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ScienceDirect
Physica B 385–386 (2006) 418–420
PHYSICA B
www.elsevier.com/locate/physb

Crystalline and magnetic structures of Sr_2FeMoO_6 double perovskites

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Abstract

Neutron diffraction and magnetic susceptibility has been used to study the crystalline and magnetic structures of Sr_2FeMoO_6. The compound crystallizes into a tetragonal I4/m symmetry. Both of the Fe and Mo moments were found to be ordered at low temperatures, with the ordered moments beginning to develop below 450 and 165 K for the Fe and Mo ions, respectively. The spin configuration may be viewed as consisting of ferromagnetic Fe/Mo planes that are mutually intersected at an angle of 120°, and form a non-collinear structure. The saturated moments for the Fe and Mo ions were $\langle \mu_Z \rangle = 3.30(4)\mu_B$ and $1.74(9)\mu_B$, respectively.

PACS: 75.30.Kz; 61.12.−q

Keywords: Neutron scattering; Perovskite; Magnetic ordering

In double perovskites of general chemical formula $A_2B'B''O_6$ (where A = alkaline-earth or rare-earth ion), the transition metal sites are alternately occupied by two different types of cations B′ and B″. It is clear that both the valence and the ionic size of B′ and B″ are crucial in affecting the physical properties of the systems. Among them, Sr_2FeMoO_6 is known as a magnetoresistive material, since it exhibits a large low-field tunnelling type of magnetoresistive effect near room temperature [1,2]. The properties related to its high Curie temperature (much higher than room temperature), high spin polarization, low operating magnetic field, and conducting ferrimagnetic character have made Sr_2FeMoO_6 a suitable material for spin devices. For the magnetic behaviour, it has been suggested [3,4] that the superexchange interaction between the Fe^{3+}($3d^5$, $S=\frac{5}{2}$) moments in the FeO_6 octahedra and the Mo^{5+}($4d^1$, $S=\frac{1}{2}$) moments in the MoO_6 octahedra may produce a large ferromagnetic magnetization at low temperatures when both the Fe and Mo moments order. In this article, we report on the results of studies made on the magnetic behaviour of the Fe and Mo moments in an ordered Sr_2FeMoO_6 at low temperatures.

A polycrystalline sample of Sr_2FeMoO_6 was prepared by the standard solid-state reaction techniques. Stoichiometric mixtures of $SrCO_3$, Fe_2O_3, and MoO_3 powders were thoroughly mixed and heated at 800 °C for 12 h, followed by slowly cooling to room temperature at a rate of 5 °C/min. After regrinding and repressing, the resultant powder was then heat treated at 1000 °C for 28 h in a flowing H_2/N_2 (5%/95%) atmosphere.

The crystal and magnetic structures of the compound were studied by neutron powder diffraction. The neutron diffraction measurements were performed at the NIST Center for Neutron Research. The high-resolution neutron powder diffraction pattern was collected on BT-1 diffractometer, using a Cu(3 1 1) monochromator crystal to extract neutrons of wavelength 1.5401 Å. Whereas the magnetic diffraction patterns were taken on BT-7 triple-axis spectrometer, using PG(0 0 2) monochromator crystal and filters to extract 2.4701 Å neutrons.

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doi:10.1016/j.physb.2006.05.140

Fig. 1 shows the observed and refined high-resolution neutron powder diffraction pattern taken at room temperature. The pattern was analysed using the GSAS program, following the Rietveld method. The observed diffraction pattern can be described very well by the tetragonal I4/m symmetry as reported [5] in a previous study. No unexpected peaks are present in the diffraction pattern, showing that it is single phase to within the 2% neutron resolution limitation. Superstructure peaks, {0 1 1} and {0 1 3} arising from the Fe/Mo are clearly observed in the diffraction pattern, which are absent in the disordered sample, and a so-called ordered structure with Fe and Mo placed right on B′ and B″ sites is formed [6]. The chemical composition that we obtained from the structural analysis is Sr_2FeMoO_6, which is consistent with the stoichiometric one.

Fig. 2 shows the variations of the in-phase component of the AC magnetic susceptibility with temperature, measured using a weak driving field with an rms strength of 1 Oe and a frequency of 10^4 Hz. The main features seen are the peak at around 165 K and the weakening of the magnetic response at low temperatures. This behaviour cannot be due to the ordering of the Fe moments, since they order at around 450 K (see data below). We believe that it is associated with the ordering of the Mo moments, which results in a decrease in the magnetic response.

A portion of the magnetic diffraction patterns taken at 25 K is shown in Fig. 3, where the diffraction pattern taken at 480 K, serving as the non-magnetic background, has been subtracted. All of the magnetic peaks appear at the same positions as the nuclear ones do. This may not indicate a simple ferromagnetic arrangement for the spins, since there is more than one magnetic ion in the nuclear unit cell. If Mo carries no ordered moment, the best fit that we obtained was a simple ferromagnetic arrangement for the Fe ions, with the moments pointing along the *b* crystallographic axis direction. This spin structure gave a very poor fit. As an example, the calculated intensity ratios between the {0 0 2} + {1 1 0} and {0 1 1} + {1 0 1} reflections and between the {1 1 2} and {0 1 1} + {1 0 1} reflections are, respectively, 0.51 and 0.70, while the observed ratios are, respectively, 0.20 and 0.23. Significant improvement in the fits may be obtained by assuming Mo moments were ordered at low temperature. We went through many models, and finally settled with the one shown in Fig. 4. The calculated pattern based on this proposed model is shown as the solid line in Fig. 3, which agrees very nicely with the observed one. In this model, it consists of ferromagnetic Fe/Mo planes that mutually intersect at an angle of 120°. The moments for both of the Fe/Mo spins lie in the *b–c* or *a–c* crystallographic plane. We, unfortunately, cannot resolve the *b–c* from the *a–c* planes, due to the similarity between the *a* and *b* axes. The non-parallel arrangement between the Fe and Mo moments is consistent

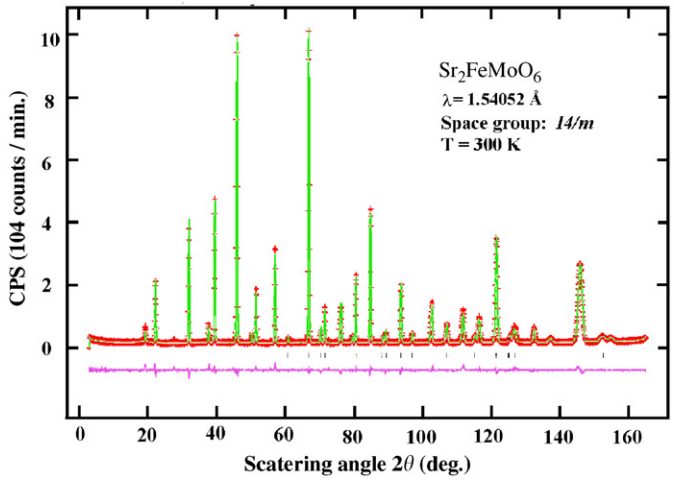

Fig. 1. The observed (crosses) and fitted (solid lines) high-resolution neutron powder diffraction pattern of Sr_2FeMoO_6 taken at room temperature.

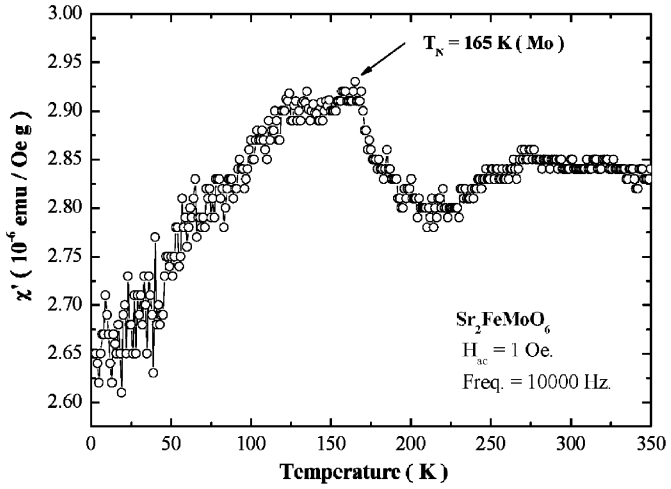

Fig. 2. Plot of the temperature dependence of the in-phase component of the ac magnetic susceptibility. An anomaly at around 165 K is evident, signalling the ordering of the Mo moments.

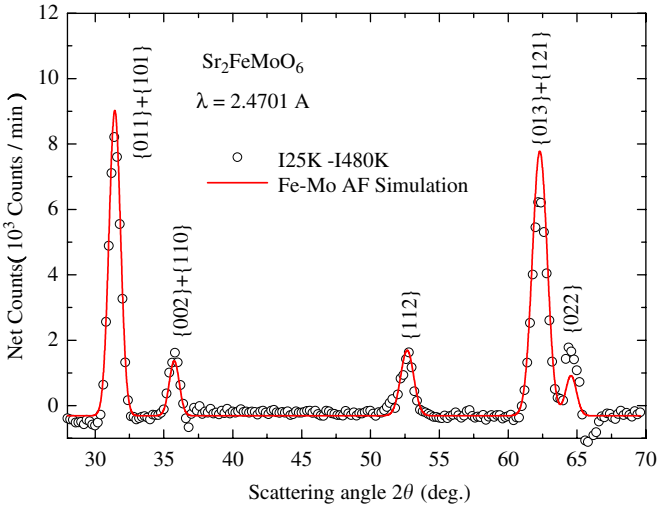

Fig. 3. The magnetic diffraction pattern obtained at 25 K, where the solid line indicates the calculated pattern, using the proposed model. It appears that the calculated pattern fits nicely to the observed one.

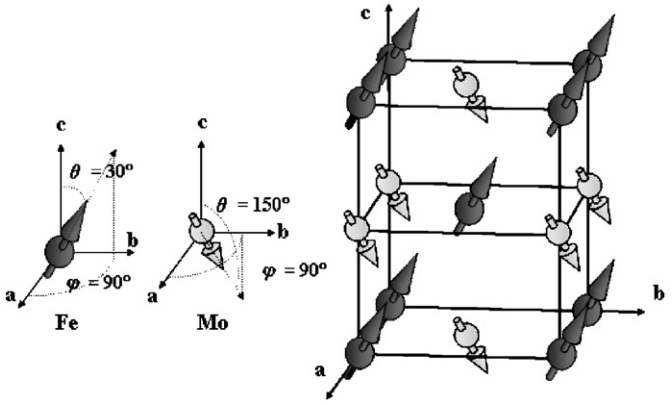

Fig. 4. Plot of the proposed spin arrangement of Fe and Mo in Sr_2FeMoO_6 at low temperatures.

with the observations that the magnetic response decreases below 165 K. The saturated moments that we obtained for the Fe and Mo ions were $\langle \mu_Z \rangle = 3.30(4)\mu_B$ and $1.74(9)\mu_B$, respectively.

Fig. 5 shows the variations of the representative $\{0\,1\,1\}+\{1\,0\,1\}$ and $\{0\,0\,2\}+\{1\,1\,0\}$ integrated intensities with temperature. These two curves display the same temperature dependence, and show an ordering temperature of $T_C \approx 450$ K for the Fe spins, which agrees with a separate study [7]. We finally remark that there is a small kink on the $\{0\,0\,2\}+\{1\,1\,0\}$ curve at around 165 K, that may be related to the Mo ordering. Whether there is a definite link is not clear from the data.

The work at NCU was supported by the NSC of the ROC under Grant no. NSC 94-2120-M-008-003.

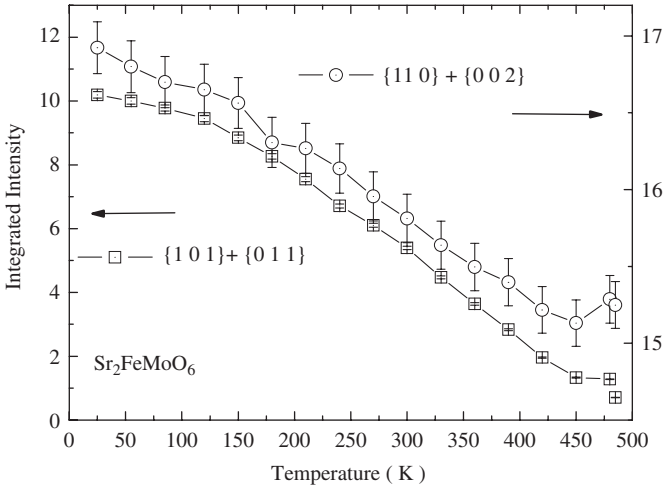

Fig. 5. The temperature dependence of the integrated intensities of two representative magnetic reflections, showing an ordering temperature of $T_C \approx 450$ K for the Fe spins.

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