Magnetic Behavior of the $LiFeTiO_4$ Spinel

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The $LiFeTiO_4$ spinel obtained by the "liquid mix" technique has been studied by neutron powder diffraction, ac and dc magnetic susceptibility, and magnetization measurements. The cationic distribution in the tetrahedral (A) and octahedral (B) sites was determined to be $(Li_{0.47}Fe_{0.53})_A(Li_{0.53}Fe_{0.47}Ti)_BO_4$. The dc magnetic susceptibility measurements show two maxima at 29 and 282 K (at $H = 1000$ Oe) and a Curie−Weiss behavior is not observed in the temperature range 282−800 K. Neutron diffraction patterns shows that the B-site magnetic moments at 2 K temperature are lower than those expected for a collinear arrangement of spins. Careful analyses of the low-temperature neutron diffraction patterns of this material suggest a localized canting of spins (LCS) type of magnetic ordering where a long-range order (LRO) of longitudinal component of moments coexists along with a totally disordered transverse component of moments. The conclusion is also supported by the features seen in complementary magnetic measurements.

Introduction

Spinels of general formula $Li_{0.5+0.5x}Fe_{2.5-1.5x}Ti_xO_4$ are of interest because they show order−disorder phase transitions that are mainly governed by composition and temperature. These structural transitions are also accompanied by noticeable variations in the magnetic behavior and this system has been widely studied.[1−10] In particular, the attention is focused on the high transition temperature from ferromagnetic to paramagnetic state that, in the parent phase, $Li_{0.5}Fe_{2.5}O_4$, is as high as 958 K.[11−13]

Much research effort has been carried out to interpret the physical properties of this system and the main features of their structural changes and relations between them are now well-known. Nevertheless, there are still some controversies over the effect of nonmagnetic and magnetic cation substitution on magnetic structure and properties of lithium ferrites.[14−15]

During recent years, we have reported the structural characterization and magnetic behavior of some phases belonging to the system $Li_{0.5+0.5x}Fe_{2.5-1.5x}Ti_xO_4$.[7−10] Magnetic properties were interpreted on the basis of a Néel's collinear ferrimagnetic structure ($x = 0.16$) that evolves to a noncollinear model for $x = 0.44$ and 0.72, and finally gives rise to a spin-glass behavior when the content of titanium is higher ($x = 1.28$ and 1.50).

To have complete knowledge of the evolution of the magnetic behavior with composition, we are currently studying the stoichiometric lithium ferrite $LiFeTiO_4$ ($x = 1$) because its composition is intermediate between those showing a 3D magnetic ordering (either collinear or noncollinear) and those in which the ordering disappears, behaving as spin-glass. Structural refinement carried out by

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powder X-ray diffraction and electrical properties on this phase have been previously reported by us.[7] The cation distribution was $(Li_{0.47}Fe_{0.53})_A(Li_{0.53}Fe_{0.47}Ti)_BO_4$, implying that both A- and B-sublattices (subscripts in the formula) are magnetically diluted. It is noteworthy that as a consequence of substitutions by diamagnetic titanium atoms from the parent phase $Li_{0.5}Fe_{2.5}O_4$, a competition between the exchange interactions (J_{AB}, J_{AA}, and J_{BB}) appears, giving rise to a large number of disordered states such as a localized canted state (LCS),[16] Yafet-Kittel (YK) state,[17] semi-spin-glass (SSG) state,[18] spin-glass (SG) state,[19] cluster spin-glass state (CSG),[20] and so forth. According to these possibilities, there are a good number of papers devoted to the interpretation of the magnetic behavior in this system.[1,2,6,21−23]

Neutron diffraction techniques can give unambiguous evidence for any long-range magnetic ordering (LRO) but they may not provide a clear distinction between SG and SSG behavior. The aim of the present work is to clarify the magnetic behavior of the spinel LiFeTiO$_4$ ($x = 1$) by neutron diffraction and magnetic measurements.

Experimental Section

A polycrystalline sample of LiFeTiO$_4$ was prepared by the "liquid mix" technique[24] from powdered mixtures of Li_2CO_3, Fe_2O_3 and TiO_2 (all reactants were supplied by Merck, Germany), in stoichiometric ratio, at 1073 K for a day, as described elsewhere.[7]

Neutron powder diffraction data were performed at 2 and 300 K on the D1A high-resolution powder diffractometer ($\lambda = 1.911$ Å) at the Institute Laue-Langevin (Grenoble, France). The position sensitive detector D1B powder diffractometer working with a wavelength of 2.522 Å and covering a range in 2θ dispersion angle of 20−84° was used to collect the thermal patterns in the temperature range 2−900 K. Oranges cryostat and vanadium ovens allow variation of the temperature in D1B and D1A instruments. Diffraction patterns were analyzed by the Rietveld[25] method and the FULLPROF program.[26]

Magnetic susceptibility measurements were performed in a commercial superconducting quantum interference device magnetometer, Quantum Design Magnetic Properties Measurement System 5S, on powder samples in a temperature range from 2 to 800 K under an applied magnetic field of 1000 Oe and in the temperature range 2−320 K, applying a field of 1000, 500, and 50 Oe. The magnetic field isothermal variations up to 80 kOe were obtained with the aid of a Quantum Design Physical Properties Magnetic System, which allowed for the experimental setting of highly homogeneous magnetic field at specific temperatures. Thermal variations of the ac magnetization were performed at frequencies of 10−1000 Hz.

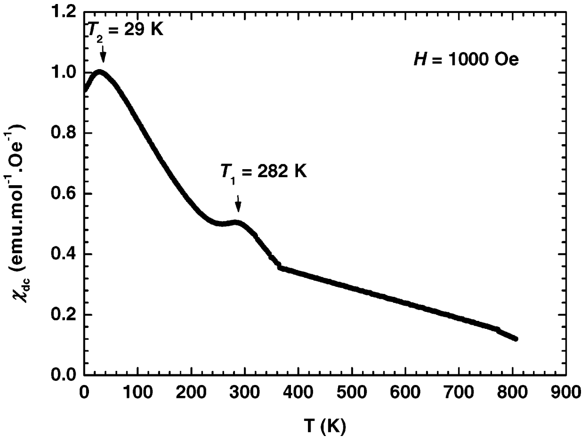

Figure 1. Variation of the dc magnetic susceptibility at 1000 Oe with temperature between 1.8 and 800 K for LiFeTiO$_4$.

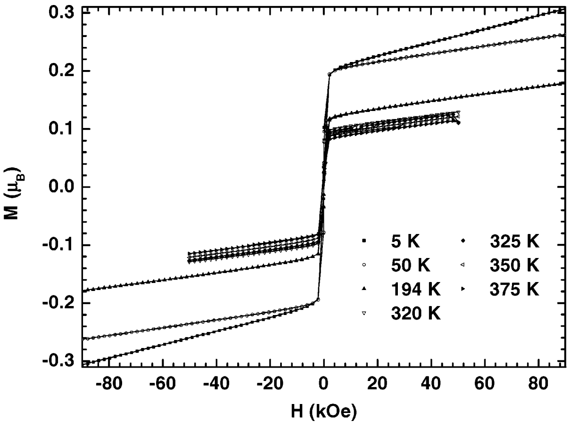

Figure 2. Isothermal magnetization vs magnetic field at 5, 25, 200, and 375 K.

Results and Discussion

Magnetic Measurements. Figure 1 shows the temperature dependence of the dc magnetic susceptibility in the range between 2 and 800 K measured at a field of 1000 Oe. The magnetic susceptibility increases with decreasing temperature and reaches a first maximum at ca. $T_1 = 282$ K. At lower temperatures another strong magnetic signal centered at $T_2 = 29$ K appears. No Curie−Weiss behavior from the dc reciprocal susceptibility (not depicted) was observed over the whole temperature range measured. The absence of linear behavior toward higher temperature data suggests that the transition to the paramagnetic state is expected for a Curie temperature $T_C > 800$ K.

Magnetization measurements were performed in the temperature range $5 \leq T \leq 375$ K and these results are shown in Figure 2. The magnetization variation with the magnetic field shows a very narrow hysteresis loop in which the coercitive fields (H_C) vary from 220 to 10 Oe when the temperature increases. The appearance of such narrow cycles is characteristic of ferrimagnetic behavior. Finally, Figure 3 shows the thermal variation of remanent magnetization, whose values slightly decrease from 0.20 to 0.08 μ_B per

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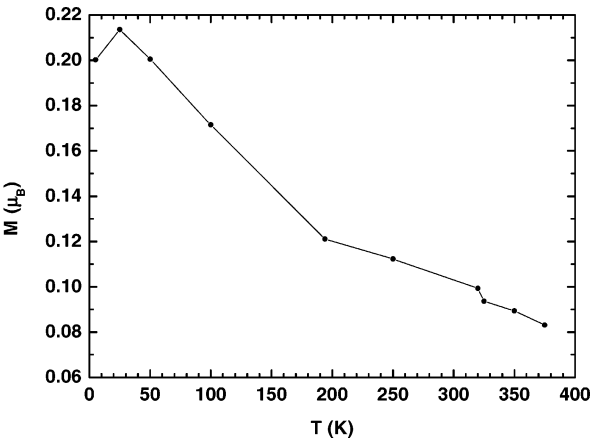

Figure 3. Saturation magnetization vs temperature for $LiFeTiO_4$.

formula unit between 5 and 375 K, respectively. In this graph a cusp is observed between 5 and 50 K that seem to correspond to the T_2 maximum obtained in the χ_{dc} graph. In turn, about 200 K a sharp decreasing of remanent magnetization is also detected and is related to the T_1 maximum in Figure 1. On the other hand, the hysteresis loops do not saturate, even for a field as high as 80 kOe, suggesting that an antiferromagnetic (AF) component is also present. Nevertheless, for other samples of the system $Li_{0.5+0.5x}Fe_{2.5-1.5x}Ti_xO_4$, the saturation is achieved from 2 to 50 kOe. This fact is characteristic of ferrimagnetic behavior.[10] This AF component observed for $LiFeTiO_4$ can be attributed to the canting of magnetic ion moments in the sublattice as a consequence of the AF interactions between ions in the same sublattice. This tendency is enhanced by a weakening of the AF interaction with the opposite sublattice. Several authors[27-31] had suggested that the competition between these different localized magnetic configurations of close energies may become the origin of a system frustration.

The real (χ'_{ac}) and imaginary (χ''_{ac}) components of the susceptibility at 100 Hz with an ac field of 0.215 Oe are shown in Figure 4. The lack of absorption in both χ'_{ac} and χ''_{ac} at around 30 K is associated with the long-range order interactions. At around T_1 strong peaks are observed, indicating the presence of a magnetic transition of a different nature than the previous ones. A more detailed analysis of the ac susceptibility has been performed around this temperature and this quantity was measured at different frequencies from 100 Hz to 10 kHz (see inset Figure 4). The χ'_{ac} values are independent of the frequency up to the proximities of the maximum whose height decreases with increasing frequency, but its position in temperature does not vary upon frequency. This behavior is consistent with a cooperative freezing of individual magnetic moments, as occurs in SG, the freezing temperature T_F being defined as that corresponding to the maximum in χ'_{ac}.

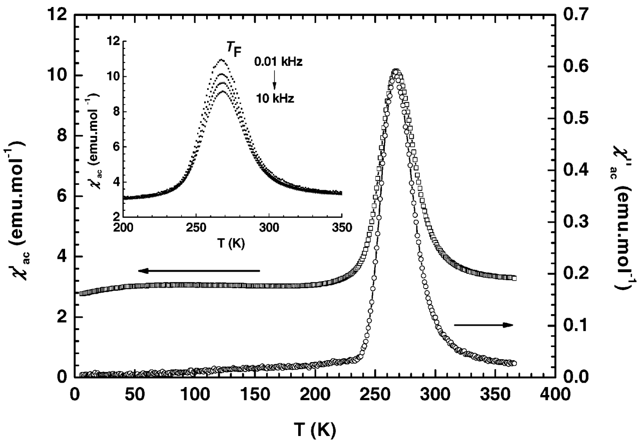

Figure 4. Real and imaginary part of the ac magnetic susceptibility as a function of temperature from 1.8 to 350 K for $LiFeTiO_4$ at $\nu = 0.1$ kHz, $H = 0.215$ Oe. Inset: Real part of the ac magnetic susceptibility as a function of temperature in the interval 200−350 K at $\nu = 0.1$ and 10 kHz.

Therefore, the magnetic behavior of $LiFeTiO_4$ observed at temperatures above 282 K can be attributed to a SG or CSG behavior that is associated with the presence of clusters, which are linked to the nonordered component of the magnetic moment. However, as commented on below, neutron diffraction data indicate that a ferrimagnetic order exists below $T_C = 805$ K, but only the longitudinal component of the magnetic moment is involved, as the transverse component remains completely disordered. Then, the spin-glass state inferred from the susceptibility measurements is associated with the presence of clusters, which are linked to the nonordered component of the magnetic moment.

As is well-known, magnetization versus temperature curves obtained during magnetic field cooling (FC) or zero-field cooling (ZFC) can be used to study SG and CSG behavior.[32] To determine the region of irreversibility, a sample was cooled to 4.2 K in zero applied field (the ZFC process). Then a constant field was applied during the temperature increase and the ZFC magnetization, $M_{ZFC}(H)$, was measured from 2 to 325 K. For field-cooling magnetization, $M_{FC}(H)$, the sample was cooled to 4.2 K under a constant field.

Figure 5 shows the ZFC and FC curves under fields of 50, 500, and 1000 Oe for $LiFeTiO_4$. The position of T_F on the M_{ZFC} curve marks the refreezing of the CG. Above T_F the system gradually approaches the ferrimagnetic (FI) state. The merging point, T_M, found in both $M_{ZFC}(T)$ and $M_{FC}(T)$ curves implies that the system is the same FI state for ZFC and FC processes above that temperature.

At the lower field applied (50 Oe) the ZFC and FC curves diverge noticeably in the whole range of temperature measured and T_F and T_M were not found at the same temperature (see Figure 5b), suggesting the presence of a mixed CG and FI state. The mixed state at this temperature disappears at higher field (e.g., 500 Oe), but this state seem to be also present at low temperature because T_F and T_M are not the same at this applied field. The difference between the FC and ZFC curves almost disappears at the higher applied field of 1000 Oe. This demonstrates that the system is always in

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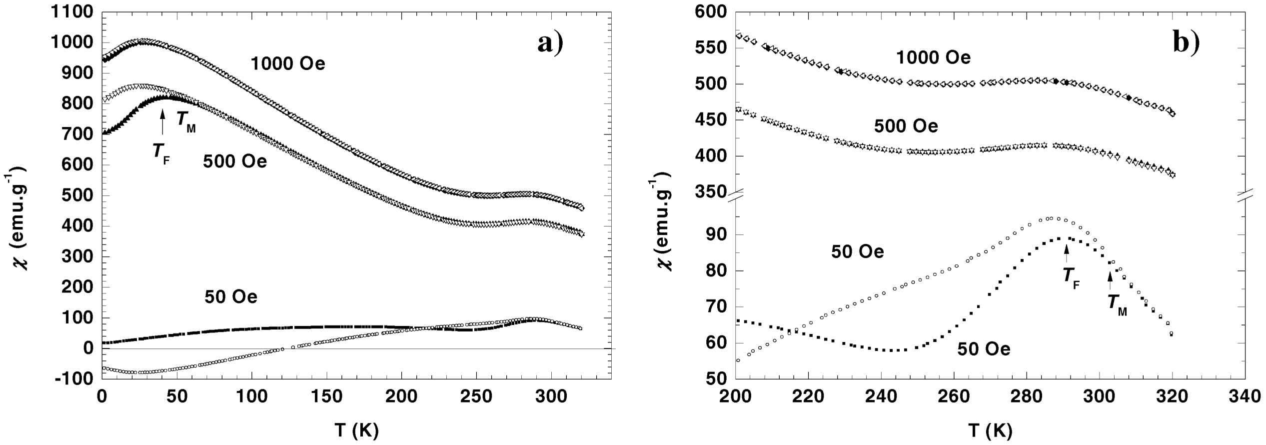

Figure 5. ZFC (solid symbols) and FC (open symbols) curves for $LiFeTiO_4$ at various applied fields in the temperature ranges: (a) 2−320 K, (b) 200−320 K.

a FI state if the magnetic field is sufficiently high. In some ferrimagnetic materials, the total contribution due to antiparallel magnetic sublattices may be canceled out at a temperature called the compensation temperature.[33] In our case the FC curve for low magnetic field shows that the compensation temperature is 127 K. Moreover, this curve presented relatively strong negative magnetization at low temperatures (below 127 K). This phenomenon has been reported for molecular-based ferrimagnets[34−36] and is certainly due to the change in direction of the magnetization in the ferrimagnetic component at the compensation temperature.

When a field is applied at high temperature, the interaction between the ferrimagnetic clusters and the antiferromagnetic matrix is very weak, allowing that the ferrimagnetic clusters rotate and point in the field direction. Then, when the temperature is decreased to a very low temperature where the interaction between clusters and matrix is progressively stronger and below a certain temperature, the field cannot rotate the ferrimagnetic clusters. Because of the compensation effect, the magnetization of the ferrimagnetic clusters now points in the opposite direction to the magnetic field and the negative signals appear. The lower applied field (50 Oe) is not sufficiently high to overcome the above-described interaction between clusters and matrix and rotate the negative magnetization to the positive direction at low temperature. Such a rotation for FI clusters is allowed in out spinel in the higher applied magnetic fields (500 and 1000 Oe) because no negative magnetization is shown in the ZFC and FC curves.

These results can be explained keeping in mind that, in general, for an AB_2O_4 spinel-type compound the main magnetic interactions between the A and B sublattices are antiferromagnetic in nature. When both A and B metal cations are paramagnetic, such an A−B coupling is the strongest, giving rise to a ferrimagnetic system (Néel-type ordering). This antiparallel ordering between the A and B sublattices magnetic moment is perturbed by partial substitutions of these paramagnetic cations by diamagnetic ones; in this case, a competition between the exchange interactions arises, giving rise to various noncollinear and perturbed states in the magnetic ordering of the spinel systems. For example, the related compound Fe_2TiO_4 is an inverse spinel that shows a weakly ferromagnetic behavior below the Curie temperature of 142 K. Its magnetic structure is fundamentally of the Néel type, but the sublattice magnetization on the octahedral sites makes a small angle with respect to that on the tetrahedral sites and the spontaneous ferromagnetic moment appears in one of the ⟨100⟩ directions, perpendicular to the sublattice magnetization. This canting angle is a consequence of the B−B interactions which are comparable to A−B interactions.

The title compound, $LiFeTiO_4$, is magnetically diluted in both A and B sublattices and in accordance with the formula $(Li_{0.47}Fe_{0.53})_A(Li_{0.53}Fe_{0.47}Ti)_BO_4$. We can consider that at lower temperatures one sublattice (e.g., A) is aligned with the applied field and therefore the other (B) is antialigned with the field. When temperature increases, the B−B interactions are progressively stronger and greater than the A−B ones, reaching thus the condition under which a compensation temperature can occur.[20,37−39] Therefore, the sublattice magnetization on the octahedral sites makes a small angle with respect to that on the tetrahedral sites. An additional consequence taken from this model is that if the spin canting on the B-sites is not fully ordered, but is accounted at a local level only, that gives rise to ferrimagnetic clusters.

In general terms, this model agrees well with the above experimental results, although the evidence for the LRO of the canting on B-sites is provided by neutron diffraction.

Neutron Diffraction Experiments. As stated above, the magnetic properties of a spinel-type complex oxide depend strongly on how the cations are distributed over the A and B sites of the crystal lattice. For these purposes, neutron diffraction patterns (NDP) for the sample under study were taken and the profiles were analyzed using the program FULLPROF[26] and the Rietveld[25] method. The $LiFeTiO_4$

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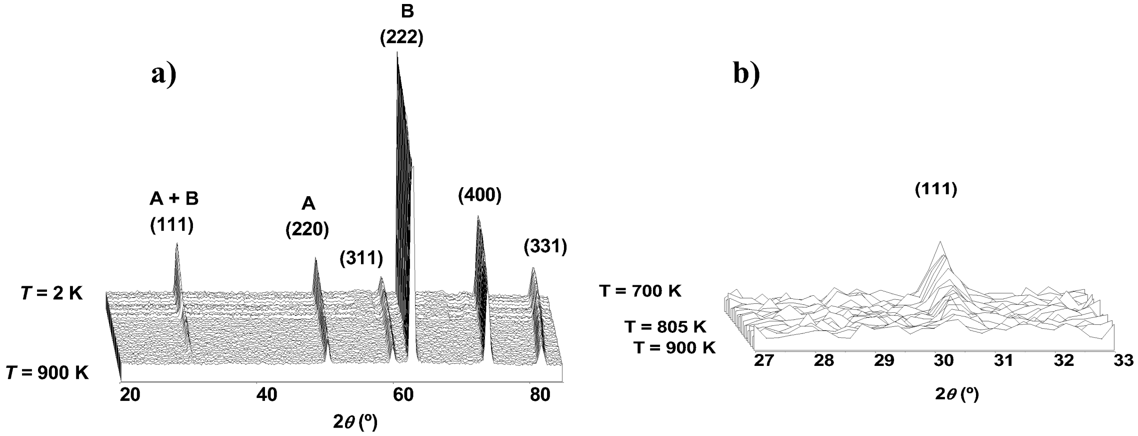

Figure 6. Thermal evolution of NDP collected at a wavelength $\lambda = 2.522$ Å in the temperature ranges: (a) 2−900 K and (b) 700−900 K.

Table 1. Crystallographic Data, Structural Parameters, and Isotropic Global Debye−Waller Factor (*B*) Obtained from the Rietveld Refinement of Powder Neutron Diffraction Pattern at 900 K of the Spinel LiFeTiO₄ ($\lambda = 2.522$ Å)

atom	site	$x = y = z$	occupancy
Li/Fe	8a	1/8	0.47/0.53
Li/Fe/Ti	16d	1/2	0.53/0.47/1.0
O	32e	0.2575(8)	1.0

space group: *Fd*3*m*
a (Å) = 8.4166(4)
R_B (%) = 2.18
B (Å2) = 0.0060(1)
R_P (%) = 3.54
$\chi^2 = 1.73$
R_{WP} (%) = 5.08

spinel exhibits the crystallographic symmetry defined by the space group *Fd*3*m* and in the data refinement process this space group was used to generate the calculated profile. In the data refinement process, the cation occupancies were varied very carefully step by step since multiple functions had to be adjusted self-consistently. Neutron diffraction is expected to be a powerful tool to clarify structural details because of the difference in the coherent scattering lengths of Li, Fe, Ti, and O atoms [b_c(Li) = −1.90, b_c(Fe) = 9.45, b_c(Ti) = −3.73, b_c(O) = 5.80 fm].

The occupation number of cations at A and B sites and other structural parameters obtained by XRD[7] at room temperature have been confirmed by ND at 900 K, i.e., in the paramagnetic phase. The cation distribution of the title compound is $(Li_{0.47}Fe_{0.53})_A(Li_{0.53}Fe_{0.47}Ti)_BO_4$ where all Ti^{4+} cations are located on octahedral coordination sites, and there is a random distribution of Li^+ and Fe^{3+} cations among the octahedral and tetrahedral sites. A summary of the structural parameters obtained in the refinement is given in Table 1.

The nuclear and magnetic Bragg peaks occur at the same scattering angle (2θ) in $LiFeTiO_4$ and therefore the magnetic unit cell is the same as the crystallographic one. Figure 6a shows the temperature evolution of the NDP with $\lambda = 2.522$ Å. The Bragg nuclear peaks such as (111), (220), (311), and (222) show a significant buildup in intensity on lowering the temperature, reflecting the increase in the magnetic contributions in this way in the temperature range between 2 and 800 K. Moreover, in the thermal variation of NDP collected between 800 and 900 K we can observe that the reflection (111) disappears and the paramagnetic phase is reached at $T = 805$ K (see Figure 6b).

Since this ferrite can be considered an ionic compound, in which the only paramagnetic cation is the Fe^{3+} one and recalling the actual cation distribution, it is possible to estimate the sublattice moments at saturation, assuming a collinear ordering. If the magnetic ions are all in such a Néel ordering, then one expects the site moments deduced from the normal Bragg reflections are to be close to the estimated free-ion moments because, in such a situation, the moments of the magnetic ions will be fully aligned along the longitudinal direction (i.e., along the axis of broken symmetry). Alternatively, if the magnetic ordering is noncollinear, then the ordered site moments deduced from the normal Bragg reflections will correspond only to the longitudinal components since the transverse components do not contribute to the intensities of these Bragg reflections, due to the extinction rules for the magnetic reflections being different from those of the space group *Fd*3*m*. Therefore, spatial ordering of the transverse magnetic components gives rise to the (2 0 0) superlattice Bragg reflection[18] which is purely magnetic.

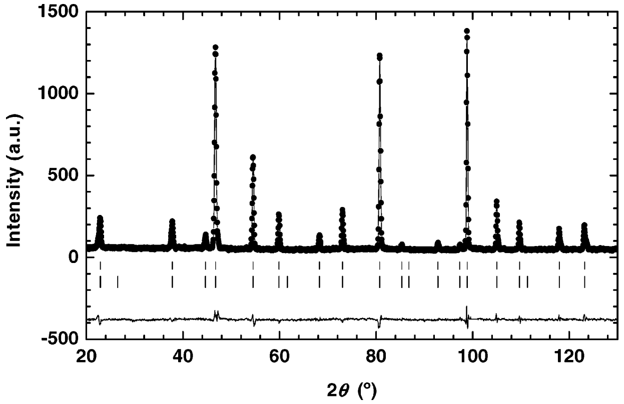

Figure 7. Observed and calculated neutron diffraction pattern at 2 K. Bragg reflections are indicated for nuclear (upper) and magnetic contributions (lower). The differences between the observed and calculated patterns are also plotted.

Rietveld refinements at 2 K were tried on the basis of a collinear ordering and Figure 7 shows the fitting results which contain both nuclear and magnetic contributions with $\lambda = 1.911$ Å. The site occupancies determined from the analysis of the high-temperature data were kept fixed and all the other parameters were varied during the refinement. Bearing in mind the actual cation distribution and considering the spin only moment for Fe^{3+} (5 μ_B), the A and B site theoretical magnetic moments have been estimated as being 2.65 and 2.35 μ_B, respectively. At 2 K reliability factors for

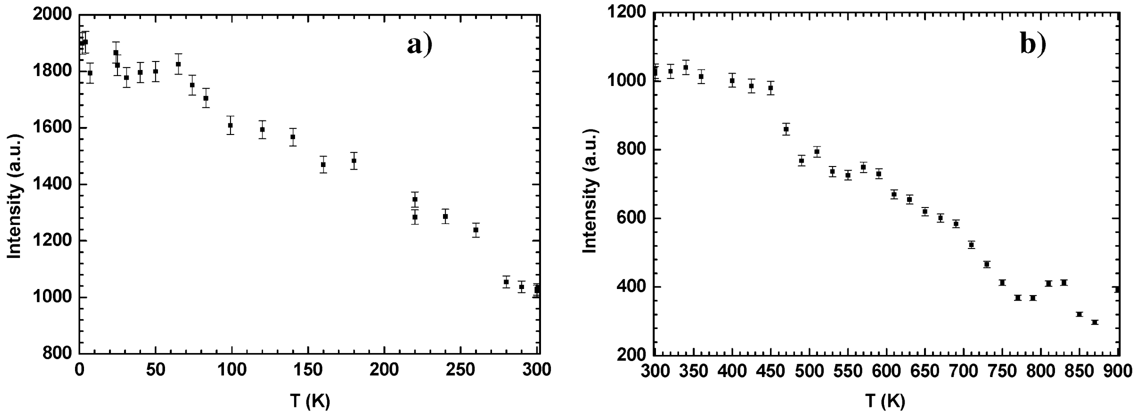

Figure 8. Temperature dependence of Bragg peak intensity (111) ($\lambda = 2.522$): (a) 2−300 K and (b) 300−900 K.

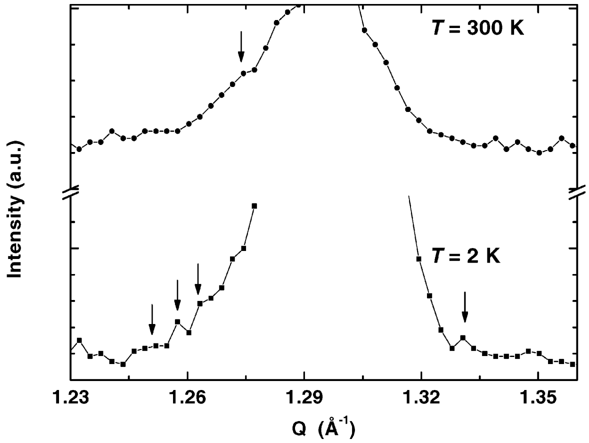

Figure 9. Comparison of the low-angle neutron diffraction patterns of intensity of the (111) Bragg peak for 2 and 300 K ($\lambda = 1.911$ Å).

the Rietveld refinement are $R_B = 2.61$ and $R_M = 3.53$, and the absolute moment values are $M_A = 2.04\ \mu_B$ and $M_B = 1.92\ \mu_B$, assuming that all the iron spins contribute to the ferrimagnetic order. By comparing theoretical and observed magnetic moments, it is evident that along with the ordered magnetic spins, which are responsible for the existence of LRO, there exists a noncollinear spin component in the system. These noncollinear spin components cannot contribute to the normal Bragg reflections and provoke a substantial loss of the ordered moments at this site.

We had remarked earlier that at increasing temperatures the intra-sublattice B−B interactions become stronger than the A−B ones, giving rise to a noncollinear ordering, and thus the spatial ordering of the transverse spin components should cause the (200) reflection. Since this (200) magnetic reflection is not present in the diffraction patterns, it indicates that the transverse components are completely disordered. Moreover, when the temperature variations of the (111) Bragg intensity (Figure 8) are analyzed, a “step-like” behavior is observed and this can be explained in terms of the presence of finite size “clusters”.[16] Some of the clusters lock themselves in phase with the infinite network and cause enhancement in Bragg intensities while some lock themselves out of phase with the infinite network to bring about the steps in temperature response of Bragg intensities. Consequently, the present neutron diffraction study provides direct evidence of the presence of LRO of the longitudinal components of spins and allow us to propose an LCS type of ordering of spins.

On the other hand, it is interesting to note the neutron diffraction patterns ($\lambda = 1.911$ Å) at low scattering angles (Figure 9) in which a significant diffuse signal, centered at the (111) peak position, could be clearly seen at 2 K. The diffuse signal broadens the (111) Bragg diffraction peak. In light of similar observations on many other spinel compounds clusters,[18,27−31] it may be assumed that, together with the LRO of the longitudinal spin components, a short-range correlation among the transverse spin components in the form of finite clusters are present in the sample. Incoherent scattering from these clusters has given rise to a diffuse signal which increases in the width of the Bragg diffraction peaks at low angles at 2 K, which is not evident at high temperatures. To clarify this point, complementary polarized neutron experiments should be carried out.

Conclusion

Complex magnetic behavior of $LiFeTiO_4$ spinel has been studied in this paper. This compound is a phase of the system $Li_{0.5+0.5x}Fe_{2.5-1.5x}Ti_xO_4$ whose composition is intermediate ($x = 1$). The magnetic properties for $x < 1$ were interpreted on the basis of a ferrimagnetic structure (in all cases the Fe^{3+} cations contained on tetrahedral sites were smaller than the ones on octahedral sites). On the other hand, the 3D magnetic ordering disappears when $x > 1$ behaves as spin-glass (in these cases, the Fe^{3+} cations contained on tetrahedral sites were bigger than ones in the octahedral sites). For a $x = 1$ sample, cation distribution was $(Li_{0.47}Fe_{0.53})_A(Li_{0.53}Fe_{0.47}Ti)_BO_4$, showing that both tetrahedral and octahedral sites have a very similar Fe^{3+} content. Because of this, we think that this fact is responsible for the complex magnetic behavior that we have found. Finally, on the basis of our observations and keeping in mind the findings of different workers[27−31] on various frustrated and diluted systems, we suggest that in our sample the disordered spin components give rise to magnetic spin clusters, which coexist with the infinite magnetic network below T_C.

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