Influence of topological frustration on the magnetic properties of the normal oxyspinel $CdFe_2O_4$

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Magnetic properties of the normal cubic spinel $CdFe_2O_4$ have been investigated on a single crystal above the spin-ordering temperature ~ 10 K, in uniform applied magnetic fields $0 < H < 70$ kG. Our measurements reveal the existence of a huge nonlinear magnetic susceptibility χ_{nl} up to room temperature, characteristic of disordered antiferromagnets in an applied field H. Our experimental results match those obtained previously on $ZnFe_2O_4$ in a field $H = 9.7$ kG. We show that the nonlinearity is responsible for the anomalous magnetic properties incorrectly attributed to the existence of magnetic clusters associated with Fe ions in tetrahedral sites Fe(A) in the previous works. In the limit $H \to 0$, the magnetic susceptibility satisfies the Curie law for $T > 30$ K, with the Curie constant in quantitative agreement with the theoretical value for Fe^{3+} ions in the $^6S_{5/2}$ state. We argue that the fraction x of Fe(A) ions, if any, is very small ($x < 10^{-2}$) so that the nonlinearity cannot be attributed to the site-dilution characteristics of random-field systems. Instead, it is attributable to the large frustration inherent in the topology of the normal spinel cubic lattice.

I. INTRODUCTION

Normal cubic spinels have been investigated for a long time,[1] and are known for their outstanding magnetic properties. Chalcogenide spinels are semiconductors which can exhibit different kinds of magnetic ordering. Some of them are ferromagnetic ($CdCr_2Se_4$ and $HgCr_2Se_4$) and provide unique examples of Mott magnetic semiconductors[2] dominated by intra-atomic Coulomb interactions;[3] others are antiferromagnetic, like $ZnCr_2S_4$,[4] or helimagnetic, like $HgCr_2S_4$ and $ZnCr_2Se_4$.[5,6] On the other hand, the normal oxyspinels AB_2O_4, where A is diamagnetic and B a magnetic ion are insulators, and they all are antiferromagnetic below a Néel temperature T_N which is small, i.e., of the order of 10 K in chromium spinels $ZnCr_2O_4$, $CdCr_2O_4$, $MgCr_2O_4$, (Ref. 7) but also in the iron oxyspinel $ZnFe_2O_4$.[8] This small value of T_N has been related to the topology of the lattice by Anderson.[9] In the normal spinel structure, the magnetic ions occupy octahedral sites (B sites). The B sites form a lattice which can be described as a lattice of corner-sharing tetrahedra, one of the anomalous lattices in which it is possible to achieve perfect short-range order while maintaining a finite zero-point entropy associated with a large degeneracy of the ground state.[9] Anderson has also shown that this high degree of topological frustration, in the lattice with nearest-neighbor antiferromagnetic interactions only, prevents long-range antiferromagnetic ordering. The next question is: Why is T_N finite in oxyspinels? This question has been addressed by Lotgering,[10] who deduced from the magnetic behavior of various spinels, including $ZnFe_2O_4$, the presence of a small fraction x of Fe^{3+} ions at tetrahedral sites (sites A). He then argues that in the surrounding of an Fe(A) ion, the spins of the 12 Fe(B) nearest neighbors are coupled to the spin of the Fe(A) ion by the A-B antiferromagnetic interaction, thus forming a magnetic cluster of 13 ions. This magnetic clustering reduces the degeneracy of the ground state, hence the frustration, and then makes possible long-range magnetic ordering.[10] The purpose of this paper is to further investigate the magnetic properties of oxyspinels, through the example of $CdFe_2O_4$. $CdFe_2O_4$ is

isomorphic with $ZnFe_2O_4$ and constitutes an end member of the Cd-Co ferrite system which has several magnetic and magneto-optic applications.[11] We argue that the anomalous temperature dependence of the magnetization of this compound is not due to the magnetic clustering envisioned in Ref. 10, but is due to the existence of a large nonlinear magnetic susceptibility characteristic of disordered antiferromagnetics. We thus conclude that the long-range antiferromagnetic ordering in the oxyspinels does not originate from the existence of 13 ion clusters generated by Fe(A) ions, contrary to previous claims.[10,12] Instead, it is more likely attributable to the small magnetic interactions connecting those B sites which are not nearest neighbors.

II. EXPERIMENTAL RESULTS

Single crystals of $CdFe_2O_4$ have been grown using the flux method. The melt contained 40 mol % of PbO and 30 mol % of PbF_2 used as a flux for the remaining reacting oxides (CdO and Fe_2O_3 in theoretical stoichiometric proportion). Electron microprobe analysis performed on the same as-grown crystal used in the magnetic measurements gives the formula $CdFe_2O_4$ (the uncertainity is less than ± 1 wt. % for Cd and Fe). Pb is found only as traces (less than 0.1%). The lattice parameter deduced from x-ray diffraction, $a_0 = 8.699 \pm 0.003$ Å, is in agreement with previous data,[13] which confirms this composition.

Preliminary runs indicated the absence of magnetic anisotropy within experimental uncertainty ($\pm 2\%$), but, nevertheless, magnetic measurements have been performed on [111]-oriented single crystals as a function of the magnetic field H in the range $O < H < 70$ kG in the temperature range $4.2 \leq T \leq 300$ K. The magnetization curves $M(H)$, illustrated in Fig. 1 at two characteristic temperatures $T = 50$ and 300 K, show a downward curvature which decreases upon heating. This nonlinearity is best evidenced in Fig. 2, where we have reported the temperature dependence of the magnetic susceptibility

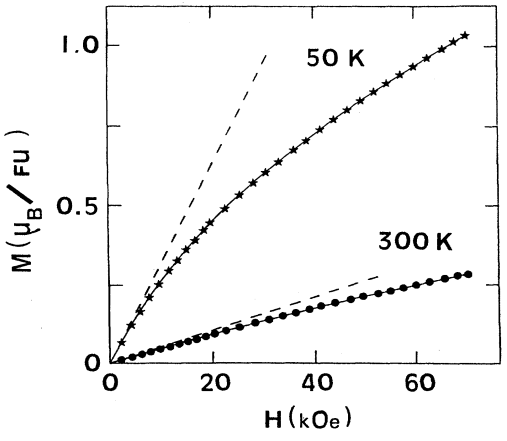

FIG. 1. Magnetization curves of $CdFe_2O_4$ in Bohr magneton per formula unit (FU), at two temperatures $T = 50$ and 300 K. The dashed lines are theoretical, according to the Brillouin law [Eq. (2)], which reduces to the Curie law in the low fields investigated.

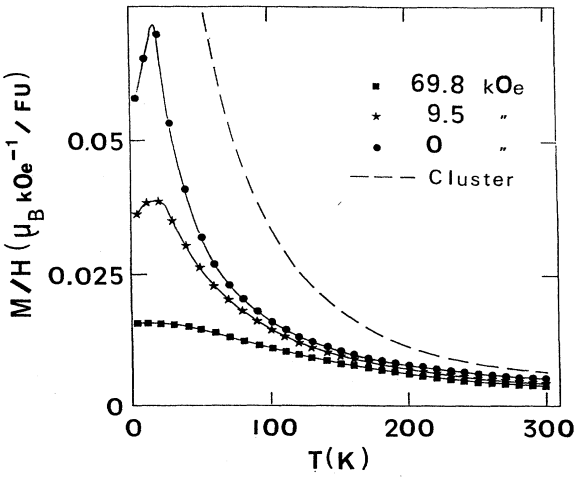

FIG. 2. Magnetic susceptibility of $CdFe_2O_4$ as a function of temperature. The solid circles ($H = 0$) correspond to the inverse of the initial slope in the $M(H)$ curves (see Fig. 1). The deviation of the two other curves with respect to this $H = 0$ curve represents the nonlinear magnetic susceptibility at the corresponding magnetic fields $H = 9.5$ and 69.8 kOe. The dashed curve represents the theoretical curve [Eq. (4) in the text] obtained if one assumes the existence of a fraction $x = 0.05$ of Fe ions on tetrahedral sites. For $x = 0$, the theoretical curve is superposed on the experimental $H = 0$ curve (see Fig. 3) for $T > 30$ K.

$\chi_H = M/H$ at various magnetic fields. The cusp of the susceptibility curves [the minimum in the $\chi^{-1}(T)$ curves in Fig. 3] is observed at $T \simeq 17$ K. The magnetic ordering occurs at the lower temperature T_N where $d\chi_H/dT$, not χ is maximum. Although we could not determine $d\chi_H/dT$ with a good accuracy, T_N can be estimated from data on similar compound $ZnFe_2O_4$, where the maximum of $\chi(T)$ occurs at 15 K.[10] The value deduced from either neutron experiments[10] or the peak of the

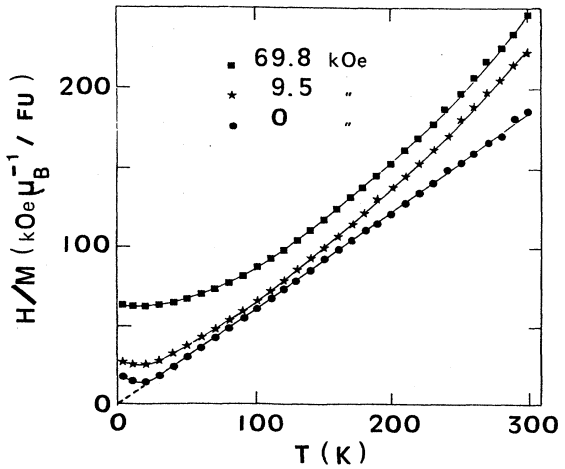

FIG. 3. Inverse of the magnetic susceptibility of $CdFe_2O_4$ vs temperature, measured at different magnetic fields. The symbols represent experimental data. The dashed curve is the theoretical Curie law, when distinct from the experimental curve at $H = 0$.

specific heat[14] is $T_N \simeq 10$ K. In the range $30 < T < 300$ K, zero-field-cooled and field-cooled susceptibility curves are the same, within experimental uncertainty, so that the material can be considered in the reversible paramagnetic state.

The experimental data at $H=0$ in Figs. 2 and 3 correspond to the initial slope χ_0 of the magnetization curves illustrated in Fig. 1. Figure 3 shows that, above 30 K, $\chi_0(T)$ satisfies the Curie law

$$\chi_0(T)=\frac{C}{T} \tag{1}$$

with $C=4.38$ K emu/g atom Fe in quantitative agreement with the theoretical value of the Curie constant predicted for Fe^{3+} ions in the quantum state $^6S_{5/2}$. Hund's rule always applies to ^6S ions in an oxide, and our result shows that the case of Fe^{3+} in oxyspinels is no exception. The application of the external magnetic field, however, induces strong deviations with respect to the Curie law, due to the existence of a strong nonlinear magnetic susceptibility $\chi_{nl}=\chi_H-\chi_0$ (see Fig. 2). Note the deviation $\chi_H^{-1}-\chi_0^{-1}$ in Fig. 3 is an increasing function of T at high temperature. This is because the plot of $\chi_H^{-1}(T)$ instead of $\chi_H(T)$ overemphasizes nonlinear effects in this temperature range where χ_H is small. Figure 2 shows that $|\chi_{nl}|$ is actually a monotonic decreasing function of temperature in the paramagnetic state.

III. DISCUSSION

Figure 3 allows a direct comparison with former results reported for the isomorphic compound $ZnFe_2O_4$ at $H=9.7$ kG.[10] Indeed, the data of Ref. 10 compare well with the curve in Fig. 3 for $CdFe_2O_4$ with the same magnetic field. The susceptibility cusp is observed at $T \simeq 15$ K in $ZnFe_2O_4$ and at 17 K in $CdFe_2O_4$. In the paramagnetic configuration, in the range $30 < T < 300$ K, the $\chi_H^{-1}(T)$ curves have the same features in both materials, i.e., the same deviation from the Curie law.

Another property common to $ZnFe_2O_4$ and $CdFe_2O_4$ is the value $\Theta \simeq 0$ of the paramagnetic Curie temperature. In Ref. 10, this result has been considered as an evidence of very small B-B nearest-neighbor interactions. We believe, however, that this interpretation of the data is not correct, and this anomalous small value of Θ is attributable to the high degree of frustration of the spinel lattice so that the material is a disordered antiferromagnet down to low temperatures. First, the strength of the exchange interaction $J(r)$ is not measured by $\Theta=\sum_r J(r)$. Instead, it is measured by the mean-field transition temperature $\bar{J}=\sum_r(-1)^r J(r)$ in antiferromagnetic systems.[15] Second, our experimental results have revealed the existence of a large nonlinear magnetic susceptibility. In the mean-field approximation (MFA), the magnetization per g atom Fe is given by

$$\frac{M}{H}=\frac{2NS}{H}B_s\left[\frac{\mu_B H}{k_B T}\right]. \tag{2}$$

B_S is the Brillouin function for a spin $S=\frac{5}{2}$, N is the Avogadro's number, and other notations are conventional.

Equation (2) reduces to Eq. (1) in the low field only, and at finite H, the nonlinear magnetic susceptibility

$$\chi_{nl}^{MFA}=\frac{2NS}{H}B_S\left[\frac{\mu_B H}{k_B T}\right]-\chi_0 \tag{3}$$

does not vanish. However, χ_{nl}^{MFA} is found to be at least 2 orders of magnitude smaller than the experimental value χ_{nl} in the whole range of magnetic fields investigated, and is then negligible for $30 < T < 300$ K. Therefore, the huge nonlinear susceptibility observed in our materials is an outstanding deviation with respect to the MFA (see Fig. 1), characteristic of disordered antiferromagnets. In the random-field Ising model (RFIM), for example, the large χ_{nl} is due to the random field generated by the application of a uniform field.[16] In particular, it has been argued[17] that the case $\Theta=0$, $J\neq 0$ corresponds to the so-called direct random field,[18] so that the RFIM is already one model which predicts a large χ_{nl} in systems with $\Theta=0$. Although the physical realization of RFIM systems is in dilute antiferromagnets in uniform applied field, we expect large χ_{nl} effects in other systems where magnetic disorder is generated , not by the site dilution, but instead by the topological frustration. It is worth noticing, however, that a large χ_{nl} in disordered antiferromagnets is usually observed only in the vicinity of the spin-freezing temperature. The fact that a large χ_{nl} is observed even at temperatures $T \gg 17$ K thus appears as an outstanding property of our material. Although the nonlinear magnetic susceptibility is decreasing as a function of temperature, it is still not negligible at room temperature, which shows that J_{BB} is actually large, contrary to previous claims.[10]

Lotgering has considered the effect of a fraction $x\neq 0$ of Fe ions in tetrahedral sites. In this case, the strong A-B exchange interaction I couples a Fe(A) ion with spin S_A to the 12 neighboring Fe(B) spins S_{Bi} indexed by i, to form a magnetic cluster of 13 Fe ions. Therefore, Eq. (2) must be modified and replaced by

$$\frac{M}{H}=\frac{N\mu_B}{H}\left[(2-13x)SB_s(\alpha)+x\frac{\sum_{S_B=0}^{12S} g(S_B)\sum_{J=S_B-S}^{S_B+S}\sinh[(J+\frac{1}{2})\alpha]JB_J(\alpha)e^{\frac{If(J,S_B)}{2k_BT}}}{\sum_{S_B} g(S_B)J\sinh[(J+\frac{1}{2})\alpha]e^{\frac{If(J,S_B)}{2k_BT}}}\right], \tag{4a}$$

with

$$f(J,S_B)=J(J+1)-S(S+1)-S_B(S_B+1)\ ,$$
$$\alpha=\frac{2\mu_B H}{k_B T}\ . \tag{4b}$$

The degeneracy factor $g(S_B)$ is equal to the number of combinations of the 12 spins $S_{B_i}=\frac{5}{2}$ with total spins S_B. The contribution of the cluster is from Ref. 10, after the summation over the azimuthal eigenvalues m_J of the total cluster spin $J=S_B+S_A$ has been carried out.

We have computed χ_H from Eqs. (4), assuming $I=-44$ K.[10] Again we find that the nonlinearity of M versus H in Eqs. (4) is negligible in the range of temperature and magnetic field investigated. The result is illustrated in Fig. 2 for $x=0.05$, and shows that the magnetic clustering increases the magnetic susceptibility which then becomes much larger than the experimental value at all temperatures.[19] Our results then show unambiguously that x is very small.

One consequence of this analysis is that the magnetic ordering at low temperatures in those materials cannot be attributed to the existence of the magnetic clusters envisioned in previous works.[10,12] The concentration of such clusters, if any, is smaller than the lower value which can be detected by our least-squares fitting procedure of the (T) curves, i.e., $x<10^{-3}$. We can understand this result if we note that the exchange interaction I induces a spin polarization of the 12 Fe(B) ions surrounding the Fe(A) ion, in the same direction opposite to that of the Fe(A) magnetic moment. Then the cluster carries a large magnetic moment as a result of this ferromagnetic indirect coupling between the Fe(B) ions nearest neighbors of the Fe(A) ion, responsible for an increase of the magnetization and $\chi(T)$. To overcome this effect, Ligenza[20] has assumed existence of a large crystal-field interaction $D[3\langle s^{z'}\rangle^2-s(s+1)]$ with z' the axis of a presumed trigonal electric field. In that case, however, $|D|$ must be extremely large ($D=-0{,}667$ meV), i.e., 1 order of magnitude larger than in any paramagnetic material. This interaction results in a huge anisotropy which should lead to a spin freezing of the magnetic clusters, hence a remanent magnetization and magnetic irreversibilities at laboratory time scale, not observed experimentally. Finally, this crystal-field interaction implies a temperature dependence of $\langle s^z\rangle$ in the range $30<T<300$ K, hence a deviation of the $\chi^{-1}(T)$ curve from the Curie-Weiss law, in contradiction with our low-field data. Actually, the failure of the cluster model is evidenced by the fact that the fit of the experimental $M(T)$ curves is achieved for values of Θ and x (or the equivalent fitting parameters Θ and A in Ref. 20), which strongly depend on H.

The cluster model, however, is based on the assumption that the B-B interaction is negligible. If the antiferromagnetic B-B coupling of the spin of the next-nearest Fe(B) neighbors of Fe(A) is not negligible, the magnetization will be reduced with respect to the cluster-model prediction [hence our estimation $x<10^{-3}$ of the Fe(A) ion concentration might be underestimated]. In this case, a Fe(A) ion will generate a contribution to the local exchange field, extending beyond the nearest neighbor over a sphere of radius $r>a$ (a is the lattice parameter) as a result of the competing ferro- and antiferromagnetic interactions. The magnetic properties of the material will be affected if the concentration x of such spheres is such that their total volume is smaller than but has the order of magnitude of the crystal volume, i.e., $8(4\pi r^3/3)(x/a^3)\lesssim 1$, or $x<10^{-2}$. The extreme sensitivity of the magnetic properties to a residual concentration of Fe(A) ions in this case might explain the outstanding differences in the magnetic properties observed on different $ZnFe_2O_4$ samples, with an asymptotic paramagnetic Curie temperature ranging from $\Theta=0$ (Ref. 10) to $\Theta=-40$ K (Ref. 21). Anderson[9] has already pointed out that the spin ordering may be enforced by what one expects to be rather small second-neighbor forces, or even more distant interactions.[22] The remarkable similarity of the magnetic properties in both $CdFe_2O_4$ and $ZnFe_2O_4$, not only in the paramagnetic state, but also regarding the spin-ordering temperature of the peak in the $\chi(T)$ curves suggests that the diamagnetic ion does not play a significant role in exchange interactions. This supports the suggestion of Lotgering[4] that in spinels AFe_2O_4 the dominant next-nearest-neighbor interactions are Fe-O-O-Fe, rather than the Fe-O-A-Fe interaction proposed by different authors.[23,24]

The large nonlinear magnetic effects and the sensitivity of the magnetic properties to defects, illustrated in this work for spinels, should be considered as main features of the frustrated lattices. Another example is provided by MnO. In this case, the Mn ions form an fcc lattice which is also a frustrated lattice.[25] For this material, a reentrant spin-glass behavior has been linked to a slight off-stoichiometry MnO_{1+x} with $x\leq 10^{-2}$.[26] Unfortunately, χ_{nl} has not been investigated in this compound. The critical behavior of χ_{nl} has been evidenced only as one approaches spin-glass freezing temperature T_g by cooling in the paramagnetic phase.[27] In this context, it might be desirable to investigate χ_{nl} also in materials like MnO_{1+x} which are in an antiferromagnetic phase at $T>T_g$ rather than in a paramagnetic phase.

IV. CONCLUSION

A large nonlinear magnetic susceptibility has been evidenced in $CdFe_2O_4$ in the whole temperature range $30<T<300$ K. This property, usually observed in dilute spin systems or in amorphous materials, is observed here in a crystal. It thus gives an outstanding example where the disorder in the magnetic interactions at the origin of χ_{nl} arises from the topological frustration inherent in the normal spinel cubic lattice. In such a lattice, even a residual concentration of defects, presumably Fe(A) ions, $x<10^{-2}$ may greatly influence the magnetic properties of the material.

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