Three Dimensional Magnetic Correlations in Multiferroic $LuFe_2O_4$

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Multiferroic materials have been investigated for many years, but only recently have materials been found which exhibit effects large enough to be useful in devices. In this new class of materials, the ferroelectricity originates as part of a more complex phenomenon [1]. For example, in $LuFe_2O_4$ at high temperatures, Fe^{2+} and Fe^{3+} ions are found in equal numbers but are randomly distributed. At temperatures below 320 K, the Fe^{2+} and Fe^{3+} ions order (charge order) leading to the formation of a ferroelectric polarization [2]. At 240 K, magnetic order appears along with a simultaneous anomaly in the electric polarization indicating a coupling between the magnetic and ferroelectric degrees of freedom in $LuFe_2O_4$. An additional demonstration of coupling between magnetic and electric degrees of freedom in $LuFe_2O_4$ is provided by dielectric constant measurements under applied magnetic fields which show a giant magnetocapacitance at room temperature [3]. Hence, $LuFe_2O_4$ appears to be a promising multiferroic material.

To provide further insight into the interesting behavior of $LuFe_2O_4$ we have performed neutron diffraction measurements on high quality single crystals. These measurements were performed on the N5 and C5 (for the polarized work) triple-axis spectrometers, Chalk River, Canada. Further measurements were also performed with the HB1 triple-axis spectrometer at HFIR at Oak Ridge National Laboratory. For the non-polarized experiment at N5, pyrolytic graphite (PG-002) flat monochromator and flat analyzer were used. Measurements were performed with a fixed final neutron energy of E_f = 13.7 meV and a PG filter in the incident beam to remove higher order contamination. Horizontal collimations were set to (none, 0.6°, 0.27°, 1.1°). For polarized experiments on C5, flat Heuser-111 crystals were used both as monochromator and analyzer with a fixed final energy of E_f = 13.7 meV and collimations set to (none, 0.8°, 0.85°, 2.4°). A Mezei flipper coil was placed on the incident side and two graphite filters were used on the scattered side to suppress the higher order neutrons. The Mezei flipper allowed spin-flip and non-spin-flip cross sections to be measured. At the sample position a pair of coils applied a weak vertical field perpendicular to $\boldsymbol{Q}$ (of ~ 3-5 G) to control the direction of the neutron spin at the sample. A flipping ratio of ~ 15:1 was achieved for this vertical field configuration.

Our study shows that in contrast to previous work, there are two transitions, one at 240 K (T_N) and another at 175 K (T_L) [4]. The nature of ordering which occurs at each of these transitions can be examined by comparing scans along the (1/3 1/3 L) direction (Figure 1a) at various temperatures. The scan at 280 K shows weak peaks at large values of L with ½ integer indices. These peaks are not magnetic and in accord with previous work they are attributed to the onset of 3D charge order at 320 K [5]. Comparing the data at 220 K to that at 280 K (where there is no long range magnetic order) shows new intensity appearing on peaks at integer and half-integer values of L with strongest enhancement at small L values. Such enhanced scattering at small L values is expected for scattering from the ordered magnetic moments of Fe^{2+} and Fe^{3+}.

To explicitly check which contributions of the scattering are due to magnetic and/or charge order we performed polarized neutron diffraction measurements on the C5 spectrometer. The results of these measurements are shown in Figure 1(b). The scattering in the spin flip channel is magnetic and the lack of scattering in the non-spin flip channel at small L values provides confirmation that the magnetic moments point along the *c*-axis. Thus, the neutron scattering data demonstrates 3D magnetic correlations below 240 K in $LuFe_2O_4$.

To constrain models for the spin configuration in $LuFe_2O_4$, a large number of reflections were measured at 220 K by scanning along the (1/3 1/3 L), (2/3 2/3 L), and (4/3 4/3 L) directions. To solve for the magnetic structure, representational analysis was performed to consider those magnetic structures that are symmetry allowed from the parent R-3m space group. From this analysis we concluded that the spin configuration is described by a ferrimagnetic structure with ordering wavevector (1/3 1/3 0), the presence of ½-integer reflections occurring as a result of the charge ordering which decorates the lattice with differing magnetic moment on Fe^{2+} and Fe^{3+} sites with a periodicity of (1/3 1/3 ½). A ferrimagnetic model consistent with the representational analysis provides good agreement with the data. The proposed magnetic structure shown in Figure 2 has 2/3 of the spins pointing in one direction and 1/3 in the opposite direction.

Below T_L, profound changes occur in the magnetic scattering as shown in Figure 1 (a). In particular, a component to the scattering builds up which is extremely broad along (1/3 1/3 L) but sharp along (HH0). Figure 1 (a) also shows that below T_L significant changes occur in the magnetic peaks along (1/3 1/3 L). The intensity along (1/3 1/3 L) for

magnetic reflections changes rather dramatically with some peaks becoming more intense (e.g. (1/3 1/3 1)) and some peaks becoming less intense (e.g. (1/3 1/3 0)). Thus, 3D magnetic correlations persist below T_L albeit with a shorter correlation length than found for T_N. Finally, we note that scans along (110) have revealed the existence of a new set of satellite peaks indexed as (1/3±δ 1/3±δ 3L/2) where δ ~ 0.027 (not shown) below T_L.

In conclusion, we show that that $LuFe_2O_4$ has two transitions below 300 K. Both of these transitions involve a 3D magnetically correlated structure with a finite correlation length along the *c*-axis. The degree to which the correlation length is an intrinsic property or is the result of disorder, most likely oxygen stoichiometry, is yet to be elucidated. Below T_N a ferrimagnetic spin configuration is found with a magnetic propagation vector of (1/3 1/3 0) with magnetic intensity occurring at (1/3 1/3 L) where L is a half-integer arising due to the charge ordering at 320 K. Theoretical models taking into account the 3D nature of the magnetic interactions as well as the sequence of magnetic phase transitions described above should provide additional insight into the multiferroic behavior of $LuFe_2O_4$.

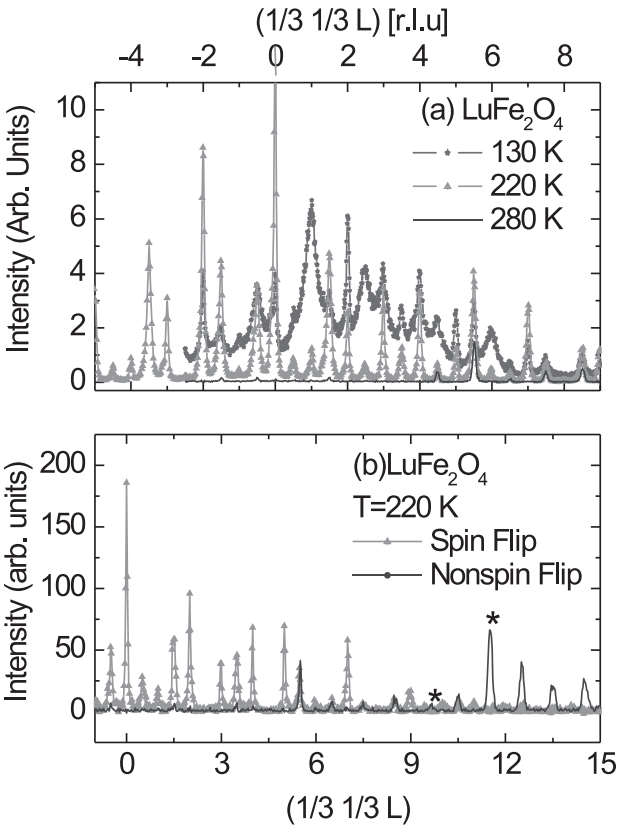

Fig 1. (a) Scans along (1/3 1/3 L) at several temperatures showing the changes to the scattering below T_N (240 K) and T_L (175 K). (b) Polarized neutron scattering data along (1/3 1/3 L). The * indicate peaks contaminated by aluminum background scattering.

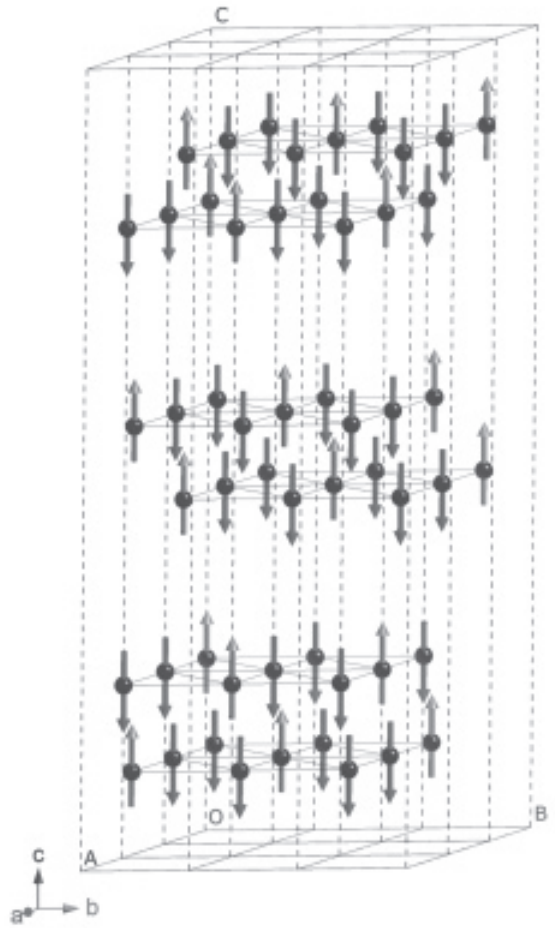

Fig 2. The ferrimagnetic structure determined below 240 K.

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