Short Communications

The Magnetic Structure of β-CrOOD

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The preparation of beta chromium oxide hydroxide, β-CrOOH, and the isomorphous deuterated compound, β-CrOOD, has been reported recently.[1,2] The magnetic properties of β-CrOOH has been investigated and the compound was found to be antiferromagnetic at temperatures below 120 K.[1] Using neutron diffraction powder methods the magnetic structure of β-CrOOD has been determined. The deuterated compound was used to obtain a better counting statistics of the powder pattern due to the low incoherent scattering of the sample in comparison with that of β-CrOOH.

A neutron powder pattern of β-CrOOD was measured at 6 K using a double axis neutron spectrometer at the DR3 reactor at Risø. The pattern was obtained with an incident neutron wavelength of 1.68 Å. The sample, approximately 30 g, was placed in a 15 mm diameter cylindrical vanadium container and was kept in a He-cryostat. The collimations in front of and behind the sample were defined by Soller slits to be 0.25 and 0.64°, respectively. The Soller slits were made of cadmiated steel. The powder pattern was measured in the 2θ interval 5 to 110° in steps of 0.1°.

The unit cell parameters of β-CrOOD are at 300 K: $a = 4.873(5)$ Å, $b = 4.332(7)$ Å, $c = 2.963(2)$ Å.[2] The space group used is $P2_1nm$ with $Z = 2$. In addition to the nuclear reflections that can be indexed with the above-mentioned unit cell, the pattern had magnetic reflections. Two of these reflections were completely resolved from the nuclear reflections and were observed at lower 2θ values than the nuclear reflections, indicating the magnetic cell to be larger than the chemical cell. All the magnetic reflections were indexed using an orthorhombic cell with $a_M = a$, $b_M = 2b$, and $c_M = 2c$ where a, b, and c are the unit cell parameters of the chemical cell.

The nuclear and magnetic structures of β-CrOOD were refined using the Rietveld least squares refinement program for powder profile
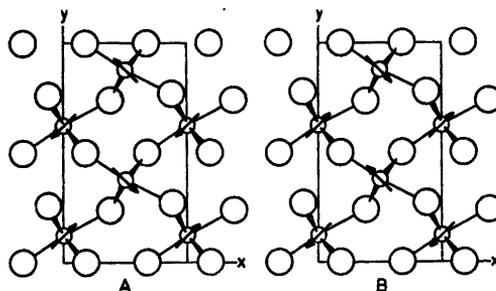
Fig. 1. Projection of the structure of β-CrOOD along 001. For clarity the positions of the deuterium atoms have been omitted. A shows the magnetic cell with the spin configuration. The chromium and oxygen atoms have $z = 0$ and $z = 0.25$. B shows the spin configuration in the magnetic cell for the chromium atoms with $z = 0.5$ and $z = 0.75$. The oxygen atoms shown in B have $z = 0.5$ and $z = 0.75$.

intensities.[3,4] The scattering lengths (in 10^{-12} cm) were: $b_{Cr} = 0.353$, $b_O = 0.580$, and $b_D = 0.667$, respectively.[5] The form factor for chromium reported by Delapalme and Sivardiere[6] was used in the calculation of the magnetic intensities. The atomic positions determined previ-

Table 1. Observed and calculated intensities for β-CrOOD. Reading from left to right the columns are: $h\ k\ l\ I_{nucl}\ I_{mag}\ I_{obs}$.

h	k	l	I_{nucl}	I_{mag}	I_{obs}
0	1	-1	0	12339	12817
0	1	1	0	8895	9240
1	1	-1	0	8346	8295
1	1	1	0	4697	4668
1	2	0	5179	0	5053
0	3	-1	0	367	418
0	3	1	0	1805	2054
1	0	2	46242	0	42200
2	0	0	10049	0	10030
0	2	2	43222	0	43346
2	1	-1	0	375	400
2	1	1	0	1852	1976
1	2	2	83314	0	88673
0	4	0	2754	0	2834
2	2	0	53645	0	55932
1	4	0	5947	0	419
1	1	-3	0	614	538
1	1	3	0	718	629
2	3	-1	0	449	433
2	3	1	0	322	310
0	4	2	3252	0	2580
2	2	2	41691	0	38418
1	4	2	15954	0	16269
2	4	0	29606	0	29812
3	2	0	1102	0	1585
0	0	4	45997	0	47663
0	6	0	3935	0	3831
3	0	2	13294	0	11718
2	4	2	13097	0	10769
0	2	4	1568	0	783
1	6	0	1388	0	576
3	2	2	8129	0	6621
1	2	4	2206	0	2093
3	4	0	7314	0	3244
0	6	2	3193	0	1410
2	0	4	6772	0	6766
1	6	2	32336	0	35181
2	6	0	15512	0	17232
4	0	0	4619	0	4911
0	4	4	2225	0	2359
2	2	4	44498	0	45922
3	4	2	41519	0	42170
1	4	4	5475	0	5920
4	2	0	5345	0	6755
2	6	2	26545	0	24504
4	2	2	36087	0	33550
2	4	4	11371	0	12372
3	6	0	304	0	341
4	4	0	28582	0	30982
3	2	4	1464	0	1448
1	8	0	9105	0	5847

Table 2. Atomic coordinates for β-CrOOD at 6 K. Standard deviations in parentheses.[a] (Refers to the chemical unit cell $a\,b\,c$).

Atom	x	y	z
Cr	0.0	0.250(2)	0.0
O1	0.306(3)	0.486(2)	0.0
O2	0.616(3)	−0.009(2)	0.0
D	0.492(3)	0.178(2)	0.0

[a] Overall scale factor = 0.0188. $R(F^2) = 11.0$ %. $R_{nucl} = 8.5$ %. $R_{mag} = 3.7$ %. (For definition of these values see Ref. 3).

ously [2] were transformed to the magnetic cell and used as starting parameters. A non-collinear antiferromagnetic model for the magnetic structure was assumed with spin waves propagating in the direction of the y- and z-axis and with the spins in planes parallel to the xy-plane. Relative to the CrO_6 coordination octahedra in the structure, the spins have directions from the chromium atoms towards oxygen atoms with same z-coordinates as the chromium atoms (see Fig. 1). This model of the magnetic structure refined to a magnetic R-value of 3.7 % (see Table 1) and gave a magnetic moment $\mu = 2.49(5)$ μ_B for the chromium atom. The spin form angles of $\pm 45(5)°$ with the x-axis. The nuclear reflections gave an R-value of 8.5 % (see Table 1). Additional scattering contributions to the powder pattern from the cryostat can account for the relatively high R-value. The atomic coordinates transformed to the chemical cell (Table 2) are within three standard deviations equal to those of β-CrOOD at at 300 K.[2]

The magnetic structure of β-CrOOD has points of resemblance with that of $CrCl_2$.[7]

1. Christensen, A. N. *Acta Chem. Scand. A 30* (1976) 133.
2. Christensen, A. N., Hansen, P. and Lehmann, M. S. *J. Solid State Chem. 19* (1976) 299.
3. Rietveld, H. M. *J. Appl. Crystallogr. 2* (1969) 65.
4. Rietveld, H. M. *Program F418 — Fortran IV Version*, Reactor Centrum Nederland, Petten, N. H., The Netherlands.
5. Shull, C. G. *Coherent Neutron Scattering Amplitudes*, Massachusetts Institute of Technology, Cambridge, Mass. 1972.
6. Delapalme, A. and Sivardiere, J. *Longeurs de Fermi, Facteurs de Forme Magnétiques, Rayons Ioniques*, Laboratoire de Diffraction Neutronique, C. E. N. G., Grenoble, France.
7. Cable, J. W., Wilkinson, M. K. and Wollan, E. O. *Phys. Rev. 118* (1960) 950.

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The Crystal Structure of Manganese(II) Diselenite

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In our investigation of manganese(II) selenites,[1] we found that the equilibrium in aqueous solution shifts towards the diselenite ion when the pH of the solution decreases. Thus, a rose-coloured, crystalline precipitate was obtained from 1 mol/dm³ selenous acid solution at 60 °C. It was identified as $MnSe_2O_5$ by chemical analyses and IR spectroscopy (*cf.* Table 1).

Thermal analysis (TG, DTG, DTA) of the compound was also carried out and the decomposition scheme in air was found to be as follows:

$$MnSe_2O_5 \rightarrow MnSeO_3 + SeO_2 \qquad (1)$$

$$2MnSeO_3 \xrightarrow{(O_2)} Mn_2O_3 + 2SeO_2 \qquad (2)$$

At a heating rate of 6 °C/min the DTA peak temperatures for reactions 1 and 2 were found to be 420 and 525 °C, respectively.

An X-ray crystallographic study of the crystals was initiated and rotation and Weissenberg photographs indicated orthorhombic symmetry. The accurate unit cell dimensions were obtained by least-squares refinement of Guinier powder data with KCl as the internal standard; *cf.* Table 2.

Table 1. Infrared absorption frequencies in the region $4000-250$ cm^{-1}.

Observed frequency	Assignment
870 s, 845 m, 830 m, 760 vs, b	ν_{Se-O} (terminal)
585 s, 555 vs, 510 m	ν_{Se-O} (bridge)
445 m, 410 w, 380 m, 330 w, sh	δ_{Se-O} (terminal)

Table 2. Crystal data of $MnSe_2O_5$.

Space group *Pbcn* (No. 60)

$a = 6.797(2)$ Å, $b = 10.617(3)$ Å, $c = 6.300(2)$ Å, $V = 454.6$ Å³;[a] $a = 6.822(3)$ Å, $b = 10.636(4)$ Å, $c = 6.323(3)$ Å, $V = 458.8$ Å³;[b] $Z = 4$, $D_m = 4.2(1)$ g cm⁻³, $D_x = 4.28$ g cm⁻³;[a] $\mu(MoK\alpha) = 168.8$ cm⁻¹.

[a] Powder data at 20 °C [a (KCl) = 6.2927 Å].[12]
[b] Diffractometer data at 25 °C.