Neutron Scattering Investigation of Multiferroic Ce$_{1-x}$Eu$_x$CrO$_3$ Nanopowders

Maryam Taheri$^1$, Zahra Yamani$^1$, Roxana Flacau$^2$, Reinhard Kremer$^3$, Fereidoon Razavi$^1$

$^1$ Department of Physics, Brock University, St Catharines, Ontario, Canada
$^2$ Canadian Neutron Beam Centre, Canadian Nuclear Laboratories, Chalk River, ON, Canada
$^3$ Max Planck Institute for Solid State Research, Stuttgart, Germany

Magnetic multiferroic materials with the coexistence of ferroelectric and ferromagnetic ordering have attracted increasing interest in recent years not only because of their potential for applications in multifunctional devices but also for the fundamental understanding of their properties. The perovskite rare-earth orthochromites with the general formula RCrO$_3$ (where R is a rare-earth ion) are one such family of multiferroic materials with the great potential applications in optics and magnetism such as catalysts, electrolytes, fuel cells and refractory ceramics. These compounds with 4 formulas per unit cell are orthorhombically distorted from the ideal cubic structure at room temperature with space group of Pbnm [1-3]. RCrO$_3$ has two antiferromagnetic sublattices consisting of Cr$^{3+}$ (3d$^3$) and R$^{3+}$ (4f$^n$) moments. The ideal bond angle of Cr-O-Cr is 180° and their magnetic moments should be antiparallel, however, the mismatch of R-O and Cr-O bond lengths causes the crystal distortion and weak ferromagnetism. Most members of the RCrO$_3$ family are canted antiferromagnetic and exhibit the magnetoelectric effect due to the Dzyaloshinskii–Moriya interaction [3, 4]. The relative size of the R$^{3+}$ appears to have an important role in the magnitude of this tilting which turn strongly affects on physical properties, including magnetization. Variations of rare earth ions also change the electronic configuration [4-6].

Recent studies [7] on pure nanocrystalline CeCrO$_3$ have revealed that it exhibits multifunctionalities such as antiferromagnetism, relaxor-like dielectric behaviour and an optical band gap in the visible region. To understand how the ionic radius size and electronic configuration affect on the structural, magnetic and electrical properties of this CeCrO$_3$ compound, we have undertaken a systematic study of this material by substituting the Ce$^{3+}$ (with 1.2 Å ionic radius size and 4f$^1$ electron configuration) with the Eu$^{3+}$ (with 0.94 Å ionic radius size and 4f$^6$ electron configuration). A new series of nano-sized powder Ce$_{1-x}$Eu$_x$CrO$_3$ (x = 0.0 to 1.0) with orthorhombic structure were synthesized using a solution combustion method. All samples were sintered at 950 °C for 12 h.

In order to determine the nuclear and magnetic structure and how they evolve with Eu-doping, we performed neutron powder diffraction measurements at C2 powder diffractometer on nanopowders Ce$_{1-x}$Eu$_x$CrO$_3$ (with x = 0, 0.1, 0.5, 0.9 and 1). The diffraction patterns were collected using 2.37 Å and 1.33 Å wavelengths. Since Eu has a large neutron absorption cross section, we used flat-plate geometry for mounting the sample in the beam [8]. With this geometry we took advantage of the large size of the beam and hence a larger sample volume but with small thickness to minimize the neutron path length within the samples. In order to determine the Neel transition temperature, we collected the diffraction pattern as a function of temperature from room temperature down to 3 K.

The refinement of the diffraction pattern at room temperature indicated that for all doping levels the nuclear structure remained orthorhombic with no additional structural phase transitions down to 3 K. Furthermore, from the temperature dependence of the observed patterns, we determined that Cr$^{3+}$ ions order below Neel temperature of $T_N$=260K in CeCrO$_3$ (Fig. 1) while it decreases with Eu-doping (180K in EuCrO$_3$). The refinement of the low-temperature neutron diffraction patterns reveals that ordering of the Cr ions leads to a G-type antiferromagnetic structure. In fact, the magnetic moments of Cr$^{3+}$ are aligned along the b-axis in a G-type antiferromagnetic arrangement where a Cr$^{3+}$ spin is aligned antiparallel to its six nearest neighbours. These results and the value of the ordered Cr$^{3+}$ moment of 2.42(±0.01) $\mu_B$ are in good agreement with previous results [7] on CeCrO$_3$. Similar analysis on EuCrO$_3$ indicates that the Cr$^{3+}$ magnetic moment is 2.5(±0.1) $\mu_B$. None of the diffraction patterns collected for different
Doping levels revealed any additional peak at low temperatures down to \( T=3K \). Thus, we couldn’t detect the magnetic ordering of the rare-earth ions in these samples which is in disagreement with the previous literature on pure CeCrO\(_3\) where weak magnetic ordering for Ce\(^{3+}\) ions was reported [7].

In order to determine the crystal field splitting level of \( R^{3+} \) ion, we also performed an inelastic neutron scattering experiment using N5 triple-axis spectrometer. These measurements on CeCrO\(_3\) sample (Fig.2) revealed the splitting energy level of \( 4.57 \pm 0.02 \) meV, in good agreement with value obtained from Schottky heat capacity anomaly at low temperatures \( 4.41 \pm 0.03 \) meV, using an equation

\[
C_{Sch} = R\frac{\Delta^2}{(1+\frac{T}{\Theta})^2}
\]

where \( \Delta \) is the energy apart between the levels and \( R \) is the gas constant.

References


Figure 1 Neutron powder diffraction of CeCrO\(_3\) at \( T=3K \) and \( T=280K \), as well as its magnetic phase transition.
Figure 2 Inelastic neutron scattering of CeCrO3 at T=3K and T=290K, (b) Schottky heat capacity of CeCrO3 at zero applied magnetic field.