Experimental report

28/09/2017

Proposal: **5-31-2464** **Council:** 4/2016

Title: Determination of the magnetic structures of the rutile-type Cr2ReO6 and CrReO4 oxides

Research area: Materials

This proposal is a new proposal

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Samples:
Cr2ReO6
CrReO4
Sr0.9R0.1TiO3 (R=Pr,Nd.Eu)
R2MnRuO6 (R=Ho,Dy)

Instrument	Requested days	Allocated days	From	To
D20	2	1	03/10/2016	04/10/2016
D2B	2	2	04/11/2016	07/11/2016

Abstract:

Oxides derived from rutile CrO2 oxide, with bi-rutile or tri-rutile crystal structures, present intriguing magnetic structures that cannot be rationalized by the Goodenough-Kanamory superexchanmge rules. Here we propose to investigate bi-rutile CrReO4 (Re5+:5d2) and tri-rutile Cr2ReO6 (Re6+:5d1) antiferromagnets that have been prepared under high-pressure conditions. The determination of the magnetic structure is of paramount importance to check a novel approach to understand the magnetic exchange interactions between Cr3+ ions when the counter-cation has a partially occupied d orbital (Re5+ or Re6+), and how the magnetic exchange interactions between Cr3+ ions change. For this purpose we ask for 2 days at D2B and 2 days at D20 to study the crystal magnetic structures and their thermal evolution across TN.

Half metallic ferrimagnets are scarce; rutile-type CrO_2 is among the few ferromagnetic half-metals with Curie temperature above RT; $T_c \approx 400$ K. The magnetic properties of the CrO_2-derived rutile-type compounds have recently attracted renewed interest due to the observation of complex magnetic behaviors. Replacing half or one-third of Cr in CrO_2 with another counter-cation in an ordered fashion can lead to bi- or tri-rutile structures. Both Cr_2TeO_6 and Cr_2WO_6 crystallize in the tri-rutile structure having the Cr^{3+} bilayers stacked alternatively with the nonmagnetic Te^{6+}/W^{6+} layers along the tetragonal c axis. It has been shown that both compounds are antiferromagnetic insulators with the Néel temperatures $T_N = 93$ K and 45 K, respectively. Such a scenario is further elaborated by our recent study on the sister compound Cr_2MoO_6 synthesized under high-pressure and high-temperature conditions [1]. These studies underscore a novel approach to tune the magnetic exchange interactions between Cr^{3+} ions via modifying the electronic states of counter-cation in the exchange pathway through orbital hybridization. As a follow-up to these studies, an interesting question to address is how the magnetic exchange interactions between Cr^{3+} ions change when the counter-cation has a partially occupied d orbital.

To this end, bi-rutile $CrReO_4$ (Re^{5+}:$5d^2$) and tri-rutile Cr_2ReO_6 (Re^{6+}:$5d^1$) are important candidate materials that deserve detailed investigations. Although both compounds have been reported to exist [2], their magnetic properties remain poorly characterized to date. Here, we have prepared nearly single-phase $CrReO_4$ and Cr_2ReO_6 polycrystalline samples (~1 gram) under **high-pressure** and high-temperature conditions. To determine the exact configuration of their magnetic structures is indispensable to understand the magnetic exchange interactions.

In this experiment, neutron powder diffraction (NPD) data were collected in the diffractometers D2B and D20 for the mentioned $CrReO_4$ and Cr_2ReO_6 rutile-type oxides. For the structural refinement, room temperature patterns were recorded in the high-resolution powder diffractometer D2B (λ = 1.594 Å); for the resolution of the magnetic structures, NPD patterns were sequentially collected across and below T_N in the high-flux diffractometer D20, given the small available sample, with a longer wavelength (λ = 2.41 Å). A standard orange cryostat was utilized to cool the samples down to 2 K. The powder samples were contained in vanadium cylinders; a time of 2 hours was required to collect full diffraction patterns at D2B, and 30' scans were dynamically recorded at D20, with longer counting times of 2 h at 2 K. The NPD data were analyzed by the Rietveld method [3] using the FULLPROF program [4]. A pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. The following parameters were refined in the final run: scale factor, background coefficients, zero-point error, pseudo-Voigt corrected for asymmetry parameters, positional coordinates and isotropic thermal factors for all the atoms, as well as the magnetic moments for the magnetic structures. The neutron scattering lengths for Cr, Re and O are, 3.635, 9.20 and 5.803 fm, respectively.

The pattern collected for Cr_2ReO_6 at 2K in the high-flux D20 diffractometer shows the appearance of some tiny additional reflections of magnetic origin, which can be indexed with the propagation vector k= [0.5,0,0.5]. The crystal structure was resolved with the MAXMAGN application using the Bilbao Crystallographic Server; the maximal magnetic space groups for the parent space group P42/mnm (No. 136) where P_a2_1/c and C_a2/m. After trying the different possibilities, the best fit between observed and calculated magnetic reflections was found for P_a2_1/c. The good agreement between observed and calculated neutron profiles is shown in Fig. 1a. The first and second reflection marks correspond to the Cr_2O_3 and $CrReO_4$ minor impurities, and the third raw belongs to the crystal and magnetic structure of Cr_2ReO_6.

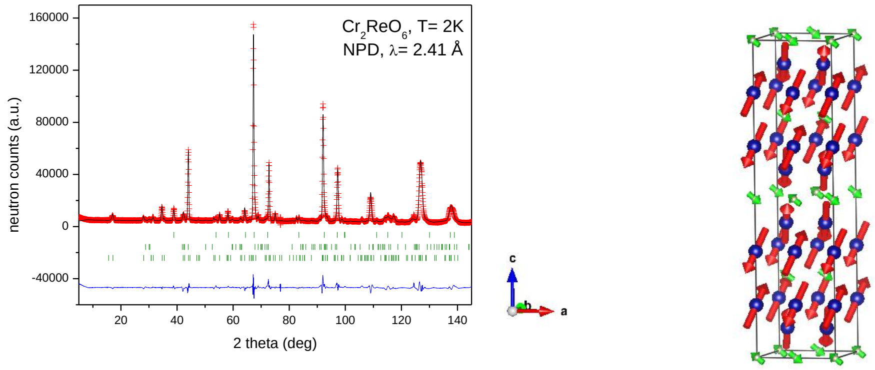

Figure 1. a) Rietveld profiles for Cr_2ReO_6 at 2 K and b) view of the magnetic structure: red arrows are Cr spins; green arrows are Re moments.

The magnetic structure regarding the coupling of the Cr magnetic moments is depicted in Fig. 1b. The Cr magnetic moments lie in the *bc* plane, showing an antiferromagnetic arrangement along *a* and *c* axes and a zig-zag orientation along *b*. The refined magnitude of the Cr moments at 2 K is 1.63 μ_B. Concerning the Re magnetic moments, they exhibit a very small refined magnitude of can present a magnetic component with the 0.26 μ_B, adopting a collinear arrangement approximately on the ac plane. Table 2 gathers the magnitudes of the components of the Cr and Re magnetic moments.

Regarding $CrReO_4$, the additional reflections observed at 2 K could be indexed with a propagation vector k= [1,0,0.5]. Using the MAXMAGN software the maximal magnetic space groups for the parent C2/m (16) space group where C_c2/c and C_c2/m, of which the best fit corresponds to C_c2/c.

The goodness of the Rietveld fit at 2 K is illustrated in Fig. 2a. A pure phase is identified in this case.

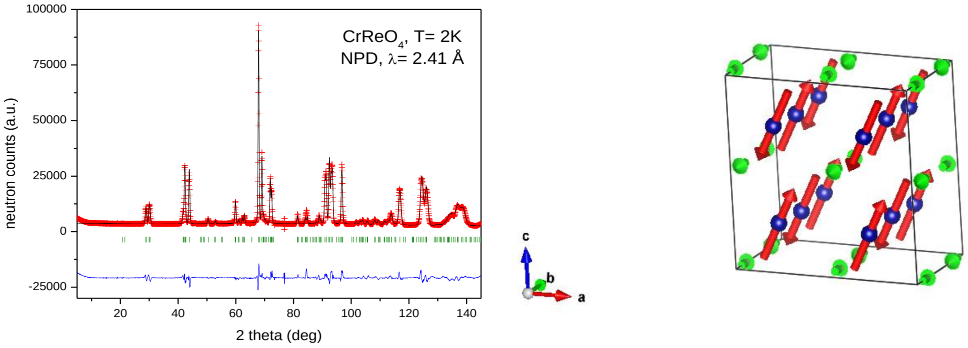

Figure 2. a) NPD profiles for $CrReO_4$ at 2 K, b) view of the magnetic structure (red arrows represent Cr spins; green arrows are the Re moments.

The magnetic structure is displayed in Fig. 2b. The ordered Cr magnetic moments lie in the ac plane, showing a perfect collinear antiferromagnetic structure that propagates along the *b* and *c* axes. The refined magnitude of the Cr magnetic moments is 1.91(3) μ_B, which is close to that expected for Cr^{4+} (t_{2g}^2) of 2 μ_B. Regarding Re moments the refined value is extremely small, of 0.3 μ_B, presenting a magnetic component in the *b* axis direction. This is presumably due to the reduced moment of Re ions with spatially much extended 5d orbitals.

References:

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[2] A. W. SLEIGHT, J. SOLID STATE CHEM. 14, 597 (1975).
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[4] J. Rodríguez-Carvajal, Physica B 192 (1993) 55