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## The spatial distribution of magnetization in cobalt tungstate, $\text{CoWO}_4$

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**Abstract.** Single-crystal neutron-diffraction measurements on cobalt tungstate,  $\text{CoWO}_4$ , at 15 K and powder measurements in the temperature interval 5–55 K have confirmed that it orders antiferromagnetically below its Néel temperature of 55 K with a magnetic propagation vector  $(\frac{1}{2} 0 0)$ . The chemical unit cell is monoclinic, space group  $P2/c$ ,  $Z = 2$  with  $a = 4.659(1)$ ,  $b = 5.667(1)$ ,  $c = 4.940(1)$  Å,  $\beta = 89.94(1)^\circ$  at 15 K. The magnetic moments on the two equivalent  $\text{Co}^{2+}$  ions within the cell are coupled ferromagnetically and lie in the  $a$ - $c$  plane at an angle  $43.4(8)^\circ$  from  $[001]$  towards  $-a$ . The magnetization density of the  $\text{Co}^{2+}$  ion is not spherically symmetric, but it can be modelled as a multipolar expansion on axes  $Z$  taken parallel to the moment direction and  $Y$  parallel to  $b$ . The moment on the  $\text{Co}^{2+}$  ion is  $3.42(3) \mu_B$  with the largest coefficients, apart from  $Y_{00}$ , being  $Y_{21+} = -0.20(2)$  and  $Y_{22+} = -0.21(2)$ . In addition, the radial form factor is expanded over that appropriate to a spin-only moment of a free ion as should be expected when there is a significant orbital moment. These observations are related to the ground-state wavefunction of the ion. There is also evidence for a small covalent transfer of moment to O amounting to  $0.04(1) \mu_B$  per ligand. The development of magnetic order is accompanied by magnetostriction, which mimics the magnitude of the ordered  $\text{Co}^{2+}$  moment and amounts to  $-3.4 \times 10^{-3} \Delta V/V$  between 5 and 55 K.

### 1. Introduction

Cobalt tungstate is isostructural with the manganese, iron and nickel tungstates and it has monoclinic symmetry, space group  $P2/c$ . The unit-cell dimensions of  $\text{CoWO}_4$  are  $a = 4.6698(9)$ ,  $b = 5.6873(23)$ ,  $c = 4.9515(17)$  Å,  $\beta = 90(\text{---})^\circ$  at ambient temperature and  $Z = 2$  (Weitzel 1976). The structure is illustrated in figure 1.  $\text{CoWO}_4$  is known to become antiferromagnetic below a  $T_N$  of 55 K (Van Uitert *et al* 1964) and powder neutron diffraction studies by Weitzel (1970) and by Weitzel and Langhof (1977) showed that the magnetic unit-cell edge is double the chemical one in the  $a$  direction and that the  $\text{Co}^{2+}$  ions carry a moment of some  $3.6 \mu_B$  oriented in the  $a$ - $c$  plane at an angle of  $46^\circ$  to  $[001]$ . The closeness of the monoclinic angle  $\beta$  to  $90^\circ$ , however, prevented these latter authors from determining whether the spin direction lay in  $\beta$  obtuse or  $\beta$  acute. A subsequent neutron single-crystal study by Wilkinson and Sprague (1977) confirmed this magnetic ordering, but the degree of extinction in their sample was severe and prevented them obtaining reliable estimates for the moment magnitude or direction. We now report a new neutron single-crystal study at 15 K, which has given an excellent data set from a sample with well characterized and small extinction. It has enabled us not only to obtain more accurate values for the magnitude and direction of the Co magnetic moment, but also to model its significant asphericity using a

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multipole expansion of the magnetic form factor on quantum axes  $Z$  parallel to the moment direction and  $Y$  parallel to  $b$ . Finally, powder diffraction profiles obtained at temperatures between 5 K and 55 K have allowed us to follow the temperature variation of the Co moment and its effect on the lattice parameters.

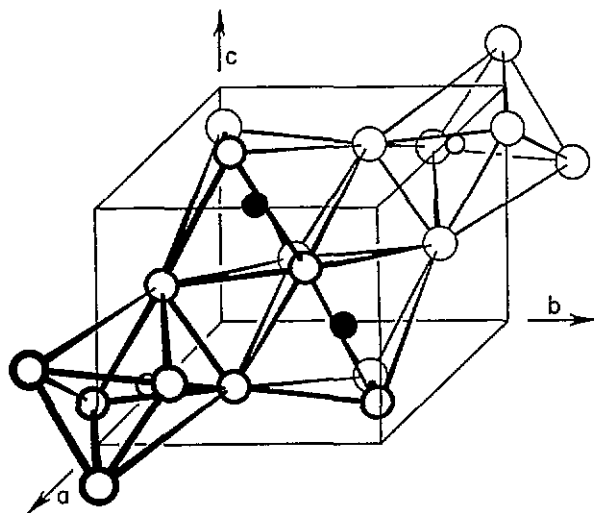


Figure 1. The crystal structure of  $\text{CoWO}_4$ . The O atoms are shown as large circles, Co and W as smaller solid and open circles, respectively.

## 2. Experimental details

The single-crystal neutron-diffraction data were obtained using the D9 diffractometer of the Institut Laue Langevin during the development of data-treatment software for its position-sensitive multidetector. This  $\text{He}^3$  detector has  $32 \times 32$  electrodes with 2 mm separation placed some 400 mm from the sample (Lehmann *et al* 1989). Only one reflection falls on the detector during each measurement and the treatment program integrates the intensity over the relevant area of the detector at each setting of the crystal required to scan the reflection. The shape of strong reflections in the  $(X, Y)$  space of the flat multidetector and the  $\omega$  rotation of the crystal are stored as a function of Bragg angle and imposed on the data for weak reflections, thereby improving the estimation of their intensities over that possible with a conventional detector (Wilkinson *et al* 1988).

A small, approximately equi-axed crystal weighing 28 mg was chosen from the same batch of crystals as prepared for Wilkinson and Sprague (1977) by Mrs B M Wanklyn of the Clarendon Laboratory using the flux-growth technique and a starting composition of 10%  $\text{CoO}$ , 75%  $\text{Na}_2\text{WO}_4$  and 15 wt%  $\text{WO}_3$  (Wanklyn 1972). After mounting on the diffractometer's Displex refrigerator, it was cooled to 15 K, well below the reported Néel temperature of 55 K. An incident wavelength of  $0.842 \text{ \AA}$  was chosen to reduce still further the effects of the small extinction and absorption. The crystal orientation matrix was refined from the coordinates of 15 centred reflections and gave cell dimensions of  $a = 4.669(8)$ ,  $b = 5.680(9)$ ,  $c = 4.951(7) \text{ \AA}$ ,  $\beta = 89.92(5)^\circ$ . Integrated intensities were measured for both the  $h$  integral (nuclear) and half-integral (magnetic) reflections. The standard deviation,  $\sigma$ , to be associated with each inequivalent structure factor was estimated from the agreement between the equivalent reflections and their associated counting statistics. A total of 2465

reflection intensities reduced to 487 and 433 inequivalent nuclear and magnetic structure factors respectively; the merging  $R$  factor on the squares of structure factors was 2.9%.

Powder diffraction measurements were made on the D2B instrument, also at the ILL, using a sample obtained by crushing a batch of small single crystals. The cylindrical specimen can, 5 mm in diameter, was located in a standard ILL 'Orange' cryostat. The incident wavelength was 1.594 Å and patterns extending to a maximum value of  $147^\circ 2\theta$  were taken at 5, 15, 25, 35, 40, 45, 50 and 55 K.

### 3. The nuclear structure at 15 K determined from the single-crystal data

The magnitude of the extinction in the sample can be judged by the relatively good agreement ( $R = 8\%$ ) obtained in a weighted least-squares refinement without an extinction correction. Including this correction following the Becker–Coppens (1974) treatment in a refinement of the nuclear data with isotropic factors on all atoms then gave an  $R$  of 3.4% with a weighted  $R$  factor,  $R_w$ , of 3.3% (weighting by  $1/\sigma^2$ ) and a  $\chi^2$  of 21. A significant improvement occurred when the O atoms were allowed to have anisotropic vibrational parameters, the  $R$  factor being 2.6%,  $R_w = 2.6\%$  and  $\chi^2 = 15$  for the 14 variables and 487 observations. An empirical correction was then made for a small contribution to the reflection intensities due to multiple scattering, which caused the weak reflections to be systematically observed as too strong. Although this correction did not make any significant changes to the refined parameters, it reduced the  $\chi^2$  to 2.9,  $R = 2.1\%$  and  $R_w = 2.0\%$  for the remaining 479 reflections. The positional parameters are little changed from their values at room temperature and they are reported, together with the thermal parameters and the standard deviations, in table 1.

Table 1. The atomic positional and thermal parameters for  $\text{CoWO}_4$  obtained from a refinement of the 15 K single-crystal data. The Co and W atoms have isotropic temperature factors (ITFs) quoted in units of Å<sup>2</sup>.

Atom	Site	$x$	$y$	$z$	ITF
Co	2f	$\frac{1}{2}$	0.668 74(20)	$\frac{1}{4}$	0.15(2)
W	2e	0	0.180 31(10)	$\frac{1}{4}$	0.12(1)
O1	4g	0.217 22(7)	0.107 17(6)	0.932 89(6)	—
O2	4g	0.256 21(7)	0.377 49(6)	0.397 30(6)	—

Atom	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{23}$	$B_{13}$
O1	0.30(2)	0.34(2)	0.18(2)	-0.033(7)	0.102(9)	-0.045(7)
O2	0.32(2)	0.35(2)	0.22(2)	-0.031(7)	0.005(8)	-0.066(7)

### 4. The magnetic structure of $\text{CoWO}_4$

#### 4.1. The single-crystal study at 15 K

The scale factor obtained from the nuclear refinement was used to place the 433 observed magnetic structure factors on an absolute scale, before undertaking a least-squares refinement of the  $\text{Co}^{2+}$  moment amplitude and direction with the extinction parameter fixed to the value found for the nuclear data. The coupling between the moments on the two

crystallographically equivalent sites is known to be ferromagnetic from previous studies and the centre of symmetry at the origin of the cell carries time inversion. The magnetic form factor was first assumed to be that corresponding to a  $\text{Co}^{2+}$  free ion (Clementi and Roetti 1974). However, the  $R$  factor on structure factors remained relatively high at 22%,  $R_w = 17\%$  and  $\chi^2 = 26$ . The observed intensities at high  $\sin \theta/\lambda$  were generally greater than calculated, which is consistent with the presence of orbital magnetization and the predictions of the dipole approximation for its scattering. Introducing an additional term  $\langle j_2 \rangle$  to the  $\langle j_0 \rangle$  of the magnetic form factor and refining its amplitude produced a significant improvement in the fit, reducing the  $R$  factor to 14.3% with  $R_w = 10.8\%$  and  $\chi^2 = 11$ . The moment direction remained essentially unchanged at  $47.7(6)^\circ$  in  $\beta$  acute and the coefficient for  $\langle j_2 \rangle$  was 1.23(5) with a moment  $\langle j_0 \rangle$  of  $3.51(3) \mu_B$ . The  $R$  factors were still significantly higher than those achieved in the nuclear refinement and a further improvement was subsequently made by allowing the Co moment to become aspherical within the constraints imposed by its site symmetry. Since the major effect of such a departure from sphericity occurs in the high-sin  $\theta/\lambda$  data, a second estimate for the moment of  $3.49(7) \mu_B$  at  $45.1(8)^\circ$  to  $[001]$  in  $\beta$  acute was obtained from a refinement of the 67 observations with  $\sin \theta/\lambda$  below  $0.4 \text{ \AA}^{-1}$  ( $R = R_w = 5.1\%$ ,  $\chi^2 = 19$ ).

#### 4.2. The temperature variation of the magnetic structure

Profile refinements of the neutron powder patterns showed that there were no significant variations in the atomic positional parameters as a function of temperature and these were fixed at the single-crystal values. However, some temperature dependence was observed in the lattice parameters. Lines of magnetic origin were visible in all the patterns, except for that measured at 55 K. Using the magnetic form factor deduced above, the Co moment was allowed to vary in magnitude and direction in profile fits to the lower-angle part of each pattern extending to  $80^\circ 2\theta$ . Figure 2 shows the variation of the spherically symmetric Co magnetization as a function of temperature; its value at 15 K ( $3.53(5) \mu_B$ ) is in good agreement with that obtained in the single-crystal study using the spherical magnetization model ( $3.54(3) \mu_B$ ). Since there is no evidence for any significant reorientation of the moment with temperature, its orientation was fixed at the mean value obtained from the single-crystal refinements. The unit-cell volume does, however, exhibit a temperature variation, which is also plotted in figure 2. There is no significant variation in the cell parameters at 5 and 15 K and their values of  $a = 4.659(1)$ ,  $b = 5.667(1)$ ,  $c = 4.940(1) \text{ \AA}$  and  $\beta = 89.94(1)^\circ$  are consistent with, but more precise than, those determined in the single-crystal experiment. The estimated standard deviations include the uncertainty in the incident wavelength. Figure 3 illustrates the quality of the fits obtained.

### 5. Magnetization density and ground-state wavefunction for $\text{Co}^{2+}$

The quality of our single-crystal data encouraged us to take the magnetic model a stage further by making a multipole fit to the magnetic structure factors with form factors expressed as a set of atom-centred products of spherical harmonics and appropriate radial integrals  $\langle j_n \rangle$  for the spin moment. The quantum axes for the expansion were chosen with  $Z$  parallel to the moment direction and  $Y$  parallel to  $[010]$ . A least-squares fit to the 433 structure factors using the nine symmetry-allowed multipoles  $Y_{00}$ ,  $Y_{20}$ ,  $Y_{21+}$ ,  $Y_{22+}$ ,  $Y_{40}$ ,  $Y_{41+}$ ,  $Y_{42+}$ ,  $Y_{43+}$  and  $Y_{44+}$  and the radial expansion term in  $\langle j_2 \rangle$  resulted in an  $R$  factor of 7.7%,  $R_w = 5.3\%$  and  $\chi^2 = 2.4$ . Initially, the direction of the  $\text{Co}^{2+}$  moment was taken to be the mean of the two estimates previously obtained for a spherically symmetric moment

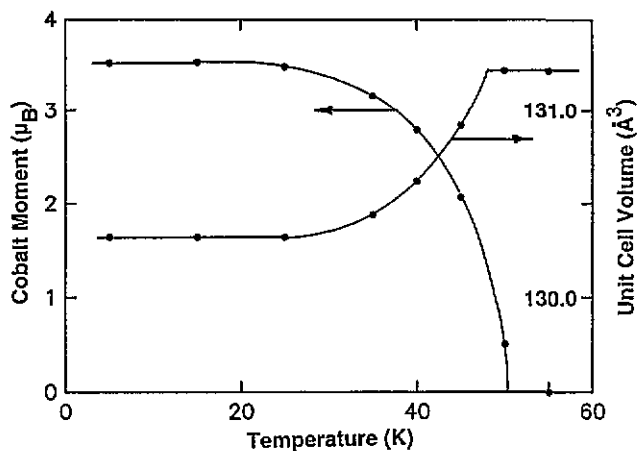


Figure 2. The temperature variation of the magnitude of the ordered  $\text{Co}^{2+}$  moment and the volume of the unit cell of  $\text{CoWO}_4$ . The solid lines are drawn as a guide to the eye; the errors on the observations lie within the plotted points except where indicated.

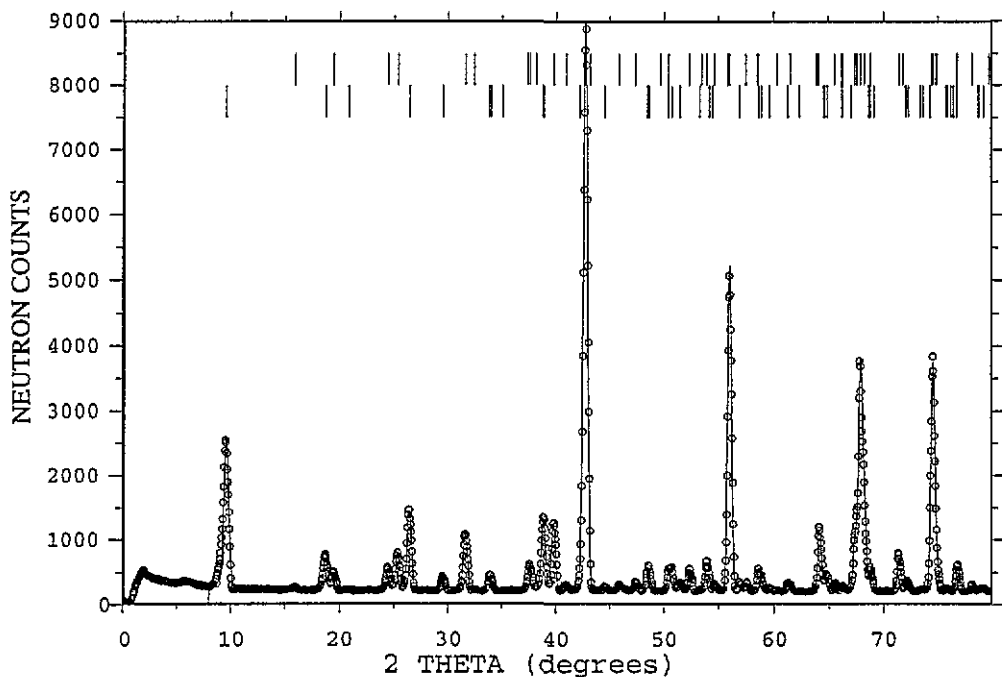


Figure 3. Profile refinement of the lower-angle part of the  $\text{CoWO}_4$  neutron powder pattern taken at 5 K with a wavelength of 1.594 Å. The positions of the nuclear and magnetic lines are shown by the upper and lower set of markers, respectively.

using either the whole data set or only those reflections with  $\sin \theta / \lambda < 0.4 \text{ \AA}^{-1}$ , namely at  $-46.3^\circ$  to  $[001]$  in  $\beta$  acute. Allowing this direction to vary showed that the angle of  $-44.3^\circ$  corresponded to the minimum in  $R$ ,  $R_w$  and  $\chi^2$  of 7.4%, 5.0% and 2.1 respectively and that significant changes in the multipole amplitudes only occurred for  $Y_{21+}$  and  $Y_{41+}$ . For this model, the best estimate for the  $\text{Co}^{2+}$  moment is  $\langle j_0 \rangle = 3.49(3)$  and  $\langle j_2 \rangle = 1.37(5) \mu_B$ .

A further improvement in fit was obtained by allowing the O atoms to have a moment oriented parallel to that of their Co neighbours which number two for O2 but only one for

O1. O moments of  $+0.05(2)$  and  $+0.08(2)$   $\mu_B$  were determined for O1 and O2 respectively, using a spherical form factor based on a free O 2p wavefunction and limiting the data to reflections with  $\sin \Theta/\lambda < 0.4 \text{ \AA}^{-1}$ . During this refinement, the multipoles describing the  $\text{Co}^{2+}$  moment and its radial expansion were held fixed at their previous best values. The agreement for the 67 reflections in this low-angle data set improved from  $R = 4.2\%$ ,  $R_w = 4.0\%$ ,  $\chi^2 = 14$  to  $R = 2.8\%$ ,  $R_w = 2.7\%$  and  $\chi^2 = 5.8$ . Clearly the magnitude of the covalently transferred moment is roughly the same for each ligand. Table 2 lists the final values for the multipoles describing the Co and O moments.

Table 2. The multipole amplitudes describing the magnetization on the Co atoms in the structure of  $\text{CoWO}_4$ . The  $\text{Co}^{2+}$  moment direction is  $44.3^\circ$  from [001] in  $\beta$  acute and the  $\langle j_2 \rangle$  addition to  $\langle j_0 \rangle$  for the  $\text{Co}^{2+}$  radial form factor is  $1.37(5)$   $\mu_B$ .

Multipole	Amplitude ( $\mu_B$ )
$Y_{00}$	3.49(3)
$Y_{20}$	-0.072(9)
$Y_{21+}$	-0.070(6)
$Y_{22+}$	-0.072(4)
$Y_{40}$	0.04(2)
$Y_{41+}$	-0.20(1)
$Y_{42+}$	-0.21(1)
$Y_{43+}$	0.06(1)
$Y_{44+}$	0.09(1)

The refined value of  $1.37(5)$  for the  $\langle j_2 \rangle$  addition to the  $\langle j_0 \rangle$  radial form factor means that the radial dependence can be written as  $\{\langle j_0 \rangle + 0.400\langle j_2 \rangle\}$  in reasonable agreement with the first two terms calculated for  $\text{Co}^{2+}$  in  $\text{CoO}$  by Mahendra and Khan (1971), whose complete expression is  $\{\langle j_0 \rangle + 0.362\langle j_2 \rangle + 0.162\langle j_4 \rangle\}$ .

It should be emphasized that the above analysis has been carried out in the framework of the dipole approximation to orbital scattering and a common direction,  $Z$ , for all the components of magnetization. However, the orbital moment will also produce small  $X$ ,  $Y$  components in the magnetization which should be modelled by  $Y_{21+}$  multipoles with a radial dependence of the form  $[\langle j_2 \rangle + \langle j_4 \rangle]$  and  $Y_{41+}$ ,  $Y_{43+}$  multipoles with  $[\langle j_4 \rangle + \langle j_6 \rangle]$  radial dependences (see, for example, Balcar and Lovesey 1989). The omission of these terms from our analysis may account, at least in part, for the relatively high values for  $\chi^2$  for the refinement using the low- $\sin \theta/\lambda$  data set, which contains the strongest and most accurately determined magnetic interaction vectors. However, the low-symmetry environment found in  $\text{CoWO}_4$  means that these multipoles, but with their normal radial dependences, may reflect the asphericity of the  $Z$  component of magnetization.

## 6. Discussion

We may first compare our results for the magnitude,  $3.49(5)$   $\mu_B$ , and direction,  $44.3(1)^\circ$  to  $c$  in the direction of  $-a$ , of the Co magnetic moment with previous studies. Galkin *et al* (1966) and Zvyagin and Khats'ko (1970) were the first to deduce a moment direction from their EPR and magnetic susceptibility measurements respectively. In both cases an angle of  $45^\circ$  to the  $a$  and  $c$  axes was proposed, though the sense of the rotation of the moment from [001] in the  $a$ - $c$  plane was not specified. Similarly, Gredescul *et al* (1972) concluded, on the basis of their single-crystal antiferromagnetic resonance (AFMR) measurements at 22 K,

that their  $y$  magnetic axis was parallel to  $b$  and that the other two axes were rotated in the  $a$ - $c$  plane such that the magnetic  $z$  axis was at about  $40^\circ$  to  $[001]$  in the direction of  $a$ . They judged that the absence of absorption for a  $z$ -polarised RF magnetic field implied that the antiferromagnetically aligned moments were parallel to their magnetic  $z$  axis. It therefore seems likely that the latter authors made an incorrect choice between  $a$  and  $-a$ , due to the fact that  $\beta$  is close to  $90^\circ$ . Weitzel (1976) also found the moments of  $3.60(5) \mu_B$  to lie in the  $a$ - $c$  plane, making an angle of  $46^\circ$  to  $[100]$ ; it is not clear that these measurements could determine whether this angle was towards  $c$  or  $-c$ . We conclude that our experiments are the first that enable the sense of the rotation of the Co moments away from  $[001]$  to be determined unequivocally. Consequently, the relationship of the  $\text{Co}^{2+}$  moment direction to its pseudo-octahedral ligand environment is also specified. The exchange pathways in  $\text{CoWO}_4$  have already been adequately discussed by Weitzel and Langhof (1977).

$\text{CoWO}_4$  exhibits strongly anisotropic magnetic properties. For example, at its Néel temperature there is a factor of about five between the extremal values of its magnetic susceptibility, which lie in the  $a$ - $c$  plane (Zvyagin and Khats'ko 1970). Gredescul *et al* (1972) have derived  $g$  values from their AFMR measurements on  $\text{CoWO}_4$  and find that the extremal values of  $6.3(7)$  and  $3.2(6)$  again lie in the  $a$ - $c$  plane with  $g_y = 4.8(6)$ .

Anisotropy in the magnetic properties of  $\text{CoWO}_4$  could in principle arise in part from the low symmetry of the crystal-field potential and in part through the anisotropic nature of the exchange potential. However, studies of  $\text{Co}^{2+}$  doped to 2% into the isomorphous  $\text{ZnWO}_4$  show that the large anisotropy in the susceptibility (Zvyagin and Khats'ko 1969) and in the  $g$  values remain when the exchange is not present. The  $g$  values obtained by Galkin *et al* (1967) from their EPR study show that the maximum and minimum values remain in the  $a$ - $c$  plane:  $g_x = 2.392(5)$ ,  $g_y = 3.345(5)$  and  $g_z = 6.78(1)$ . Both sets of authors therefore conclude that the most important contribution to anisotropy in  $\text{CoWO}_4$  is single-ion crystallographic anisotropy and, furthermore, that the crystal-field potential at the  $\text{Co}^{2+}$  site has a significant component of rhombic symmetry.

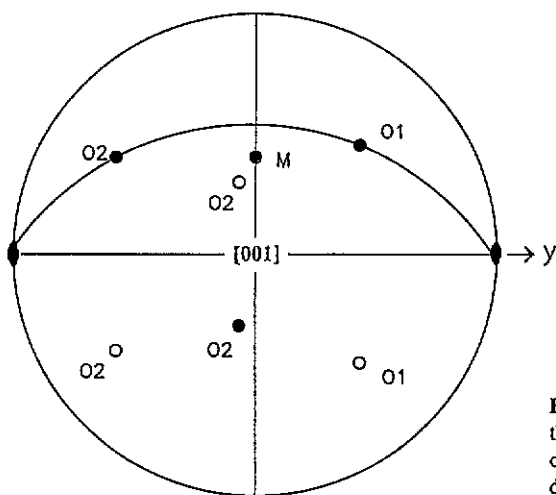


Figure 4. A stereogram showing the orientation of the  $\text{Co}^{2+}$  moment,  $M$ , with respect to the distorted octahedron of O ligands.  $M$  lies close to the pseudo-diad axis between an O1 and an O2 atom.

The orientation of the  $\text{Co}^{2+}$  moment with respect to the ligands is shown in figure 4, from which it can be seen that it lies close to the pseudo-diad roughly midway between a pair of atoms O1 and O2, which, with the true diad along  $b$ , define the orthorhombic



axes of the O octahedron. This observation supports the view that single-ion anisotropy is the principal factor orienting the  $\text{Co}^{2+}$  moment in the lattice. The presence of significant magnetostriction, deduced from the correlation between the variation in the cell volume and the growth of the ordered moment shown in figure 2, indicates the strength of the coupling.

The effects of a crystalline field of low symmetry on a  $\text{Co}^{2+}$  ion have been treated by Uryu *et al* (1966) in connection with monoclinic  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . They calculate the variation of the principal values of the  $g$  tensor and the reduced energies of the six lowest Kramers doublets of  $\text{Co}^{2+}$  as functions of the tetragonal and rhombic crystal-field parameters and find that the observed  $g$  values and heat-capacity data are consistent with the presence of pronounced orthorhombic distortion in the pseudo-octahedral ligand field at the  $\text{Co}^{2+}$  site, in addition to a tetragonal term. A similar treatment has been used by Zvyagin and Khats'ko (1969) to fit the magnetic susceptibility and  $g$  values for  $\text{Co}^{2+}$  in  $\text{ZnWO}_4$ . They estimate that the ratio of the rhombic to axial contributions to the crystalline field potential is 0.6.

A direct association between the observed anisotropy in the magnetization density and a corresponding anisotropy in the crystal field cannot be made until the contribution made by the orbital scattering has been calculated directly from the ground-state wavefunction. Perhaps the most direct experiment bearing on the choice of a ground state would be the use of zero-field neutron polarimetry (see, for example, Brown *et al* 1993) to determine the direction of the magnetic interaction vector for a few magnetic reflections. Such measurements would yield the magnitudes of the  $X$ ,  $Y$  components of orbital magnetization and provide the key to the fullest interpretation of the present observations.

## Acknowledgment

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## References

- Balcar E and Lovesey S W 1989 *Theory of Magnetic Neutron and Photon Scattering* (Oxford: Clarendon) p 138  
Becker P and Coppens P 1974 *Acta Crystallogr. A* **30** 129  
Brown P J, Forsyth J B and Tasset F 1993 *Proc. R. Soc. A* **442** 147  
Clementi E and Roetti C 1974 *At. Data Nucl. Data Tables* **14** 177  
Galkin A A, Prokhorov A D and Tsintsadze G A 1966 *Fiz. Tverd. Tela* **8** 3674 (Engl. Transl. 1967 *Sov. Phys.-Solid State* **8** 2943)  
Gredescul V M, Gredescul S A, Eremenko V V and Naumenko V M 1972 *J. Phys. Chem. Solids* **33** 859  
Lehmann M S, Kuhs W F, McIntyre G J, Wilkinson C and Allibon J R 1989 *J. Appl. Crystallogr.* **22** 568  
Mahendra A and Khan D C 1971 *Phys. Rev. B* **4** 3901  
Uryu N, Skalyo J Jr and Friedberg S A 1966 *Phys. Rev.* **144** 689  
Van Uittert L G, Sherwood R C, Williams H J, Rubin J J and Bonner W A 1964 *J. Phys. Chem. Solids* **25** 1447  
Wanklyn B M 1972 *J. Mater. Sci.* **7** 813  
Weitzel H 1970 *Solid State Commun.* **8** 2071  
— 1976 *Z. Kristallogr.* **144** 238  
Weitzel H and Langhof H 1977 *J. Magn. Magn. Mater.* **4** 265  
Wilkinson C, Khamis H W, Stansfield R F D and McIntyre G J 1988 *J. Appl. Crystallogr.* **21** 471  
Wilkinson C and Sprague M J 1977 *Z. Kristallogr.* **145** 96  
Zvyagin A I and Khats'ko 1969 *Sov. Phys.-Solid State* **10** 2970  
— 1970 *Sov. Phys.-Solid State* **12** 258