SHORT STRUCTURAL PAPERS

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Magnetic Transition Temperature of Terbium Hydroxide Oxide. Structure of Ytterbium Hydroxide Oxide

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Abstract. TbO(OH), $a = 6{\cdot}04$ (1), $b = 3{\cdot}69$ (1), $c = 4{\cdot}33$ (1) Å, $\beta = 109{\cdot}0$ (1)°, $Z = 2$, $P2_1/m$, and YbO(OH), $a = 5{\cdot}87$ (1), $b = 3{\cdot}58$ (1), $c = 4{\cdot}27$ (1) Å, $\beta = 109{\cdot}3$ (1)°, $Z = 2$, $P2_1/m$, were prepared hydrothermally. TbOOH orders magnetically and the Néel temperature was determined to be 7·6 K from neutron diffraction powder patterns measured in the temperature interval 5·7–8·2 K. YbO(OH) does not order magnetically. The structure of YbO(OH) was refined from neutron diffraction data by the powder-profile-refinement technique; $R(F) = 5{\cdot}3\%$ for 58 reflexions.

Introduction. The magnetization of the two rare-earth hydroxide oxides TbO(OH) and YbO(OH) has previously been investigated between 4·2 and 300 K (Christensen, 1972). TbO(OH) was found to order antiferromagnetically at 10 K. YbO(OH) was not found to have a magnetic transition, but the magnetization curve showed a kink at 10 K.

The magnetic structure of TbO(OH) was determined by Christensen & Quézel (1974) using powder neutron diffraction data obtained at 4·2 K. The magnetic cell is doubled along a and contains four magnetic ions. The data obtained by Christensen & Quézel (1974) showed magnetic reflexions hkl for both $h = 2n$ and $h = 2n + 1$ in the magnetic cell. (In the following, reflexions are indexed in the magnetic cell unless otherwise specified.) The suggested structure is a non-collinear arrangement of the moments on the four Tb^{3+} ions. The moment on one atom in the first half of the magnetic cell ($y = \frac{1}{4}$) makes an angle of 43° with the ac plane and the projection on the ac plane makes an angle of 59° with the a axis. The moment on the equivalent atom in the second half of the magnetic cell ($y = \frac{1}{4}$) makes an angle of −43° with the ac plane and the projection on the ac plane makes the same angle of 59° with the a axis. The moments on the two other atoms in the magnetic cell at $y = \frac{3}{4}$ are antiparallel to the moments on the atoms at $y = \frac{1}{4}$.

Because the suggested magnetic structure of TbO(OH) can formally be described by two propagation vectors (k = [000] and k = [$\frac{1}{2}$00]), the compound may have two magnetic transition temperatures, one corresponding to ordering of the ac-plane component and one corresponding to ordering of the b-axis component. To investigate this possibility the temperature dependence of the intensities of the magnetic reflexions 100, 200, $10\bar{1}$, 001, $20\bar{1}$, 300, and 010 were measured by a neutron diffraction study of the same specimen of TbO(OH) as was used in the previous investigation. In the diffraction diagrams the two reflexions 001, $20\bar{1}$ and the two reflexions 300, 010 were not fully resolved. However, the five measured peaks corresponding to the seven reflexions listed above were fitted to Gaussians to obtain the integrated intensities of the individual reflexions shown in Fig. 1. Fig. 2 shows the ordered moment as a function of temperature derived from the intensities of the 100, 200 and 010 reflexions. Within the experimental uncertainties the two types of magnetic reflexions hkl with $h = 2n$ (k = [000]) and $h = 2n + 1$ (k = [$\frac{1}{2}$00]) correspond to the same ordering temperature of 7·6 K, a value which is approximately 2 K lower than the value determined previously (on heating) from magnetization measurements. This discrepancy is presum-

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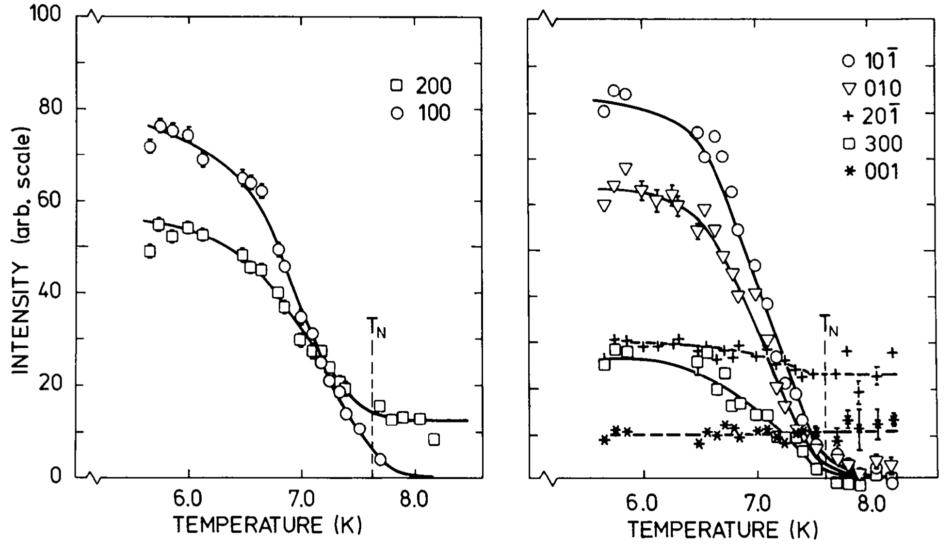

Fig. 1. Temperature dependence of the intensities of the seven low-angle peaks of TbO(OH) showing the appearance of the magnetic intensity at $T_N = 7{\cdot}6$ K.

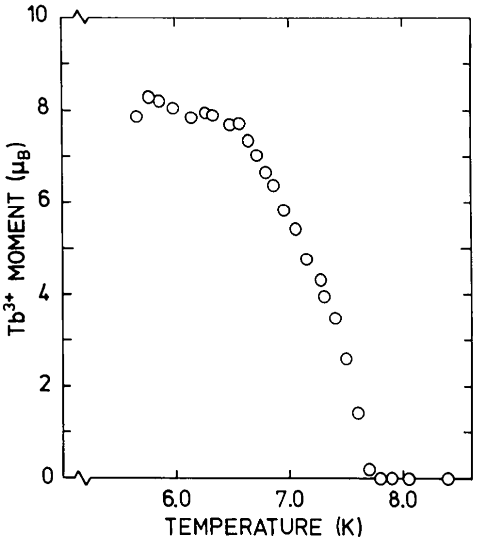

Fig. 2. Temperature dependence of the ordered moment of the Tb^{3+} ions in TbO(OH). The points shown in the figure are mean values calculated from the intensities of the 100, 200 and 010 reflexions.

ably caused by poor thermal contact between the sample and thermometer in the earlier experiment. TbO(OH) is a poor heat conductor and the neutron diffraction experiment showed that although the powdered sample was sealed in a helium-filled case in direct contact with the temperature block and thermometer there was a time lag between the change of temperature and the appearance of a Bragg peak. The Néel temperature of 7·6 K is determined on heating from 4·2 K.

The refinements of the nuclear structures of YbO(OH) and TbO(OH) were conducted as follows. A specimen of YbO(OH) was prepared hydrothermally by treating a precipitate of ytterbium trihydroxide with a 1 *M* solution of NaOH at 723 K and 46 MPa for 48 h. Neutron diffraction powder patterns of the product were measured for reciprocal-lattice vectors between 0·4 and 1·8 $Å^{-1}$ using 1·42 Å neutrons, *i.e.* the same region as was investigated for TbO(OH). One pattern was measured at 40 K and one at 4·2 K. The two patterns were identical and showed only two peaks corresponding to the three nuclear reflexions 100, 001 and 10$\bar{1}$ (nuclear cell). The compound YbO(OH) is thus not magnetically ordered at 4·2 K.

Another neutron diffraction powder pattern of YbO(OH) was measured for scattering angles between 10 and 90° in steps of 0·1° using 1·69 Å neutrons. The pattern showed 17 peaks corresponding to 58 reflexions. A refinement was made of the structure using the profile-analysis technique (Rietveld, 1969). Two sets of scattering lengths for Yb, O, and H were used: (*a*) the values suggested by Bacon (1972) to be 12·83, 5·80 and −3·74 fm, respectively, and (*b*) the values suggested by Koester (1977) to be 12·62, 5·803 and −3·7409 fm, respectively. Refinements using the two sets of scattering amplitudes give identical results within the uncertainties. The results of the refinements using (*b*) are listed in Table 1.*

The neutron diffraction data at 300 K of Christensen & Quézel (1974) were refined once more using the scattering amplitudes suggested by Koester (1977). Using $b_{\mathrm{Tb}} = 7{\cdot}38$ instead of 7·6 fm (Bacon, 1972) did

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* A list of observed and calculated intensities has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35658 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Results of the refinement of the structure of* YbO(OH)

Scattering amplitudes are, Yb: 12·62, O: 5·803 and H: −3·7409 fm. Scale factor = 0·0131 (1), $R(F)$ = 5·3%.

	Atom site	x	y	z	B (Å^2)
Yb	2(*e*)	0·1918 (7)	0·75	0·331 (1)	0·9
O(1)	2(*e*)	0·058 (2)	0·75	0·771 (3)	−0·1 (2)
O(2)	2(*e*)	0·571 (2)	0·75	0·755 (2)	1·0 (2)
H	2(*e*)	0·582 (3)	0·75	0·988 (5)	2·6 (3)

not change the atomic positions and B values significantly. Hence, we may conclude that the powder-profile-refinement technique is insensitive to small changes of the scattering amplitudes when used on the available powder diffraction data of YbO(OH) and TbO(OH).

Discussion. The investigation confirms that TbO(OH) and YbO(OH) have the same monoclinic structure, that TbO(OH) orders antiferromagnetically at 7·6 K and that YbO(OH) shows no magnetic transition down to 4·2 K. The two hydroxide oxides also exist in a more dense tetragonal modification (Gondrand & Christensen, 1971; Christensen & Hazell, 1972). For YbO(OH) the metal–oxygen distances are from 2·22 (1) to 2·45 (5) Å in the tetragonal modification and from 2·25 (1) to 2·36 (1) Å in the monoclinic modification. The O—H distance in the monoclinic form of YbO(OH) is 0·98 (1) Å and the structure is not hydrogen bonded.

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Diammonium Copper Bis(selenate) Hexahydrate

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Abstract. $Cu(NH_4)_2(SeO_4)_2.6H_2O$, M_r = 493·5, monoclinic, $P2_1/c$, a = 6·424 (1), b = 12·547 (1), c = 9·351 (2) Å, β = 105·62 (5)°, V = 725·8 (2) Å^3, Z = 2, D_c = 2·26 Mg m^{-3}. Final R = 0·050 for 1269 observed reflexions. The Cu atom has the characteristic 4 + 2 distorted coordination.

Introduction. The crystal structures of many double sulphates are known. This is not the case for the related Se compounds, with the exception of $CuK_2(SeO_4)_2.6H_2O$ (Whitnall, Kennard, Nimmo & Moore, 1975). In this paper the crystal structure of $Cu(NH_4)_2(SeO_4)_2.6H_2O$ is studied to establish its relation to that of the above-mentioned sulphates and selenate: in particular the coordination of the metal atom and the arrangement of the hydrogen bonds.

A pale-green crystal was mounted on a Nonius CAD-4 diffractometer. The cell dimensions were refined by least-squares fitting of the θ values of 20 reflexions. The intensities of all 1348 unique reflexions with $1 < \theta < 70°$ were measured at 295 K with monochromatic Cu $K\alpha$ radiation (λ = 1·54178 Å) and an $\omega/2\theta$ scan technique. There was no appreciable change in the periodically monitored standard reflexions. The intensities were corrected for Lorentz and polarization effects and 1269 of these were considered as observed with $I > 2\sigma(I)$. No absorption correction was applied because of the irregular shape of the crystal.

Scattering factors for neutral atoms and anomalous-dispersion corrections for Cu and Se were taken from *International Tables for X-ray Crystallography* (1974). The structure was solved by *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). The set of phases with the highest figure of merit gave 50% of the non-hydrogen atoms, the remainder being located in a difference synthesis. Anisotropic full-matrix least-squares refinement with unit weights led to R = 0·059.

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