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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Magnetic Properties of Cu-Mn and Cu-Fe Alloys

J. J. Hauser
Bell Laboratories, Murray Hill, New Jersey 07974
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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

concentrations (up to 1 at.%) could be maintained in solid solution by sputtering at room temperature or below, one can check with susceptibility measurements whether the Fe atoms in such concentrated alloys are indeed all paired.

II. EXPERIMENT

The various alloys were prepared by getter-sputtering films[8] from targets made from arc-melted buttons. The experimental technique used to deposit the films has already been described.[8] As shown in Table I the word "film" is used in quotation marks to indicate that although a film technique was used to deposit various alloys, these "films" are truly representative of bulk: The thickness itself ranging from 1.3 to 64 μ excludes these layers from the film category. The alloys were deposited at temperatures (T_D) ranging from 77 to 1070 °K and these temperatures are listed in the second column of Table I. The only exception is the sample $Cu_{0.8}Mn_{0.2}$ No. 4 which was deposited at 170 °K and then annealed for 1 h at 1070 °K while getter sputtering proceeded without deposition (the shutter was over the film during the annealing period).

The magnetic properties of the films were measured using two different techniques. The majority of the Cu-Mn alloys were measured on a very sensitive torque balance.[10] The other alloys were measured on a sensitive ac bridge using two balanced coils.[11] The rectangular cross section of the coils was very close to that of the sapphire substrates used in the film deposition so as to maximize the coupling between the coil and the film. The bridge was used at 200 cycles, 1 and 10 kHz and if a frequency dependence of the susceptibility was observed, the susceptibility was extrapolated to zero frequency. The bridge was calibrated both against a nickel film and at low temperatures against superconducting V_3Si and Pb films.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Cu-Mn Alloys

The various properties of the Cu-Mn "films" are listed in Table I. It was previously pointed out[8] that Cu and dilute-alloy Cu films (with up to 1 at.% Fe or Mn) deposited at 170 °K or below, have an fcc structure with a lattice parameter of 4.28 Å instead of 3.615 Å for bulk copper. This is not the case for the heavier concentrations used here and all the films listed in Table I have the structure of bulk Cu. The electron diffraction rings of films deposited at 170 and 77 °K are, however, somewhat broadened by the small grain size.

As shown in Table I the properties of films deposited at 300 and 170 °K are very similar. Comparison of $Cu_{0.95}Mn_{0.05}$ Nos. 2 and 4, of $Cu_{0.9}Mn_{0.1}$ Nos. 1 and 7, and of $Cu_{0.8}Mn_{0.2}$ Nos. 3 and 7 where in each case the thickness is varied by at least an order of magnitude without a marked change in the magnetic properties supports the statement made earlier that these films have a bulklike behavior. A further proof of this statement is given by experiments on $Cu_{0.09}Mn_{0.1}$ No. 4 and $Cu_{0.8}Mn_{0.2}$ No. 4 where the films have the same bulk behavior as described by Kouvel.[2,3] $Cu_{0.8}Mn_{0.2}$ was deposited at 170 °K like the films studied in the proximity-effect experiments[8] and then annealed at 1070 °K. This temperature of 800 °C was selected as it was the annealing temperature chosen by Kouvel[3] to anneal his bulk samples. When the sample $Cu_{0.8}Mn_{0.2}$ was

TABLE I. Properties of Cu-Mn "films."

Sample		T_D (°K)[a]	d(μ)[a]	Method of measurement	T_C (°K)[a]	M_r (emu)[a]	μ_r (μ_B/Mn atom)[a]
$Cu_{0.95}Mn_{0.05}$	No. 2	170	2.4	Torque	5.5	0.42	0.01
$Cu_{0.95}Mn_{0.05}$	No. 3	170	1.9	Torque	···	0.43	0.01
$Cu_{0.95}Mn_{0.05}$	No. 4	300	64	Susceptibility	5.9	0.26	0.006
$Cu_{0.9}Mn_{0.1}$	No. 1	170	3.6	Torque	···	0.55	0.007
$Cu_{0.9}Mn_{0.1}$	No. 2	170	1.6	Torque	12	1.65	0.02
$Cu_{0.9}Mn_{0.1}$	No. 4	1070	39	Susceptibility	···	16.2	0.21
$Cu_{0.9}Mn_{0.1}$	No. 6	77	29	Susceptibility	···	0	0
$Cu_{0.9}Mn_{0.1}$	No. 7	300	37	Susceptibility	15	0.46	0.006
$Cu_{0.8}Mn_{0.2}$	No. 2	77	1.3	Torque	···	0	0
$Cu_{0.8}Mn_{0.2}$	No. 3	170	2.4	Torque	29	3.05	0.02
$Cu_{0.8}Mn_{0.2}$	No. 4	1070[b]	2.8	Torque	···	14	0.09
$Cu_{0.8}Mn_{0.2}$	No. 6	170	6.1	Torque	···	3.5	0.02
$Cu_{0.8}Mn_{0.2}$	No. 7	300	22.6	Susceptibility	26	2	0.01
$Cu_{0.7}Mn_{0.3}$		170	2.15	Torque	···	2.6	0.01

[a] T_D is the temperature of deposition of a film of thickness d, T_C is the Curie temperature, M_r is the remanent magnetization per unit volume, and μ_r is the remanent moment per Mn atom.

[b] See Sec. II.

cooled in zero field to 4.2 °K it showed almost zero isothermal magnetization (IRM). However, after cooling $Cu_{0.8}Mn_{0.2}$ to 4.2 °K under an applied field of 10 kOe a nonzero thermoremanent magnetization (TRM) was observed. The torque was proportional to $\sin\theta$ rather than $\sin 2\theta$ as it should be for an exchange-anisotropy system.[2,3] Furthermore, the value of remanent magnetization per unit volume (M_r) and of the remanent moment per Mn atom (μ_r) are in excellent agreement with the values obtained by Kouvel on bulk.[3] The $Cu_{0.9}Mn_{0.1}$ No. 4 sample was deposited at 1070 °K and the temperature dependence of its reciprocal volume susceptibility after cooling to 4.2 °K in zero field is shown in Fig. 1. The magnitude of the susceptibility and the minimum at 44 °K are in good agreement with Kouvel's bulk measurements. Again, although the IRM was almost zero the TRM is large and the values of M_r and μ_r shown in Table I agree well with bulk data.[3] Since the atomic moment of Mn is probably[3,7] $4\mu_B$ a μ_r value of 0.2 corresponds to 5% of the Mn atoms being aligned ferromagnetically. The $Cu_{0.9}Mn_{0.1}$ No. 4 hysteresis loop shown in Fig. 2 is almost completely reversible and shifted in the negative field direction, the positive field direction being the direction of the cooling field. This shifted hysteresis loop is a clear indication of exchange-anisotropy interactions between ferromagnetic and antiferromagnetic regions which lead to a unidirectional anisotropy as shown on bulk Cu-Mn alloys by Kouvel.[3] Consequently, the results obtained on $Cu_{0.9}Mn_{0.1}$ No. 4 and $Cu_{0.8}Mn_{0.2}$ No. 4 show that thick films deposited by the getter-sputtering technique can behave like bulk if they are deposited or annealed at the same temperature as bulk.

On the other hand, films deposited at 77 °K as $Cu_{0.9}Mn_{0.1}$ No. 6 and $Cu_{0.8}Mn_{0.2}$ No. 2 show zero IRM and zero TRM. These results are in agreement with the one quoted by Dorn[7] on a $Cu_{0.95}Mn_{0.05}$ film quench evaporated at 14 °K. As previously discussed,[8] films deposited at low temperature are quasiamorphous and one can therefore expect a statistical distribution of Mn atoms.[7,8] The deviation from the statistical distribution, and therefore, the clustering tendency, will increase with increasing temperature of deposition or of annealing owing to the higher diffusion rates. Consequently, the difference between Korn's[7] and Kouvel's[3] experiments cannot be ascribed to a difference between film and bulk behavior as the experiments above described show that both behaviors can be observed in films.

We shall now turn our attention to films deposited in the intermediate temperature range (170–300 °K). A proximity-effect study[8] of a $Cu_{0.95}Mn_{0.05}$ film deposited at 170 °K revealed a ferromagnetic behavior with a Curie temperature T_C of 5.5 °K. As evidenced in Table I, all the compositions studied show ferromagnetism but one no longer has the exchange-anisotropy interactions present in the films deposited at 1070 °K. Indeed, the torque curves are proportional to $\sin 2\theta$, the hysteresis loops are symmetrical, and the IRM is almost the same as the TRM. Furthermore, the remanent moment per atom (μ_r) no longer peaks around the 10 at.% Mn composition but scatters between 0.006 and 0.02 for the range of Mn compositions investigated (5–30 at.%). In other words, the fraction of Mn atoms ferromagnetically aligned is ten times smaller than in films deposited at 1070 °K. The temperature dependence of the IRM is also quite different from alloys showing exchange anisotropy: Instead of the maximum in M_r versus T (Fig. 1 of Ref. 3), Fig. 3 shows that M_r decreases proportionally to $1/T$ as in the case of superparamagnetic systems. The observed T_C's of 5.9 °K for $Cu_{0.95}Mn_{0.05}$ No. 4 and of 5.5 °K for $Cu_{0.95}Mn_{0.05}$ No. 2 are in excellent agreement with the T_C of 5.5 °K reported for such an alloy by the

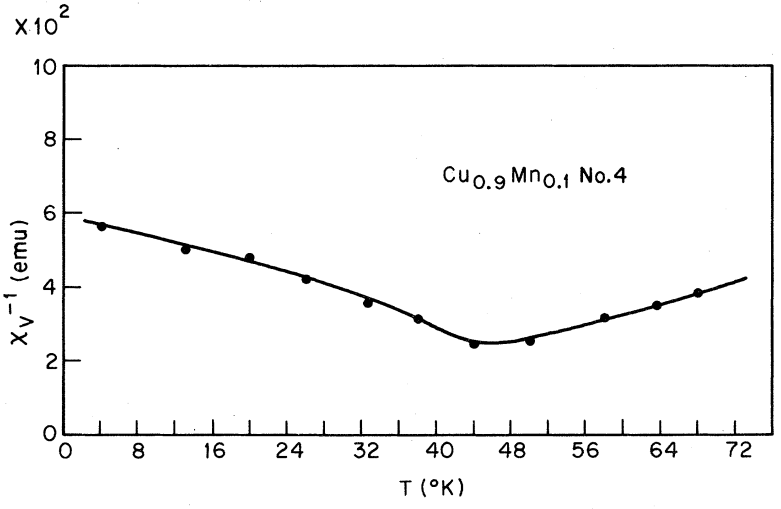

FIG. 1. Temperature dependence of the reciprocal volume susceptibility for a $Cu_{0.9}Mn_{0.1}$ film deposited at 800 °C and cooled to 4.2 °K in zero field.

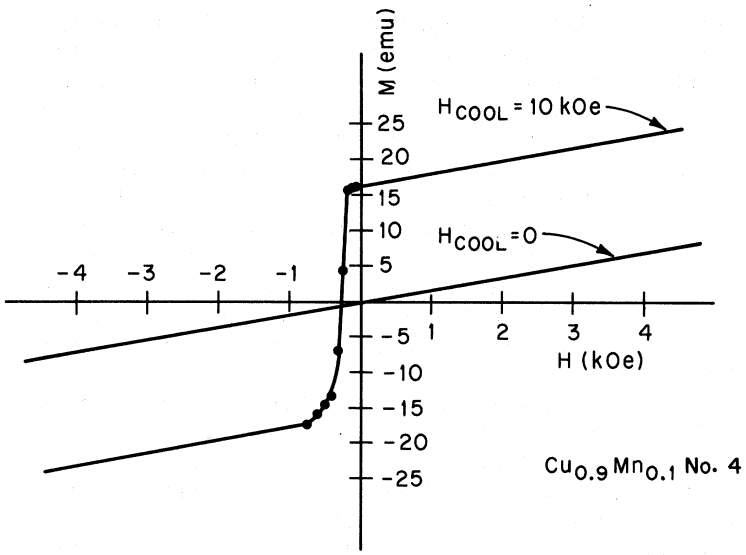

FIG. 2. Hysteresis loop measured at 4.2 °K for a $Cu_{0.9}Mn_{0.1}$ film deposited at 800 °C and cooled to 4.2 °K in 0 or +10 kOe applied parallel to the measurement axis.

proximity-effect experiments.[8] The T_C's of the other compositions seem to be approximately proportional to the Mn concentration.

Kouvel[3] reported that the unidirectional anisotropy coefficient decreases with decreasing Mn content to vanish at about 2 at.% Mn. In a similar way, we find that for a given concentration the exchange anisotropy decreases with decreasing temperature of deposition as a result of the more statistical distribution of Mn atoms. In the case of films deposited at 170–300 °K the exchange-anisotropy interactions may have disappeared for two reasons. First, the number of ferromagnetic clusters as shown by Table I is much smaller than in films deposited at 1070 °K. Second, in such low-temperature-deposited films, the antiferromagnetic order is greatly perturbed by spin-orbit scattering.[8] In conclusion, it has been shown that the magnetic properties of Cu-Mn alloys depend on the deviations from a pure statistical distribution of the Mn atoms. In increasing the temperature of deposition from 77 to 1070 °K one smoothly changes from an antiferromagnetic order, through ferromagnetic clusters of the superparamagnetic type, to the exchange-anisotropy interactions seen in bulk alloys.

B. $Cu_{0.99}Fe_{0.01}$

The proximity effect of Pb with $Cu_{0.99}Fe_{0.01}$ films

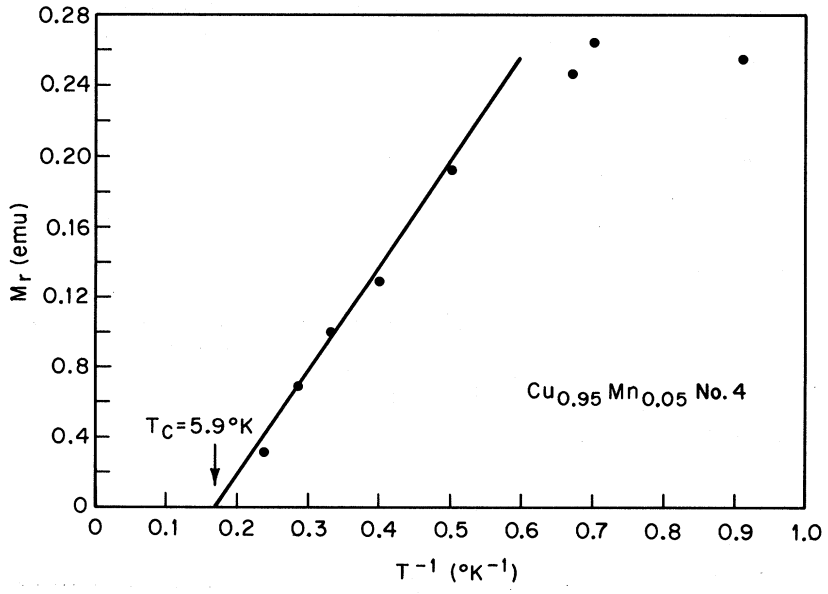

FIG. 3. Temperature dependence of the isothermal remanent magnetization for a $Cu_{0.95}Mn_{0.05}$ film deposited at room temperature.

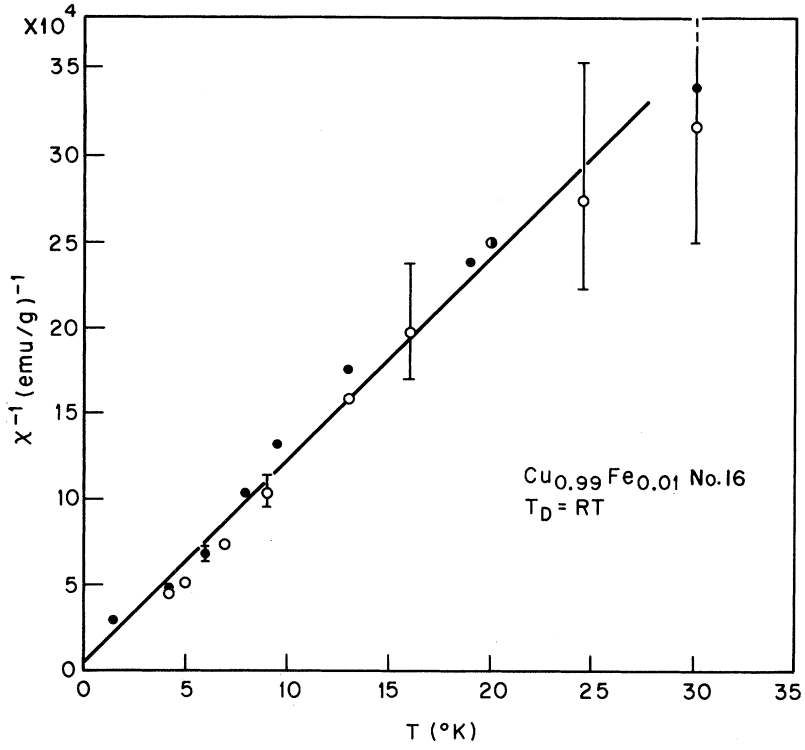

FIG. 4. Temperature dependence of the reciprocal specific susceptibility for a 57-μ $Cu_{0.99}Fe_{0.01}$ film deposited at room temperature (RT). The closed and open dots indicate two different runs on the same sample.

deposited at 530 °C, 200 °C, room temperature, and − 100 °C showed[8] that in the temperature range of the measurements (1–7 °K) the $Cu_{0.99}Fe_{0.01}$ film was compensated when deposited at 530 °C, 200 °C, and room temperature and the full spin-depairing effect was present when deposited at − 100 °C. This latter behavior was explained by the lowering of the Kondo temperature (T_K) as a result of the stretched lattice of such low-temperature-deposited film. It was also pointed out in that study[8] that Fe clusters in films deposited at high temperatures and it was concluded from resistivity measurements that 0.1 at.% Fe is free in a film deposited at 800 °C while 0.2 at.% Fe is free in a film prepared at 200 °C. Susceptibility measurements on a $Cu_{0.99}Fe_{0.01}$ film deposited at 800 °C lead to the conclusion that 0.5 at.% Fe was clustered.[12] On the other hand, susceptibility measurements on a $Cu_{0.99}Fe_{0.01}$ film deposited at room temperature showed no sign of clustering. The temperature dependence of the reciprocal specific susceptibility for such a film is shown in Fig. 4. Although the scatter is quite large, the data can be fitted by a Curie-Weiss law $\chi = C(T + T_K)^{-1}$ with $T_K \simeq 0$ °K and $C = 9.3 \times 10^{-5}$ emu °K/g. Tholence and Tournier[9] showed that the initial susceptibility of dilute Cu-Fe alloys (up to 600 ppm) can be decomposed into a term linear in the concentration c corresponding to isolated impurities, and one proportional to c^2 due to Fe pairs. The importance of pairs to the magnetization of dilute Cu-Fe alloys has also been shown recently by Hirschkoff *et al.*[13] using susceptibility measurements in the few millidegrees temperature range. Consequently, the departure from a pure Curie-Weiss law with $T_K = 29$ °K at low temperatures is caused by the pairs. The concentration of impurities tied up in both antiferromagnetic pairs (assuming an equal number of both) was found to be $520c^2$. Consequently, if the extrapolation of the data of Tholence and Tournier remains valid, one expects all the Fe atoms to be paired up at a concentration of 1.92×10^{-1} at.%. Therefore three magnetic species are present in general in such Cu-Fe alloy films: single spins, pairs of spins, and clusters of more than two spins. The clusters can either originate from the same magnetic interaction that leads to the pairing of spins, or from the limited solubility of Fe in Cu which results in the rejection of Fe into second-phase clusters. Consequently, films deposited at higher temperatures and which show the largest clustering will have a lower concentration of Fe in solid solution. It is possible that this lower concentration of free spins (both single and pairs) will result in less pairing. Furthermore, the initial susceptibility of pairs was found[9] to follow a Curie-Weiss law with $0 < T_K < 5$ °K and a Curie constant of $10.2c^2$. The data shown in Fig. 4 are therefore convincing evidence that most if not all Fe atoms are paired up. Indeed, the data of Fig. 4 follow a Curie-Weiss law with $T_K \simeq 0$ °K, which is the Kondo temperature for

pairs. Furthermore, by equating the experimental slope of Fig. 4 to $10.2c^2$ one finds that the concentration of Fe atoms in ferromagnetic pairs is 3×10^{-3}. If one further assumes as Tholence and Tournier[9] that the number of antiferromagnetic and ferromagnetic pairs is equal, the concentration of paired Fe atoms is then 6×10^{-3}. It is therefore possible that an appreciable fraction of the spins (up to 4×10^{-3}) remains unpaired. Indeed, the scatter present at high temperatures ($T>15$ °K) in the data shown in Fig. 4 does not exclude a line of lower slope, which would correspond to a higher T_K and therefore to the presence of isolated spins. This could also mean that the remaining Fe atoms (4×10^{-3}) are gathered in microscopic clusters undetectable by susceptibility measurements. On the other hand it is equally possible that at such large concentrations the number of antiferromagnetic pairs becomes larger than the number of ferromagnetic pairs and that actually all the Fe atoms in the 1% alloy are paired up. At any rate, the fact that most if not all Fe atoms are paired explains why some spin depairing was observed in the proximity effect with the $Cu_{0.99}Fe_{0.01}$ film deposited at room temperature (Fig. 7 of Ref. 8). The large scatter in Fig. 4 and in the pair-susceptibility data of Tholence and Tournier[9] only establishes that $0<T_K<5$ °K. However, as compared to $T_K=29$ °K for isolated impurities, this will still imply a less complete compensation in the 1–7 °K range. The proximity effect with films deposited at 200 °C and above showed almost complete compensation. This could be explained by the fact that a large amount of clustering takes place in such films and the lower concentration of Fe in solid solution could give rise to a greater single-impurity contribution and thus to a higher T_K.

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