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The magnetic structure of antiferromagnetic $DyVO_4$

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Abstract. The magnetic and crystallographic structure of $DyVO_4$ has been determined by neutron diffraction on a powdered sample. The two observed λ-type anomalies in the specific heat at 13·8 and 3·0 K are explained by a quadrupole ordering followed by an antiferromagnetic transition. At 3·0 K $DyVO_4$ undergoes a transition to a collinear antiferromagnetically ordered state with the moments parallel to the b axis. The magnetic moment is 9·0 μ_B at 1·85 K. The nuclear scattering does not allow for a crystallographic phase transition, either at 13·8 K or at 3·0 K. In order to describe the magnetic structure properly the symmetry has to be reduced, however, to orthorhombic symmetry, space group I*mma* – D_{2k}^{28}.

1. Introduction

$DyPO_4$ and $DyVO_4$ seem to be ideal and simple examples of an antiferromagnetic Ising-like system and these two compounds have attracted great activity recently (Rado 1969. Wright and Moos 1969). The low temperature magnetic properties have been reported in a number of publications, which clearly indicate a transition from a paramagnetic to an antiferromagnetically ordered state at respectively 3·5 and 3·0 K. Most reliable evidence of magnetic ordering is found in recent specific heat measurement on $DyPO_4$ by Colwell *et al.* (1969) and on $DyVO_4$ by Becker *et al.* (1970) and by Cooke *et al.* (1970).

Interpretation and understanding of the exchange mechanism depends on the knowledge of the magnetic structure and the sublattice magnetization, and we have, therefore, undertaken a neutron diffraction study to establish the magnetic order and the type of ordering in these compounds. In this paper we wish to report the results on $DyVO_4$.

2. Experimental details

The diffraction experiments were done with a powdered sample of 7 mm diameter and 30 mm high. The powder, which had been ground from crystals grown by a flux method (Hintzmann and Müller-Vogt 1969), was kindly provided by Professor Kahle of the Technical University of Karlsruhe. Neutron diffraction diagrams were run at the DIDO research reactor in Jülich at 293 K, 4·2 K and at 1·85 K with a neutron wavelength of 0·97 Å in steps of 0·1° in 2θ. The absorption in the centre of the cylindrical sample was measured to 81 %.

3. Crystallographic data and crystal structure refinement

$DyVO_4$ crystallizes isomorphous with $ErPO_4$, $ErVO_4$, and $DyPO_4$ with the zircon structure in the tetragonal space group I $4_1/amd$ – D_{4h}^{19} (Wyckoff 1965). There are four formula units of $DyVO_4$ in the unit cell, with the ions occupying the following positions (International Tables of Crystallography 1965)

Dy^{3+} in	4 (a)	0	0	0
V^{5+} in	4 (b)	0	0	$\frac{1}{2}$
O^{2-} in	16 (h)	0	x	z

The structure consists of slightly distorted VO_4 tetrahedra with vanadium in the centre. The magnetic Dy^{3+} ions, which are located between the VO_4 tetrahedra, form a diamond-like lattice of point symmetry $\bar{4}2m$ with four nearest Dy neighbours at the corners of a distorted tetrahedron. Since the oxygen ions of the VO_4 tetrahedra are in general positions with free parameters x and z, and since the neutron scattering intensity is quite sensitive to the oxygen positions due to the quite large scattering length of oxygen, we have attempted to determine accurate positional parameters. The nuclear scattering also serves to establish an absolute scale for the calculation of the magnetic moments and allows the determination of a possible crystallographic phase transition. Neutron diffraction data were therefore collected with increased statistics at room temperature out to $2\theta = 45°$. Refinement of the parameters from the diffraction data was accomplished with a full matrix least squares program designed to take into account overlapping powder peaks, which had been used previously in a number of refinements with great success (Will and Eberspächer 1968). The function minimized is $\Sigma w . (G_0 - G_c)^2$, with $G_0 = I_{obs}/L . A$, where I_{obs} are the observed intensities and LA is the product of Lorentz and absorption correction factors. $(w)^{1/2}$ is $1/\sigma$, where σ is the estimated standard error in the observed intensities. G_c is $\Sigma j . F_c^2$, the sum over all overlapping reflections which are considered to contribute to an observed peak, j being the multiplicity factor. With a total of 15 peaks the refinement resulted in an R factor $R = \Sigma |G_0 - G_c| / \Sigma G_0$ of 5·3% and the parameters

$$x(O^{2-}) = 0{\cdot}185 \pm 0{\cdot}002$$
$$z(O^{2-}) = 0{\cdot}321 \pm 0{\cdot}002$$

The neutron scattering lengths used are $b(\mathrm{Dy}) = 16{\cdot}9$ fm $b(\mathrm{V}) = -0{\cdot}5$ fm, $b(\mathrm{O}) = 5{\cdot}77$ fm (1 f = 1 Fermi = 10^{-13} cm). A temperature factor of 0·2 was used. Table 1 lists the observed and calculated values of $\Sigma j . F^2$.

Table 1. Comparison of observed and calculated quantities $\Sigma j . F^2$ for the nuclear reflections of $DyVO_4$ at 293 K and 1·85 K.

(hkl)	Bragg angle 2θ observed	$\sum j . F^2$ observed at 293 K	$\sum j . F^2$ calculated	$\sum j . F^2$ observed at 1·85 K
101	11·80	174	188	167
200	15·65	247	272	257
211	19·70	65	78	64
112	20·95	161	153	161
220		0	0	0
202 + Al	23·85	–	310	–
301	25·20	901	938	
103 + Al	27·90	–	800	
321	29·80	1206	1072	
312	30·70	1148	1109	
400	31·55	497	495	
213	32·20	170	175	
411	33·85	214	160	
420, 004, 303, 402	35·90	580	604	
332	38·25	1216	1202	
204, 323, 422 + Al	39·70	–	407	
501, 431	40·85	1327	1386	
224, 413	42·70	1014	1055	

The main bond distances and angles are listed in table 2. The values are in close agreement with $ErVO_4$ (Patscheke *et al.* 1968). For the magnetic interaction, we calculate distances of 3·90 Å for the four nearest Dy^{3+} neighbours (nn). There are four next nearest neighbours (nnn) at 5·91 Å and eight further neighbours at 5·95 Å.

Table 2. Comparison of main bond distances and angles for $ErVO_4$ and $DyVO_4$

	$ErVO_4$	$DyVO_4$
x(O)	0·187	0·185
z(O)	0·325	0·321
V – O	1·72	1·73
O(1) – O(2)	2·66	2·64
O(1) – O(3)	2·89	2·92
Er – O(1)	2·44	
Er – O(4)	2·27	
Dy – O(1)		2·41
Dy – O(4)		2·29
Dy – Dy		3·90
O(1) – V – O(2)	100·8	100·7
O(1) – V – O(3)	114·0	114·9
Dy – O – Dy		111·9

Special attention was paid to a possible crystallographic phase transition of $DyVO_4$ to a configuration of lower symmetry at lower temperatures, which had been suggested by Cooke *et al.* (1970). Their recent specific heat measurements in the temperature range 0 to 22 K yielded two γ-type anomalies at 3·0 K and at 13·8 K, the latter being attributed to a first order phase transition for tetragonal to orthorhombic symmetry. The suggested crystallographic distortion below 13·8 K has been attributed to a Jahn–Teller splitting of an accidentally degenerate ground state quartet into two doublets. We could not detect such a crystallographic transition in the neutron diffraction diagrams. We have determined the lattice parameters by least squares calculation at 293 K and at 1·85 K with no detectable deviations from a tetragonal unit cell; $a = 7{\cdot}135$ Å, $c = 6{\cdot}288$ Å at 293 K.

A more rigorous test for a possible phase transition can be drawn from the diffracted nuclear intensities, which are especially sensitive to shifts in the oxygen nuclei due to the comparatively large scattering power of oxygen for neutrons. Any distortion of the tetragonal cell to, for example, an orthorhombic cell must change the relative position and/or orientation of the oxygen tetrahedra and therefore of the intensities. No such difference in the intensities of the nuclear peaks observed at 1·85 K and at 293 K can be detected (see table 1), so that the proposed distortion (Cooke *et al.* 1970) has to be doubted and there is no change in the symmetry of the *nuclear* or atomic structure.

4. The magnetic structure

In the neutron diffraction diagram taken at 1·85 K (figure 1) additional peaks are observed as a result of antiferromagnetic alignment of the magnetic moments. Figure 2 depicts for clarity the temperature difference diagram with only the magnetic peaks and intensities left. All reflections can be indexed on the basis of the original tetragonal cell with no change in the *size* of the unit cell.

The magnetic ions Dy^{3+} occupy the positions 0 0 0, $0\,\frac{1}{2}\,\frac{1}{4}$, $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$, $\frac{1}{2}\,0\,\frac{3}{4}$ in the unit cell. If we choose the nomenclature of Bertaut–Wollan–Koehler A (+ − − +), C (+ + − −), G (+ − + −), F (+ + + +) the configurations G and F can be excluded immediately on the grounds of the observed extinctions: 100, 001, 111 are absent. The remaining configurations A and C are shown in figure 3. Both configurations A and C are however equivalent and undistinguishable in the tetragonal symmetry, as can be seen from figure 3. They can be transformed into each other by a rotation around [001] by 90° followed by a rotation by 180° around a twofold axis parallel to respectively a or b at a distance $z = \frac{1}{2}$.

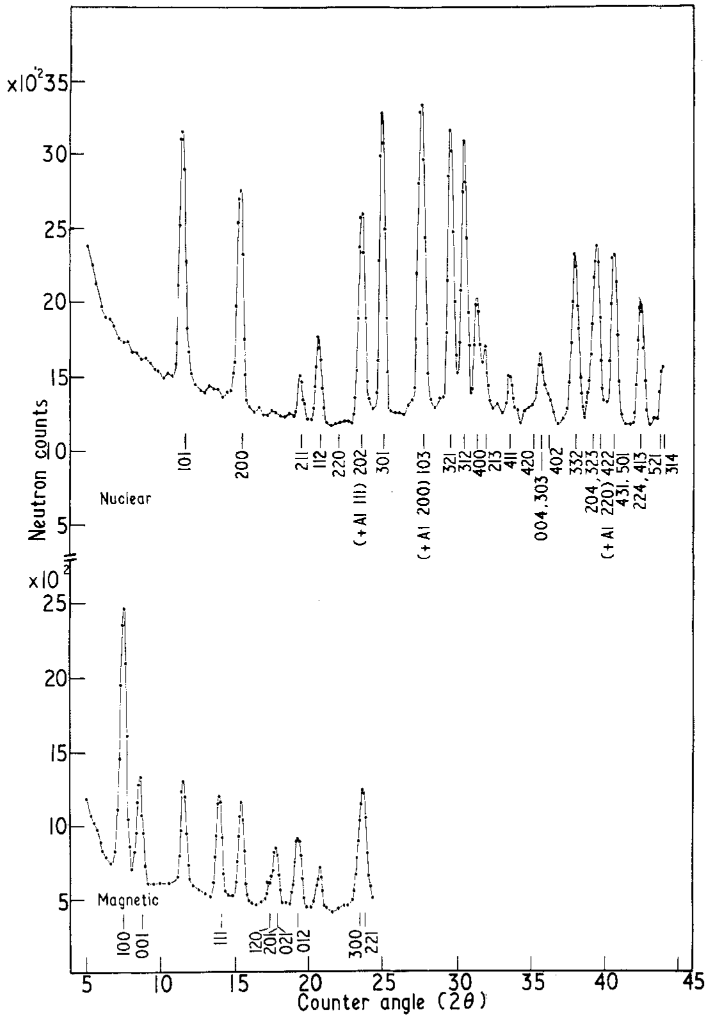

Figure 1. Neutron diffraction diagrams of $DyVO_4$ at 293 K (top) and 1·85 K (bottom); $\lambda = 0{\cdot}97$ Å.

In order to describe the magnetic structure of figure 3 properly, the symmetry has to be lowered from the tetragonal symmetry of space group $I\,4_1/amd - D_{4h}^{19}$ to orthorhombic symmetry, for the reason that the fourfold screw axis 4_1 of the original tetragonal cell is lost in the magnetic transition, and there is only a twofold, coloured screw axis $2_1'$ left. From tables published by Asher (1968) listing equi-translation subgroups of space groups the proper symmetry is then orthorhombic $I\,mma - D_{2h}^{28}$. In this space group the ions then occupy the following positions (with the origin shifted by $0\,\frac{1}{4}\,\frac{\bar{1}}{8}$)

Dy^{3+} in 4 (e): $0\,\frac{1}{4}\,z$ with $z = \frac{7}{8}$

V^{5+} in 4 (e): $0\,\frac{1}{4}\,z$ with $z = \frac{3}{8}$

$O(1)^{2-}$ in 8 (i): $x\,\frac{1}{4}\,z$ with $x = 0{\cdot}315$, $z = 0{\cdot}946$

$O(2)^{2-}$ in 8 (h): $0\,y\,z$ with $y = 0{\cdot}065$, $z = 0{\cdot}196$

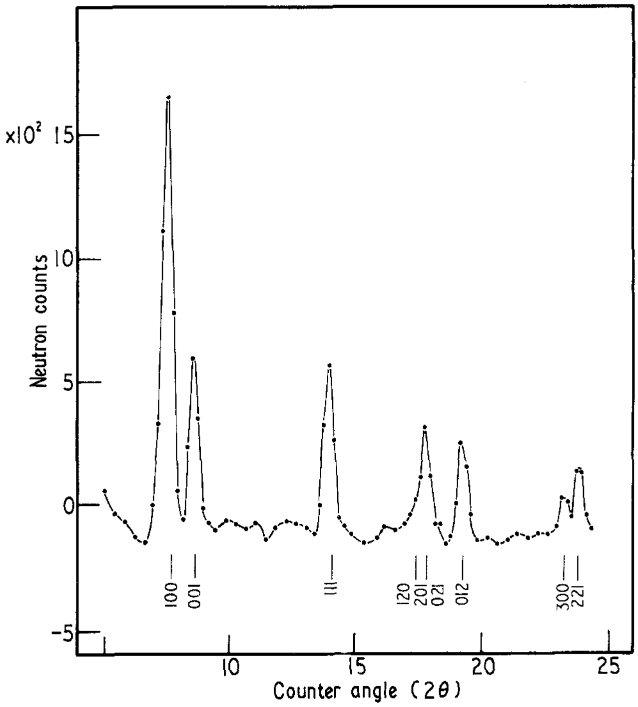

Figure 2. Temperature difference diagram of DyVO$_4$ showing the magnetic scattering contributions at 1·85 K. The difference pattern is given by I(1·85 K) − I(293 K).

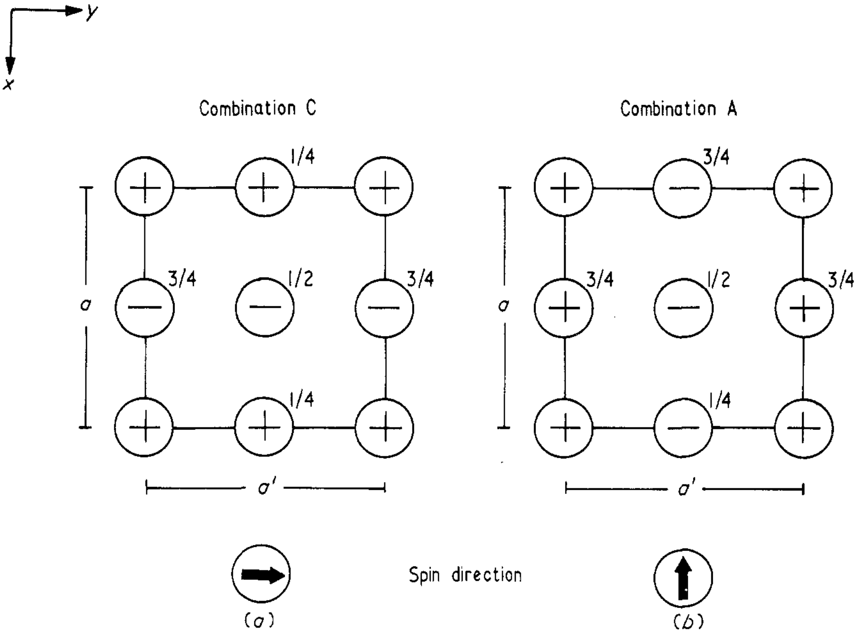

Figure 3. The two possible, undistinguishable and equivalent magnetic configurations of the Dy^{3+} ions in the antiferromagnetically ordered state in a tetragonal unit cell (space group I, $4_1/amd$). The magnetic moments are parallel to [010] in case (a), and parallel to [100] in case (b). The two configurations can be transformed into each other by two consecutive rotations (see text).

We did not attempt to distinguish between different coordinates of O(1) and O(2) at 1·85 K, as would be possible in I *mma*.

The orientation of the magnetic moments can be calculated from the observed magnetic scattering intensity through the angle-dependent magnetic interaction vector $\boldsymbol{q}$:

$$I = \frac{Kq^2F^2}{LA} = \frac{Kq^2\left|\sum_i p_i \exp\{2\pi i(hx_i + ky_i + lz_i)\}\right|^2}{LA} = \frac{K16q^2p^2}{LA}$$

$$\boldsymbol{q} = \boldsymbol{\epsilon}\,.\,(\boldsymbol{\epsilon}\,.\,\boldsymbol{k}) - \boldsymbol{k}.$$

For tetragonal symmetry and a powder sample

$$\langle q^2\rangle = 1 - \{\tfrac{1}{2}(h^2 + k^2)\,a^{*2}\sin^2\phi_c + l^2c^{*2}\cos^2\phi_c\}\,d^2,$$

which means from powder diffraction data we can only determine the angle ϕ_c between the moments and the c axis.

For orthorhombic symmetry however we have

$$\langle q^2\rangle = 1 - (h^2a^{*2}\cos^2\phi_a + k^2b^{*2}\cos^2\phi_b + l^2c^{*2}\cos^2\phi_c)\,d^2$$

with ϕ_a, ϕ_b, ϕ_c the angles of the magnetic moment vector $\boldsymbol{k}$ with the crystallographic axes a, b, c. This means, the angles can be determined uniquely, at least in principle.

The magnetic moment μ per Dy^{3+} is calculated from p

$$p = \tfrac{1}{2}\cdot\left(\frac{e^2\gamma}{mc^2}\right)\mu f.$$

The absolute scale for the calculation of the magnetic moment is established through the nuclear diffraction to $K/A = 1{\cdot}023$ (A = absorption). f is the magnetic form factor for Dy^{3+}, which has been taken from Bideaux and Meriel (1968). All other quantities are known. We have performed least squares calculations on the observed magnetic quantities $\Sigma j\,.\,F^2_{\mathrm{mag}}$ and derived, referring to the configuration C = (+ + − −):

$$\phi_a = 90^\circ \qquad \phi_b = 0^\circ \qquad \phi_c = 90^\circ$$

For the magnetic moment we calculate $\mu = 9{\cdot}0\ \mu_B$ at 1·85 K with an agreement factor $R = 3{\cdot}3\,\%$. Table 3 lists the observed and calculated magnetic quantities $\Sigma j\,.\,F^2_{\mathrm{mag}}$. The first three magnetic peaks (100), (001) and (111) were also measured at 2·35 K yielding a value of $\mu = 8{\cdot}2\ \mu_B$. They are included in table 3.

Table 3. Comparison of observed and calculated quantities $\Sigma j\,.\,F^2$ for the magnetic reflections of $DyVO_4$ at 1·85 K and 2·35 K

		1·85 K		2·35 K	
(*hkl*)	Bragg angle 2θ observed	$\sum j\,.\,F^2_{\mathrm{mag}}$ observed	$\sum j\,.\,F^2_{\mathrm{mag}}$ calculated	$\sum j\,.\,F^2_{\mathrm{mag}}$ observed	$\sum j\,.\,F^2_{\mathrm{mag}}$ calculated
100	7·80	193	186	156	154
001	8·85	90	92	78	76
111	14·20	224	230	185	189
120, 201, 021	17·95	233	241		
012	19·45	246	236		
300, 221 + Al	24·10	†	257		

† Al-(111) from the cryostat superimposed

The moments are thus aligned in a collinear antiferromagnetic pattern perpendicular to the *c* axis, as inferred from optical and specific heat measurement, and parallel to the *b* axis. There is no additional component yielding a canted or helical structure.

5. Temperature dependence

The Neel temperature is known from specific heat measurements (Becker *et al.* 1970) to be 3·038 K. We have studied the temperature dependence of the magnetic scattering by following the strongest magnetic reflection (100), in order to determine the type of transition. The result is shown in figure 4 indicating a second order phase transition with a Neel point at 3·0 K. In figure 5 the normalized data I/I_0 are plotted versus T/T_N and compared with a Brillouin-dependence of an effective spin $\frac{1}{2}$. I_0 was taken to be $I_0 = 9{\cdot}5\ \mu_B$ at $T = 0$ K, corresponding to the theoretical magnetic moment value of a three positive dysprosium ion in the ordered state with $g = 19$.

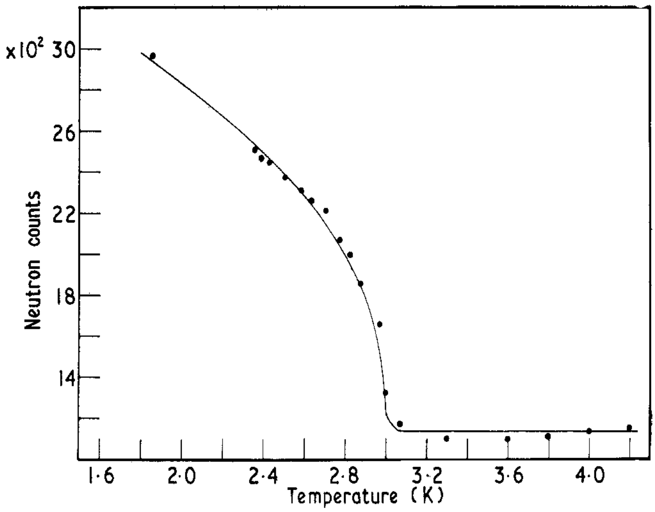

Figure 4. Temperature dependence of the intensity of the (100) magnetic reflection for DyVO$_4$, indicating a Neel temperature of 3·0 K.

6. Discussion

The observed temperature dependence of the magnetic transition in comparison with a Brillouin function clearly indicates, that the magnetic interactions in DyVO$_4$ are exchange plus dipolar.

The observed magnetic moment of 8·2 μ_B at 2·35 K and of 9·0 μ_B at 1·85 K yields an extrapolated moment of 9·5 μ_B at 0 K. Together with the observed highly anisotropic g-factors: $g_a = 19$, $g_b = 0$, $g_c = 0{\cdot}5$ we calculate a fictious spin-value of $\frac{1}{2}$ in agreement with an expected ground state Kramers doublet.

For the observed anomaly in the specific heat at 13·8 K we propose a quadrupole ordering, as suggested by Blume (private communication 1970). This interpretation is in agreement with the fact, that no crystallographic phase transition could be found together with the fact, that the Mössbauer spectrum shows a sharp line splitting into a

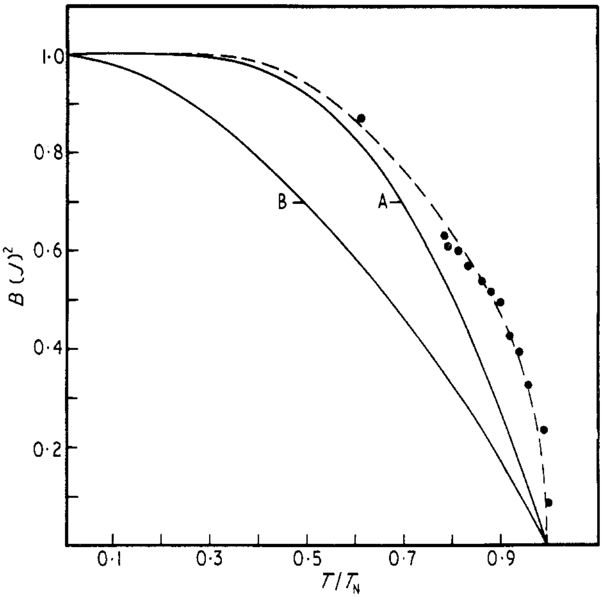

Figure 5. Normalized magnetic scattering from (100) planes of DyVO$_4$ compared with a Brillouin dependence for $J = \frac{1}{2}$ (curve A) and $J = \frac{15}{2}$ (curve B). $I_0 \simeq 9{\cdot}5\ \mu_B$, $T_N = 3{\cdot}0$ K. (●) denotes DyVO$_4$ (100).

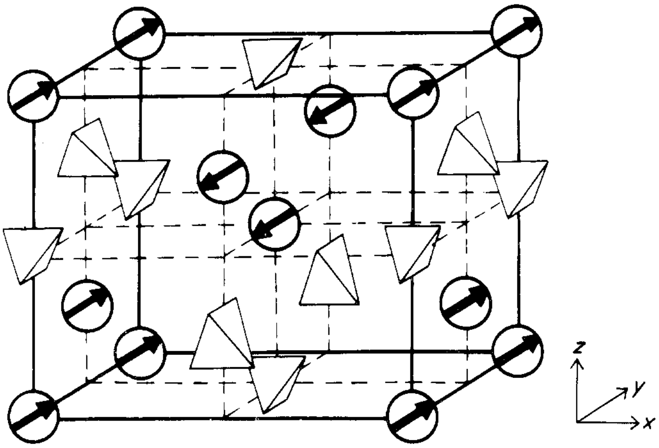

Figure 6. Crystallographic and magnetic structure of DyVO$_4$ at 1·85 K. The small tetrahedra represent the VO$_4$ tetrahedra, with vanadium in the centre and oxygen at the corners.

line rich pattern between 14 and 13 K (Belakovsky, private communication 1970). Quadrupole ordering would also be in agreement with the observed optical spectra (Ellis *et al.* 1970) above, between and below the two λ anomalies.

As a further check we are planning X ray diffraction measurements around 13·8 K and neutron diffraction measurements on single crystals.

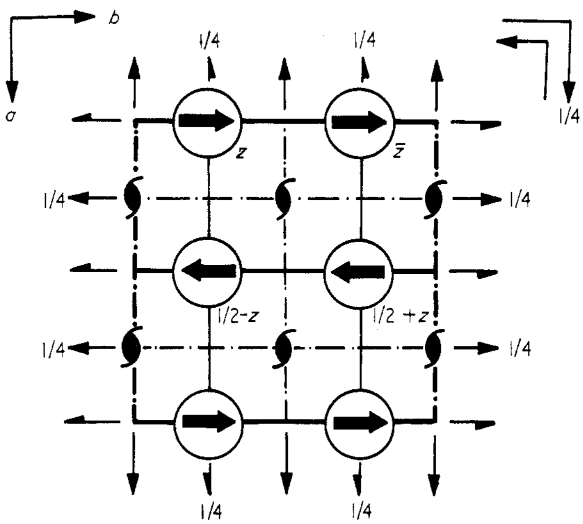

Figure 7. Magnetic structure of $DyVO_4$ in the orthorhombic setting of space group I *mma.*

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References

ASHER, E., 1968, *Lattices of Equi-Translation Subgroups of the Space Groups* (Geneva: Battelle Institute).
BECKER, P. J. *et al.*, 1970, *Phys. Lett.*, **31**A, 499–500.
BIDAUX, R., and MERIEL, P., 1968, *J. Phys.* (*Paris*), **29**, 220–4.
COLWELL, J. H. *et al.*, 1969, *Phys. Rev. Lett.*, **23**, 1245–7.
COOKE, A. H., *et al.*, 1970, *Solid St. Commun.* **8**, 689–92.
ELLIS, C. J. *et al.*, 1971, *Int. Conf. on Magnetism, Grenoble* 1970 (*J. Phys.-Paris*, 1971, in press).
HINTZMANN, W., and MÜLLER-VOGT, G., 1969, *J. Cryst. Growth* **5**, 274–8.
International Tables for X-Ray Crystallography, 1952 (Birmingham: Kynoch Press).
PATSCHEKE, E., FUESS, H., and WILL, G., 1968, *Chem. Phys. Lett.* **2**, 47–50.
RADO, G. T., 1969, *Phys. Rev. Lett.*, **23**, 644–7.
WILL, G., and EBERSPÄCHER, O., 1969, *Z. anorg. allg. Chem.*, **356**, 163–71.
WRIGHT, J. C., and MOOS, W. H., *Phys. Lett.*, **29**A, 495–6.
WYCKOFF, R. W. G., 1965, *Crystal Structures* (New York: Interscience).