Magnetic resonance of the insulating spin-glass spinel solid solution $CdCr_{2x}In_{2-2x}S_4$ $(0.25 \leq x \leq 0.85)$

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A microwave resonance study has been performed in the temperature range $4.2 \leq T \leq 300$ K on the system $CdCr_{2x}In_{2-2x}S_4$ in the spin-glass region $(0.25 \leq x \leq 0.85)$. The low-temperature line broadening and the down shift of the resonant field are better interpreted in terms of topological arguments rather than on the basis of a critical-dynamics model. Evidence of ferromagnetic short-range correlations in the spin-glass phase is presented.

I. INTRODUCTION

A common feature of magnetic resonance studies on metallic[1] and the insulating[2] spin-glass systems is the linewidth increase and low-field shift of the resonance line on approaching the freezing temperature T_f. Two models[3,4] have been proposed to explain these phenomena. In the former[3] the increase of the linewidth is attributed to a broadening from a distribution of internal fields and the line shift is assumed to arise from dipolar anisotropic fields. In the latter[4] the line broadening as well as the shift originate, in the limit of the exchange-narrowing model, from a slowing down of the spins-relaxation rate on approaching T_f. Salamon's predictions[4] have been supposed valid in a limited temperature range in some metallic spin-glasses,[5,6] while they have been considered inadequate to explain the observed properties in $Eu_{0.4}Sr_{0.6}S$ (Ref. 7) and $Gd_{0.06}La_{0.94}Al_2$.[8]

In a preceding paper we have reported the electron-paramagnetic-resonance (EPR) behavior of the insulating spin-glass $CdCr_{1.6}In_{0.4}S_4$, for which an inapplicability of Salamon's model was suggested because of the failure of the exchange-narrowing model well above T_f.[9] We report here a microwave resonance study of the solid solution $CdCr_{2x}In_{2-2x}S_4$ in the spin-glass region $(0.25 \leq x \leq 0.85)$, and we show the properties are a function of the composition x and can be related to the magnetic homogeneity of the system.

II. EXPERIMENTAL

Sample preparation is reported elsewhere.[10] The EPR spectra of polycrystalline specimens have been recorded at $\nu = 9230$ MHz in the temperature range $4.2 \leq T \leq 300$ K using a Varian E9 spectrometer with an Oxford continuous-flow cryostat (ESR9). The temperature was measured with an Au plus 0.03 at.% iron-versus-Chromel thermocouple positioned in the helium flow path just below the samples. The field was measured by a Bruker NM-20 Gaussimeter and the frequency by a Sistron Donner (Model 6246A) counter. EPR experiments were carried out after zero-field cooling of the samples.

III. RESULTS AND DISCUSSION

A. Magnetic properties of the system $CdCr_{2x}In_{2-2x}S_4$

The pure $CdCr_2S_4$ spinel has a normal structure with the Cd^{2+} ions in tetrahedral (A) sites and the trivalent chromium ions in octahedral (B) sites. As found by Baltzer *et al.*[11] $CdCr_2S_4$ is a ferromagnet ($T_c = 84$ K; $\Theta = 152$ K). The interactions with the six nearest-neighbor Cr^{3+} ions (through overlap of d_{xy} orbitals at right angles via the intermediate sulfur ion) are ferromagnetic ($J_1/k = 11.8$ K), while the interactions with 30 more distant neighbors are weaker and antiferromagnetic ($J_2/k = -0.33$ K)

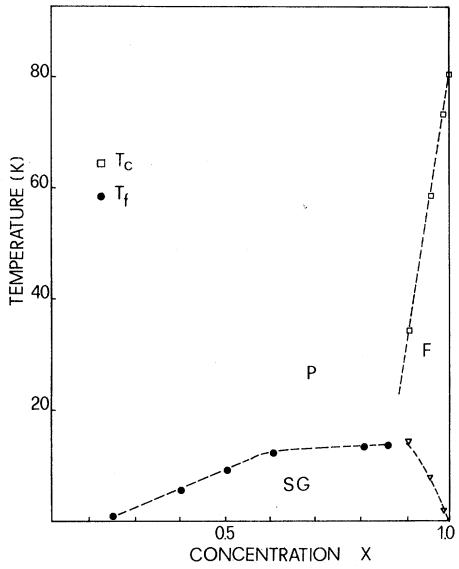

FIG. 1. Magnetic phase diagram of $CdCr_{2x}In_{2-2x}S_4$ (from Ref. 14).

(Ref. 11). On introducing nonmagnetic In^{3+} ions, the chromium ions are always in B sites in the whole range of composition x.[12,13] The site occupancy of indium was shown to be a function of composition x.[13]

By dc and ac susceptibility measurements ($\nu=17$ Hz) the magnetic phase diagram shown in Fig. 1 has been established.[14] Particularly, the insertion of nonmagnetic ions first produces a sharp decrease of T_c, and the ferromagnetic phase disappears well above the nearest-neighbor percolation threshold p_c ($p_c=0.401$) calculated by Monte Carlo simulations for the octahedral spinel sublattice.[15] In the composition range $0.25 \leq x \leq 0.85$ the system shows magnetic properties characteristic of a spin-glass phase.

Generally speaking the spin-glass phenomenon results from bond frustration. While in metallic spin-glasses the character of the frustration is related to the oscillatory form of Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions; in the insulating $CdCr_{2x}In_{2-2x}S_4$ system it arises from the simultaneous presence and competition between ferromagnetic and antiferromagnetic interactions. This paper deals with an EPR study of the spin-glass phase only; the investigations on the ferromagnetic samples will be reported elsewhere.[16]

B. Temperature dependence of the linewidth

For all the samples studied, the room-temperature EPR signal consists of a strong

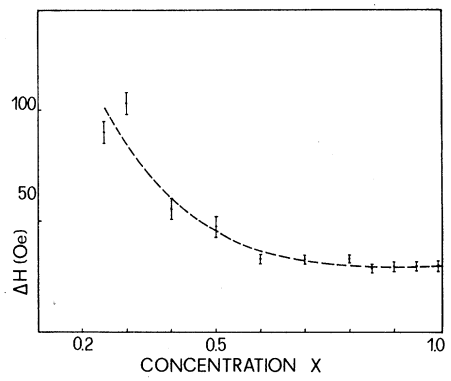

FIG. 2. Concentration dependence of ΔH (half-power half-width of the EPR signal).

symmetrical absorption with $g=1.99$; a value very close to that found for isolated Cr^{3+} ions in $CdIn_2S_4$ single crystals.[17] The line shape is strictly Lorentzian and this spectrum can be attributed to large clusters of chromium ions coupled by exchange.

A study of the temperature dependence of the peak-to-peak linewidth ΔH_{pp} has shown that the linewidth reaches a constant value above $T \simeq 200$ K, and therefore it seems justified to apply at T_{room} the high-temperature theories of the exchange-narrowed spectra.[18,19] The concentration dependence of

$$\Delta H=(3^{1/2}/2)\Delta H_{pp}$$

is reported in Fig. 2. Following Kittel and Abrahams[20] in a solid solution

$$\Delta H(x)=\Delta H(1)x^{1/2},$$

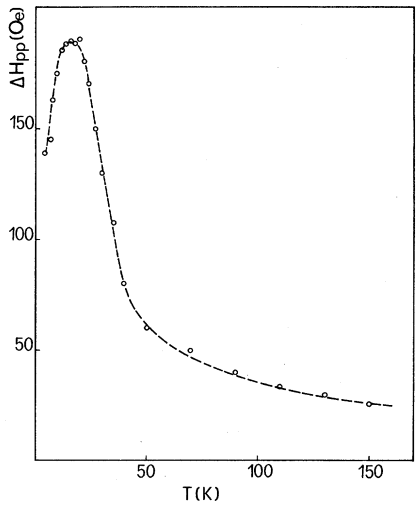

FIG. 3. Temperature dependence of ΔH_{pp} (peak-to-peak linewidth) for $x=0.60$.

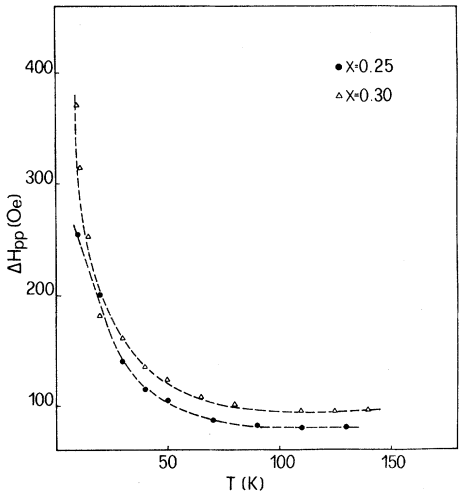

FIG. 4. Temperature dependence of ΔH_{pp} for $x=0.25$ and 0.30.

where $\Delta H(1)$ is the half-power half-width of the absorption in the pure compound $CdCr_2S_4$. It can be seen that in $CdCr_{2x}In_{2-2x}S_4$ system (Fig. 2) the $x^{1/2}$ law is not followed. The disagreement may arise from a diminution, with decrease in the concentration x, of the effective number of Cr^{3+} ions coupled by exchange. An alternative explanation is offered from the observed slight increase of ΔH_{pp} (above $T\simeq 200$ K) for the more diluted samples: It is probably due to spin-lattice relaxation of fast relaxing impurities (Cr^{2+} and/or Cr^{4+}) originated by slight deviations from the stoichiometry.

Below $T\simeq 200$ K ΔH_{pp} begins to increase for all the compositions x studied; a rounded maximum has been found in the region of T_f for $0.50\leq x\leq 0.85$, and below T_f the linewidth decreases continuously down to $T=4.2$ K. A typical behavior is reported in Fig. 3. For the compositions $0.25\leq x\leq 0.40$ the study of the linewidth has been performed down to $T\simeq 10$ K (Fig. 4), below which several signals develop, preventing accurate determinations of ΔH_{pp} and of the resonant field $H_{\rm res}$ shift. As the linewidth and the line-shape behavior is strongly dependent on the chromium concentration for $T<200$ K, we will discuss the experimental data as a function of the composition x.

1. $0.70\leq x\leq 0.85$

In the range $110\leq T\leq 180$ K we observe a slight line broadening. An analysis of the line shape has been performed considering the analytical expressions of the first derivative for a Gaussian and a Lorentzian absorption line. For the Gaussian,

$$Y'=1.649\,Y'_m\left[\frac{2(H-H_0)}{\Delta H_{pp}}\right]\times\exp\left[-\frac{1}{2}\left[\frac{2(H-H_0)}{\Delta H_{pp}}\right]^2\right], \quad (1)$$

and for the Lorentzian,

$$Y'=\frac{16\,Y'_m\left[\frac{2(H-H_0)}{\Delta H_{pp}}\right]}{\left[3+\left[\frac{2(H-H_0)}{\Delta H_{pp}}\right]^2\right]^2}, \quad (2)$$

where Y'_m denotes the maximum amplitude, H_0 is the field at the center of the line, and Y' is the amplitude at field H.

The experimental results show that down to $T=110$ K the line shape remains Lorentzian and, following the critical dynamics model,[4] we have calculated the relaxation rate τ^{-1}, in the range $110\leq T\leq 300$ K, from the equation

$$\gamma\Delta H=\chi_T^{-1}\omega_d^2\tau, \quad (3)$$

where χ_T is the magnetic susceptibility determined at $H=3$ kOe, γ is the gyromagnetic ratio, and ω_d is the dipolar frequency $\gamma g\mu_B S r^{-3}$ for two Cr^{3+} ion separated by $r=3.7$ Å. The results indicate that the criterion $\omega_0\tau\ll 1$ is valid in this temperature range and, therefore, the observed slight increase of ΔH_{pp} can be attributed to a slowing down of the fluctuations.

Below $T\simeq 100$ K the linewidth increases more rapidly as the temperature decreases, and a progressive deviation from a Lorentzian towards a Gauss-

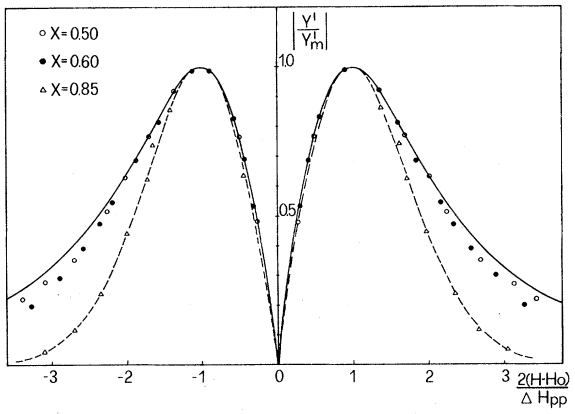

FIG. 5. Reduced amplitude $|Y'/Y'_m|$ vs $[2(H-H_0)/\Delta H_{pp}]$ at $T=4.2$ K; Lorentzian (——) and Gaussian (— — —) curves.

ian line is observed. At $T=4.2$ K the line is purely Gaussian for $x=0.85$ and 0.80, but not yet for $x=0.70$. These results are presented in Fig. 5, where the reduced amplitude

$$\left|\frac{Y'}{Y'_m}\right|$$

is plotted as a function of the ratio

$$\frac{2(H-H_0)}{\Delta H_{pp}}.$$

The progressive deviation towards a Gaussian curve for $T<100$ K indicates that the exchange narrowing breaks down well above T_f and, therefore, the observed increase of ΔH_{pp} ($T<100$ K) can be explained on the basis of topological arguments[3] rather than by dynamical effects.[4] The line broadening may originate from the presence, in samples close to the boundary region between the spin-glass and the ferromagnetic phase, of ferromagnetic internally strongly correlated clusters surrounded by a medium with more competing (ferromagnetic and antiferromagnetic) interactions. When weakly coupled with the medium, these magnetic regions give an inhomogeneously broadened line approaching Gaussian behavior and the observed resonance cannot be considered as a single resonance mode. A tendency to short-range ferromagnetic order has been observed in insulating[21] as well as metallic[3,22] concentrated spin-glasses.

In the vicinity of $T\sim 2T_f$ a slowing down of the ΔH_{pp} increase is observed, and this phenomenon may be related to a blocking of local fields, as reported for other insulating spin-glasses.[2,7] In the vicinity of T_f, a maximum in ΔH_{pp} is found.

2. $0.50 \leq x \leq 0.60$

On diluting the Cr^{3+} ion, the influence of the short-range order becomes progressively less important and a more "pure" spin-glass phase may be predicted. If in the system the exchange coupling is sufficiently strong, all the spins respond as a unit originating a Lorentzian line. This picture can explain the results for the samples $x=0.50$ and 0.60 (Fig. 5).

As the exchange-narrowing limit is valid in this case, an effective relaxation rate τ^{-1} can be calculated following Salamon,

$$\tau^{-1}=\frac{\gamma\Delta H}{\Delta g} \tag{4}$$

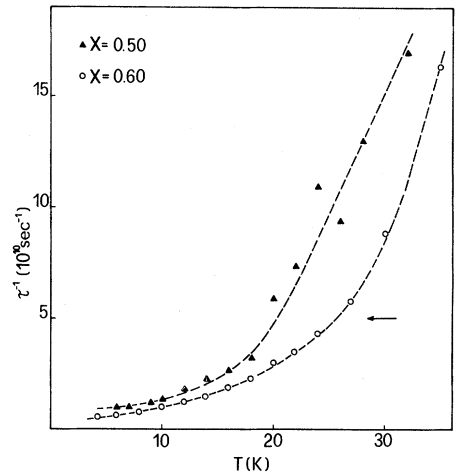

FIG. 6. Temperature dependence of the effective relaxation rate τ^{-1} for $x=0.50$ and 0.60. Arrow indicates the limit of the validity of the criterion $\omega_0\tau<1$.

where γ is the gyromagnetic ratio for the Cr^{3+} ion and Δg is the g shift from the paramagnetic value.

The temperature dependence of τ^{-1} is reported in Fig. 6, where an arrow indicates the value of the angular microwave frequency. According to Salamon, when the relaxation time becomes comparable to the measuring time, static dipolar fields would give rise to a Gaussian line and, therefore, the exchange-narrowing model should be invalid below

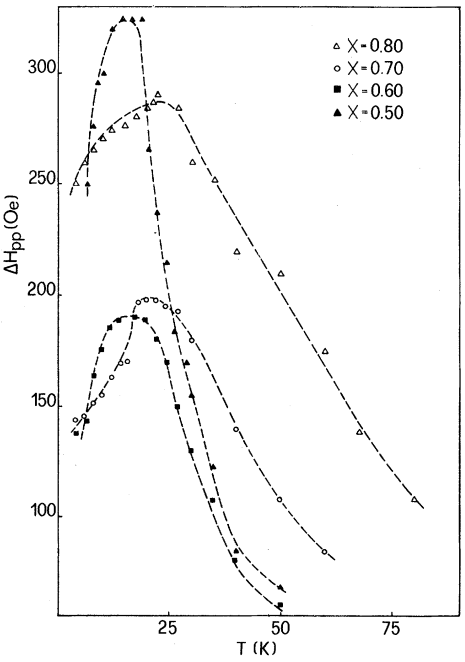

FIG. 7. Temperature dependence of ΔH_{pp} for $0.50\leq x\leq 0.80$. Results for $x=0.85$ are not reported for sake of clarity.

$T \sim 28$ and 22 K for $x = 0.60$ and 0.50, respectively (Fig. 6). This hypothesis is in disagreement with the experimental results (Fig. 5), indicating that, below T_f, the exchange coupling is still operating as found in the insulating spin-glass $Eu_{0.4}Sr_{0.6}S$.[7]

We tentatively propose an explanation of the maximum in ΔH_{pp} observed for $0.50 \leq x \leq 0.85$ (Fig. 7). Above T_f only superparamagnetic-type clusters, with distribution of relaxation times, block progressively. At $T = T_f$ the freezing process becomes collective and the relaxation modes of different clusters are no longer independent. The narrowing of the line below T_f could be due to a more efficient exchange coupling as a consequence of the cooperative nature of the freezing process. A study of the frequency dependence of T_f should permit us to clarify the characteristic of the freezing process (collective phenomenon or blocking of independent clusters).

Nevertheless, it must be remembered that the EPR experiments, performed at different frequencies on metallic spin-glasses, have shown a dramatic influence of the measuring frequency on the divergence of the linewidth near T_f.[8,23,24] This effect may be due to an influence of the applied field on the blocking of the fluctuations or to a different picked up part of the fluctuations spectra. Therefore, we believe that caution must be exercised in interpreting the linewidth behavior at only one measuring frequency.

3. $0.25 \leq x \leq 0.40$

For the sample $x = 0.40$[$T_f = 7$ K (10)] the line remains Lorentzian down to $T = 16$ K, below which an anisotropic signal appears. This anisotropy increases on decreasing the temperature although two well-separated signals are never observed. The situation becomes more complex for the more diluted samples ($x = 0.25$ and 0.30): On decreasing the temperature, several signals appear in the range $1 \leq H \leq 2$ kOe near the principal absorption centered at $H = 3315$ Oe (Fig. 8). This behavior is associated with the increased dilution of the magnetic ions and the low-field signals are perhaps due to small isolated clusters of Cr^{3+} ions. The presence of several independent resonance modes suggests an increased magnetic inhomogeneity of the system and prevents, therefore, an analysis of the line shape and of the relaxation time for these samples.

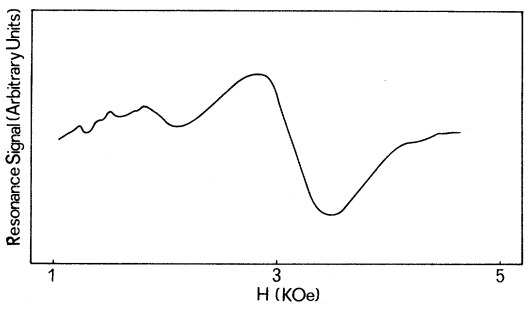

FIG. 8. EPR spectrum at $T = 4.2$ K for $x = 0.30$.

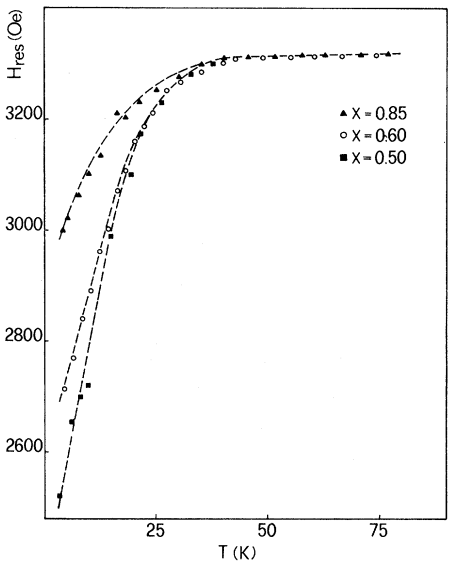

FIG. 9. Temperature dependence of the resonant field H_{res} ($\nu = 9320$ MHz).

C. Resonance field shift

On decreasing the temperature the resonant field H_{res} at $\nu = 9230$ MHz shifts to lower values (Fig. 9), and this shift can be related to the formation of internal fields in the system[3] or to a change of the g value.[4] As the critical dynamics model is not applicable in our case we suggest this shift originates

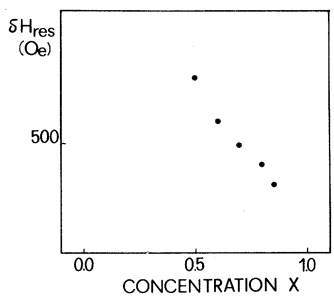

FIG. 10. Concentration dependence of $\delta H_{res} = H_{res(300\ K)} - H_{res(4.2\ K)}$.

from local fields. For all the compositions $0.50 \leq x \leq 0.85$, H_{res} begins to deviate from the paramagnetic value well above T_f indicating the presence of regions of internally strongly correlated clusters at $T \sim 3T_f$. The shift increases rapidly below $T \simeq 30$ K and is continuous down to $T = 4.2$ K without showing any anomalies at freezing temperature. In Fig. 10 we report the concentration dependence of the shift $\delta H = H_{res(300\ K)} - H_{res(4.2\ K)}$, showing it increases on decreasing the chromium concentration; i.e., moving away from the ferromagnetic region. These results are similar to those found in AuMn (Ref. 22) and GdAl (Ref. 3) alloys. Following Jamet and Malozemoff[3] the H_{res} shift arises from an anisotropy which is field induced and is related, in the limit of strong exchange coupling, to the magnetic inhomogeneity of the system. The H_{res} shift may therefore be considered as a probe of a transition from a "pure" spin-glass state to a spin-glass with strong ferromagnetic short-range correlations. If the exchange coupling is weak, the anisotropy (and consequently the shift of the resonant field) are reduced.

In our case the lower value of δH for compositions $0.70 \leq x \leq 0.85$ (Fig. 10) may be a consequence of the failure of a strong exchange model. For $x = 0.50$ and 0.60, for which the line remains Lorentzian, the hypothesis of an increasing inhomogeneity should be valid. These results lead us to suppose that in the sample $x = 0.85$ short-range ferromagnetic regions play an important role. On decreasing the chromium concentration, the probability of nearest-neighbor magnetic ions is reduced, the influence of ferromagnetic clusters become less important and a system with more competing ferromagnetic and antiferromagnetic interactions will be formed.

D. Temperature dependence of IT

In Figs. 11 and 12 the temperature dependence of the relative number of spins, IT (area of resonance times the temperature), is reported. In the range $200 \leq T \leq 300$ K the quantity IT is constant as expected for a well-behaved paramagnet without low-energy excited states and if $h\nu \ll kT$. Below $T \simeq 200$ K and for $0.50 \leq x \leq 0.85$, the product IT shows a rapid increase with a maximum at $55 \leq T \leq 75$ K and a subsequent decrease through T_f down to $T = 4.2$ K.

This behavior can be explained as follows: Regions of spins become correlated at relatively high temperature and the rapid increase of IT is attributed to the formation of clusters bearing giant moments (due to chromium-chromium ferromagnetic nearest-neighbor interactions) causing an apparent increase in the relative number of spins. Decreasing the temperature, such magnetic regions evolve in size as more distant spins become correlated, originating clusters where ferromagnetic and antiferromagnetic correlations are present. The simultaneous presence and competition between these interactions will originate a random distribution of the spin directions and, consequently, a decrease of the magnetization with respect to the temperature range where ferromagnetic correlation predominate.

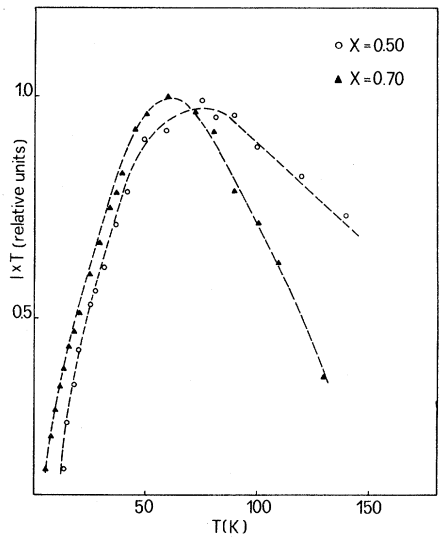

FIG. 11. Temperature dependence of the product IT (area of resonance times the temperature).

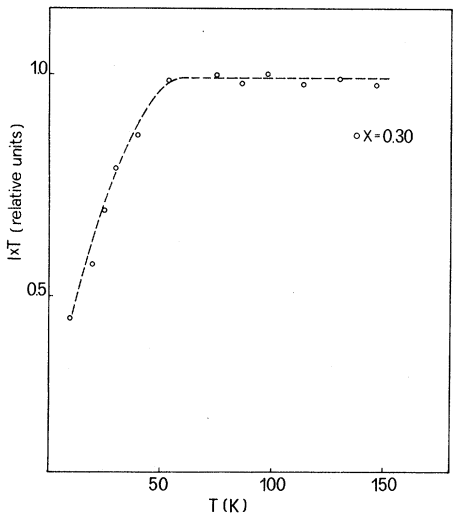

FIG. 12. Temperature dependence of the product IT for $x = 0.30$.

The decreased relative importance of the ferromagnetic with respect to the antiferromagnetic contributions, diluting the Cr^{3+} ion, may be inferred from the shift of the maximum of IT from $T=55\pm5$ K for $x=0.85$ to $T=75\pm5$ K for $x=0.50$ (Fig. 11) and from the disappearance of a significant increase in the relative number of spins for $x=0.30$ (Fig. 12).

The continuous decrease of IT at lower temperatures (Figs. 11 and 12) cannot be related, in our opinion, to the intervening antiferromagnetic correlations only, but it may reflect the freezing of the magnetization in random directions when the relaxation time τ of the clusters becomes comparable with the measurement time.

IV. CONCLUSIONS

The low-temperature EPR properties (line broadening, line shape, H_{res} shift) of the spin-glass phase in the system $CdCr_{2x}In_{2-2x}S_4$ are a function of the composition x. The line broadening below $T=100$ K for the more concentrated samples ($0.70\leq x\leq0.85$) is related to the appearance of several resonance modes precessing independently. The high concentration of magnetic Cr^{3+} ions may be at the origin of the observed phenomenon: Ferromagnetic internally correlated clusters should be present and weakly coupled to a matrix with competing magnetic interactions.

On diluting the Cr^{3+} ions, the short-range effects are progressively reduced and the exchange-coupled part of the system becomes predominant originating in a Lorentzian line shape ($x=0.50$ and 0.60). The EPR spectra of more diluted samples ($0.25\leq x\leq0.30$) show the appearance of several signals (probably associated with the formation of small isolated clusters) reflecting an increased magnetic inhomogeneity with increasing chromium dilution.

The down-field shift of the resonance line can be interpreted in terms of Jamet and Malozemoff's model[3] as arising from the presence of local demagnetizing fields. The low-temperature line broadening and H_{res} shift are, therefore, better interpreted in terms of topological arguments rather than of the critical-dynamics model. This does not necessarily imply a general invalidity of Salamon's predictions, as the inapplicability of that assumption may be a consequence of the relatively high concentrations of magnetic ions originating local order.

In conclusion, the spin-glass phase cannot be regarded as having the same characteristics within the range $0.25\leq x\leq0.85$: Increasing the chromium concentration, short-range effects (presumably ferromagnetic) become progressively important with respect to an exchange-coupled medium with competing magnetic interactions. The study of the temperature dependence of IT gives indications of the contemporaneous presence and relative importance of ferromagnetic and antiferromagnetic interactions, which are responsible for the spin-glass behavior in $CdCr_{2x}In_{2-2x}S_4$ solid solution.

ACKNOWLEDGMENT

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