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High-temperature susceptibility of the *Cu*Mn spin-glass

A. F. J. Morgownik and J. A. Mydosh
Kamerlingh Onnes Laboratorium der Rijks-Universiteit, Leiden, The Netherlands

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We have measured the static susceptibility χ of a series of *Cu*Mn spin-glass alloys with concentrations 1 to 6 at.% Mn in the temperature range 4 to 300 K. A sensitive pendulum magnetometer was used with external fields up to 6000 G (0.6 T). For temperatures above $5T_f$ (T_f is the freezing temperature), a Curie-Weiss law is obeyed with an effective Bohr magneton number $p_0 = (5.07 \pm 0.10)\mu_B$ which is, within 2%, independent of concentration, and a paramagnetic Curie temperature Θ which is a strong, linear function of the concentration. Below $5T_f$ there are deviations, which increase with decreasing temperature, in the susceptibility from the Curie-Weiss law. We analyze these deviations by means of the temperature derivative of the inverse measured susceptibility, a quantity which becomes very large near T_f. This behavior demonstrates that short-range ferromagnetic correlations and fluctuations exist among the Mn spins far above T_f and further that these interactions are a precursor of the cooperative freezing at T_f. Our results illustrate the need for a new theoretical approach to describe spin-glass freezing.

I. INTRODUCTION

The temperature dependence of the susceptibility of a dilute magnetic alloy has once again become an important parameter for characterizing the magnetic behavior of such systems. This time it is with respect to the susceptibility χ above the freezing temperature T_f in spin-glass alloys, as for example *Cu*Mn and *Au*Fe. For many years there have been studies of $\chi(T)$ in the dilute Mn or Fe concentration limit regarding the effective magnetic moment (or spin) in a metal.[1,2] In addition significant deviations exist from a simple Curie law when Kondo effects[3] are present and when interactions manifest themselves at low temperatures.[2] More recently the sharp cusp in the susceptibility at T_f of the strongly interacting spin-glass alloys[4,5] has generated an enormous amount of experimental and theoretical activity in attempting to understand the nature of the spin-glass state[6] at and below T_f. However, less attention has been given to the question of high-temperature ($T >> T_f$) correlations between the moments and the evolution of the spin-glass state as the temperature is reduced to T_f. Beck, in a series of papers,[7] has measured the Faraday susceptibility $\chi(T)$ and the magnetization $M(H,T)$ (via a Foner method) as a function of applied magnetic field H for some higher concentration, $c \geqslant 9$ at.% Mn, *Cu*Mn alloys. By applying a Brillouin function analysis,[8] he concluded that at $T >> T_f$ there was a gradual evolution of ferromagnetic clusters with very large effective moments and an effective cluster concentration which decreased with decreasing temperature. The $\chi(T)$ reflected this behavior with a Curie-Weiss dependence at high temperatures, $\chi(T) = C/(T-\Theta)$, for which $\Theta > 0$. At lower temperatures, as $T \rightarrow T_f$, there were strong deviations from Curie-Weiss behavior which were associated with the development of this short-range ferromagnetic order. In contrast to these results, Nagata *et al.*[9] used a very sensitive low-dc (5 G)-field, magnetic-susceptibility superconducting quantum interference device (SQUID) to determine the $\chi(T)$ behavior for *Cu*Mn with 1 and 2 at.% Mn up to 50 K. From just above T_f (9.9 and 14.7 K, respectively), and until their maximum temperature (50 K) the data obeyed a simple Curie law ($\chi = C/T$ and $\Theta = 0$). Such a fit, giving an effective Bohr magneton number $p_0 = 4.8\mu_B$, was taken as strong support for the Edwards-Anderson phase-transition theory,[10] since this theory predicts $\chi(T) = (C/T)[1-Q(T)]$ where $Q(T)$ is the Edward-Anderson order parameter, which is zero for $T > T_f$.

In order to describe the nature of the spin-glass freezing at T_f and the unusual magnetic properties for $T < T_f$, it is essential to comprehend the spin-glass behavior far above T_f. This is especially true now that compelling experimental evidence of various sorts[11] is available which indicates the existence of short-range magnetic correlations for $T >> T_f$. Any viable theory must take into account these noncooperative superparamagneticlike effects and their influence on spin-glass freezing. Thus, measurements which can clarify the high-temperature experimental situation should be of particular significance in guiding the proper theoretical treatment of both the freezing and the frozen state.

We have performed a series of systematic and sensitive pendulum magnetometer measurements on five concentrations of Mn in the Cu host, an archetypal spin-glass. Our chosen concentrations were from 1 to 6 at.% Mn, a regime where spin-glass effects are clearly visible and the metallurgical difficulties minimal compared to higher concentrations. The available temperature range was 4 to 300 K thereby reaching 10 to 30 times the various T_f. The susceptibility data exhibit high-temperature deviations from the Curie-Weiss law, and the temperature at which these deviations occur are correlated to the freezing temperature for the different concentrations. By analyzing the effective Mn moments and the paramagnetic Curie temperature Θ we find definite evidence for magnetic interactions far above T_f and we can follow the temperature evolution of these ferromagnetic clusters down to T_f. A phenomenological model for the spin-glass freezing is suggested which, it is hoped, will lead to a full mathematical description of these effects.

II. EXPERIMENTAL DESCRIPTION

In the present experiments *Cu*Mn alloys have been studied in the concentration range from 1 to 6 at.% Mn. The samples were made by melting the two components under 2 atm of argon with 5% hydrogen gas in a high-frequency induction furnace. A quartz crucible was used and the melt was maintained above the alloy melting point for about 15 min at a temperature of 1150 °C. The solidified ingots were then turned over in the crucible and melted again to ensure homogeneity. The final ingots were shaped into the form of cylinders by means of spark erosion. After these preparations the samples were annealed for 2 h at 950 °C to eliminated dendritic concentration gradients which may occur due to the sluggish diffusion during the solidification process.[12] The samples are then slowly furnace cooled to room temperature with an exponential cooling rate and a decay constant of 400 sec. After the measurements we have given one of the samples (see Table I) a different heat treatment in order to check if a possible atomic short-range order could influence the magnetic behavior. This different heat treatment consists of a renewed anneal at 900 °C followed by quenching into water. The exact Mn concentrations were determined by spectrophotometric analysis and are listed in Table I.

The static susceptibility was measured with a pendulum magnetometer. The magnetic field gradient required by this method is produced by spherical poleshoes of an electromagnet. In this method the symmetric field gradient produces a force on the sample which is determined by measuring the change in oscillation frequency of the pendulum on which the sample is attached. Typical frequencies ranged from 0.7 to 1.2 Hz. The frequencies were measured with an accuracy of 2×10^{-5} Hz by means of an optic-electronic counter. The measurements were usually performed in a field of 6000 G (0.6 T). The field inhomogeneities due to the required field gradient for this type of measurement are very small ($\Delta H = 6$ G) and can be neglected to within an accuracy of 0.1%. Two of the samples were additionally measured in fields of ≈ 1000 to 7500 G (0.1 and 0.75 T). Data were taken at 150 different temperatures to cover the range from 4.2 to 300 K. The temperature was measured with a calibrated Au-0.03 at.% Fe versus Chromel thermocouple. The absolute value of the magnetization is determined through calibration with the standard paramagnet, $Mn(NH_4)_2(SO_4)_2 \cdot 6H_2O$, and with a magnetically soft Fe specimen. The accuracy of the calibration is 1% but the relative accuracy in comparing the measurements of a sample at different temperatures is always better than 0.2% depending upon the strength of the force on the sample. All measurements are corrected for the weak di-

TABLE I. Summary of the metallurgical and susceptibility properties of the *Cu*Mn alloys. "*A*" refers to the slow-cooled samples and "*B*" refers to the quenched samples (see Sec. II). T_f are literature values obtained from the susceptibility cusp.

Nominal c (at.% Mn)	Analyzed c (at.% Mn)	Heat treatment	p_0 (μ_B)	Θ (K)	T_d (K)	T_f (K)	T_f/T_d
1	1.03	*A*	5.16	3.8	51	10.0	0.20
2	2.08	*A*	5.06	14.1	80	16.2	0.20
2	2.08	*B*	5.06	17.6	96	16.2	0.17
3	2.96	*A*	5.19	25.2	106	20.2	0.19
4	4.04	*A*	5.04	34.2	130	24.5	0.19
6	5.94	*A*	4.90	55.0	160	31.9	0.20

amagnetism of the host material (Cu) by subtracting this contribution from the alloy susceptibility.

III. EXPERIMENTAL RESULTS

The susceptibility of the *Cu*Mn alloys exhibits deviations from Curie-Weiss behavior [$\chi^{\mathrm{CW}} = C/(T-\Theta)$] at relatively high temperatures as is shown in Fig. 1, where the reciprocal susceptibility is plotted as a function of temperature for the different Mn concentrations. The data in Fig. 1 are all from measurements with an external field of 6000 G. When extracting the effective Bohr magneton number p_0 and in particular the paramagnetic Curie temperature Θ from the measurements, one should take extreme care that the temperature is high enough to establish Curie-Weiss behavior completely. As we will show in the following analysis there exists a characteristic temperature T_d which marks the onset of these deviations from Curie-Weiss behavior. T_d is as large as 5 times the freezing temperature T_f (see Table I).

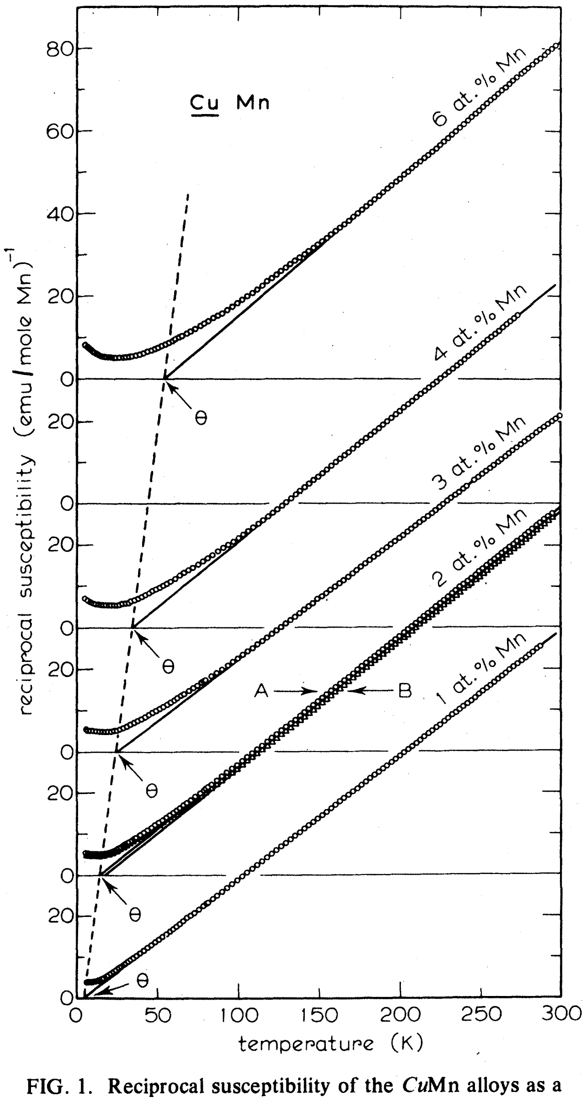

FIG. 1. Reciprocal susceptibility of the *Cu*Mn alloys as a function of temperature. The dashed line connects the intercepts (paramagnetic Curie temperature Θ) of the high-temperature extrapolation (solid line) for the slow-cooled samples. The "*A*" (slow cooled) and "*B*" (quenched) refer to the different heat treatments of the 2 at.% Mn sample (see Sec. II).

The experimental results given in Fig. 1 are analyzed by computer fitting procedure that searchs for Curie-Weiss behavior of the susceptibility within the accuracy of our measurements (0.2%). The derivative of the reciprocal susceptibility with respect to the temperature at a given T_i is calculated by fitting $\chi^{-1}(T_j)$ from T_{i-5} to T_{i+5}, where the $\chi^{-1}(T_j)$ are equidistant measured points. $P(T)$ is then defined as

$$P(T) \equiv \left[\frac{N\mu_B^2}{3k_B}\right]^{-1/2} \left[\frac{d}{dT}(\chi^{-1})\right]^{-1/2} . \tag{1}$$

Here k_B is the Boltzmann constant, μ_B the Bohr magneton number, and N the number of magnetic (Mn) ions. In the case of a Curie-Weiss behavior $P(T)$ is simply the usual effective Bohr magneton number p_0

$$P(T \rightarrow \infty) = p_0 = g[J(J+1)]^{1/2} , \tag{2}$$

where g is the Landé g factor and J the total angular momentum quantum number. $P(T)$, as defined in Eq. (1), is plotted in Fig. 2 as a function of temperature for the various Mn concentrations. T_d is then defined as the temperature below which the susceptibility deviates more than the experimental scattering from a high-temperature Curie-Weiss fit (see insert in Fig. 2). $P(T)$ is constant above T_d, while for temperatures below T_d, $P(T)$ gradually increases with decreasing temperature. However, at temperatures near the maximum of the susceptibility ($T < 2T_f$) $P(T)$ is strongly increasing and becomes field dependent. In Fig. 3 we have plotted the uninverted values of the $\chi(T)$ data for the 4 at.% Mn in comparison with the Curie-Weiss extrapolation showing that at $2T_f(\approx 50$ K) the susceptibility is twice as small as the Curie-Weiss law. Also the field dependence of the susceptibility near T_f is shown in Fig. 3 for fields of 2000 and 5000 G. For the 6 at.% Mn alloy we have varied the external field from 1000 G to 7500 G, the limits of our technique. While there is more scatter in the χ data at low fields, no field dependences were observed for $T > 2T_f$ in χ^{-1} vs T. In addition we have compared our χ measurements with the ac susceptibility measurements of Mulder *et al.*[5] performed in fields of ≈ 1 G on *Cu*Mn alloys of 1 and 2 at.% Mn. A good overall agreement of these two different χ experiments in 1 and 6000 G exists when χ^{-1} is plotted against T until the region about T_f, i.e., $T < 2T_f$.

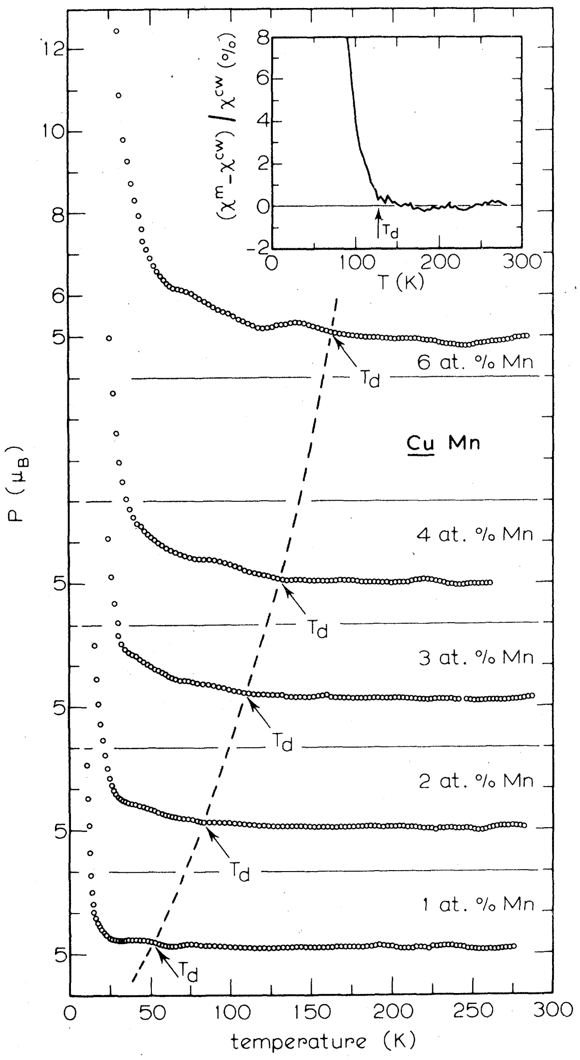

FIG. 2. P as a function of temperature. T_d indicates the deviation from Curie-Weiss behavior $[\chi^{CW}=C/(T-\Theta)]$. In the insert we have plotted the digression of the measured points (χ^m) from the high-temperature Curie-Weiss fit (χ^{CW}) for the 4 at.% Mn alloy.

At T_f the maximum of χ is reduced by the field of 6000 G by 9 to 17% compared to the 1-G data for the 2 and 1 at.% Mn alloys, respectively. See Ref. 5 for more about the field dependence of χ near T_f. In particular, the ac, 1 G, susceptibility data also show definite deviations from Curie behavior below 50 K as is demonstrated in Fig. 9 of Ref. 5. Furthermore, our determination of p_0, Θ, and T_d agree rather well with those obtained for 1 and 2 at.% Mn in Cu from the ac χ measurements in a 1-G field. Thus, based upon this comparison, we feel that our values of p_0, Θ, and T_D, all obtained at $T >> 2T_f$, are field-independent values.

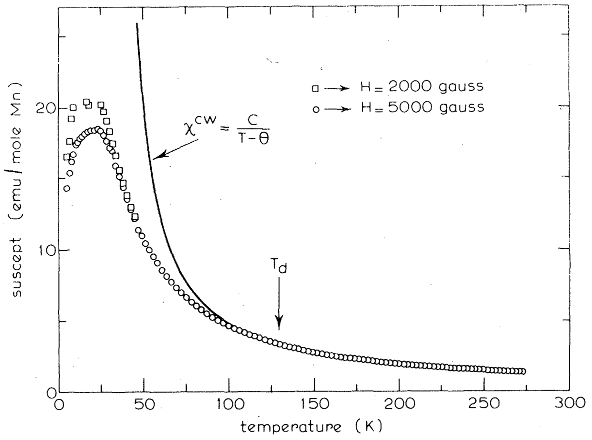

FIG. 3. Field dependence of the susceptibility of the 4 at.% Mn alloy as a function of temperature. The solid line represents the extrapolation of the high-temperature Curie-Weiss susceptibility with $\Theta=34$ K.

After determining T_d the effective Bohr magneton p_0 the paramagnetic Curie temperatures Θ are calculated from least-square fitting of all susceptibility data for temperatures above T_d. In Fig. 4 p_0 and Θ are plotted as a function of concentration. Θ shows a linear dependence upon concentration c between 1 and 6 at.% Mn

$$\Theta=-6.9+(10.4)c \ . \tag{3}$$

Note that the extrapolation of this linear dependence to zero concentration does not go through zero,[13] as

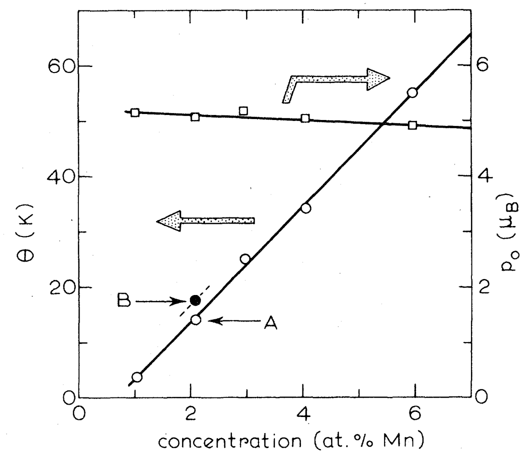

FIG. 4. Effective Bohr magneton number p_0 and the paramagnetic Curie temperature Θ as a function of concentration. p_0 and Θ are determined from least-squares fitting of the susceptibility for temperatures above T_d. The "A" and "B" mark the values for the slow cooled and the quenched 2 at.% Mn sample. All other values are for slow-cooled samples.

is expected for an alloy which has no atomic short-range order. Although atomic order is probably small for low-concentration *Cu*Mn alloys,[15] we have found a small increase in Θ ($\Delta\Theta = 3.5$ K) when we reduce the atomic short-range order by quenching the sample. In Fig. 4 the Θ obtained for the quenched sample is marked by "*B*," while the other paramagnetic Curie temperatures are obtained for the slow-cooled "*A*" samples (see also Fig. 1 and Table I). p_0 is unaffected by these two different heat treatments. The value of p_0 is nearly independent of concentration, ranging from 4.90 to $5.16\mu_B$ for concentrations varying from 6 to 1 at.% Mn. In order to consistently explain this value of p_0 we have taken $g = 2$, $S = 2$, and $L = 0$.[9,14–16]

It is interesting to note that outside the CW regime the increase of $P(T)$ with decreasing temperature is relative large for the 6 at.% Mn alloy, where $\Theta = 55$ K, and minimal for the 1 at.% Mn, where Θ is approaching zero ($\Theta = 3.8$ K). This suggests that the appearance of short-range ferromagnetic order is a precursor to the lower-temperature spin-glass freezing at T_f. Ferromagnetic clusters could gradually be formed, giving rise to $P(T)$, when the temperature is lowered from T_d. We are presently attempting to develop a model which takes into account these short-range correlations by using a cannonical ensemble for all possible magnetic states of the first 11 configurations in which magnetic impurities can be grouped in an fcc lattice. In order to explain the susceptibility behavior observed here, this "cluster" model requires ferromagnetic first- and second-nearest-neighbor interactions of 50 and 20 K, respectively.[16]

A summary of the metallurgical and susceptibility properties of the *Cu*Mn alloys is given in Table I. The two different heat treatments of the 2 at.% Mn sample do not have an effect on the value of $p_0(5.06\mu_B)$, but do affect the value of T_d, indicating that magnetic clusters are formed at a higher temperature for the quenched sample. This interpretation is consistent with the higher Θ which is found for the quenched sample and hence a stronger ferromagnetic, short-range interaction is present. We have also listed in Table I the quotient of the freezing temperature T_f and the previously defined T_d, showing scaling of T_d with respect to T_f. The scaling factor is found to be about 0.20 for the slow-cooled samples.

IV. CONCLUSIONS

For temperatures below $T_d(\approx 5T_f)$ there are deviations, which increase with decreasing T, in the susceptibility from the Curie-Weiss law (see Fig. 1). This behavior demonstrates that short-range correlations and fluctuations exist among the Mn spins and these interactions are a precursor to the cooperative freezing at T_f. The $P(T)$, as defined from our susceptibility data analysis, rapidly increase as T_f is approached from above (see Fig. 2). This indicates that the correlations are becoming stronger and lead to the formation of ferromagnetic clusters at $T \rightarrow T_f$. Further evidence for a net ferromagnetic exchange in these alloys comes from the high-temperature susceptibility where the Curie-Weiss law is obeyed. Here the linear extrapolation of the χ data results in a positive (ferromagnetic) Θ which increases linearly with the concentration (see Fig. 4). It should be noted that $\Theta(c)$ increases more strongly with concentration than $T_f(c)$. Also at these high temperatures, the effective Bohr magneton number p_0 is nearly independent of the Mn concentration and has a mean value of $5.07\mu_B$ which is consistent with $g = 2$, $S = 2$, and $L = 0$. The field dependence of $\chi(T)$ depicted in Fig. 3, occurs only near T_f and there are no field-dependent effects in the region around T_d. The behavior of $\chi(T)$ in an external field has been discussed in a previous paper.[5] The main effect of varying the heat treatment of these *Cu*Mn samples has been to increase Θ and T_d by quickly quenching the samples, thereby introducing more ferromagnetic exchange into the system. From previous measurements in *Cu*Mn,[5] T_f is unaffected by heat treatment and here we observe no change in p_0.

From the relative strong deviations from Curie-Weiss law and the high values of T_d we expect a broad spectrum of interaction strengths and that, at a given temperature, a part of this interaction spectrum is too small compared with k_BT to establish magnetic coupling. This part of the spin system will therefore remain noninteracting or paramagnetic. The other part of the spectrum, containing the stronger interactions, will, in spite of the disordering effect of the temperature, couple various groups of spins together. We expect that at temperatures above T_d the disordering effect of temperature will be large enough to prevent most spins from coupling. The dominant type of interaction in the above-mentioned spectrum will be ferromagnetic, as we have concluded from our measurements, namely, a positive Θ increasing from 3.8 to 55 K for the concentration range of 1 to 6 at.% Mn. When the temperature is lowered from T_d the dominant ferromagnetic interactions will start to couple the nearest spins into ferromagnetic clusters. The coupling of these spins is felt in the behavior of the susceptibility and deviation from the Curie-Weiss law will occur. In the present study we have carefully measured these deviations and found that the onset of these deviations occurs at a temperature, defined as T_d, which is correlated to the freezing temperature ($T_d \approx 5T_f$). A mathematical description of the susceptibility, in the case where all clusters are already formed (static clusters), has been proposed by Eiselt *et al.*[17] for the $Eu_xSr_{1-x}S$ system

$$\chi T \propto \sum_k m_k^2 n_k(c)\left[\frac{1}{1+0.05m_k^2c^2/T^2}\right] . \tag{4}$$

The susceptibility here is formed by a summation over n_k clusters of configuration k with an effective moment m_k. The last factor in Eq. (4) represents the effect of the (dipolar) interactions between the clusters of type k. The value of all parameters in Eq. (4) can be calculated, assuming only that the ratio between a nearest-neighbor ferromagnetic coupling and a next-nearest-neighbor antiferromagnetic coupling is equal to 2.[17] However, in our temperature range the different types of clusters are gradually formed (dynamical clusters) when the temperature is lowered from T_d. Therefore the number of type k clusters is not only concentration dependent as in Eq. (4) but also temperature dependent: $n_k(c,E_k/k_BT)$, where E_k is a function of all bonds which take part in the configuration of the cluster type k. So this model calculation must be extended to include the evolution and growth of spin correlations and the resulting cluster formation before it can be applied to our case of *Cu*Mn.

The results of our experiments suggest that the spin correlations far above T_f are very important and must be considered in any theoretical description of the spin-glass freezing. For, it is the development of these correlations and clusters which generate the spin-glass state. At present there is little theoretical guidance to describe the high-temperature susceptibility of a spin-glass. The available theories do not treat a dynamical cluster growth process, at best they focus upon the freezing of already existing clusters at T_f. Nevertheless the concept of dynamically evolving clusters is implicit in the magnetic cluster-percolation models.[18] Here the cusp in χ at T_f occurs when an infinite cluster of randomly frozen spins is generated. The dynamics appear through a competition between intracluster interactions, intercluster interactions, and the disordering effect of temperature. However, this magnetic percolation model is presently only able to give a qualitative description of the spin-glass freezing. It needs to be quantified and fully tested with experiment, also for $T >> T_f$. We are presently considering a dynamical cluster model along these lines.[16]

Another theoretical approach is to create a new form of nonequilibrium critical phenomenon which is time dependent over a wide temperature range surrounding T_f. Such a dynamical theory, with a time-dependent order parameter, would treat a metastable type of phase transition and would be able to trace the behavior of the interacting spins from the onset of correlations through the freezing temperature and into the region of low-temperature excitations.

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