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# Magnetic structures of the tri-rutiles $NiTa_2O_6$ and $NiSb_2O_6$

H. Ehrenberg[a,]*, G. Wltschek[a], J. Rodriguez-Carvajal[b], T. Vogt[c]

[a] *Fachgebiet Strukturforschung, Fachbereich Materialwissenschaft, Technische Universität Darmstadt, Petersenstr. 23, D-64287 Darmstadt, Germany*

[b] *Laboratoire Léon Brillouin, Centre d'Etudes de Saclay, F-91191 Gif sur Yvette Cedex, France*

[c] *Brookhaven National Laboratory, Associated Universities, Inc., Upton, NY 11973-5000, USA*

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## Abstract

The magnetic structures of the tri-rutiles $NiSb_2O_6$ and $NiTa_2O_6$ were determined by neutron powder diffraction. In both cases the magnetic moments are collinear aligned parallel to [1 1 0]. In the tetragonal plane ferromagnetic and antiferromagnetic chains exist, which are perpendicular to each other. But in antimonate these chains run along the [1 0 0]- and [0 1 0]-directions in contrast to [1 1 0] and $[1\,\bar{1}\,0]$ for the tantalate. Along the [0 0 1]-direction the orientations are alternating for both compounds, i.e. $k_z = \frac{1}{2}$. © 1998 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The compounds $NiTa_2O_6$ and $NiSb_2O_6$ crystallize in the tri-rutile structure type [1–3]. In previous articles short-range magnetic ordering is discussed for both compounds based on the very broadened maximum in the temperature dependence of magnetic susceptibility [3–7]. Long-range magnetic ordering below $T_N = 2.5$ K is reported for $NiSb_2O_6$, based on the appearence of extra reflections in neutron diffraction patterns [7]. But neither the magnetic unit cell nor the magnetic structure were given. In the case of $NiTa_2O_6$ long-range magnetic ordering below $T_N = 10.55(5)$ K is deduced from specific heat measurements [8]. This paper is concerned with the determination of the magnetic structures of both compounds at 1.5 K.

## 2. Experimental

The synthesis of $NiTa_2O_6$ and $NiSb_2O_6$ was carried out by subsolidus reaction of stoichiometric mixtures of NiO (99.9% Aldrich) and either $Ta_2O_5$ (99.99% Aldrich) or $Sb_2O_5$ (99.99% Aldrich). The reactants were intimately mixed in an agate mortar under acetone, placed in a platinum crucible and

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* Corresponding author. Tel.: + 49 40 8998 2918; fax: + 49 40 8998 4475; e-mail: helmut@steno.st.mw.tu-darmstadt.de.

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heated at a rate of 300°C/h to 1450°C. After 48 h the reaction products were cooled down at a rate of 180°C/h to room temperature. In both cases trifling impurities of NiO were detected.

Neutron powder diffraction experiments on $NiTa_2O_6$ were performed at the High Flux Beam Reactor (HFBR) of the Brookhaven National Laboratory, using the High Resolution Neutron Powder Diffractometer (H1A1) with a wavelength of 1.8857 Å. In the case of $NiSb_2O_6$ the powder diffractometer G4.2 at Laboratoire Léon Brillouin (LLB), Saclay, was used with a wavelength of 2.95 Å. For both compounds intensity data have been recorded at $T = 1.5$ and 50 K.

## 3. Results

The atomic parameters are summarized in Tables 1 and 2 as refined from the 50 K data. The corresponding diffraction patterns are shown in Figs. 1 and 2, where the bottom lines of reflection markers belong to the nuclear and magnetic peaks of the NiO-impurities. Long-range magnetic ordering was confirmed for both compounds by neutron powder diffraction at 1.5 K, where additional peaks appear in the patterns compared to the 50 K data, see Figs. 3 and 4. These reflections can be indexed by the propagation vector $\boldsymbol{k} = (\frac{1}{2}, 0, \frac{1}{2})$ for $NiSb_2O_6$, but a twice as large magnetic unit cell is needed in the case of $NiTa_2O_6$. If the crystallographic cell is

Table 1
Atomic parameters for $NiSb_2O_6$ at 50 K as derived from neutron powder diffraction

| Space group | $a$ [Å] | $c$ [Å] | |
|---|---|---|---|
| $P4_2/mnm$ | 4.62957(7) | 9.19811(20) | $Z = 2$ |
| Atom | $x$ | $y$ | $z$ |
| Ni | 0 | 0 | 0 |
| Sb | 0 | 0 | 0.3333(10) |
| O(1) | 0.3107(10) | 0.3107(10) | 0 |
| O(2) | 0.3021(6) | 0.3021(6) | 0.3270(5) |

Table 2
Atomic parameters for $NiTa_2O_6$ at 50 K as derived from neutron powder diffraction

| Space group | $a$ [Å] | $c$ [Å] | |
|---|---|---|---|
| $P4_2/mnm$ | 4.71581(4) | 9.11627(11) | $Z = 2$ |
| Atom | $x$ | $y$ | $z$ |
| Ni | 0 | 0 | 0 |
| Ta | 0 | 0 | 0.3320(3) |
| O(1) | 0.3091(4) | 0.3091(4) | 0 |
| O(2) | 0.2970(2) | 0.2970(2) | 0.3270(5) |

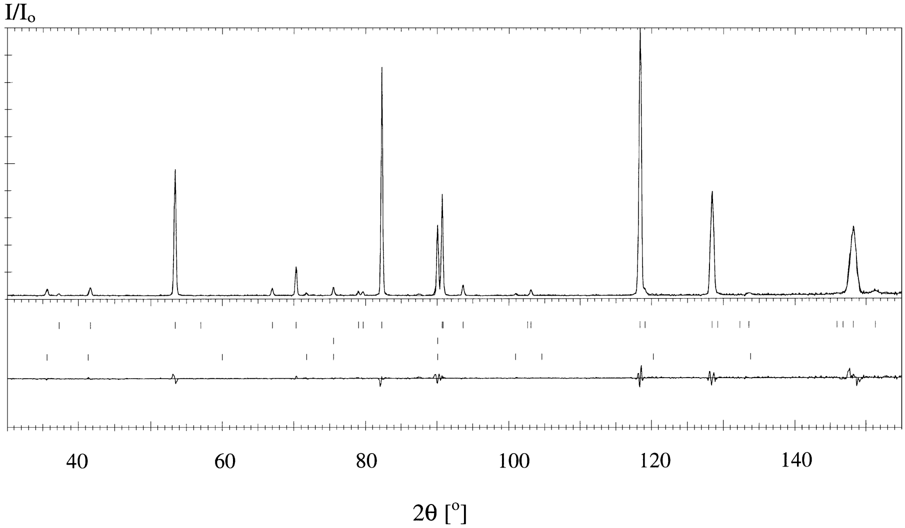

Fig. 1. Neutron diffraction pattern for $NiSb_2O_6$ at 50 K with $\lambda = 2.95$ Å. The lower lines of reflection markers belong to nuclear and magnetic reflections of the NiO-impurity.

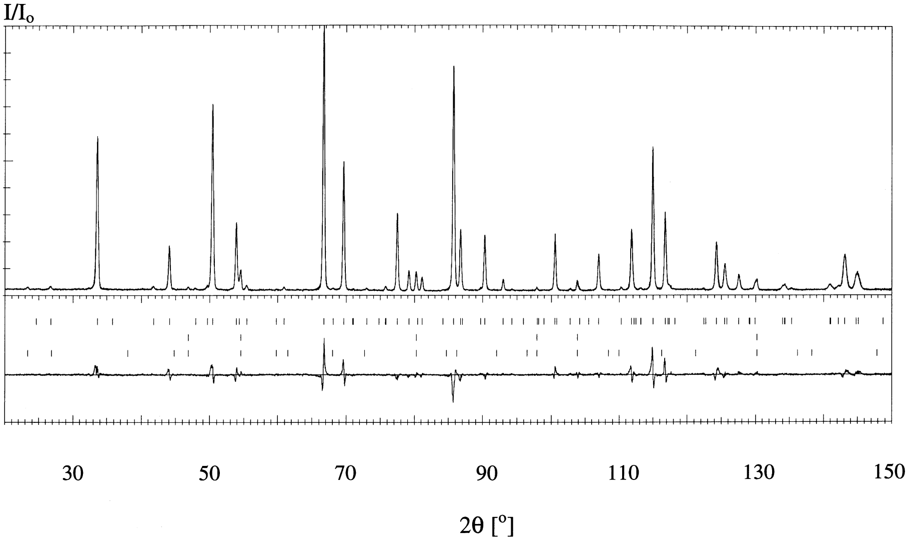

Fig. 2. Neutron diffraction pattern for $NiTa_2O_6$ recorded at 50 K with $\lambda = 1.8857$ Å. The lower lines of reflection markers belong to nuclear and magnetic reflections of the NiO-impurity.

transformed according to

$$\boldsymbol{a}' = \boldsymbol{a} + \boldsymbol{b}, \quad \boldsymbol{b}' = \boldsymbol{a} - \boldsymbol{b}, \quad \boldsymbol{c}' = \boldsymbol{c}\,,$$

the non-standard symmetry group $C4_2/mmn$ is achieved, and the propagation vector becomes $\boldsymbol{k}' = (\frac{1}{2}, 0, \frac{1}{2})$. Therefore, in both cases the little groups are generated by the inversion and the two-fold rotation axis along [0 0 1], but for $NiTa_2O_6$ four independent Ni-sites have to be distinguished in contrast to only 2 for $NiSb_2O_6$. The magnetic moments on all sites are restricted to be either within the *ab*-plane or perpendicular, depending on whether the rotational symmetry is combined with time-reversal or not. For all possible spin configurations the intensities of the magnetic reflections were calculated and compared to the observed data. The best agreement was achieved with the magnetic structures as illustrated in Fig. 5, and the corresponding profiles are shown in Figs. 3 and 4. For both compounds the magnetic moments are

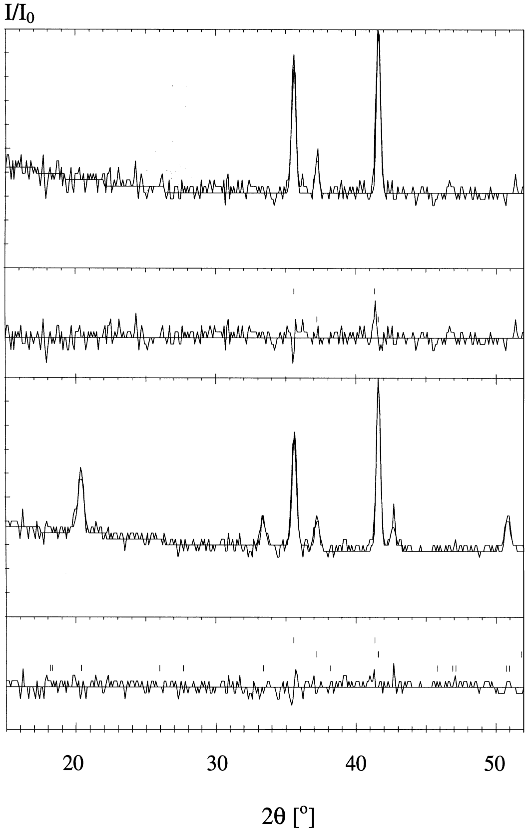

Fig. 3. Neutron diffraction pattern for $NiSb_2O_6$ at 50 K (upper picture) and 1.5 K (lower picture) in the range of magnetic reflections with highest intensities. The upper line of reflection markers belongs to the magnetic reflections of the NiO-impurity and the intermediate one to nuclear reflections of $NiSb_2O_6$.

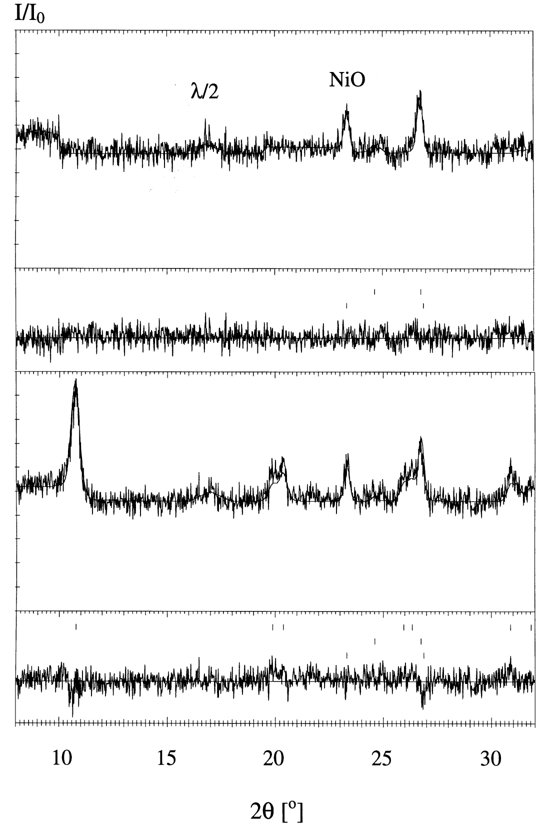

Fig. 4. Neutron diffraction pattern for $NiTa_2O_6$ at 50 K (upper picture) and 1.5 K (lower picture) in the range of magnetic reflections with highest intensities. The lower line of reflection markers belongs to the magnetic reflections of the NiO-impurity and the intermediate one to nuclear reflections of $NiTa_2O_6$.

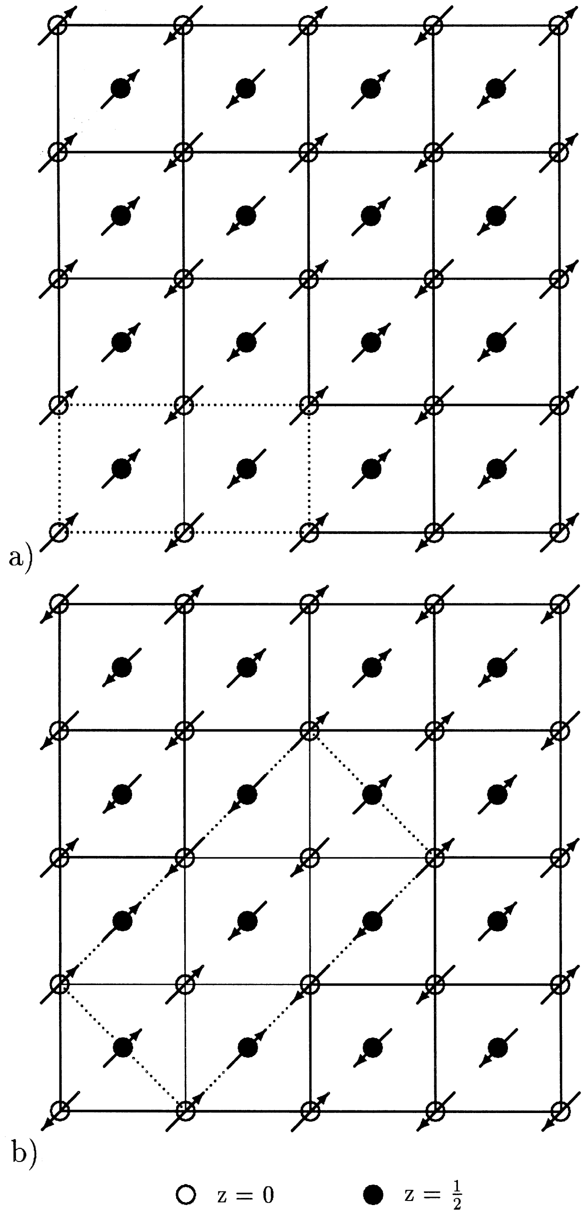

Fig. 5. Schematic representation of the spin arrangement within the tetragonal ab-plane for $NiSb_2O_6$ (a) and $NiTa_2O_6$ (b). The dotted lines indicate possible choices for the magnetic unit cells.

collinearly aligned parallel to [1 1 0] and build an arrangement of ferromagnetic and alternating chains, which are perpendicular to each other. But in the antimonate these chains run along the directions [1 0 0] and [0 1 0] in contrast to [1 1 0] and [1 $\bar{1}$ 0] for the tantalate. Equivalent directions are not given here. It should be emphasized that the cell transformation in the case of $NiTa_2O_6$ is not necessary at all. The magnetic structure can also be described in the original cell with propagation vector $\boldsymbol{k} = (\frac{1}{4}, -\frac{1}{4}, \frac{1}{2})$ or whatever of its star. The new cell has been chosen to point out the similarity of both magnetic structures under consideration. The absolute values of the magnetic moments at 1.5 K are refined to $1.6(1)\mu_B$ for both compounds and have to be compared to $g_0 \cdot m_S = 2\,\mu_B$ indicating that the spins are not completely ordered.

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