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ON THE MAGNETIC STRUCTURE OF $DyCrO_3$

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Résumé. — Cette communication décrit une nouvelle détermination de la structure magnétique de $DyCrO_3$ par diffraction neutronique. L'arrangement des moments de Dy proposé par Bertaut et Mareschal doit être modifié. On n'observe pas une coexistence des deux modes G et A selon chaque axe **a** et **b**, ce qui indique qu'une contribution à l'énergie, quoique permise par la symétrie, n'existe pas. Bien que la section efficace d'absorption du dysprosium pour les neutrons thermiques soit assez élevée, il a été possible de déterminer les paramètres des positions atomiques dans la maille.

Abstract. — A new investigation of the magnetic structure of $DyCrO_3$ by means of neutron diffraction is described. The Dy moment arrangement as reported by Bertaut and Mareschal has to be modified. No mixing of G and A modes along one crystallographic axis is observed which means that one type of interaction, though allowed by symmetry, is not present. Although the absorption cross section for thermal neutrons of Dy is rather high it was possible to determine the positional parameters of the atoms in the lattice.

Introduction. — The compound $DyCrO_3$ crystallizes in the orthorhombic space group Pbnm(D_{2h}^{16}). There are four molecules per unit cell [1]. The atoms occupy the following positions :

4 Cr at 4(b) : $\frac{1}{2}, 0, 0$
4 Dy at 4(c) : $x, y, \frac{1}{4}$
4 01 at 4(c) : $x, y, \frac{1}{4}$
8 02 at 8(d) : x, y, z

Neutron diffraction work showed the existence of two different Néel temperatures. The Cr moments order at $T_N(Cr) = 146$ °K while ordering of the Dy moments occurs at $T_N(Dy) = 2.2$ °K [2], [3]. The Cr moments are arranged in a G_z mode [2], [3], i. e. the moments are along the *c* axis, those at $(\frac{1}{2}, 0, 0)$ and $(0, \frac{1}{2}, \frac{1}{2})$ being parallel to each other and antiparallel to the moments at $(\frac{1}{2}, 0, \frac{1}{2})$ and $(0, \frac{1}{2}, 0)$. A model for the ordering scheme of the Dy moments is given by Bertaut and Mareschal [3]. From a neutron diffraction diagram it was deduced that this scheme is based on a propagation vector $\mathbf{k} = [\frac{1}{2}, \frac{1}{2}, 0]$ which means that the periodicity of the magnetic structure in the **a** and **b** direction is twice that of the crystallographic structure.

Group theoretical considerations as given by Bertaut and Mareschal show that the Dy structure either has *z* components only or *x* and *y* components. Another result of these considerations is that the directions of the moments on atoms 1 and 3 (Table I) are uncorrelated. This is a consequence of the fact that in all irreducible representations of the group of **k** the symmetry elements that connect the atoms 1 and 3 (and 2 and 4) are represented by $\pm i$. This is equivalent to saying that these elements, the twofold screw axes along **a** and **b** and the two glide planes *n* and *b*, are not present in the magnetic space group and hence the magnetic symmetry is monoclinic. The

TABLE I

Definition of G and A modes in the ordering scheme of the Dy moments.
The positional parameters in the table refer to the crystallographic cell

Nr.	Position	G	A
1	$x, \quad y, \quad \frac{1}{4}$	+	+
2	$\bar{x}, \quad \bar{y}, \quad \overline{\frac{1}{4}}$	−	−
3	$\frac{1}{2} + x, \frac{1}{2} - y, \overline{\frac{1}{4}}$	+	−
4	$\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{4}$	−	+

moments on atoms 1 and 2 (and 3 and 4) remain correlated.

Bertaut and Mareschal observed that the magnetic reflections due to the Dy moments are strong for $h, k, l = 2n + 1$ and weak for $h, k = 2n + 1, l = 2n$, where h, k, and l refer to the magnetic unit cell. As pointed out by them the fact that reflections with $h + k = 4n$ and with $h + k = 4n + 2$ have equivalent intensities, indicates that in the Dy arrangement the modes G and A are both present, these modes being defined as given in Table I. This implies that no z components are present in the structure.

It follows from Table I that the moments on atoms 1 and 2, are antiparallel as are the moments on atoms 3 and 4. The relative and absolute orientation of these two pairs are not yet known at this stage.

In reference [3] it is stated that the ratio of the observed intensities of the (131) and (311) reflections implies that the modes A and G coexist along both the x and y directions. The deduced directions for the moments on the Dy atoms 1 and 3 are not related by any symmetry operation. This would have been the first known example of an orthorhombic compound in which atoms belonging to one crystallographic position carry moments not related by symmetry. A recalculation of the magnetic intensities by the present authors revealed, however, that it is not necessary to allow the coexistence of A and G modes along both the x and y direction to fulfil the above mentioned condition. This observation, together with the possibility to obtain better intensity data, led to a new investigation of the magnetic structure of $DyCrO_3$ described in the present paper.

Experimental. — The sample has been prepared by heating an intimate mixture of Dy_2O_3 and Cr_2O_3 at 1 400 °C in air for some days.

Neutron diffraction data at 300 °K, 4.2 °K, and 1.2 °K have been collected at the H. F. R. in Petten. The neutron wavelength was 2.5796 (4) Å, obtained from the (111) planes of a copper crystal. As a second order filter, a block of pyrolytic graphite with a thickness of 10 cm was employed [4]. Between reactor and monochromator and in front of the BF_3 counter Soller slits with a horizontal angular divergence of 30′ were placed.

The sample, which was contained in a cylindrical vanadium sample holder with a diameter of 20 mm and a volume of 17.7 ml consisted of a mixture of 4.46 g $DyCrO_3$ and 17.93 g Al powder. The ratio of the effective density of $DyCrO_3$ and its theoretical density was therefore 0.03. Although the volume of the sample is much decreased by this dilution technique, the absorption by the sample is also less than in a pure $DyCrO_3$ powder to such an extent that an intensity gain of about a factor 7 was obtained. Nevertheless it was necessary to correct the data for absorption.

Crystallographic and magnetic structures. — ROOM-TEMPERATURE. — In reference [3] the atomic position parameters in $DyCrO_3$ were not determined but taken as intermediate between those in $TbCrO_3$ and $ErCrO_3$. The present data allowed a direct determination of these parameters. The refinement of the structure has been performed by means of the profile refinement method described by Rietveld [5]. This method determines the estimates of the various parameters by finding a least squares fit between the observed and calculated diffraction diagrams, minimizing the quantity

$$\chi_\nu^2 = \sum_i w_i[y_i(\text{obs}) - y_i(\text{calc})]^2/\nu ,$$

where y_i (obs) and y_i (calc) are the observed and calculated values of the i-th measuring point and w_i is its statistical weight. The number of points minus the number of parameters is indicated by ν. The coherent scattering lengths used are :

$$b_{\text{Dy}} = +\ 1.69 \times 10^{-12}\ \text{cm},\quad b_{\text{Cr}} = +\ 0.352 \times 10^{-12}\ \text{cm},$$

and

$$b_0 = +\ 0.577 \times 10^{-12}\ \text{cm}.$$

The final least squares parameters are listed in Table II. The observed and calculated diffraction profiles are shown in figure 1. The deduced position parameters are not much different from those adopted in reference [3].

TABLE II

Structural parameters and magnetic moments in Bohr magnetons in $DyCrO_3$ *at different temperatures.*

Standard deviations in units of the last decimal are given in parentheses.

T(K)	300 °K	4.2 °K	1.2 °K
a (Å)	5.271 (1)	5.266 (1)	5.258 (1)
b (Å)	5.525 (1)	5.522 (1)	5.514 (1)
c (Å)	7.561 (1)	7.547 (1)	7.536 (1)
x (Dy)	-.015 (1)	-.016 (1)	-.003 (1)
y (Dy)	.065 (1)	.067 (1)	.068 (1)
x (01)	.103 (2)	.103 (2)	.108 (3)
y (01)	.446 (2)	.466 (2)	.467 (3)
x (02)	-.305 (2)	-.306 (2)	-.303 (3)
y (02)	.302 (1)	.297 (2)	.301 (3)
z (02)	.052 (1)	.053 (1)	.056 (2)
μ_x (Dy)	—	—	4.2 (2)
μ_y (Dy)	—	—	7.5 (1)
μ (Dy)	—	—	8.5 (1)
α (°)	—	—	90 (-)
β (°)	—	—	29 (2)
μ_z (Cr)	—	2.6 (1)	2.7 (1)
χ_ν	1.4	1.5	4.6

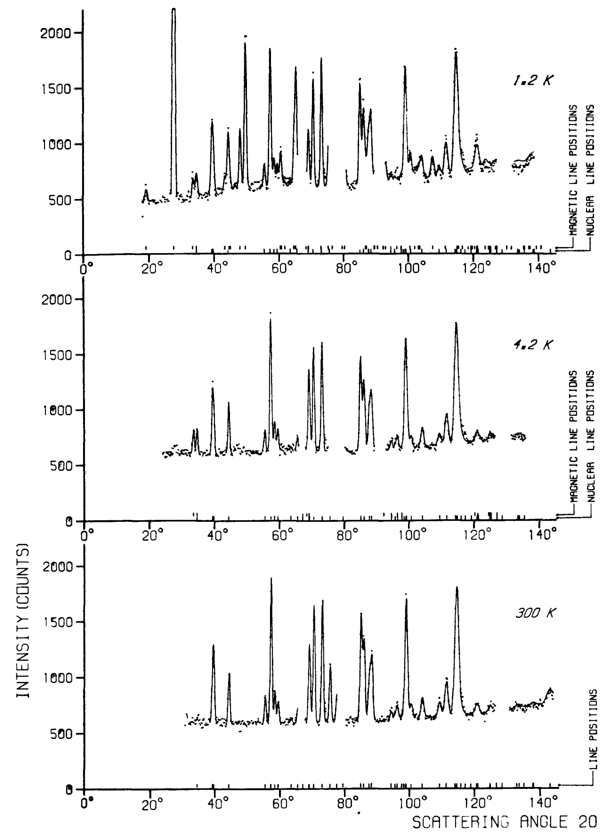

FIG. 1. — Observed and calculated neutron diffraction profiles of DyCrO$_3$ at three different temperatures. The dots represent the observed profile, the full line the calculated profile. Observed peaks due to the aluminium in the sample and the copper of the cryostat have been omitted.

4.2 °K. — From the diffraction data at 4.2 °K the Cr spin arrangement given in references [2, 3] and described in the introduction of this paper, was confirmed. In the refinement of the crystallographic and the magnetic parameters by means of the profile method the spherical Cr^{3+} formfactor given by Watson and Freeman [6] was used. Final parameters are listed in Table II. The observed and calculated profiles are shown in figure 1. The value for the Cr^{3+} moment is not significantly different from that determined by Bertaut and Mareschal [3].

1.2 °K. — The neutron diagram at 1.2 °K had the same overall appearence as that published in reference [3]. The extra peaks due to the Dy moment could be indexed by adopting the **k** vector [$\frac{1}{2}$, $\frac{1}{2}$, 0). The observed ratio of I(131) + I(13$\bar{1}$) and I(311) + I(31$\bar{1}$) was 0.37 which agrees well with the value of 0.36 given by Bertaut and Mareschal. The model for the Dy spin arrangement given by these authors, was used as a starting model in the least squares refinement with the present data. In this refinement the Dy^{+++} formfactor calculated by Blume, Freeman, and Watson [7] was used. In all refinements the moments on the four Dy atoms were constrained to have the same value, though symmetry requires only the equality of the moments within the pairs 1-2 and 3-4. The moments 1 and 2 are antiparallel as are 3 and 4. In the first part of the refinement the directions of moments 1 and 3 were left free. This resulted in spin directions such that the angle α between **a** and $\mathbf{S}_1 - \mathbf{S}_3$ and the angle β between $\mathbf{S}_1$ and $\mathbf{S}_1 - \mathbf{S}_3$ had the values (93 ± 3)° and (30 ± 3)° respectively. In the last cycles α was constrained to 90° which resulted in a value of (29 ± 2)° for β and an increase of χ^2_ν from 4.54 to 4.58 which is insignificant. This means that, within the accuracy of the observation, in the Dy spin arrangement the G mode only exists along **a** and the A mode only along **b**. This situation is summarized in figure 2, which should be compared with figure 2 of reference [3]. A picture of the whole Dy arrangement is given in figure 3.

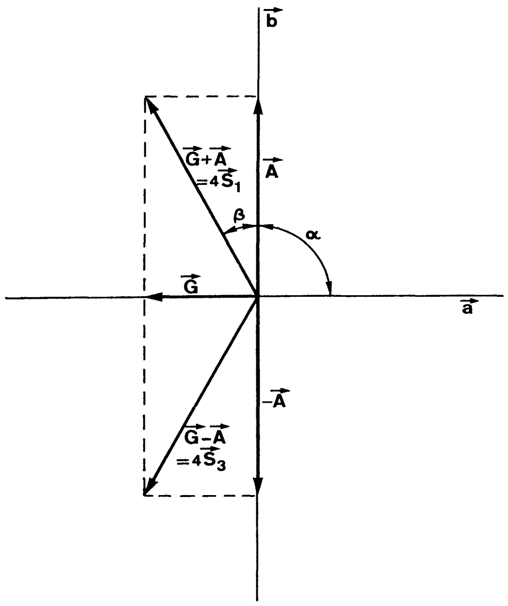

FIG. 2. — Diagram of the vectors **G** and **A** characterizing the Dy spin arrangement in DyCrO$_3$.

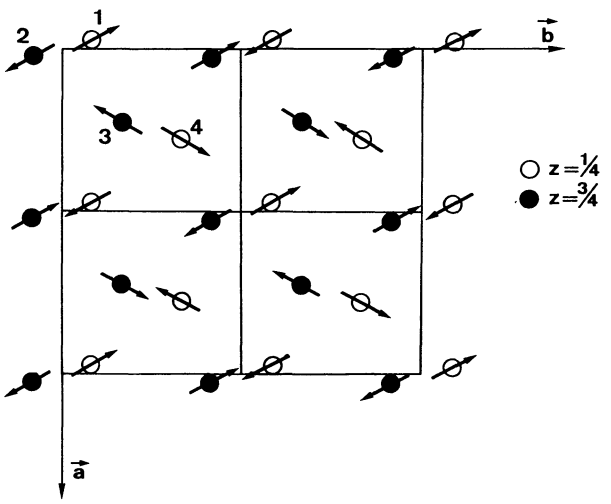

FIG. 3. — Magnetic spin arrangement of Dy in DyCrO$_3$. One magnetic unit cell with sides 2 **a** and 2 **b** is shown in projection along **c**.

The final parameters are listed in Table II and the observed and calculated profile is found in figure 1.

The Hamiltonian. — Bertaut and Mareschal [3] construct the Hamiltonian as a linear combination of all invariants of order two and arrive at :

$$\begin{aligned} H = {} & 4\,\mathrm{S}^2\,\mathrm{b} - 2\,b(\mathrm{S}_1.\mathrm{S}_2 + \mathrm{S}_3.\mathrm{S}_4) + \\ & + (a - b)\left[(\mathrm{S}_{1x} - \mathrm{S}_{2x})^2 + (\mathrm{S}_{3x} - \mathrm{S}_{4x})^2\right] \\ & + c\left[(\mathrm{S}_{1x} - \mathrm{S}_{2x})(\mathrm{S}_{3y} - \mathrm{S}_{4y})\right. \\ & \left. + (\mathrm{S}_{1y} - \mathrm{S}_{2y})(\mathrm{S}_{3x} - \mathrm{S}_{4x})\right] \\ & + d\left[(\mathrm{S}_{1x} - \mathrm{S}_{2x})(\mathrm{S}_{1y} - \mathrm{S}_{2y})\right. \\ & \left. - (\mathrm{S}_{3x} - \mathrm{S}_{4x})(\mathrm{S}_{3y} - \mathrm{S}_{4y})\right] . \end{aligned}$$

Expressing the various terms of this expression in the angles α and β defined above and differentiating with respect to α and β leads to the stability conditions, with :

$$- (a-b) \sin 2\,\alpha \cos 2\,\beta - c \cos 2\,\alpha - d \sin 2\,\alpha \sin 2\,\beta = 0$$

$$- (a-b) \cos 2\,\alpha \sin 2\,\beta + d \cos 2\,\alpha \cos 2\,\beta = 0$$

with :

$$- (a-b) \cos 2\,\alpha \cos 2\,\beta + c \sin 2\,\alpha - d \cos 2\,\alpha \sin 2\,\beta > 0$$

$$- (a-b) \cos 2\,\alpha \cos 2\beta - d \cos 2\,\alpha \sin 2\,\beta > 0$$

Inserting the values $\alpha = 90^\circ$ and $\beta = 29^\circ$ found in the present work leads to :

$$d/(a - b) = + 1.65 \; ; \; c = 0$$

with d and $(a - b)$ both positive.

Discussions. — From the new data described in this paper it is concluded that the ordering scheme of the Cr moments agrees with the model reported by Bertaut and Mareschal. Their model for the Dy moment arrangement is, however, not correct. They may have been mislead by the fact that the intensities for the (hkl) and $(hk\bar{l})$ reflections are different, due to the fact that the Dy spin arrangement does not have an orthorhombic symmetry but is monoclinic.

Though magnetic symmetry does not require any correlation between the direction of the moments on atoms related via one of the twofold screw axes, such a correlation still appears to be present, i. e. along each axis only one mode is existent. It has already been pointed out in reference [3] that the symmetry in the magnetic state allows four interaction types which is reflected by the fact that the expression for the Hamiltonian consists of four parts :

i) With coefficient b. This part is isotropic, it depends only on the relative orientation of $\mathbf{S}_1$ and $\mathbf{S}_3$.

ii) With coefficient $(a - b)$. This part favors a uniaxial structure with $\mathbf{S}_1$ and $\mathbf{S}_3$ parallel or antiparallel to each other and oriented along **a** or **b**.

iii) With coefficient c. This part tends to orient the moments such that $\mathbf{S}_1 \pm \mathbf{S}_3$ is parallel to

$$(\mathbf{a}/|\,\mathbf{a}\,|) \pm (\mathbf{b}/|\,\mathbf{b}\,|) .$$

iiii) With coefficient d. This part is minimized in an arrangement in which $\mathbf{S}_1 \perp \mathbf{S}_3$ and both moments along $(\mathbf{a}/|\,\mathbf{a}\,| \pm (\mathbf{b}/|\,\mathbf{b}\,|)$.

It has been shown above that interaction iii) which is reponsible for a mixing of G and A modes along each axis is not present in the actual structure though it is allowed by symmetry. The contribution to the energy of the other interaction containing cross products, interaction iiii), is somewhat higher than that of the uniaxial anisotropy ii), but not as much as indicated by Bertaut and Mareschal.

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