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# MAGNETIC STRUCTURES OF $CoNb_2O_6$

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We have carried out neutron diffraction and susceptibility measurements on a $CoNb_2O_6$ single crystal. Below 2.96 K, we found a screw structure with the $y$ axis as screw axis and a screw angle of 133°. This angle increases with decreasing temperature to a constant angle of 180° at and below 1.97 K. The magnetic structure below 1.97 K is a non-collinear antiferromagnetic structure of the type $\beta_x\beta_z$ with a doubled $y$ axis and belongs to the magnetic space group $P_b2_12_12_1$ ($=P_{2b}2_12'2_1$).

## 1. Introduction

The compound $CoNb_2O_6$ crystallizes in the columbite structure [1] with the space group Pbcn. Early neutron diffraction experiments [2] on a powder sample at 2.0 K showed magnetic reflections which could be indexed in a magnetic unit with a doubled $c$ axis. A collinear two-sublattice arrangement of the moments with directions along the crystallographic $a$ axis was proposed. Magnetization measurements at 1.4 K [3] on a single crystal gave evidence for a four-sublattice model. In agreement with the neutron diffraction results, no $y$ component of the magnetic structure could be detected. The Néel point was found to be at 2.95 [3].

## 2. Results and discussion

To look for a magnetic phase transition we carried out susceptibility measurements and further neutron diffraction work on single crystals and powder samples, but now in the whole temperature range between 1.5–4.5 K. Fig. 1 shows the results of the susceptibility measurements. Decreasing the temperature there is a change at (2.95 ± 0.02) K from the paramagnetic phase to an ordered spin structure. The unusual behaviour of $\chi_c$ suggests that changes in the spin structure take place between 2.95–1.97 K. Below 1.97 K a fixed antiferromagnetic structure is stable in zero field. One can see that the groundstate of the spin directions must be perpendicular to the $y$ axis, because the absolute value of $\chi_b$ does not change below 4 K.

For the neutron diffraction measurements, we used a single crystal of 10 $mm^3$ volume grown from a $Na_2B_4O_7/Nb_2O_5$ mixture as flux [4]. The exact temperatures of the transitions were found to be (1.97 ± 0.01) K and (2.96 ± 0.01) K. The result at 1.65 K, observed on 20 magnetic reflections, is identical to a powder measurement performed at 1.8 K. Table 1

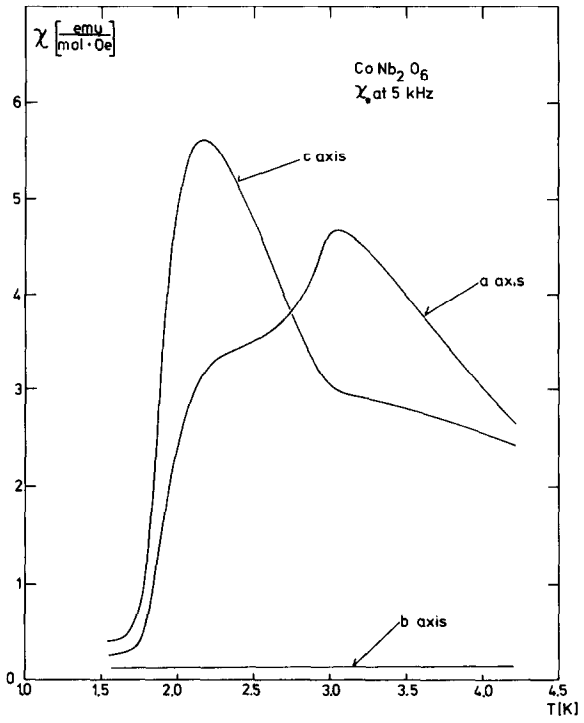


Fig. 1. Zero-field ac susceptibility of $CoNb_2O_6$ along the crystallographic *a*-, *b*- and *c*-axis.

Table 1
Intensities of the magnetic reflections of $CoNb_2O_6$ at 1.65 K
$I_{calc}$ for a canting angle of 59°

| Reflection | $I_{obs}$ | $I_{calc}$ |
|---|---|---|
| 0 1/2 0 | 100 | 97.4 |
| 0 −1/2 0 | 96.3 | 97.4 |
| 1 1/2 0 | 65.4 | 66.2 |
| −1 1/2 0 | 64.6 | 66.2 |
| 2 1/2 0 | 39.3 | 37.5 |
| −2 1/2 0 | 38.2 | 37.5 |
| 0 1/2 1 | 4.8 | 5.3 |
| 0 −1/2 1 | 4.4 | 5.3 |
| 3 1/2 0 | 23.9 | 23.3 |
| −3 1/2 0 | 23.3 | 23.3 |
| 0 3/2 0 | 0 | 0 |
| 0 −3/2 0 | 0 | 0 |
| 4 1/2 0 | 15.0 | 15.2 |
| 0 3/2 1 | 17.0 | 16.9 |
| 0 −3/2 1 | 16.4 | 16.9 |
| 5 1/2 0 | 11.4 | 10.0 |
| 5 −1/2 0 | 8.7 | 10.0 |
| 0 5/2 0 | 10.3 | 11.6 |
| 1 5/2 0 | 10.2 | 11.2 |
| −1 5/2 0 | 9.4 | 11.2 |
| 2 5/2 0 | 8.0 | 9.9 |
| −2 5/2 0 | 6.0 | 9.9 |

$R = \Sigma |I_{calc} - I_{obs}| / \Sigma I_{obs} = 0.042$

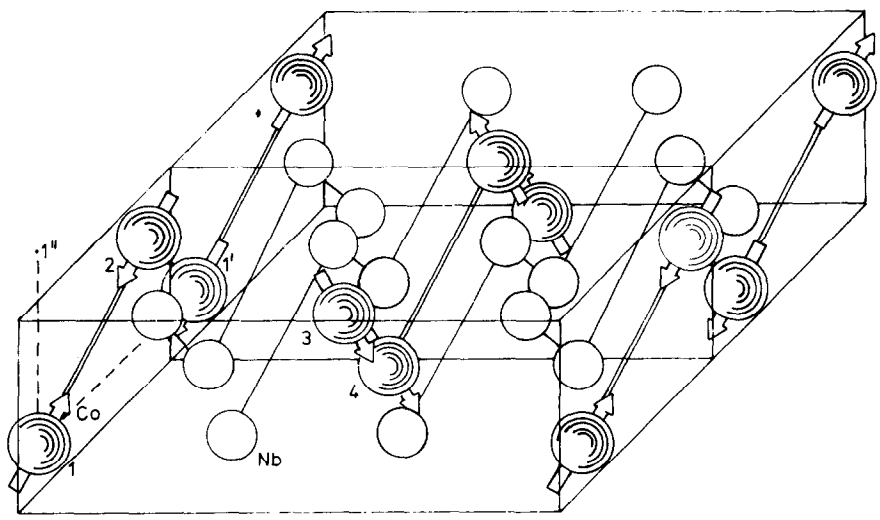


Fig. 2. Antiferromagnetic structure of $CoNb_2O_6$ below 1.97 K.

Table 2
Positions and directions of the magnetic moments in $CoNb_2O_6$ at 1.65 K ($a$, $b$, $c$ = lattice constants of the chemical unit)

| Atom | Co-positions | | | Direction cosines with respect to the $x$, $y$, $z$-directions | | |
|---|---|---|---|---|---|---|
| | $x/a$ | $y/b$ | $z/c$ | $x$ | $y$ | $z$ |
| 1 | 0 | 0.1818 | 0.25 | +0.515 | 0 | +0.857 |
| 2 | 0 | 0.8182 | 0.75 | −0.515 | 0 | −0.857 |
| 1′ | 0 | 1.1818 | 0.25 | −0.515 | 0 | −0.857 |
| 2′ | 0 | 1.8182 | 0.75 | +0.515 | 0 | +0.857 |
| 3 | 0.5 | 0.3162 | 0.75 | +0.515 | 0 | −0.857 |
| 4 | 0.5 | 0.6818 | 0.25 | +0.515 | 0 | −0.857 |
| 3′ | 0.5 | 1.3162 | 0.75 | −0.515 | 0 | +0.857 |
| 4′ | 0.5 | 1.6818 | 0.25 | −0.515 | 0 | +0.857 |

gives the intensities. Fig. 2 and table 2 show the magnetic structure below 1.97 K.

One can see that we have a doubled $y$-axis because we find pairs (1–2′, 2–1′, 3–4, 3′–4′) of parallel coupled magnetic moments which are all coupled together antiferromagnetically within the $y-z$ planes. The magnetic moments are canted in the $x-z$ plane with a canting angle of ±59° ± 2° from the $x$-axis; there is no $y$ component. The effective magnetic moment is found to be $\mu = (3.05 \pm 0.03)\,\mu_B$. This magnetic structure should be called $\beta_x\beta_z$ [5] with the magnetic space group $P_b2_12_12_1$ (= $P_{2b}2_12'2_1$).

Increasing the temperature into the region between 1.97 K and 2.96 K, we find a splitting of all magnetic reflections into two satellite reflections along the $b^*$-axis of the reciprocal lattice. Fig. 3, for example, shows $0k0$ scans near the 0 1/2 0-reflection in the temperature range between 4.2–1.7 K. One can see the splitting of the 0 1/2 0-reflection into two satellites above 1.97 K. With increasing temperature the distance between the satellites becomes larger, and at 2.2 K we can call these reflections 0 2/5 0 and 3 3/5 0. This implies a magnetic structure with a screw angle of 72° or 144° between two neighbouring chemical units along the $y$-axis. Intensity calculations rule out the case of an angle of 72°. Fig. 4 shows the temperature dependence of this screw angle from 137° ± 4° at $T$ = 2.96 K up to 180° at and below 1.97 K. This last angle implies a doubling of the $y$ axis in this phase as

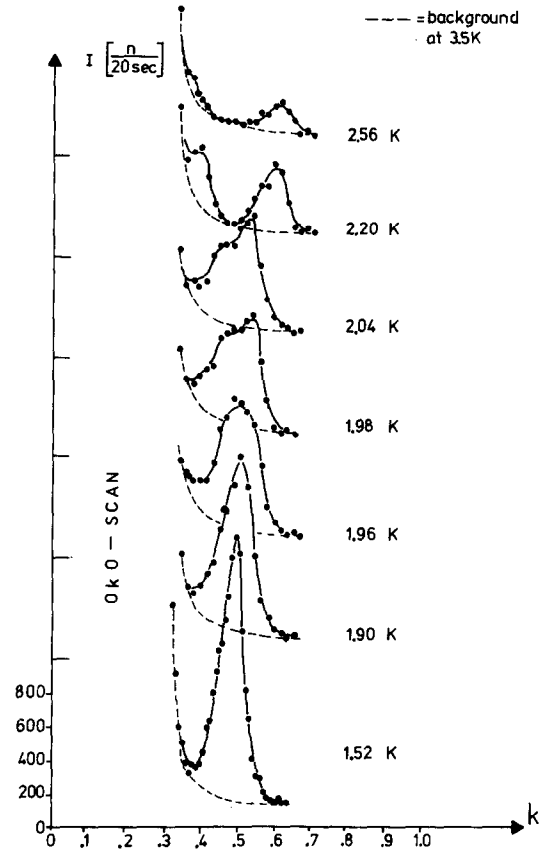


Fig. 3. $0k0$-scan of $CoNb_2O_6$ as function of the temperature.

shown in fig. 2.

The low temperature phase $\beta_x\beta_z$ of $CoNb_2O_6$ is very similar to the magnetic structure of $FeNb_2O_6$ [5] and is well understood [6]. This result is also in good

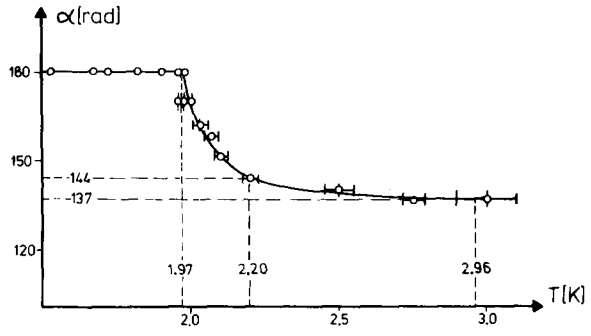


Fig. 4. Screw angle along the $y$-axis of $CoNb_2O_6$ as function of the temperature.

agreement with the magnetic structure of four sublattices inferred from field-induced phase transitions at 1.4 K [3]. The strongest interaction is $I_{21}$, between the atoms 2 and 1′ (see [6], fig. 7). This 90°–Co–O–Co superexchange interaction is a ferromagnetic pσ–dγ-bonding [7], which is responsible for the Néel point of this compound. But the interaction $I_{12}$ between the atoms 1 and 2 is weaker and antiferromagnetic coming from superexchange- and dipole–dipole-interactions. The moments are arranged collinearly within $y - z$ planes, and following the symmetry non collinearly between neighbouring $y-z$ planes. The direction of the moments nearly corresponds to the direction built up by the three ions $O_2$–Co–$O_2$ in the $x - z$ plane. This was also found for the moments in the magnetic structures of the wolframites $MeWO_4$ (Me = Mn, Fe, Co, Ni), of the columbites $Mn(Nb, Ta)_2O_6$ and of the trirutile $FeTa_2O_6$ [6]. The directions of the moments of ±59° to the $a$-axis in $CoNb_2O_6$ result from the single-ion anisotropy of the $Co^{2+}$ ion. This anisotropy must be similar to that in the compound $CoWO_4$, because there are nearly the same distorted oxygen octahedra around the $Co^{2+}$ ion. In the case of $CoWO_4$, the direction of the moments was found by neutron diffraction to be at 46° ± 2° [6]; the easy axis was determined by magnetization and susceptibility measurements to be 50° ± 5° [8] and 45° [9] to the $x$-axis, both in good agreement with our result. The magnetic moment $\mu$ = $(3.05 \pm 0.03)\,\mu_B$ seems to be nearly a spin only value, whereas in $CoWO_4$ $\mu = (3.6 \pm 0.05)\,\mu_B$ was found [6]. The screw structure of the incommensurable phase will be reported elsewhere in more detail.

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