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Isolated spin 3/2 plaquettes in Na₃RuO₄

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Abstract

The crystal structure of Na₃RuO₄ determined by powder neutron diffraction is reported. The structure consists of isolated tetramers of edge sharing RuO₆ octahedra in the *ab* plane, creating isolated four-member plaquettes of Ru atoms comprised of two equilateral triangles sharing an edge. Magnetic susceptibility measurements reveal an antiferromagnetic transition at ~29 K, with $\theta_w = -141 K$. Neutron diffraction data indicate the onset of three-dimensional magnetic ordering at 29 K. © 2005 Elsevier Inc. All rights reserved.

Keywords: Ruthenates; Na₃RuO₄; Magnetic properties.

1. Introduction

Ruthenates are rich in structure and varied in properties. Perovskite-based alkaline earth ruthenates $(MRuO_3 \text{ or } M_{n+1}Ru_nO_{2n+1}, \text{ where } M = Ca, Sr, Ba),$ exhibit properties varying from ferromagnetism in SrRuO₃ [1], to weakly temperature dependent Pauli paramagnetism in BaRuO₃ [2] to superconductivity in Sr₂RuO₄ [3]. Characterization of Sr₃Ru₂O₇ at higher temperatures point towards ferromagnetic interactions between the Ru atoms, while at lower temperatures, the compound crosses over to antiferromagnetic-like behavior [4] and becomes metamagnetic at high applied fields [5]. $CaRuO_3$ can be viewed in the same manner: its paramagnetic behavior can be tipped toward ferromagnetism by doping [6,7]. Such varied behavior of properties suggests that ruthenates sit on the boundary between magnetic and non-magnetic states.

The alkali metal ruthenates have not been as extensively studied. Recent work on the hollandites, KRu_4O_8 and $RbRu_4O_8$, revealed temperature independent Pauli paramagnetism [8] and metallic conductivity. Pauli paramag-

netism has also been observed in Li₂RuO₃ [9]. Although the magnetic properties of these three compounds are relatively ordinary, a further investigation of the alkali metal ruthenates may expose compounds that exhibit more unusual properties. For instance, Li₃RuO₄ exhibits short range antiferromagnetic ordering, with the possibility of spin freezing at ~10 K [10]. The Na–Ru–O system, for example, has not been thoroughly investigated, with several previously reported phases only superficially characterized [11]. Recently, Darriet et al. reported the structure and the magnetic properties of NaRuO₂ as well as Na₂RuO₄ [12,13]. NaRuO₂ displays paramagnetic behavior, while Na₂RuO₄ exhibits antiferromagnetic behavior attributed to short range ordering.

Although Na₃RuO₄ has been reported as being analogous in structure to Na₃NbO₄, the crystal structure was not previously refined, and magnetic data had only been collected from 77 to 600 K [14]. Mössbauer ⁹⁹Ru data were interpreted in terms of an antiferromagnetic long range ordering in Na₃RuO₄ at low temperature [15]. In this paper, we present the neutron diffraction refinement of Na₃RuO₄ and low temperature magnetic characterization. It is postulated that long range ordering of the spin 3/2 Ru⁵⁺ magnetic moments is frustrated by the isolated equilateral plaquettes present in the structure.

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2. Experimental

Polycrystalline samples of Na_3RuO_4 were synthesized using stoichiometric amounts of NaOH pellets (Merck, 97.0%) and RuO₂ powder (Alfa Aesar, Ru 54% min). The RuO₂ powder was heated prior to sample preparation at 700 °C for 2 h to remove any absorbed water. Reaction mixtures were placed in dense alumnia crucibles and heated first at 500 °C under flowing O₂ for 18 h and then at 650 °C under N₂ for 18 h, with an intermediate grinding.

Phase purity was determined via powder X-ray diffraction using $CuK\alpha$ radiation. Resulting patterns corresponded with previously reported peak positions [14]. Magnetic characterization was performed using a Quantum Design PPMS magnetometer. The neutron powder diffraction intensity data of Na₃RuO₄ were collected at the NIST Center for Neutron Research, on a high resolution powder neutron diffractometer, with monochromatic neutrons of wavelength 1.5403 A produced by a Cu(311) monochrometer. Collimators with horizontal divergences of 15', 20' and 7' of arc were used before and after the monochrometer and after the sample, respectively. Data were collected in the 2θ range of 3° and 168° , with a step size of 0.05'. The structural parameters were refined using the program GSAS [16]. The neutron scattering amplitudes used in the refinement were 0.363, 0.721, and 0.581 (10^{-12} cm) for Na, Ru and O, respectively. The magnetic peak intensity at $2\theta =$ 23.1° as a function of temperature for Na₃RuO₄ was measured with neutrons of wavelength 2.359 Å on the BT-2 triple-axis spectrometer at the NIST Center for Neutron Research, with a PG filter employed to suppress higher order wavelength contaminations.

3. Results

The structure of Na₃RuO₄ was refined to a monoclinic space group C2/m (#12) with lattice parameters of a = 11.0295(6) A, b = 12.8205(7) A, c = 5.7028(3) A, and $\beta = 109.90(3)^{\circ}$, and the initial atomic positions were taken as those of Na_3TaO_4 [14]. The neutron diffraction pattern is shown in Fig. 1. Atomic positions and thermal parameters are listed in Table 1: the final structure was very close to that of Na₃TaO₄. Relevant Ru-O and Na-O bond distances, as well as Ru-O bond angles, are listed in Tables 2 and 3, respectively. The average Ru–O bond length (= 2.01 Å) is similar to that reported for other Ru⁵⁺ compounds [17–19]. The oxygen coordination to the Ru atom creates two distinct octahedral environments (see Fig. 3). The octahedra are distorted both in bond lengths and bond angles. The distortions are similar to those seen in other ruthenates, such as β -La₃RuO₇ and La₂Sr₂LiRuO₈ [20,21]. In the present case, the irregular Ru–O bond lengths in the RuO₆



Fig. 1. Observed intensities (crosses) and calculated neutron diffraction pattern (solid line) Na₃RuO₄ at 295 K. Vertical lines show reflection positions. Differences between the observed and calculated intensities are shown at the bottom of the figure.

Table 1

Atomic positions and thermal parameters of Na₃RuO₄, e.g., C2/m(#12) a = 11.0295(6)Å, b = 12.8205(7)Å, c = 5.7028(3), $\beta = 109.908$ (3), Z = 4

Atom	Site	x	у	Ζ	$U_{iso} \times 100 (\AA^2)$
Ru1	4g	0	0.1252(7)	0	0.59(11)
Ru2	4i	0.2550(9)	0	0.01777(16)	0.59(11)
Na1	4g	0	0.3759(15)	0	1.28(13)
Na2	4e	$\frac{1}{4}$	$\frac{1}{4}$	0	1.28(13)
Na3	8j	0.2421(13)	0.1254(10)	0.	1.28(13)
Na4	2c	0	0	1/2	1.28(13)
Na5	4h	0	0.2565(14)	1/2	1.28(13)
Na6	2d	0	1/2	1/2	1.28(13)
01	4i	0.1147(14)	0	0.2019(27)	1.07(6)
O2	8j	0.1032(8)	0.2278(6)	0.2285(17)	1.07(6)
O3	4i	0.1528(12)	0	0.1969(23)	1.07(6)
O4	8j	0.1197(9)	0.1119(7)	0.8111(17)	1.07(6)
05	8j	0.1455(8)	0.3924(7)	0.7636(16)	1.07(6)

 $R_{\rm p} = 5.38, R_{\rm w} = 6.45, \chi^2 = 1.078.$

*Temperature parameters for Ru, Na and O were constrained to be equal, respectively.

octahedra result in equilateral Ru plaquettes, suggesting that Ru–Ru repulsion may play a role in the overall Ru–O geometry.

In a previous publication [14], the structure of Na_3MO_4 (M = Nb, Ru, and Ta) was viewed as a derivative of the NaCl structure with ordering of the NaO₆ and RuO₆ octahedra in planes parallel to the *b*-axis. However, from the magnetic point of view, it is advantageous to look at the structure with respect to the coordination and packing of the RuO₆ octahedra only, as it is the Ru that are responsible for the observed magnetic behavior. By doing so, the structure of Na₃RuO₄ can be viewed as consisting of isolated tetramers of edge-sharing RuO₆ that lie in the *ab* plane. The planes of RuO₆ octahedra are separated by a layer

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