A. I. Schindler and C. Mackliet, Phys. Rev. Letters 20, 15 (1968).

[3] C. Chouteau, R. Fourneaux, K. Gobrecht, and R. Tournier, Phys. Rev. Letters 20, 193 (1968).

[4] E. Fawcett, E. Bucher, W. F. Brinkman, and J. P. Maita, Phys. Rev. Letters 21, 1183 (1968).

[5] P. Lederer and D. L. Mills, Phys. Rev. 165, 837 (1968).

[6] S. Englesberg, W. F. Brinkman, and S. Doniach, Phys. Rev. Letters 19, 1040 (1968); referred to in the text as EBD.

[7] P. Soven, Phys. Rev. 156, 809 (1967); 178, 1136 (1969).

[8] B. Velicky, S. Kirkpatrick, and H. Ehrenreich, Phys. Rev. 175, 747 (1968).

[9] G. Stocks, R. W. Williams, and J. S. Faulkner, Phys. Rev. Letters 26, 235 (1971).

[10] J. Hubbard, Proc. Roy. Soc. (London) A276, 238 (1963).

[11] See also K. Levin and K. Benneman, Bull. Am. Phys. Soc. 16, 424 (1971).

[12] E. C. Stoner, Proc. Roy. Soc. (London) A17, 371 (1932).

[13] O. K. Anderson and A. R. Mackintosh, Solid State Commun. 6, 285 (1968); O. K. Anderson, Phys. Rev. B 2, 883 (1970); A. J. Freemann, A. M. Furdyana, and O. J. Dimmock, J. Appl. Phys. 37, 1256 (1966).

[14] S. Wakoh, J. Phys. Soc. Japan 20, 1894 (1965).

[15] M. Shimizu (private communication).

[16] A. Misetich and R. E. Watson, J. Appl. Phys. 40, 1211 (1969); A. Misetich (private communication).

[17] T. M. Geballe, B. T. Matthias, A. M. Clogston, and H. J. Williams, J. Appl. Phys. 37, 1181 (1966).

[18] P. Wohlfarth, J. Appl. Phys. 41, 1205 (1970).

[19] C. Sadron, Proc. Roy. Soc. (London) A17, 371 (1932); V. Marian, Ann. Phys. (Paris) 7, 459 (1937).

[20] J. Crangle and W. R. Scott, J. Appl. Phys. 36, 921 (1965).

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High-Temperature Entropy and Specific Heat of Interacting Electrons in a Solid*

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The virial expansion for a fermion system is employed to derive an expression for the high-temperature entropy of electrons which interact according to the Hubbard Hamiltonian. The results are applied to an itinerant electron ferromagnet at temperatures well above the Curie temperature. In contrast with the results of the Stoner theory, a nonvanishing interaction contribution to the entropy and specific heat is obtained above T_C.

INTRODUCTION

In two previous reports, the virial expansion has been considered for a system of electrons in a solid[1,2] which interact with an effective short-range repulsion (the Hubbard Hamiltonian[3]). The virial-expansion technique is applicable to low-density systems at high temperatures. While these are not the usual conditions which prevail in solid-state problems, it is possible to use this technique to study an itinerant electron ferromagnet, for example, at temperatures higher than the Curie temperature. In some such systems it is possible to satisfy this condition and still have the temperature quite small relative to other characteristic parameters (e.g., bandwidth).

In the usual treatments of itinerant electron ferromagnetism, it is found that the magnetic entropy and specific heat vanish above the Curie temperature.[4] Such results are characteristic of molecular field theories, and are at variance with nature. In contrast, the virial expansion is an exact procedure which will yield nonvanishing results for these quantities. The specific heat of the ferromagnet Sc_3In ($T_C = 6.7$ °K) has been measured by Isaacs and Knapp.[5] The present theory should be applicable to such a system.

Our previous calculations have yielded exact expressions for the second virial coefficient for a system of electrons interacting according to the Hubbard model. An exact expression has also been obtained for the third virial coefficient, but we are unable to evaluate it completely. The results presented here should be essentially exact in regard to the first-order correction to the results for a noninteracting system, but are only approximate in the next order.

THEORY

Let Z be the grand partition function for the system, which has temperature T. The free energy F and entropy S are given by

$$F = -k_B T \ln Z , \tag{1}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,\mu} \tag{2}$$

(in which V is the volume and μ is the chemical potential of the system). The virial expansion for Z is

$$Z = 1 + Z_1 e^{\nu} + Z_2 e^{2\nu} + Z_3 e^{3\nu} + \cdots ,$$

in which Z_j refers to a cluster of j particles

$$Z_j = \mathrm{Tr}\ (e^{-H_j/k_B T}) .$$

The trace is taken over j-particle states of proper symmetry. H_j is the Hamiltonian for j interacting particles. The quantity $\nu = \mu/k_B T$ is determined by the condition that the number of particles in the system is fixed. Let this number by denoted by n:

$$n = \left(\frac{\partial}{\partial \nu} \ln Z\right)_V . \tag{3}$$

The virial coefficients b_n are obtained by expanding $\ln Z$:

$$\ln Z = Z_1 (e^{\nu} + b_2 e^{2\nu} + b_3 e^{3\nu}) , \tag{4}$$

in which

$$\begin{aligned} b_2 &= (Z_2 - \tfrac{1}{2} Z_1^2)/Z_1 , \\ b_3 &= (Z_3 - Z_1 Z_2 + 1/3 Z_1^3)/Z_1 . \end{aligned} \tag{5}$$

In Ref. 2 we have shown that these expressions may be simplified:

$$b_2 = [(\Delta Z_2)_c - \mathcal{S}_2]/2\mathcal{S}_1 , \tag{6}$$

$$b_3 = [(\Delta Z_3)_c + \tfrac{2}{3}\mathcal{S}_3]/2\mathcal{S}_1 . \tag{7}$$

In these expressions $(\Delta Z_j)_c$ is the completely connected part of the contribution from clusters of j particles to the partition function. The second-order term (ΔZ_2) can be expressed in terms of phase shifts for two-particle scattering.[1] We are substantially ignorant of the nature of ΔZ_3, except that it vanishes if the first-order approximation to the Faddeev equations is valid in which the three-body t matrix is expressed in terms of two-body t matrices.

The quantity $\mathcal{S}_j$ is given by

$$\mathcal{S}_j = \sum_{\vec{k}} e^{-jE(\vec{k})/k_B T} , \tag{8}$$

in which $E(\vec{k})$ is the single-particle energy. Spin directions have been included explicitly in (6) and (7). Note also that

$$Z_1 = 2\mathcal{S}_1 . \tag{9}$$

The factor of 2 above takes account of spin directions. Thus (4) becomes

$$\ln Z = 2\mathcal{S}_1 e^{\nu} + [(\Delta Z_2)_c - \mathcal{S}_2] e^{2\nu} + [(\Delta Z_3)_c + \tfrac{2}{3}\mathcal{S}_3] e^{3\nu} . \tag{10}$$

We may now proceed to compute the entropy. According to (2), (10) is to be differentiated for fixed μ ($= k_B T \nu$). Afterwards, μ must be determined from (3). Equation (3) becomes

$$n = 2\mathcal{S}_1 e^{\nu} + 2[(\Delta Z_2)_c - \mathcal{S}_2] e^{2\nu} + 3[(\Delta Z_3)_c + \tfrac{2}{3}\mathcal{S}_3] e^{3\nu} . \tag{11}$$

Equation (11) can be solved by iteration to determine e^{ν}. After some algebra, we obtain a fairly lengthy expression for the entropy S. It is convenient to break this expression into two parts:

$$S = S_F + S_I , \tag{12}$$

in which S_F pertains to a gas of noninteracting particles, and S_I involves the interaction explicitly: That is, S_I would vanish if the connected parts $(\Delta Z_2)_c$ and $(\Delta Z_3)_c$ are set equal to zero;

$$\begin{aligned} \frac{S_F}{nk_B} = 1 - \nu_0 + \frac{\beta\mathfrak{F}_1}{\mathcal{S}_1} - \frac{n\mathcal{S}_2}{4\mathcal{S}_1^2}\left(1 - \frac{2\beta\mathfrak{F}_1}{\mathcal{S}_1} + \frac{2\beta\mathfrak{F}_2}{\mathcal{S}_2}\right) \\ + \frac{n^2\mathcal{S}_3}{12\mathcal{S}_1^3}\left(1 - \frac{3\beta\mathfrak{F}_1}{\mathcal{S}_1} + \frac{3\beta\mathfrak{F}_3}{\mathcal{S}_3}\right) - \frac{n^2\mathcal{S}_2^2}{8\mathcal{S}_1^4} \\ \times\left(1 - \frac{4\beta\mathfrak{F}_1}{\mathcal{S}_1} + \frac{4\beta\mathfrak{F}_2}{\mathcal{S}_2}\right) , \end{aligned} \tag{13}$$

in which

$$\nu_0 = \ln(n/2\mathcal{S}_1) \tag{14}$$

and

$$\mathfrak{F}_j = \sum_{\vec{k}} E(\vec{k})\, e^{-jE(\vec{k})/k_B T} . \tag{15}$$

The contribution from the electron interaction to the entropy is

$$\begin{aligned} \frac{S_I}{nk_B} = \frac{n(\Delta Z_2)_c}{4\mathcal{S}_1^2}\left(1 - \frac{2\beta\mathfrak{F}_1}{\mathcal{S}_1} + B\right) + \frac{n^2(\Delta Z_3)_c}{8\mathcal{S}_1^3} \\ \times\left(1 - \frac{3\beta\mathfrak{F}_1}{\mathcal{S}_1} + C\right) - \frac{n^2\mathcal{S}_2(\Delta Z_2)_c}{4\mathcal{S}_1^4}\left[\left(\frac{(\Delta Z_2)_c}{2\mathcal{S}_2} - 1\right)\right. \\ \left. \times\left(1 - \frac{4\beta\mathfrak{F}_1}{\mathcal{S}_1}\right) - \frac{2\beta\mathfrak{F}_2}{\mathcal{S}_2} + B\left(\frac{(\Delta Z_2)_c}{\mathcal{S}_2} - 1\right)\right] , \end{aligned} \tag{16}$$

in which

$$B = T\frac{\partial}{\partial T} \ln(\Delta Z_2)_c \tag{17}$$

and

$$C = T\frac{\partial}{\partial T} \ln(\Delta Z_3)_c . \tag{18}$$

The virial expansion enables us to express both contributions to the entropy as power series in the particle density. Both expression (13) and (16) are accurate through terms of second order in the density. The series for S_F is just that which would be obtained for an assembly of free fermions. The convergence of this series is governed by a dimensionless parameter which is the number of particles in a volume which is the cube of a Debye wavelength. This number is large for metals at ordinary temperatures. However, other parameters must be evaluated to determine the convergence of the series for S_I. These depend on the interaction strength as measured, for example, by the two-body t matrix. This will appear more clearly below. We argue that the interaction-dependent corrections S_I may still be meaningful at temperatures at which the electrons are degenerate ($k_BT < \epsilon_F$, where ϵ_F is the Fermi energy at 0 °K), as is the case in ordinary metals. It is, however, necessary that the temperature be large compared to that at which magnetic ordering takes place. These requirements can be satisfied in a material with a small number of electrons in a nearly empty band, or a small number of holes in a nearly full band. In such systems, even the condition $k_BT > \epsilon_F$ may be obeyed. It will always be assumed here that k_BT is much smaller than the bandwidth E_M.

It was shown in Ref. 1 [see Eq. (43) of that paper] that $(\Delta Z_2)_c$ is given for the Hubbard Hamiltonian exactly by

$$(\Delta Z_2)_c = -\sum_{\vec{K}}\left(e^{-\beta E_m(\vec{K})} - e^{-\beta E_B(\vec{K})}\right) - \frac{\beta}{\pi}\sum_{\vec{K}}\int_{E_0(\vec{K})}^{E_m(\vec{K})} \delta_{\vec{K}}(E)\, e^{-\beta E}\, dE \ . \tag{19}$$

In this expression $\vec{K}$ is the total wave vector of a system of two interacting particles and β is $1/R_BT$. In terms of the single-particle energy-band function $E(\vec{k})$, it is useful to define

$$E(\vec{K},\vec{k}) = E(\tfrac{1}{2}\vec{K}+\vec{k}) + E(\tfrac{1}{2}\vec{K}-\vec{k}) \ . \tag{20}$$

The quantities $E_0(\vec{K})$ and $E_m(\vec{K})$ are the minimum and maximum values of $E(\vec{K},\vec{k})$. The repulsive two-body interaction may cause a bound state to appear above the band for some $\vec{K}$ at an energy $E_B(\vec{K})$. The first sum extends over only those values of $\vec{K}$ for which such a bound state exists.

The quantity $\delta_{\vec{K}}(E)$ is the scattering phase shift for two particles with fixed total wave vector. It is shown in Ref. 1 that

$$\delta_{\vec{K}}(E) = \tan^{-1}\frac{\pi V_0 G_{\vec{K}}(E)}{1+V_0\mathcal{G}_{\vec{K}}(E)} \ . \tag{21}$$

In Eq. (21) V_0 is the interaction strength which appears in the Hubbard Hamiltonian, $G_{\vec{K}}(E)$ is the density of two-particle (noninteracting) states of fixed $\vec{K}$, and

$$\mathcal{G}_{\vec{K}}(E) = P\int\frac{G_{\vec{K}}(E')}{E'-E}\,dE' \ . \tag{22}$$

Equations (16)–(22) make possible an exact calculation of the leading high-temperature-interaction correction to the entropy of electrons interacting according to the Hubbard Hamiltonian. The next term in S_I (proportional to n^2) can be obtained in an approximation in which the third-order connected part $(\Delta Z_3)_c$ is neglected.

Evaluation of the integrals required for this calculation is a task requiring numerical integration employing an actual or model band structure. Such calculations are in progress and will be reported subsequently.

In this paper attention will be restricted to a model in which analytic approximations are possible. A situation is considered in which k_BT is small compared with the bandwidth but large compared to the Curie temperature of a possible ferromagnetic transition. A sequence of plausible approximations described in Ref. 1 leads to an explicit formula for $(\Delta Z_2)_c$ [see Eq. (83) of that paper]

$$\frac{n(\Delta Z_2)_c}{\mathcal{S}_1^2} = -\rho\frac{8\mathcal{S}_2^2}{\mathcal{S}_1^2}\frac{t_0}{k_BT} \ , \tag{23}$$

in which $\rho = n/N$ is the ratio of the number of particles to the number of sites,

$$t_0 = \frac{V_0}{1+\frac{1}{2}V_0\mathcal{G}} \ , \tag{24}$$

and $\mathcal{G}$ is given by

$$\mathcal{G} = \int\frac{G(E)}{E}\,dE \ , \tag{25}$$

in which $G(E)$ is the density of *single*-particle states [in contrast with Eq. (22), which contains the density of two-particle states].

We find with the use of (23) that B [Eq. (17)] is given by

$$B = -1 + \frac{4\beta\mathfrak{F}_2}{\mathcal{S}_2} \ . \tag{26}$$

Equations (23) and (26) are substituted into (16). This becomes, with the neglect of $(\Delta Z_3)_c$,

$$\begin{aligned}\frac{S_I}{nk_B} = {} & -\rho\frac{8\mathcal{S}_2^2}{\mathcal{S}_1^2}\frac{t_0}{k_BT}\left(\frac{\beta\mathfrak{F}_2}{\mathcal{S}_2} - \frac{1}{2}\frac{\beta\mathfrak{F}_1}{\mathcal{S}_1}\right) \\ & + \rho^2\frac{8\mathcal{S}_2^2}{\mathcal{S}_1^2}\frac{t_0}{k_BT}\left\{\left(\frac{N\mathcal{S}_2}{\mathcal{S}_1^2}\right)\left(\frac{\beta\mathfrak{F}_1}{\mathcal{S}_1} - \frac{3}{2}\frac{\beta\mathfrak{F}_2}{\mathcal{S}_2}\right)\right. \\ & \left. + \frac{\mathcal{S}_2^2}{\mathcal{S}_1^2}\frac{t_0}{k_BT}\left[1 - 8\left(\frac{\beta\mathfrak{F}_2}{\mathcal{S}_2} - \frac{1}{2}\frac{\beta\mathfrak{F}_1}{\mathcal{S}_1}\right)\right]\right\} \ .\end{aligned} \tag{27}$$

It remains to evaluate the quantities $\mathcal{S}_j$ and $\mathfrak{F}_j$, and this requires specific assumptions about the density of states. The values of $\mathcal{S}_j$ and $\mathfrak{F}_j$ depend significantly on such assumptions. Even the sign of the contribution can vary.

The simplest case is that of a parabolic band. Suppose

$$E(\vec{k}) = \gamma k^2 \ .$$

In this case,

$$\begin{aligned}&\mathcal{S}_j = V(k_BT/4\pi\gamma j)^{3/2} \ , \\ &\beta\mathfrak{F}_j/\mathcal{S}_j = 3/2j, \ \ 8\mathcal{S}_2^2/\mathcal{S}_1^2 = 1 \ .\end{aligned} \tag{28}$$

The leading term in S_I vanishes, and the remainder simplifies to

$$\frac{S_I}{nk_B} = \rho^2 \frac{t_0}{8k_BT}\left[\frac{t_0}{k_BT} + \frac{3N}{V}\left(\frac{2\pi\gamma}{k_BT}\right)^{3/2}\right]. \qquad (29)$$

The interaction contribution to the entropy is positive and proportional to $(k_BT)^{-2}$ at high temperatures. If a fourth-order term in $E(\vec{k})$ is considered, the leading term in S_I no longer vanishes, and an entropy proportional to $t_0/(k_BT)^2$ at high temperatures is obtained. The sign of this contribution is the negative of the sign of the fourth-order term in $E(\vec{k})$.

The parabolic-band situation is not typical of itinerant electron ferromagnetism, which is favored by the presence of a sharp peak in the density of states near the zero-temperature Fermi energy.[6] A model density of states which can exhibit the desired features and still be simple enough so that the required integrals can be performed is

$$\begin{aligned} G(E) &= aE^{\mu}(E_m - E)^{\mu} + bE^{\tau}(E_0 - E)^{\tau}\,\theta(E_0 - E), \quad 0 < E < E_m \\ &= 0 \qquad \text{otherwise}. \end{aligned} \qquad (30)$$

In (30), θ is a unit step function $\theta(x) = 1$ for $x > 0$, $\theta(x) = 0$ for $x < 0$. The parameters of Eq. (30) can be chosen so that the density of states has a peak at $E_0/2$. The sharpness of the peak is controlled by the parameter τ.

We will normalize $G(E)$ so that

$$\int_0^{E_m} G(E)\, dE = N, \qquad (31)$$

in which N is, as before, the number of atomic sites in the system. It is convenient to replace the parameters a and b by the number of states in the background n_bN, and the number of states in the peak, n_pN. Thus, choose a and b so that

$$\begin{aligned} a\int_0^{E_m} E^{\mu}(E_m - E)^{\mu}\, dE &= n_bN, \\ b\int_0^{E_0} E^{\tau}(E_0 - E)^{\tau}\, dE &= n_pN. \end{aligned} \qquad (32)$$

The basic integral required is

$$\begin{aligned} \int_0^{E_m} e^{-j\beta E} E^{\mu}(E_m - E)^{\mu}\, dE &= (\pi)^{1/2} E_m^{2\mu+1}\,\Gamma \\ &\times(\mu+1)(j\beta E_m)^{-\mu-1/2}\, e^{-j\beta E_m/2}\, I_{\mu+1/2}(1/2j\beta E_m), \end{aligned} \qquad (33)$$

in which I is a modified Bessel function. The model density of states will be considered in the limit in which $\beta E_m \gg 1$, $\beta E_0 < 1$. This situation describes a low-energy peak in an otherwise structureless density of states. After a straightforward but somewhat lengthy calculation we find that the dominant contributions to the terms in (27) are

$$\beta\mathfrak{F}_j/\mathcal{S}_j \approx \tfrac{1}{2}\beta E_0, \quad \mathcal{S}_2^2/\mathcal{S}_1^2 \approx (1 - \beta E_0), \quad N\mathcal{S}_2/\mathcal{S}_1^2 \approx 1/n_p. \qquad (34)$$

We then obtain from (27), correct to order $1/(k_BT)^2$,

$$\frac{S_I}{nk_B} = -2\rho\frac{t_0E_0}{(k_BT)^2}\left(1 + \frac{\rho}{n_p}\right) + 8\rho^2\left(\frac{t_0}{k_BT}\right)^2. \qquad (35)$$

In a situation particularly favorable to ferromagnetism, we might expect $\rho \approx \frac{1}{2}n_p$, so that the zero-temperature Fermi energy would fall close to the maximum of the peak in the density of states.

In this case, as in (29), we obtain an interaction entropy proportional to $1/T^2$ at high temperatures.

The specific heat can be obtained immediately:

$$C = T\left(\frac{\partial S}{\partial T}\right).$$

The interaction contribution to the electron specific heat is then

parabolic band:

$$\frac{C_I}{nk_B} = -\rho^2\frac{t_0}{4k_BT}\left[\frac{t_0}{k_BT} + \frac{15}{4}\frac{N}{V}\left(\frac{2\pi\gamma}{k_BT}\right)^{3/2}\right], \qquad (29')$$

density of states with low-energy peak:

$$\frac{C_I}{nk_B} = 4\rho\frac{t_0E_0}{(k_BT)^2}\left(1 + \frac{\rho}{n_p}\right) - 16\rho^2\left(\frac{t_0}{k_BT}\right)^2. \qquad (35')$$

DISCUSSION AND CONCLUSIONS

In contrast to the predictions of the Stoner theory of collective electron ferromagnetism, we have shown that a nonvanishing contribution to the entropy and specific heat from the interaction that produces magnetic order should exist at high temperatures. A general expression for these quantities has been obtained on the basis of a one-band Hubbard Hamiltonian. These expressions are exact in the high-temperature limit to first order in the particle density.

The general expressions were evaluated for two models. One surprising result emerges. For a particularly simple band of parabolic form, the interaction contribution to the entropy is positive. This result is also obtained for any system with a density of states which is a power of the energy, or in which a negative fourth-order term (in $\vec{k}$) is added to the k^2 dependence of the single-particle energy. This means that the system is, in effect, more disordered than is the case for free fermions under the same conditions. Since this results from the term of order n^2 in the virial expansion, it remains possible that inclusion of the neglected $(Z_3)_c$ could alter this conclusion. In the case of a model in which the density of states has a peak at low energy, the expected negative sign is obtained for the leading term in the entropy (with respect to the particle density). The predictions of the entropy and specific heat remain to be determined for realistic band models. Calculations of this type are in progress.

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[1] J. Callaway and D. M. Edwards, Phys. Rev. 136, A1333 (1964).

[2] J. Callaway and A. K. Rajagopal, Phys. Rev. B 3, 1763 (1971).

[3] J. Hubbard, Proc. Roy. Soc. (London) A276, 238 (1963).

[4] See A. H. Wilson, *Theory of Metals* (Cambridge U.P., New York, 1953), Chap. 7.

[5] L. L. Isaacs and G. S. Knapp, Bull. Am. Phys. Soc. 15, 1623 (1970).

[6] G. S. Knapp, F. Y. Fradin, and H. V. Culbert, J. Appl. Phys. 42, 1341 (1971).

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Magnetic Properties of Cu-Mn and Cu-Fe Alloys

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Cu-Mn alloys with a Mn content ranging from 5 to 30 at.% were sputtered at temperatures ranging from 77 to 1070 °K. The films deposited at 77 °K showed an antiferromagnetic spin ordering. On the other hand, films deposited at 1070 °K had the mixed antiferromagnetic-ferromagnetic behavior of the bulk which can be explained by an exchange-anisotropy mechanism. Films deposited at 170 or 300 °K displayed a ferromagnetism similar to that observed with superparamagnetic particles with a Curie temperature proportional to the Mn content. These magnetic properties are consistent with the idea that the low-temperature-deposited films (77 °K) have a random distribution of Mn atoms and that the degree of clustering of Mn atoms increases with increasing deposition temperature. $Cu_{0.99}Fe_{0.01}$ films sputtered at 800 °C show a large amount of clustering, while films deposited at room temperature do not. The susceptibility of the $Cu_{0.99}Fe_{0.01}$ films deposited at room temperature follows a Curie-Weiss law from which one can extract a Kondo temperature (T_K) very close to 0 °K. One can deduce from the slope of χ^{-1} versus T and from the fact that $T_K \simeq 0$ °K that most, if not all, of the Fe atoms in such a film are paired.

I. INTRODUCTION

Cu-Mn alloys have been the subject of many investigations. Most experiments have shown an antiferromagnetic behavior at low temperature with a Néel temperature depending on the method of measurement.[1–5] Kouvel[2,3] made the most extensive study on Cu-Mn alloys annealed at 800 °C and quenched in water and concluded that they consisted of a mixture of ferromagnetic and antiferromagnetic regions coupled by exchange-anisotropy interactions. If such an alloy is cooled in a field, one observes a unidirectional anisotropy as evidenced by the shifted hysteresis loop and a torque curve proportional to $\sin\theta$ and not $\sin 2\theta$ as in materials with uniaxial anisotropy. Furthermore, the remanence which is very low at 1 °K increases with temperature, passes through a maximum and then decreases; the maximum remanence occurs around 12 at.% Mn and corresponds to about 5% of the Mn atoms being ferromagnetically aligned. Scheil and Wachtel[6] found short-range atomic order in Cu-Mn alloys (20–25 at.% Mn) annealed between 100 and 450 °C. On the other hand, Korn[7] quench evaporated at 14 °K a $Cu_{0.95}Mn_{0.05}$ film and reported a pure antiferromagnetic behavior. Recently,[8] a proximity-effect study of such alloys showed that a $Cu_{0.95}Mn_{0.05}$ film sputtered at − 100 °C became ferromagnetic at 5.5 °K. In view of the wide variety of results, it would be interesting to find out the material properties which lead to the various magnetic properties.

Tholence and Tournier[9] have recently studied the magnetization of very dilute Cu-Fe alloys (up to 600 ppm of Fe). They showed that the magnetization could be split up in two terms: one proportional to the concentration c of Fe impurities and one proportional to c^2 which can be attributed to Fe pairs. The Kondo temperature which was 29 °K for isolated impurities decreased to a value between 0 and 5 °K for the pairs. An extrapolation of their analysis[9] predicts that all the Fe atoms should be paired up when the concentration reaches 2×10^{-3} at.%. As it was shown in the proximity-effect study[8] that such