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Local canted spin behaviour in the disordered spinel $Zn_xCo_{1-x}FeCrO_4$: a magnetization study

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Abstract. Zero-field-cooled magnetization, field-cooled magnetization and hysteresis measurements on $Zn_xCo_{1-x}FeCrO_4$ ($x = 0.45$ and 0.50) ferrite samples are reported using a SQUID magnetometer. The data have been analysed using a model of ferrimagnetic arrangement of local canted spins, in the light of our earlier neutron diffraction data reported on these systems.

1. Introduction

Spinel ferrites constitute an important class of magnetic materials. Their magnetic structures depend upon the types of magnetic ion residing on the A (terahedral) and B (octahedral) sites and the relative strengths of the inter-sublattice interactions J_{AB} and intra-sublattice interactions J_{AA} and J_{BB}. Since in most of the spinels all the three exchange interactions, namely J_{AA}, J_{BB} and J_{AB} are negative, there exists a competition between intra- and inter-sublattice interactions, often resulting in 'frustration effects'. Further, as spinels offer the possibility of selective magnetic dilution of A and B sites, one finds a rather rich variety of magnetic behaviours [1–6] in this family. A wide spectrum of magnetic structures ranging from ferrimagnetism, antiferromagnetism, local canted spin (LCS) to semi-spin-glass, spin-glass, etc, has been observed [1]. Recently a magnetic phase diagram was proposed for the disordered spinel $Zn_xCo_{1-x}FeCrO_4$ on the basis of the χ_{AC}, low-field DC magnetization and Mössbauer studies [7]. The investigations led Muraleedharan *et al* [7] to conclude that, as the non-magnetic atom concentration increases ($x \geqslant 0.40$), the ferrimagnetic phase disappears and a spin-glass freezing is observed at low temperatures. On the other hand, a neutron diffraction study on the same disordered ferrites $Zn_xCo_{1-x}FeCrO_4$ ($x = 0.45$, 0.50 and 0.55) showed the existence of long-range ferrimagnetic ordering of the longitudinal components S_z of the spins and disorder of the transverse components S_t of the spins for all three compositions. Moreover, for $x \geqslant 0.50$, at low temperatures, the long-range magnetic order of S_z was found to coexist with short-range correlation in S_t [8]. In view of this situation, we decided to perform magnetization measurements to obtain a better understanding of these disordered spinels. In particular, we have investigated two compositions, namely those with $x = 0.45$ and 0.50, and report our results on zero-field-cooled (ZFC) magnetization, field-cooled (FC) magnetization and hysteresis measurements. These studies have been made using the Quantum Design SQUID magnetometer (model MPMS).

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2. Experimental details

The present work has been carried out on the same samples (prepared using the wet chemical method) as were used in the earlier neutron diffractions studies [8]. ZFC, FC and hysteresis measurements were made on powder samples which were compacted in the form of pellets. Studies were carried out over the temperature ranges 5–300 K (for $x = 0.50$) and 5–400 K (for $x = 0.45$) and over fields of up to ± 3 kOe. The following procedures were used for ZFC and FC measurements on both the samples. In ZFC measurements the sample was cooled from room temperature to 5 K in zero magnetic field (except for a small residual field of about ± 1–2 Oe in the superconducting solenoid of this magnetometer which is difficult to eliminate without using the quench option). A field of 10–20 Oe was applied at 5 K, and then the isofield magnetization was measured in the warming cycle after an adequate pause (about 300 s) at each temperature for thermal stability. For the FC case, the magnetization measurements were performed in the cooling cycle as the sample temperature was being lowered towards 5 K in the presence of the same fixed magnetic field as was used for measurement in the ZFC case. The applied fields on the $x = 0.45$ sample were about 20 Oe and 1 kOe, whereas the $x = 0.50$ sample was studied with approximately 10 Oe and 3 kOe fields.

The hysteresis measurements on both the compositions were carried out in the field range of ± 3 kOe at several temperatures starting from 5 K to about room temperature. Prior to performing the hysteresis measurement at each temperature, the sample temperature was raised to about 350 K, kept there for sometime under the zero-field condition and then lowered to the desired temperature with zero field.

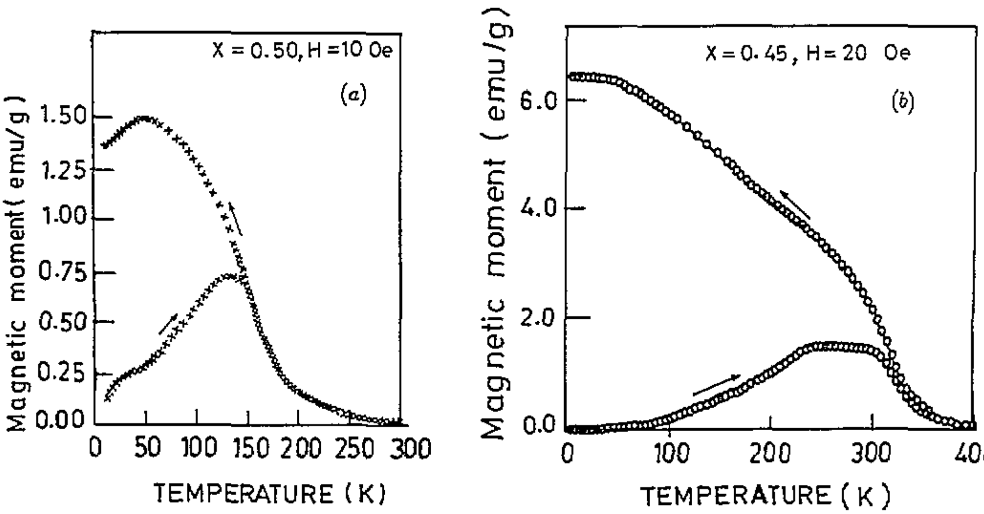

Figure 1. ZFC and FC magnetization data for (*a*) the $x = 0.50$ sample with $H_{external} = 10$ Oe and (*b*) the $x = 0.45$ sample with $H_{external} = 20$ Oe.

3. Experimental results

Figures 1(*a*) and 1(*b*) show the ZFC and FC results for both the ferrites. For the $x = 0.50$ sample the ZFC curves deviate from the FC curves below 145 K (figure 1(*a*)), and for the

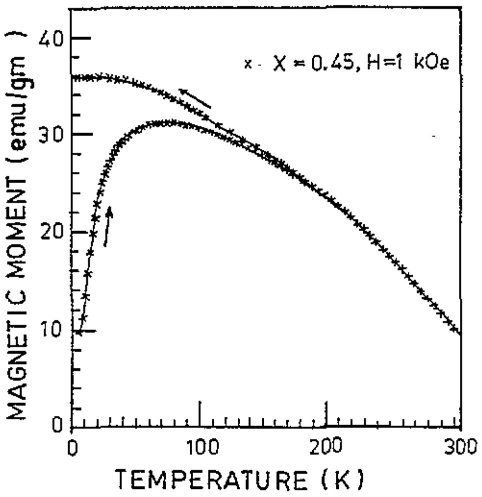

Figure 2. ZFC and FC magnetization data for the $x = 0.45$ sample with $H_{external} = 1$ kOe.

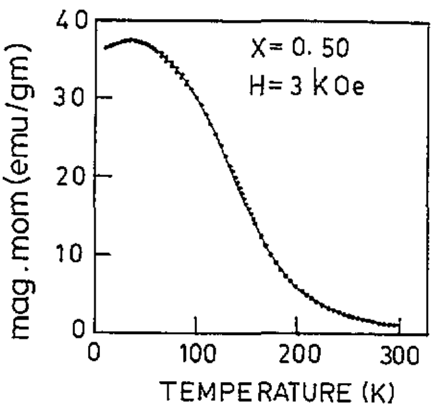

Figure 3. High-field ($H_{external} = 3$ kOe) magnetization data for the sample with $x = 0.50$, measured in ZFC and FC experiments.

$x = 0.45$ sample the curves deviate below 350 K (figure 1(*b*)). The ZFC curves are identical in shape with the χ_{AC} curves for both compositions [8]. The low-field ZFC curves show broad maxima at about 135 K and 280 K for the $x = 0.50$ and $x = 0.45$ samples, respectively, while the FC magnetization (in the same field) continuously increases until about 43 K for both the compositions; thereafter it remains almost constant for the $x = 0.45$ sample and marginally decreases for the $x = 0.50$ sample. The difference between the ZFC and FC curves decreases as the external field is increased to 1 kOe (figure 2). No difference between the ZFC and the FC behaviours was observed when the field was raised to 3 kOe for the $x = 0.50$ sample (figure 3). It should be noted that the low-field ZFC curve for $x = 0.50$ shows a shoulder at around 25 K as also seen in the χ_{AC} data [8]. For the $x = 0.50$ sample the small reduction in magnetization observed below 43 K at a field of 10 Oe (figure 1(*a*)) shifts to 34 K when the field is increased to 3 kOe (figure 4).

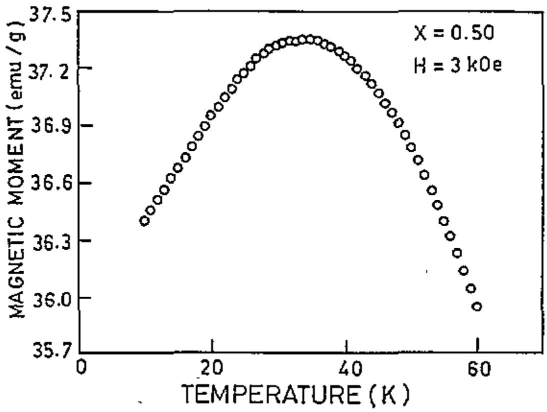

Figure 4. Reduction in magnetization below 34 K for the $x = 0.50$ sample (FC measurement; $H_{external} = 3$ kOe).

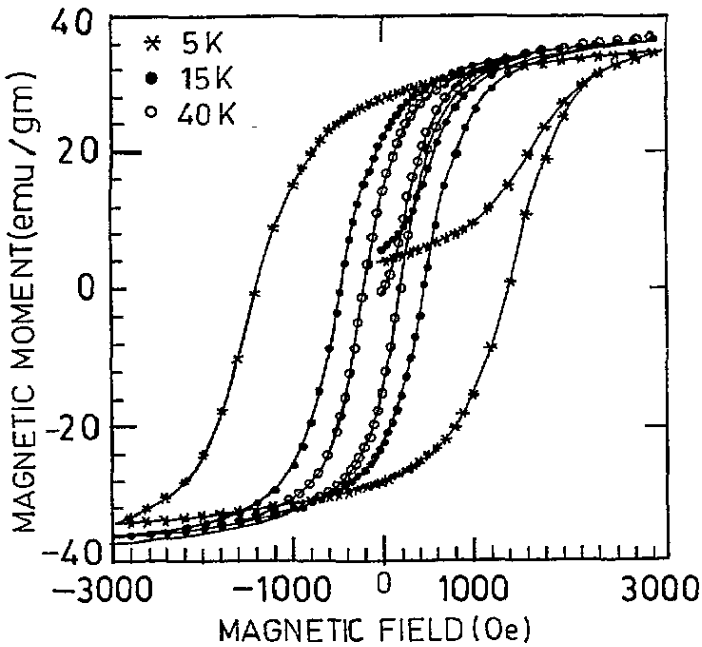

Figure 5. Hysteresis loops for the $x = 0.50$ ferrite at low temperatures $T = 5$, 15 and 40 K.

The hysteresis measurements were performed at different temperatures on both the samples. For the $x = 0.50$ sample the results are shown in figures 5 and 6. A slow rise in magnetization can be observed up to a 1 kOe field at 5 K. It should be noted that the sample exhibits wide hysteresis loops up to 120 K. For the $x = 0.45$ sample, a similar behaviour was observed up to 220 K. We have computed $(\mathrm{d}M/\mathrm{d}H)_{H=H_c}$ at different temperatures using figures 5 and 6 and the results are shown in figure 7. From the hysteresis measurements for both the samples we have derived the coercive field H_c versus temperature and remanent magnetization σ_r versus temperature. These results are presented in figures 8 and 9. Figure 8 clearly shows that, for both the $x = 0.50$ and the 0.45 samples, H_c is very large at low temperatures. Turning to figure 9, we find that, at low temperatures, σ_r is large for both the compositions. For $x = 0.45$, σ_r exhibits a saturation character at low temperatures (and follows the typical Brillouin-like function) while, for the $x = 0.50$ sample, no such saturation is observed. However, for the latter sample a change in slope above 25 K is observed (figure 10), similar to that seen in the H_c versus temperature curve.

4. Discussion

From figures 1–3 it is clear that the FC–ZFC branching is strongly field dependent for both the compositions. While FC–ZFC differences are found up to about the Néel temperature T_N for the $x = 0.45$ sample at 20 Oe field, for the $x = 0.50$ sample the difference appears only for temperatures below about 145 K ($T_N \simeq 320$ K) at 10 Oe. This observation suggests that even a field of 10 Oe is quite high for depressing the temperature at which branching occurs for the $x = 0.50$ composition. We may recall here that such differences between ZFC and FC magnetization have been observed in spin-glass or spin-glass-like materials [9, 10] and also in LCS ferrites [11, 12], amongst others. However, some further clues are needed to

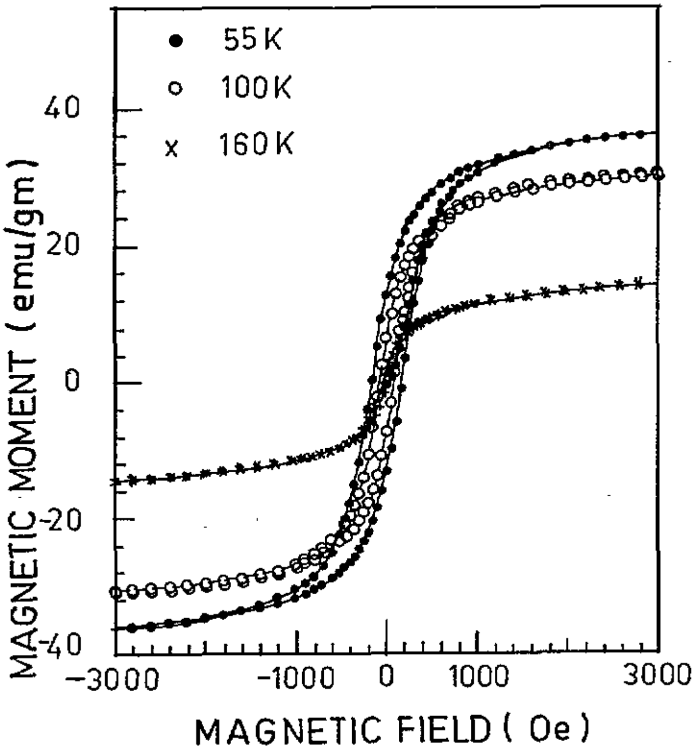

Figure 6. High temperature ($T = 55$, 100 and 160 K) hysteresis loops for the $x = 0.50$ sample.

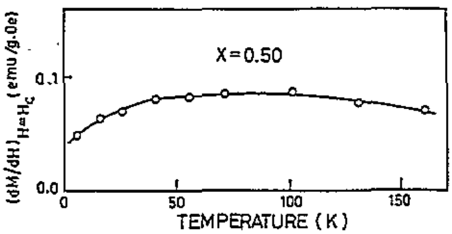

Figure 7. $(dM/dH)_{H=H_c}$ as a function of temperature for the $x = 0.50$ sample (computed from figures 5 and 6).

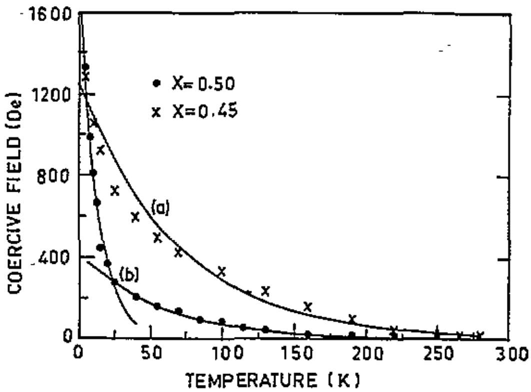

Figure 8. Temperature variation in the coercive field H_c for the $x = 0.45$ sample (curve (a)) and for the $x = 0.50$ sample (curve (b)), solid lines: exponentially fitted curves (see text).

identify the nature which the present materials possess. Magnetic neutron diffraction results provide help.

For both $x = 0.50$ and $x = 0.45$ samples the presence of long-range magnetic ordering (ferrimagnetic ordering) of the longitudinal spin components is confirmed from

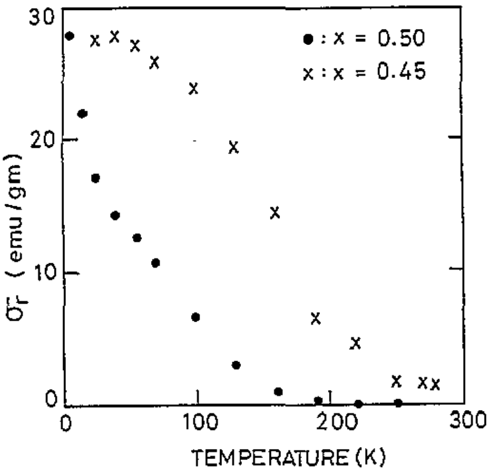

Figure 9. Remanent magnetization as a function of temperature for the samples with $x = 0.45$ and 0.50 (derived from hysteresis measurements).

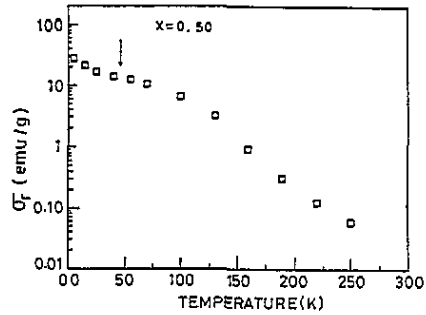

Figure 10. Temperature variation in remanent magnetization for the $x = 0.50$ sample (obtained from hysteresis measurements). The downward arrow indicates the change in slope.

the presence of magnetic contributions to the Bragg intensities of the normal reflections over all temperatures below T_N. On the other hand, for both samples the observed B-site magnetic moment is substantially lower than the estimated free-ion moments (collinear structure). The possibility of uniform canting relative to the average magnetization (Yafet–Kittel-type structure) is ruled out from the absence of a sharp (200) Bragg peak in the neutron diffraction pattern [8]. However, for the $x = 0.50$ sample a broad hump is seen around the (200) Bragg position at $T \leqslant 20$ K, which indicates the existence of only short-range correlation of the transverse components of spins. In brief, neutron diffraction measurements for both $x = 0.45$ and $x = 0.50$ indicate that the magnetic structure is highly non-collinear, favouring LCS-type ordering [13, 14].

For the systems where long-range order is involved, the contributions to the difference between ZFC magnetization and FC magnetization can arise from domains, from domain walls and from disorder. Our sample is a perturbed ferrimagnet and possibly both domain and disorder effects could contribute. As already noted, the ZFC–FC branching point is rather sensitive to the applied field and branching starts at rather high temperatures. As neutron diffraction shows, the short-range correlation of transverse spin components occurs at quite low temperatures ($T \leqslant 20$ K for the $x = 0.50$ sample); so, if the FC–ZFC branching were to be related to spin-glass or spin-glass-like freezing, presumably it should have appeared at a lower temperature. In passing, we may note that in LCS systems the FC–ZFC branching behaviour has been interpreted in terms of domains, i.e. as a consequence of the temperature variation in the hysteresis loop [1, 15].

We may note the presence of a broad asymmetrical peak centred around T_{max} (the temperature at which the magnetization becomes a maximum) in low-field ZFC magnetization (figures 1(*a*) and 1(*b*)) and also χ_{AC} measurements [8]. Similar asymmetrical peaks have been observed for other diluted ferrite systems [16, 17]. These have been attributed to effects arising from anisotropy in these ferrites. It is to be noted that the presence of Co^{2+} in our ferrite systems introduces uniaxial random anisotropy [18].

Coming to the observed shoulder in ZFC at about 25 K (and also seen in χ_{AC} measurements [8]) we may note that this is consistent with the short-range correlation of transverse spin components at 20 K for the $x = 0.50$ sample as seen by neutrons [8]. It is to be noted that for the $x = 0.45$ sample no such shoulder has been observed either in our low-field ZFC measurements or in χ_{AC} measurements reported elsewhere [8]. This observation indicates that for the $x = 0.45$ sample there is no correlation in the transverse spin components, which is again consistent with the neutron data. It is very interesting to note that our low-field ZFC or χ_{AC} data on the $x = 0.50$ sample do not show any sharp transition (around 25 K) for the transverse component of spins but only progressive freezing. This is generally the case for the LCS structure [1, 19], unlike that for the semi-spin-glass model [1], where a sharp spin freezing of S_t is expected.

The field dependence of the FC maximum temperature T_{max} is clear from figures 1(a) and 4 and this has also been observed in other ferrite systems [11]. This behaviour can arise either from a decrease in the magnetic order at low temperatures or because of a different variation in the magnetization of each sublattice [1] (in fact, a neutron diffraction study on these ferrites shows different temperature responses of the individual A-site and B-site moments [8]). It can also be visualized as an activation phenomenon of domain wall movements [11].

Turning to figures 5 and 6, hysteresis measurements clearly show that loops open when the temperature decreases. A similar behaviour has been observed in other systems including LCS ferrite systems [1]. Figure 8 shows that the coercive force, which is a measure of magnetic hardness, varies considerably with temperature; H_c is small at higher temperatures (below T_N), as in ferrimagnets. A similar rapid increase in H_c at low temperatures has also been observed in LCS ferrite systems [11]. The coercive field was found to be reasonably well described by a single-exponential function of the form $H_c \simeq 1253\ \exp(-T/67.5)$ for $x = 0.45$ ferrite (figure 8, curve (a)). Such an exponential temperature dependence has previously been observed in LCS ferrite systems [20]. Figure 8 (curve (b)) shows the temperature dependence of the coercive field for the $x = 0.50$ sample. It was not found possible to fit these data to a single exponential (as was the case for the $x = 0.45$ sample) and we needed two exponentials of the form of $A\ \exp(-T/T_0)$. The law $H_c \simeq 1789\ \exp(-T/12.6)$ fits very well for the low-temperature range $5\ K \leqslant T \leqslant 25\ K$, whereas in the range 25–300 K the observed form is $H_c \simeq 424\ \exp(-T/56.4)$. In the LCS structure the canting angle of a given site depends on the fraction of magnetic atoms in the neighbourhood and the associated exchange integrals. However, the transverse spin component has some preferential directions which minimize the energy. As noted before, the transverse component is frozen in an energy minima at low temperatures ($T \leqslant 25$ K) for the $x = 0.50$ sample. Thus the domain wall structure can be rather complex. The energy barrier between energy minima is high and correspondingly, the cost in energy to move the walls is also high. As H_c is a measure of the field required to displace the domain wall over the largest potential energy barrier on its path, it increases very rapidly at low temperatures. At high temperatures ($T < T_N$), the energy barrier between the preferential directions can be overcome more easily, and as a result H_c is low. It should be mentioned that the domain wall pinning can also arise owing to the uniaxial anisotropy and random distribution resulting from Co^{2+} in our sample. The temperature dependence of domain and domain wall motion is very clear from the double-exponential behaviour of H_c versus T. The existence of two values of T_0 for the $x = 0.50$ sample indicates that there are two activation barriers. The change in slope of the σ_r versus temperature curve (figure 10) above 25 K is consistent with the H_c versus temperature behaviour (figure 8, curve (b)). This type of $\ln \sigma_r$ variation has been observed in LCS ferrite systems [20]. The fact that H_c and σ_r go to zero only near the expected Néel temperatures suggests the existence of a semi-disordered state, which is in the mean ferrimagnetic. The observed plateau over the temperature range from about 30 to 130 K in the $(dM/dH)_{H=H_c}$ versus temperature curve (figure 7) also indicates at least mean ferrimagnetic order. A similar feature has been found in [11, 19]. While for the $x = 0.45$ sample we have not seen the freezing of S_t at any temperature, the observed characteristics of hysteresis loops for this sample can also be understood using the same LCS model of spin arrangements [1].

5. Summary

We have performed magnetization measurements on $Zn_xCo_{1-x}FeCrO_4$ ($x = 0.45$ and 0.50) using a SQUID magnetometer. We have reported ZFC and FC isofield magnetization versus temperature studies and hysteresis measurements at several temperatures. The present measurements together with the reported neutron data [8] reveal that these disordered spinels exhibit local spin canting behaviour. There is no sharp transition exhibited by the transverse components of spin at low temperatures for the $x = 0.50$ sample, but only progressive freezing. On the other hand, the $x = 0.45$ sample does not show any evidence of progressive transverse spin freezing at any temperature. The observed temperature-dependent features of ZFC and FC magnetizations, coercive field and remanent magnetization for both the samples have been explained in terms of the domain properties of a LCS state governed by a thermally activated process. In conclusion, for the spinels studied in this paper an explanation in terms of a LCS state is more appropriate than a description of the semi-spin-glass state.

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