Crystal and magnetic structure of the YSrCuFeO$_{5+y}$ compound

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Abstract

We studied the crystal and magnetic structure of the oxygen deficient perovskite YSrCuFeO$_{5+y}$. The structure was refined from neutron powder diffraction data by assuming both substitutional and displacement disorder. Three-dimensional (3D) antiferromagnetism with $T_N = 400 \pm 10$ K occurs and all the magnetic peaks were indexed with two propagation vectors $k_1 = [\frac{1}{2} \frac{1}{2} \frac{1}{2}]$ and $k_2 = [\frac{1}{2} \frac{1}{2} 1]$ from 300 down to 2 K.

Keywords: Antiferromagnetism; Perovskite compounds; Powder diffraction; Rietveld refinement

1. Introduction

YBaCuFeO$_5$ has a tetragonal structure similar to that of YBa$_2$Cu$_3$O$_{6-\delta}$, but with the chain levels absent [1]. $^{57}$Fe Mossbauer spectroscopy revealed a single Fe site typical of Fe$^{+3}$ ($S = \frac{5}{2}$) with the Fe moments antiferromagnetically ordered ($T_N = 442$ K) [2]. The substitution of Y with other rare earths leads to a variation in $T_N$, probably due to the different amount of extra oxygen incorporated for each rare earth within the Y layer. In this work, we focus on the structural and magnetic properties of YSrCuFeO$_{5+y}$ and report the results of a neutron powder diffraction (NPD) study in the temperature range 2–300 K.

2. Experimental methods

The synthesis procedure of an YSrCuFeO$_5$ sample along with a detailed study of the structure and of the magnetic properties (by means of Mossbauer spectroscopy) will be published elsewhere. NPD experiments were performed in the flat-cone E2 and E6 focusing single crystal diffractometers of the reactor BERII in Berlin. The (3 1 1) reflection of a Ge monochromator with $\lambda \approx 1.2$ Å and the (0 0 2) reflection of a pyrolytic graphite monochromator with $\lambda \approx 2.4$ Å were used.

3. Results and discussion

The major question of a structural study is to decide which is the more appropriate space group. For YSrCuFeO$_5$, the X-ray powder diffraction data certainly cannot decide between the P4mm (model I) and P4/mmm space groups (model II when $Z_{Cu} = Z_{Fe}$, model III when $Z_{Cu} \neq Z_{Fe}$). The NPD patterns were refined using the FULLPROF program [3]. The obtained lattice parameters at 2 K are $a = 3.8317(1)$ Å and $c = 7.6076(4)$ Å, while $R_B$ is lower for model II (5.42%) than for models I and III (6.48% and 6.52%, respectively).

Since the amount of extra oxygen is very small, we cannot prove its presence by NPD. However, there is indirect evidence from Mössbauer spectroscopy for both YSrCuFeO$_5$ and PrBaCuFeO$_5$ [4]...
that \( \sim 15\% \) of Fe is in octahedral coordination. Moreover, in oxygen saturated PrBaCuFeO\(_5\), the location of the extra oxygen was proved with NPD [4].

Fig. 1 shows the refined NPD pattern at 2 K. In addition to the nuclear structure peaks, there are peaks, whose intensity decreases with increasing temperature and are therefore attributed to antiferromagnetic ordering. Mössbauer spectroscopy determined \( T_N \) to be 400 \( \pm 10 \) K. These peaks were indexed with superlattice indices \((h_1/2, k_1/2, l_1/2)\) and \((h_2/2, k_2/2, l_2)\), where \( h_1, k_1, h_2, k_2, l_1, l_2 \) are odd integers (like in PrBaCuFeO\(_5\) [4]). The former family of reflections comes from a spin arrangement with propagation vector (PV) \( k_1 = [\frac{1}{2} \frac{1}{2} \frac{1}{2}] \), i.e. the unit cell is doubled along all three axes. The latter comes from a spin arrangement with PV \( k_2 = [\frac{1}{2} \frac{1}{2} 1] \), i.e. the unit cell is doubled only along the \( a- \) and \( b- \) axis.

The observed reflections can be interpreted either as an incoherent mixture of domains with different PVs and with the same ordered moment, but occupying different volumes or by a canted spin configuration which is the vector sum of two collinear magnetic structures with different ordered moments but occupying the same volume [5].

The expression of the magnetic structure factor for a magnetic unit cell with cell constants \( a_M = b_M = \sqrt{2}a_N \) and \( c_M = c_N \) (corresponding to \( k_2 \)) points out that the absence of the \( l = 0 \) peak means that \( p_A = -p_B \), where A and B are the (Cu, Fe) layers above and below the Y layer. This occurs only when layers A and B are equivalent. Due to the small number of magnetic reflections, we had to consider the magnetic ions at the \( z = 0.25 \) position and represent them by a mean magnetic moment. This assumption corresponds to model II. Regarding \( k_1 \), it can be either \( p_A = p_B \) or \( p_A = -p_B \), but our data cannot distinguish between them. Thus, three are the possible collinear magnetic models for \( k_1 \) and one for \( k_2 \) (Fig. 2).

For the canted structure model, the ordered moments per ion at 2 K are \( S[k_1] = 1.5(1)x + 0.2(5)y\mu_B \) (\( R_B = 2\% \)) and \( S[k_2] = 1.6(1)y\mu_B \) (\( R_B = 5.6\% \)). Thus, the magnetic moment is nearly perpendicular to the \( c- \) axis. \( S[k_1] \) is equal to 1.4, 1.2 and 1.0\( \mu_B \), while \( S[k_2] \) is equal to 1.6, 1.2 and 1.0\( \mu_B \) at 100, 200 and 300 K, respectively. For the model with the incoherent mixture of domains and with the two PVs having the same moment (\( S \approx 2\mu_B \)), the two domains \( k_1 \) and \( k_2 \) represent 41\% and 59\%, respectively, of the total crystal volume at 2 K.
The existence of two PVs cannot be explained by some kind of interactions between (Cu, Fe) and the rare-earth ions (Y or Pr), because in YSrCuFeO$_5$, Y$^{3+}$ unlike Pr$^{3+}$, does not carry a magnetic moment.

References