Electron-spin resonance in the spin-glass-like system $Fe_{1-x}Ga_xSbO_4$

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We report ESR measurements in the spin-glass-like system $Fe_{1-x}Ga_xSbO_4$ for $0 \leq x \leq 0.8$. A single broad line associated with the resonance of Fe^{3+} is observed at $g = 2.00(5)$. The temperature dependence of the ESR linewidth shows two different regimes. Between 200 and 640 K the temperature dependence is discussed in terms of a mean-field approximation for the magnetic interactions between neighboring Fe ions, and the experimental data have been correlated to the behavior of the static magnetic susceptibility. From this analysis we have determined the high-temperature limit of the linewidth, $\Delta H_{pp}(\infty)$, for different values of x. Below approximately 200 K a strong enhancement of the linewidth is observed, and, from the temperature dependence measured in this region, we have estimated values of the spin-freezing temperature for different concentrations of magnetic ions and determined a concentration of Ga atoms, $x_0 = 0.285(15)$, above which there is no evidence of spin freezing for $T > 4.2$ K. The large absolute value of the high-temperature linewidth for $FeSbO_4$ and its increase when the system is magnetically diluted through Ga substitution indicate the importance of spin-diffusion processes in these materials. This observation, together with the comparatively high magnetic-percolation concentration determined from the x dependence of the freezing temperature, suggest that large portions of the system may present low-dimensional magnetic behavior. This possibility is analyzed in terms of the antisite cationic order proposed for these compounds.

I. INTRODUCTION

Iron antimonate, $FeSbO_4$, is a compound with a rutile-related structure that presents interesting magnetic properties. Electron-diffraction experiments[1] in this material have been interpreted in terms of a partially ordered array of the Fe and Sb cations, which form a superlattice with three rutile units stacked along the c axis, as shown in Fig. 1. $FeSbO_4$ presents a complex magnetic behavior[2,3] sharing many characteristics with canonical spin-glass materials. The low-field (0.01-T) magnetic susceptibility[3] shows two peaks at ≈ 70 and 25 K, while magnetic irreversibility has been observed below 80 K. In addition, a finite magnetic correlation length has been measured below 160 K in neutron-diffraction experiments,[3] which saturates at a value of ≈ 30 Å below 70 K. The functional dependence of the magnetization about the maximum at 70 K is very sensitive to the strength of the applied magnetic field and a peak of the nonlinear part of the magnetic susceptibility has been recently measured[4] at 72 K. However, this nonlinear contribution varies less than an order of magnitude around the freezing temperature unlike the 3 orders of magnitude change observed in spin-glass systems like CuMn.[5] This has been taken[4] as an indication that the observed freezing should be interpreted as inhibited antiferromagnetism, rather than as a true spin-glass transition. It has been suggested[2,3] that the origin of the complex observed spin-glass-like behavior may be associated with the particular antisite cationic ordering proposed[1] for the crystallographic structure of this compound. A study of the freezing process in $Fe_{1-x}Ga_xSbO_4$ has shown that[6] this magnetic system is strongly affected by the dilution of the magnetic species

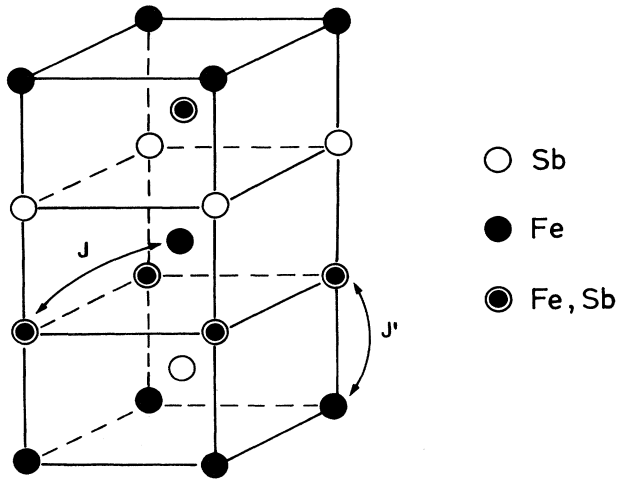

FIG. 1. Atomic ordering proposed in Ref. 1 for the Sb and Fe ions in the $FeSbO_4$ structure, where oxygen positions have been omitted for clarity. J indicates the nearest-neighbor coupling constant and J' that corresponding to next-nearest neighbors.

(through the Ga substitution for Fe) and for $x \simeq 0.30$, no maximum of the susceptibility has been observed above 4.2 K.

We report here an electron-spin resonance (ESR) study of this system, where we analyze the temperature dependence of the linewidth for different Fe concentrations. In Sec. II we present the experimental results in two different temperature ranges: (a) the high-temperature limit where the system is paramagnetic and (b) the intermediate-temperature region where the linewidth evolves in correspondence with the developing of antiferromagnetic correlations. In Sec. III we analyze the concentration dependence of the ESR linewidth in terms of a spin-diffusion model[7] and discuss qualitatively the possible relation between the observed linewidth behavior and the magnetic structure expected for the antisite cationic order proposed in Ref. 1, which may induce two-dimensional (2D) behavior in large portions of the system.

II. EXPERIMENTAL RESULTS

Polycrystalline samples of $Fe_{1-x}Ga_xSbO_4$, with nominal compositions $0 \leq x \leq 0.8$ were prepared as described in Ref. 1. ESR measurements were made at the X band (9.3 GHz) in the temperature range from 77 to 640 K using conventional techniques. For all the samples studied, a single broad line with a peak-to-peak linewidth $\Delta H_{pp} > 0.16$ T, was observed with a temperature-independent g value, $g = 2.00(5)$. We associate this line to the resonance of Fe^{3+} ions in their ground-state configurations: $3d^5\,{}^6S_{5/2}$. No hysteresis was observed in the ESR experiments or differences in the spectra related to the magnetic history of the samples, i.e., differences between cooling them in zero applied field [zero-field cooled (ZFC)] or in a finite field [field cooled (FC)]. The absence of these characteristic effects of spin-glass materials[8] is in agreement with magnetization measurements[4] which also show no hysteresis or dependence on the magnetic history of the sample in the magnetic field and temperature ranges of our ESR measurements.

A. High-temperature linewidth ($210 < T < 640$ K)

In the high-temperature limit, the ESR linewidth of a magnetic system results from the competition between broadening through dipolar interactions and exchange narrowing. In this limit, the ESR line is generally assumed to have a truncated Lorentzian line shape with a temperature-independent linewidth given by[9]

$$\Delta H_{pp} = \Delta\omega/\gamma = (1/\gamma)\omega_p^2/\omega_e \ , \tag{1}$$

where $\Delta\omega$ is the linewidth in frequency units, γ is the gyromagnetic ratio, ω_p is the rms dipolar perturbation frequency, and ω_e is the exchange frequency. When $\omega_e \gg \omega_p$, the rapid exchange-induced fluctuations produce the loss of the dipolar-induced spin correlations. From Ref. 9 we have that

$$\omega_p^2 \propto \sum_j{}'(1+\cos^2\theta_{ij})/R_{ij}^6$$

and (2)

$$\omega_e \propto \left[\sum_j{}' J_{ij}^2\right]^{1/2} \ ,$$

where the sums are performed over all magnetic ions and the result is statistically independent of the ith atom taken as a reference. Here R_{ij} is the distance and J_{ij} is the exchange constant between the spins in the lattice sites i and j, and θ_{ij} is the angle between R_{ij} and the applied magnetic field H.

The temperature range where this expression is expected to remain valid corresponds to the regime where the system is paramagnetic and the magnetic correlations are negligible, i.e., the magnetic susceptibility, $\chi(T)$, follows a Curie law. In $FeSbO_4$, $\chi(T)$ follows[2] a Curie-Weiss law for $T > 600$ K, with an effective moment, $\mu_{\text{eff}} = 6.0\mu_B$/Fe atom, and an antiferromagnetic Curie-Weiss temperature, $\Theta = 580$ K. No evidence of magnetic correlations has been found in the neutron-diffraction patterns[3] at 600 K. We approach this paramagnetic regime in the upper temperature limit of our ESR experiments (640 K). At lower temperatures, a progressive deviation from the Curie-Weiss behavior has been observed indicating a longer range for the magnetic correlations, giving rise to the formation of ordered spin clusters.[2]

In this temperature range the ratio of dipolar to exchange energies corresponding to the spin clusters changes continuously and this process is reflected in the ESR linewidth.[10] In this regime the temperature dependence of the linewidth shows significant variations that can be related to the measured magnetic susceptibility through the expression[10]

$$\Delta H_{pp}(T) = [C/T\chi(T)]\Delta H_{pp}(\infty) \ , \tag{3}$$

where C is the Curie constant for Fe^{3+} ions and $\Delta H_{pp}(\infty)$ is the high-temperature limit for the linewidth, given by Eq. (1).

For a paramagnetic system in a temperature range where the magnetic interaction with neighboring spins is described, in a mean-field approximation, through a Curie-Weiss law the temperature variation is given by a factor $(1+\Theta/T)$. This dependence is most noticeable[10] in magnetic systems with strong competing interactions such that the paramagnetic regime extends down to ordering (or freezing) temperatures much smaller than Θ. In $FeSbO_4$, the ratio between Θ and the freezing temperature T_f, is $\Theta/T_f \approx 8$ and we have found that the functional temperature dependence of the linewidth is well described by Eq. (3) in the temperature range $200 < T < 640$ K, where the magnetic susceptibility closely follows a Curie-Weiss law. Typical spectra are shown in Fig. 2 for the case $x = 0$, and the temperature dependence of the linewidth is presented in Fig. 3. A comparison of the experimental data with the predictions of Eq. (3) is also made in Fig. 3, using in the calculations the magnetic susceptibility reported in Ref. 2. From this comparison we have obtained an extrapolated value, $\Delta H_{pp}(\infty) = 0.082(5)$ T, for undiluted $FeSbO_4$. From the measured linewidth at room temperature, we have estimated the high-temperature limit for the linewidth of all the samples, using Eq. (3) and values of the Curie-Weiss temperature interpolated from the results of Ref. 2. We have found a continuous increase of $\Delta H_{pp}(\infty)$ as a function of x, as shown in Fig. 4. We have also explicit-

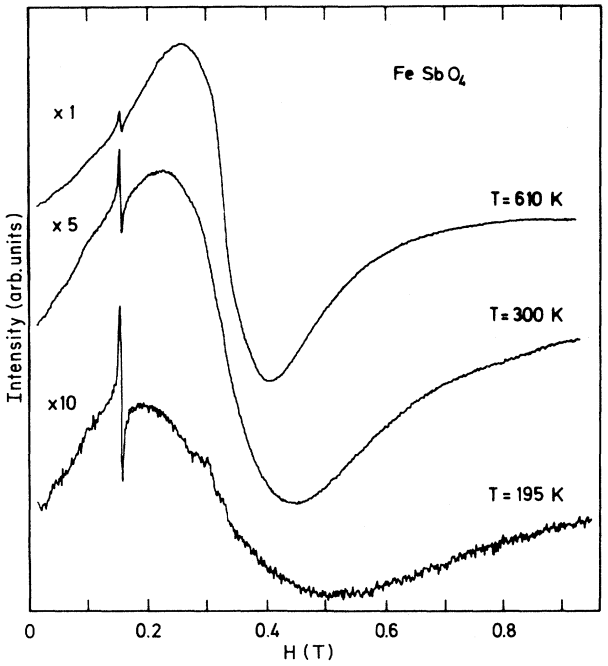

FIG. 2. ESR spectra of $FeSbO_4$ taken at different temperatures. The narrow signal at low fields is due to magnetic impurities in the quartz dewar.

ly verified the agreement between the calculated temperature dependence and the experimental results for $x=0.15$ and 0.50, in the temperature range $200<T<450$ K.

B. Intermediate-temperature region ($140<T<210$ K)

Below a characteristic temperature, $T_0=210$ K, the measured linewidth for $FeSbO_4$ increases, as a function of decreasing temperature, more rapidly than predicted by Eq. (3), indicating that other contributions to the linewidth are present, probably due to fluctuations associated to the onset of a new magnetic state. Consequently, the ESR signal amplitude decreases and we were no longer able to observe the spectrum below ~ 140 K. This behavior below T_0 is accompanied with a strong deviation of the magnetic susceptibility from the high-temperature Curie-Weiss regime. This deviation has been interpreted[2] as a stabilization of spin clusters which interact antiferromagnetically. For the dilute samples with $x=0.10$ and 0.15, the temperature range where the ESR linewidth is enhanced starts at about the same characteristic temperature T_0. However, the magnitude of the

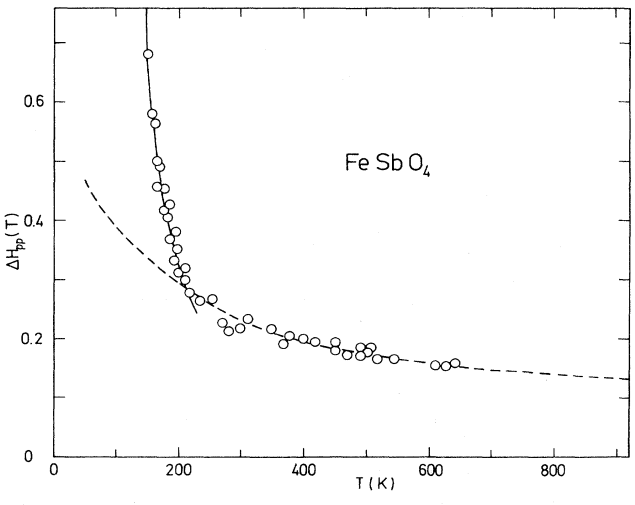

FIG. 3. Temperature dependence of the ESR linewidth, $\Delta H_{pp}(T)$, for $FeSbO_4$. The dashed line corresponds to a fit of the high-temperature data of Eq. (3) and the solid line to a fit of the low-temperature data of Eq. (4).

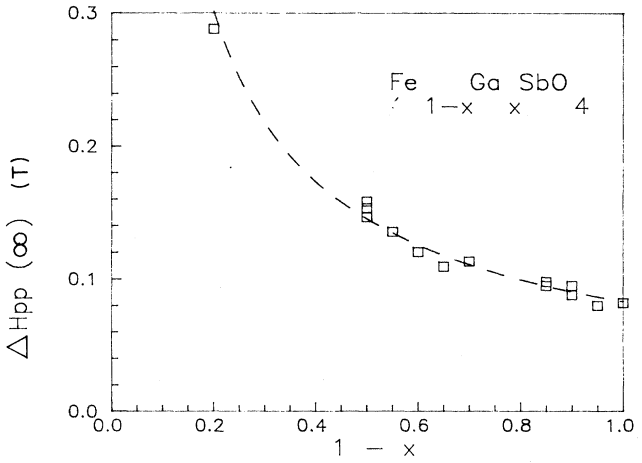

FIG. 4. High-temperature limit of the ESR linewidth, $\Delta H_{pp}(\infty)$, as a function of the Fe concentration. The dashed line is a guide for the eye.

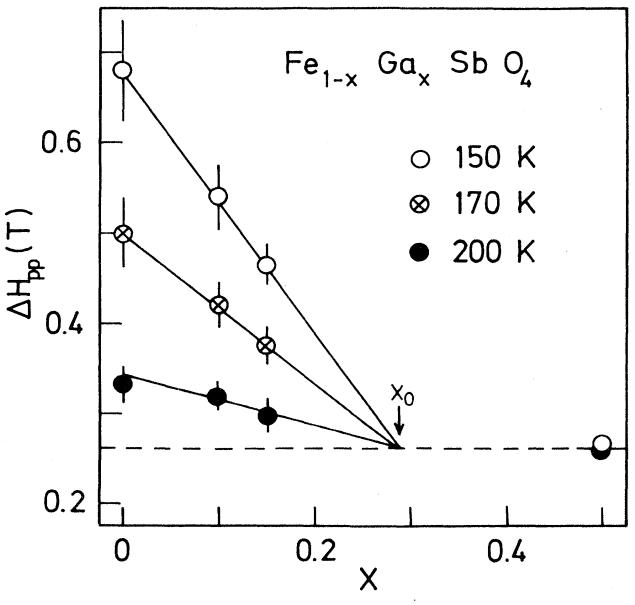

FIG. 5. $\Delta H_{pp}(T)$ as a function of x for $Fe_{1-x}Ga_xSbO_4$, taken at different temperatures.

low-temperature contribution to the line broadening is strongly dependent on the Ga concentrations x. At any given temperature in the range 140 K $< T < T_0$, we have found a linear decrease of the linewidth with x, the slope being a function of the temperature, as it is shown in Fig. 5. From the experimental data we have extrapolated a limiting Ga concentration, $x_0 = 0.285(5)$ above which no extra contributions to the linewidth were observed.

III. DISCUSSION

In order to discuss our results we have chosen for comparison two different compounds that share some characteristics with our materials: MnF_2 and $Mn_{1-x}Cd_xTe$. In both compounds the Mn^{2+} ions are isoelecronic with the Fe^{3+} ions. MnF_2 has the same basic crystalline structure as $FeSbO_4$ and orders in a 3D antiferromagnetic configuration.[11] In $Mn_{1-x}Cd_xTe$, the Mn^{2+} ions form a spin-glass or a random antiferromagnetic state for a wide range of solid solutions,[12] as it seems to be the case for $Fe_{1-x}Ga_xSbO_4$.

Some peculiarities are observed in the $Fe_{1-x}Ga_xSbO_4$ compounds when we compare the measured values of $\Delta H_{pp}(\infty)$ with those corresponding to the reference materials. A comparison of $\Delta H_{pp}(\infty)$ for the two isostructural compounds MnF_2 and $FeSbO_4$ shows that the ESR line is wider for $FeSbO_4$ (0.082 T as compared[13] to 0.026 T for MnF_2). However, according to Eq. (1), the linewidth would be expected to be much smaller since the dipolar energies are of comparable magnitude in the two compounds and the exchange interaction is much stronger for $FeSbO_4$. In fact, an estimate[2] of $J \approx 25-50$ K has been made from the measured Curie-Weiss temperature $\Theta = 580$ K, and this value should be compared to $J \approx 3.5$ K, determined[11] for MnF_2.

Also, when a comparison is made on the dependence of $\Delta H_{pp}(\infty)$ on the concentration of the magnetic species, we observe an important difference between $Fe_{1-x}Ga_xSbO_4$ and the cubic spin-glass-like system $Mn_{1-x}Cd_xTe$. In the latter, the linewidth decreases with the random dilution of the magnetic ions. This is an expected result from Eqs. (1) and (2), where the dipolar and exchange energies vary with concentration according to the relations

$$\omega_p^2(x) = (1-x)\omega_p^2(0)$$

and

$$\omega_e(x) = (1-x)^{1/2}\omega_e(0)$$

since the probability of having each term contributing to the sums in Eq. (2) is proportional to $(1-x)$, which is the concentration of magnetic ions.[14] These relations predict a linewidth decrease with magnetic dilution given by

$$\Delta H_{pp}(x) = (1-x)^{1/2}\Delta H_{pp}(0) .$$

In the $Fe_{1-x}Ga_xSbO_4$ system, instead, we have observed that the linewidth increases when the Fe species are diluted with nonmagnetic Ga ions. In order to explore the possible connection between these observations and the particular antisite ordering proposed for these compounds, we have made numerical evaluations of $\Delta H_{pp}(\infty)$ for magnetically diluted systems using the exact expressions given in Ref. 13 rather than the approximations given by Eq. (2). The sums have been carried out over ≈ 12 atomic cells finding negligible contributions to the linewidth from dipolar interactions with magnetic ions beyond this limit. We have analyzed two different cases: random distribution of magnetic sites and cationic ordering as shown in Fig. 1. For the two cases we have obtained the same $(1-x)^{1/2}$ dependence already anticipated from general considerations. The absolute values calculated for the linewidth are slightly smaller in the case of antisite ordering. We conclude, then, that the simple exchange-narrowing mechanism expressed by Eq. (1) is not enough to correctly describe our experimental results, even if we take into account effects of cationic ordering.

However, based on the particular ordering proposed for the Fe ions (see Fig. 1), it is possible to expect 2D characteristics in the magnetic properties of this material since planar arrays of Sb ions separate atomic layers where the Fe ions are concentrated. Thus, it is expected that the exchange-narrowing process will be affected in this magnetic configuration. As pointed out in Ref. 7, the expression given by Eq. (1) "assumes that the exchange-induced fluctuations are sufficiently rapid to average to zero the dipolar field seen by a spin in a time $\tau_c \approx 1/\omega_e$, which is much less than the relaxation time $1/\Delta\omega$." In magnetic systems with low dimensionality, the rate at which the spin correlation decays as a function of time is reduced as compared with 3D systems because of the limitation in the possible paths of diffusion. As a consequence, the exchange narrowing is much less effective giving rise[7,15] to larger values of $\Delta H_{pp}(\infty)$. For analogous reasons, the presence of diamagnetic impurities in the paths of diffusion cannot be so easily avoided as it is done in 3D systems.[16] Thus, further reduction of the exhange-narrowing effectiveness is also expected when the magnetic ions are diluted.[15,16] Consequently, the high-temperature linewidth of $Fe_{1-x}Ga_xSbO_4$ may be expected to increase with the addition of Ga, as it does, for instance, in the 2D dilute antiferromagnet[16] $Rb_2Mn_{1-x}Mg_xFe_4$.

The temperature T_0, below which the linewidth enhancement is observed, has been found to be independent of the Ga concentration x. This fact is taken as an indication that, at this temperature, the thermal energy is of the same order of magnitude of the exchange coupling constant ($zJ \approx 200$ K) related to the formation of the first spin cluster in the system. In the $FeSbO_4$ crystal structure it is expected that the magnetic coupling would be dominated by the exchange interaction (J) between the magnetic ions located at the center and corners of each rutile unit (see Fig. 1), as it does in similar magnetic systems[17] like MnF_2. The cationic ordering shown in Fig. 1 implies that the number of nearest neighbors involved in the cluster formation varies from $z = 1$ to 4. Assuming that T_0 corresponds to the freezing of clusters with highest energy ($z = 4$), we obtain an estimate of $J \approx 50$ K. The low-temperature region, where the linewidth is enhanced above the predictions of Eq. (3), extends well

above the spin-glass freezing temperature,[3] $T_f \simeq 72$ K, that corresponds to the maximum value of the ZFC magnetization measured in a field of 0.01 T. Referred to the freezing temperature, $T_f = 72$ K, we found that the region of enhanced linewidth extends, for undiluted $FeSbO_4$, up to temperatures $\approx 3T_f$, which resembles the behavior of spin glasses[12] such as $Mn_{1-x}Cd_xTe$. The extension of this temperature region is in accordance with the observation of a finite correlation length in neutron-diffraction experiments[3] up to at least 160 K.

In $Mn_{1-x}Cd_xTe$, the temperature dependence of the linewidth has been adequately described by the expression[12]

$$\Delta H_{pp} \propto [T/T_f(\mathrm{ESR}) - 1]^{-\beta} , \quad (4)$$

where the exponents adopt a value, $\beta = 1.5$, independent of the Mn concentration for $x < 0.7$, and $T_f(\mathrm{ESR})$ is determined from the experimental data. Although the temperature range where we can observe the ESR line is well above the freezing temperature of $Fe_{1-x}Ga_xSbO_4$, we have been able to fit our data to Eq. (4) assuming a fixed value $\beta = 1.5$. From this fit we have determined values of $T_f(\mathrm{ESR})$ for different Ga concentrations. For $x = 0$ we have found $T_f(\mathrm{ESR}) = 59(8)$ K, in reasonable agreement with the determination made from magnetic susceptibility and neutron-diffraction experiments.[3,4] For $x = 0.1$, a lower value, $T_f(\mathrm{ESR}) = 47(7)$ K, was required for the fit and, for $x = 0.15$ we obtained $T_f(\mathrm{ESR}) = 4(13)$ K. This decrease of the freezing temperature has also been observed in magnetic susceptibility[6] measurements, where no maximum appears above 4 K for $x = 0.30$. The critical concentration, $x_0 = 0.285(5)$, determined in Fig. 4, is consistent with the fast depression observed for the freezing temperature as a function of Ga concentration. From this value, and taking into account that the diamagnetic Sb ions also dilute the magnetic Fe lattice (down to 50%), we have determined a percolation concentration of $p_c = 0.357$. This value for p_c is larger than that found in other compounds with the same rutile crystal structure,[18] such as $Mn_{1-x}Zn_xF_2$, where $p_c = 0.24$. In this latter case the measured value is very close to the percolation concentration calculated for a bcc lattice, which is the effective magnetic structure[18] for MnF_2. The larger value found for $Fe_{1-x}Ga_xSbO_4$ may also be taken[18] as an indication of low dimensionality in these compounds, although p_c is still far from the value, $p_c = 0.59$, calculated[19] for a 2D square lattice.

In conclusion, we have shown that the behavior of the high-temperature limit of the ESR linewidth, $\Delta H_{pp}(\infty)$, cannot be explained in terms of a purely 3D exchange-narrowing process. The experimental data would be better described within a spin-diffusion model[7] with the paths of diffusion strongly reduced from a perfect 3D magnetic lattice. This kind of behavior is possible in the rutile structure if (a) the cations have the proposed[1] antisite ordering shown in Fig. 1 and (b) the exchange interactions (J) between nearest neighbors dominate the magnetic coupling, as it has been found in other compounds with the same rutile structure.[11] In this array, large portions of the spin system will behave as in a 2D magnetic lattice, although the absence of a long-range correlation of this cationic order and non-negligible next-nearest-neighbor interactions (J' in Fig. 1) actually lead to 3D magnetic coupling within the system. This partial reduction of the magnetic dimensionality is also supported by the concentration found for percolation, $p_c = 0.357$, determined from the dependence on Ga concentration of both the freezing temperature and the magnitude of the linewidth enhancement below T_0. Since the proposed spin-diffusion mechanism should have strong effects on the angular dependence of the ESR line shape and linewidth,[7,15,16] experiments with single crystals would be very interesting in order to obtain a more detailed characterization of the spin dynamics of this magnetic system.

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