ext}}, c, T)$ is given by Eq. (4.8). A comparison of the MRF theory to measured magnetization at 1.6°K for Cu(Mn)-4A and Cu(Mn)-5A is shown in Fig. 16. Here we have taken $\gamma = 2.8 \times 10^3$ K/at. fraction, as determined earlier.

In order to compare the Ising-model theory to experiment it was necessary to assume that the moment was $qS\mu_B = 4\mu_B$ rather than simply μ_B , as in the original theory. The agreement with experiment is surprisingly good in view of the Ising-model approximation and the approximate value used for γ ($\approx \pm 30\%$).

VII. SUMMARY AND CONCLUSIONS

In this work we have attempted to understand the magnetic properties of the two alloy systems Cu(Fe) and Cu(Mn) in the finite concentration region, i. e., not in the extreme-dilution limit. We have used our susceptibility and high-field magnetization results, but also have relied heavily on the results of other experiments as explained above. The major results for Cu(Fe) are as follows:

(i) We have confirmed in part the results of Tholence and Tournier: there exist in Cu(Fe) alloys isolated iron and pair terms in the magnetization. The pair magnetization saturates at ~ 60 kOe for $T \approx 4^\circ\text{K}$, and each pair has associated with it a spin of approximately 3.

(ii) By comparing several completely different sets of samples, it was shown that the pair density

depends on sample-preparation procedures such as quench rate and cold work. This, along with Mössbauer evidence⁴⁴⁻⁴⁶ for nearest-neighbor Fe-Fe interactions, indicates that the magnetic pairs are not due to long-range RKKY-type couplings to distances of $\sim 11 \text{ \AA}$. Rather, the pairs should be regarded as nearest-neighbor Fe atoms (in a sense, a diatomic Fe molecule) dissolved in the copper matrix. The pairs form as a result of the great tendency for iron atoms to stick together or cluster in these supersaturated alloys.

(iii) It was shown that the magnetic remanence exhibited by two 0.6-at. % alloys was proportional to the pair densities in the respective samples. This lends additional support to the suggestion¹⁰ that the "ordering" seen in dilute Cu(Fe) alloys at very low temperatures and concentrations is pair-pair ordering.

(iv) It was shown that the resurgence of spin-glass transitions in cold-worked alloys, where they did *not* exist before the working, could be understood on the basis of the breaking up of Fe pairs and clusters with a resulting randomizing effect on the impurity spin position. Thus the magnetic properties of dilute alloys are intimately related to the details of the structure of the alloy.

(v) With respect to the Kondo problem, it was shown that the isolated Fe-atom spin polarization in fields to ~ 100 kOe and $T \ll T_K$ cannot be described by a Brillouin function appropriate to an independent spin. However, a Brillouin function of the form $B_{3/2}(\alpha)$, where $\alpha = g\mu_B S_1 H / T + 29$, was able to represent the data rather well. So far as we are aware, there is no first-principles theory which is able to describe this result.

For the Cu(Mn) alloys the present work has shown that the recent mean-random-field theory of Klein is able to explain the concentration dependence of the initial susceptibility in a certain low-temperature limit ($kT \ll \gamma c$) in which the spins are strongly interacting. In this same limit the theory is able to explain semiquantitatively the field dependence of the magnetization to ~ 100 kOe. The success of this theory in the present work and also in recent high-temperature work makes it apparent that the theory is indeed a good first-order theory, at least for alloys which approximate well the idealized *random* solid solution.

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