ONE-IMPURITY AND INTERACTION EFFECTS ON THE Cu:Fe MAGNETIZATION

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(Received 27 July 1970)

The magnetization of very dilute Cu:Fe alloys contains one term proportional to c due to the isolated impurities and another proportional to c^2 which is attributed to nearly magnetic or magnetic pairs. The susceptibility of the isolated iron atoms follows a Curie-Weiss law $C(T+T_k)^{-1}$ with $T_k = 29$ K well below T_k. The c^2 term which is nearly saturated in 60 kOe at 1.3 K is responsible for the important temperature dependence of the initial susceptibility below T_k.

The Cu:Fe system is considered as a characteristic example of the Kondo effect at very low temperatures.[1] The existence of a compensated spin being suggested by the experiments of Daybell and Steyert,[2,3] the nonexistence of the magnetic moment of the iron atom in copper was shown by Mössbauer effect,[4] NMR,[5-7] magnetization,[8] and magnetoresistance measurements.[9] The apparent existence of a magnetic moment at high temperatures is confirmed by the Curie-Weiss behavior of the susceptibility measured either directly or by NMR, Mössbauer effect, and by the logarithmic dependence of the resistivity on the temperature. The experimental results on the temperature dependence of the physical properties in the nonmagnetic region are very important for testing the different theories on the ground state of the impurity. Unfortunately the experimental situation is as complicated as the theoretical one. The susceptibility was found to follow a $T^{-1/2}$ law.[3] The difference between the magnetization deduced from Mössbauer effect on iron and from NMR on copper was interpreted as due to the formation of a conduction-electron cloud around the impurity.[6,7] The resistivity varies like $1-\alpha(T/T_k)^2$ and some interaction effects appear when the concentration reaches several hundred ppm.[10] The variation of the specific heat seems to be proportional to T rather than to $T^{1/2}$.[11]

We present here some new results on the Cu:Fe system which show the effects of the interactions on the magnetic properties of the alloys, when the one-impurity effects are separated from the interaction effects. The magnetization of our alloys has been measured between 0.05 and 33 K in fields up to 70 kOe. The method consists in the movement of the cylindrical sample ($\phi = 7$ mm, $l = 20$ mm) in the uniform field (10^{-3} over 6 cm) produced by a superconducting solenoid, inside two detection coils connected in series opposition. The variation of the magnetization of our alloys when the temperature is decreasing from 1.3 to 0.05 K corresponds essentially to the nuclear magnetization of copper [$\chi \simeq (3.5\times10^{-7})/T$ in emu/at. g], and we cannot distinguish with good accuracy the contribution of the iron atoms. Therefore, we shall present here only our measurements above 1.3 K.

All the samples were prepared from 99.999% Cu and 99.99% Fe. A first set of Cu:Fe samples has been obtained by fusion for 4 h in high vacuum at 1250°C in an alumina crucible. The sample A (455 ± 5 at. ppm) after annealing at 950°C for 24 h in a hydrogen atmosphere was quenched in a jet of gaseous hydrogen. The samples B (153 ± 3 ppm) and C (74 ± 2ppm) were annealed at 1000°C for 24 h in quartz tubes sealed under vacuum, then quenched in cold water. The sample D (46 ± 2ppm) was cooled in 2 h (natural cooling of the furnace). This first set allowed us to clarify the metallurgical problems involved and to observe their effects on the magnetization. Better quenched samples with more reproducible characteristics were obtained in a vacuum induction furnace, where the melting was followed by direct casting in a water-cooled mold (second set). The concentrations of these samples, determined by absorption spectroscopy analysis, are 11 ± 2, 33 ± 2, 108 ± 3, 200 ± 4, 314 ± 6, 337 ± 9, and 603 ± 9 at. ppm Fe. All the samples were kept in liquid nitrogen when not in use (the magnetization of 0.1% Cu:Fe may become twice as great after aging at 300 K for several months).

In Fig. 1(a), the magnetization curves at 1.3 K of all our alloys are represented. Similar curves were obtained at 4.2, 10, 20, and 33 K. For the calibration of the apparatus we have used the value of 0.881×10^{-7} emu/g[12] for the susceptibility between 1.3 and 4 K of a pure copper sample ($c < 2$ ppm Fe). The magnetization due to the iron impurities is given by the difference between the magnetization of the alloy and that of the pure copper sample. The slope $(dM/dH)_{H\sim60\text{ kOe}}$ is

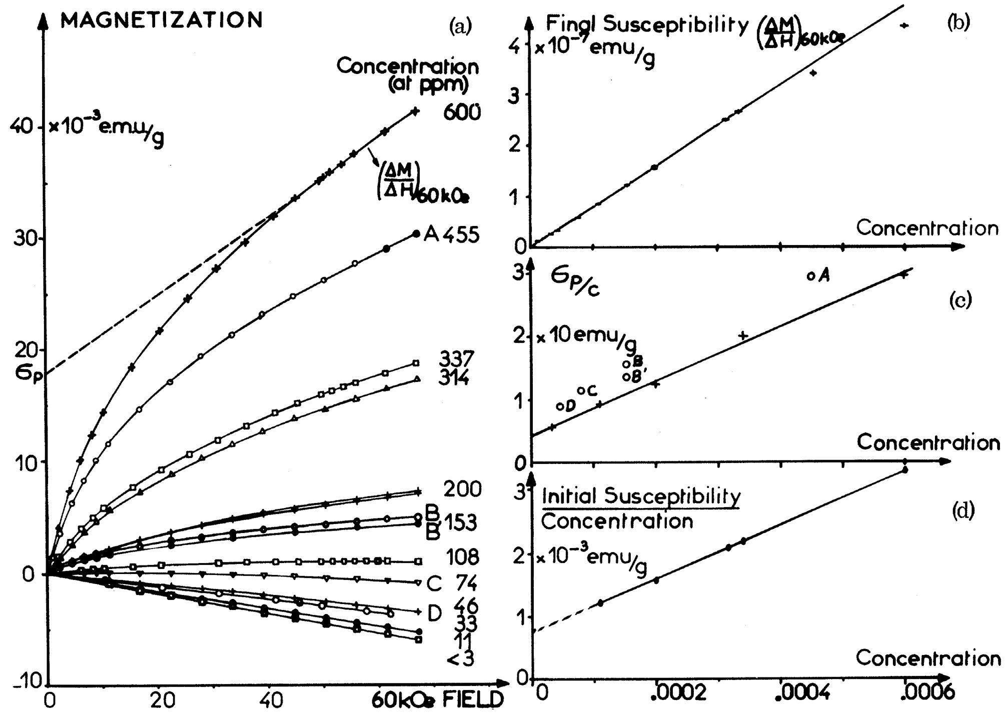

Fig. 1. (a) Magnetization curves $M(H)$ at 1.3 K before subtracting the diamagnetism of copper. (b) dM/dH at $H = 60$ kOe versus the concentration presents a linear dependence up to $c = 0.00034$. (c) σ_P/c vs c is fitted by a straight line for the second set of samples (crosses). The first set gives higher values (circles). (d) The initial susceptibility ($H < 1$ kOe) contains a c^2 term.

plotted as a function of the analyzed concentration in Fig. 1(b). We observe a linear variation with the concentration up to $c \simeq 0.00034$ at. This behavior shows that the one-impurity effects govern the variations of the magnetization in high fields. Let us study now the part of the magnetization σ_P which seems to be saturated in high field. σ_P is obtained by a linear extrapolation to zero field from $H = 60$ kOe [Fig. 1(a)] and its variation as a function of the concentration is well represented by a straight line in the diagram of $\sigma_P/c = f(c)$ [Fig. 1(c)]. σ_P is equal to $4.5c + 4.3\times 10^4 c^2$ emu/g. Moreover, for the insufficiently quenched samples (first set) the σ_P value is higher. The magnetization of the samples of the second set is smaller and less sensitive to the temperature than that of the first set of samples. The initial susceptibility ($H < 2$ kOe) contains also a c^2 term [Fig. 1(d)]. All these observations imply that some interaction effects are superposed on the one-impurity properties. The c^2 term may be attributed to the effects of pairs of impurities. The curvature of the magnetization as a function of the field, also observed in NMR experiments, cannot be attributed only to a negative polarization because, in this case, the magnetization should be proportional to the concentration at all fields.

From what has been pointed out above we postulate that the magnetization may be given by an expression of the form $M(H) = M_1(H)c + M_2(H)c^2$. We have then plotted for different temperatures M/c versus c for several values of the field [Fig. 2(a)]. [Since the accuracy on the final slope $(dM/dH)_{60\ \mathrm{kOe}}$ is very good we have considered it a better measurement of the concentration than the analysis in the region where it is seen to be linear in concentration. Therefore the values which are used for c in Fig. 2(a) for the samples of the second set are, respectively, 13, 111.5, 195, 316, and 337 at. ppm, which are easily seen to fall within the error bars of the analysis.] For all the alloys of the second series $M(H)/c$ is seen in Fig. 2(a) to be a linear function of c, for the lowest values of c ($c < 0.00034$ at.), where we expect the above approximation to be valid. $M_1(H)$ is obtained from the intercept at zero concentration. $M_2(H)$ is the slope of $M(H)/c$ vs c. $M_1(H)$ is almost proportional to the applied field up to 50 kOe [Fig. 2(b)]. Above, we observe a small curvature. The thermal behavior of $M_1(H)$ follows a Curie-Weiss law $\chi_1 = [dM_1(H)/dH]_{H=0} = C_1/(T + T_{k_1})$ [Fig. 2(c)]. The Curie constant corresponds to an effective mo-

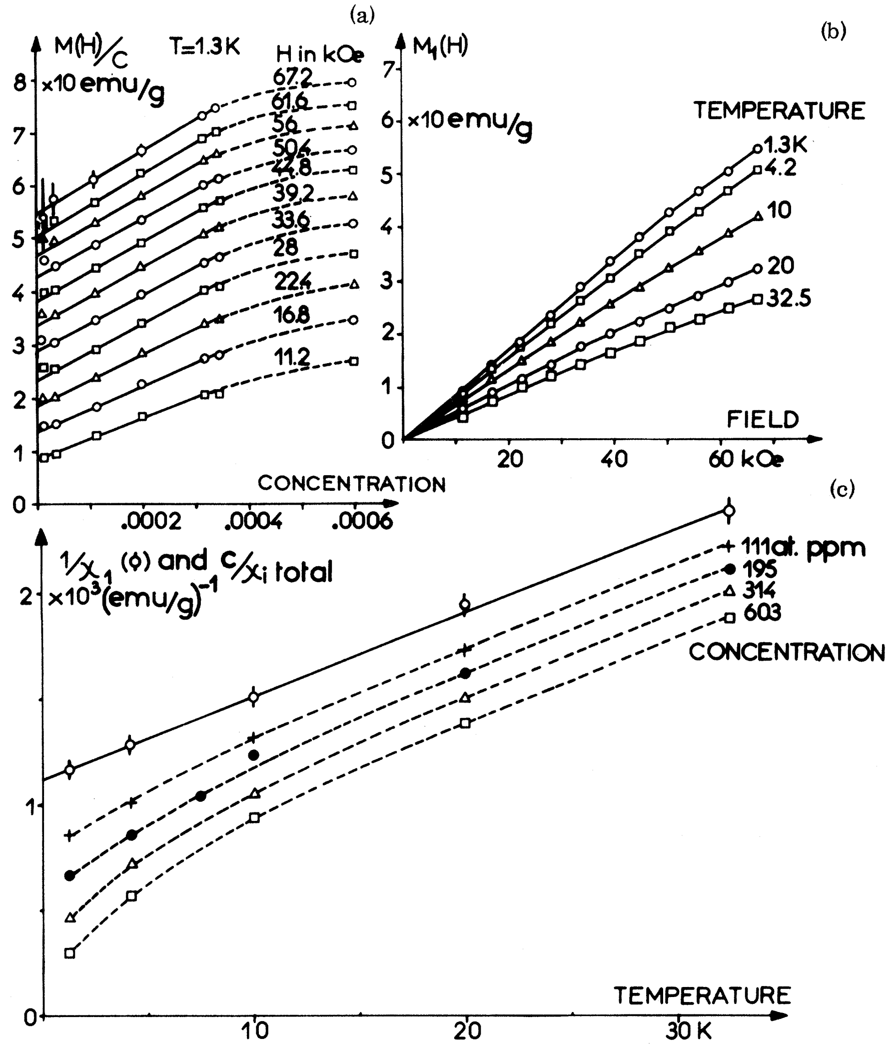

Fig. 2. (a) $M(H)_c$ is plotted versus c, to separate the c and c^2 terms of $M(H)$ [$M(H) = M_1(H)c + M_2(H)c^2$ up to $c = 0.000\,34$]. (b) Temperature and field dependence of $M_1(H)$. (c) The initial susceptibility of isolated impurities $\chi_1(H) = dM_1(H)/dH$ follows a Curie-Weiss law and may be compared to the total initial susceptibility (dashed curves).

ment $\mu_{\rm eff} = 3.4\mu_{\rm B}$ and T_{k_1} is equal to 29 ± 1 K. These results are in a good agreement with the results of Hurd[12] obtained above T_k. The small curvature in high fields of $M_1(H)$ is not very surprising. Such an effect has been observed for some nearly magnetic impurities of nickel in palladium.[13] The Curie-Weiss behavior of the magnetization due to the isolated impurities is well established for all temperatures either smaller than T_k $(T < T_k/10)$ or higher. The $M_2(H)$ term is represented in Fig. 3(a). The pairs seem to be saturated in a field of 60 kOe at 1.3 K. The susceptibility $\chi_2 = (dM_2/dH)_{H=0}$ may be fitted by the law $\chi_2 = C_2/(T + T_{k_2})$ with $0 < T_{k_2} < 5$ K. Let n be the concentration in moment carriers of spin S, then $(N/\mathfrak{M})2n\mu_{\rm B}S = 6.1 \times 10^4c^2$ emu/g (at 1.3 K and 60 kOe) and $(N/\mathfrak{M}) \times n4S(S+1)\mu_{\rm B}^2/3K = 10.2c^2$ (emu/g) are the saturation and the Curie constant for the impurities responsible for the $M_2(H)$ term (N = Avogadro's number, $\mathfrak{M}$ = molar mass). This gives $n = 130c^2$ and $S = 2.7 \pm 0.1$. This last value corresponds to the spin of two iron impurities ferromagnetically coupled and confirms the validity of our analysis of the c^2 term as being due to pairs.

Let us suppose that the condition of magnetism of the iron atom $U_{\rm eff}\rho_d(E_{\rm F}) = 1$ is not satisfied [$U_{\rm eff}$ = effective Coulomb interaction in Anderson's Hamiltonian, $\rho_d(E_{\rm F})$ = density of states for one spin direction at the Fermi level]. In such a model of nearly magnetic impurities, we can imagine that the oscillating change[14] in the den-

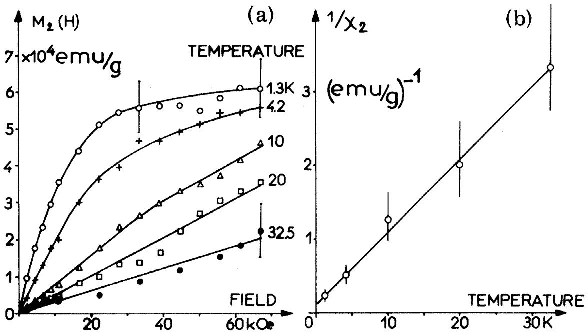

Fig. 3. (a) The c^2 term $M_2(H)$ is nearly saturated in 60 kOe at 1.3 K. (b) The initial susceptibility of pairs varies like $C_2/(T+T_{k2})$ with $0<T_{k2}<5$ K.

sity of states introduced by one neighbor impurity modifies the condition of magnetism, so that some pairs of impurities may have a Kondo temperature smaller than that of the isolated impurities. This has already been shown for the Au:Co and Cu:Co alloys.[15] But here the pairs are not restricted to near-neighbor impurities, as evidenced by the high value which is found for n. Then, the oscillating character of the Ruderman-Kittel-Kasuya-Yosida interaction, which probably couples the pairs, suggests that an equal number of antiferromagnetic pairs should exist. Then $260c^2$, the concentration of pairs, i.e., $520c^2$ concentration of impurities actually contributes to $M_2(H)$.[16] Such a value implies that a neighbor may be found to build a pair in any of 520 given sites around an impurity and we suggest a critical radius (of the order of 11 Å in the fcc lattice of Cu) where this pair formation occurs. However, it remains to distinguish whether $M_2(H)$ is due to the ferromagnetic coupling between two magnetic or two nearly magnetic impurities. Such nearly magnetic pairs exist in the Au:Co and Cu:Co alloys, and in an external field they may be magnetized more easily than the isolated impurities.[15]

In the Cu:Fe system, the existence of nearly magnetic pairs is suggested by the more rapid increase of the linewidth of NMR on copper between 2 and 40 kOe.[7] The contribution of really magnetic pairs to the linewidth would be independent of H and we suggest it is responsible for the linewidth found in zero field (extrapolated from 2 kOe) which was formerly interpreted as due to ferromagnetic clusters. The ratio of magnetic to nearly magnetic pairs obtained from the linewidths in zero field extrapolated from 2 and 50 kOe, respectively, would be about $\frac{1}{5}$.

Let us now compare our results with those of Daybell and Steyert.[3] First, the total susceptibility in zero field may be written $\chi(h=0)=\chi_0+C_m/T$ rather than $\chi=\alpha T^{-1/2}$ for $T<1$ K ($\chi_0=0.15\times10^{-8}$ emu/g ppm). Since their measurements were made at low temperature (<1 K) and low field (<1 kOe) we may expect that their value of χ_0 contains the contribution of all isolated impurities and nearly magnetic pairs. C_m/T is then the contribution of pairs which are really magnetic below 1 K. The values of C_m (respectively 1.19×10^{-8}, 2.9×10^{-8}, and 16.5×10^{-8} emu/g for the samples of 54, 145, and 330 ppm of Daybell and Steyert) are about 6 times smaller than our value of $10.2c^2$ emu/g deduced from Fig. 3(b). As from NMR results, about $\frac{1}{6}$ of the pairs are magnetic; at low temperatures they can be saturated in low fields (1 kOe).

To conclude, we have separated the properties of the isolated atoms from those of the pairs of impurities. One iron atom may be considered isolated (properties proportional to c) only if it has no neighbor iron atom in a sphere of radius $r_c\simeq 11$ Å. The susceptibility of the isolated impurities follows a Curie-Weiss law $\chi=C/(T+T_k)$, to well below $T_k\simeq 29$ K, and their magnetization is almost proportional to the applied field up to 70 kOe. For impurities within a distance $<r_0$ the criterion for magnetism is modified and they constitute a nearly magnetic or a magnetic pair.

The susceptibility in zero field and the linewidth of NMR of copper cannot be attributed only to one-impurity effects: The nearly magnetic pairs contribute to these properties by some terms proportional to c^2, which are more field and temperature dependent below T_k than the terms proportional to c due to the isolated impurities. A careful study over a large region of concentration is necessary to separate this c^2 dependence.

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[16] Antiferromagnetic interactions at a distance $<r_c$ are not destroyed even by a field of 60 kOe, so that the saturation value measured is only due to ferromagnetic pairs. The Curie constant is nearly the same for $4N$ impurities with spin S or N superparamagnetic pairs with spin $2S$ plus N pairs with spin 0.

PHASE TRANSITION IN HUBBARD MODEL

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(Received 16 March 1970; revised manuscript received 4 August 1970)

We investigate the appearance of magnetism in the Hubbard model. In the limit of large value of the interaction U, we show that localized moments appear below a critical temperature T_L. We find a Ruderman-Kittel interaction between these moments, which gives an ordered magnetic phase at a critical temperature T_c smaller than T_L.

For many years, there has been important activity in the fields of itinerant ferromagnetism, metals which exhibit localized-moment behavior above the transition temperature and the Mott transition. A particularly important start for this problem is the Hubbard Hamiltonian,[1] where one assumes a nondegenerate band of width Δ studied in tight binding and where electrons interact only when they are on the same atom, i.e., on the same Wannier state, the interaction being U, in that case.

In this Letter, we want to show that for this model magnetism can occur in two stages. For large values of the ratio U/Δ, there exists a first critical temperature T_L below which localized moments appear on each site. These localized moments interact and one can take into account only a two-body interaction which is a Ruderman-Kittel type. As a result of this interaction one can have a transition to a ferromagnetic or antiferromagnetic state at a second critical temperature T_c smaller than T_L. For small values of U/Δ, $T_L = T_c$ and the appearance of localized moments is connected with the appearance of magnetism if any. These results are in qualitative agreement with a model for magnetism in transition metals suggested by Friedel, Leman, and Obsewski.[2] The differences in approach and in choice of model have made if difficult to compare the present results in detail with previous works. However our results are different from the Hartree-Fock calculation of Blandin and Lederer,[3] although we agree with the qualitative features.

We support these conclusions with the calculation of the free energy using a functional integral representation.[4] This replaces the interaction U by an arbitrary magnetic field varying from site to site and having a Gaussian probability. We show that the free energy can be written as a series $F_1 + F_2 + \cdots$ of functions of the local field on one, two, $\cdots$ sites. For large U/Δ, the main term is the first one and F_1 is strongly peaked over two symmetrical values of the local field for temperature smaller than T_L. This shows the existence of local moments. This magnitude is a function of temperature and gives a susceptibility which deviates from a Pauli law. The second term of the series gives the interaction between moments. So one obtains an ordering temperature of these local moments of the order of $T_c \cong F_2$. For small U/Δ, F_1 and F_2 are comparable and greater than the remaining terms. We obtain $T_L = T_c$ when magnetism can occur.

As a start we have a Hubbard Hamiltonian:

$$H = \sum_{ij\sigma} T_{ij\sigma} C_{i\sigma}^{\dagger} C_{j\sigma} + \tfrac{1}{2} U n_{i\sigma} n_{i-\sigma}. \tag{1}$$