

2062 (1973). The paper by R. W. Cochrane and W. P. Wolf [Solid State Commun. **9**, 1997 (1971)] quotes a different set of values: $\nu_{nm} = 0.1800$ °K and $\nu_{nm} = -0.0173$ °K; with these values the lowest-lying eigenvalue is negligibly different from the one given in this paper.}

¹¹W. P. Wolf, H. Meissner, and C. A. Catanese, J. Appl. Phys. **39**, 1134 (1968).

¹²A. H. Cooke, D. T. Edmonds, F. R. McKim, and W. P.

Wolf, Proc. R. Soc. A **252**, 246 (1959); A. H. Cooke, D. T. Edmonds, C. B. P. Finn, and W. P. Wolf, Proc. R. Soc. A **306**, 313 (1968); Proc. R. Soc. A **306**, 335 (1968).

¹³C. Kittel, Phys. Rev. **82**, 965 (1951).

¹⁴R. B. Griffiths, Phys. Rev. **176**, 655 (1968).

¹⁵C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1971), p. 452. The "demagnetization factor" is similar to the "depolarization factor."

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Magnetic Structure of DySb[†]

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A neutron-diffraction study of a single crystal of DySb has shown that at about 9.5 K the compound has a crystallographic as well as a magnetic transition. Below the transition DySb is monoclinic (almost tetragonal) with type-II antiferromagnetic ordering. The direction of the magnetic moment is close to the tetragonal axis at low temperature and tilts away with increasing temperature. The extrapolated saturation moment is $(9.8 \pm 0.2)\mu_B$ /dysprosium atom.

I. INTRODUCTION

DySb is an antiferromagnetic substance with its Néel temperature (T_N) at about 9.5 K.¹ Above T_N the crystal structure of the antimonide is strictly of NaCl type. At T_N the lattice undergoes a slight contraction along one of the cubic axes.² A neutron-diffraction study on powder sample³ indicated an antiferromagnetic ordering compatible with a type-II structure: a rhombohedral spin arrangement in which + spins and - spins are assigned alternately to every other (111) plane of cations. Magnetic measurements at⁴ 1.5 K indicated that the easy axis for the magnetic moments is along one of the [100] axes of the distorted cube. The ordered magnetic moment for dysprosium is close³⁻⁵ to the expected saturation value for the free ion. The rhombohedral symmetry of the type-II magnetic structure seems to contrast with the tetragonal nature of the distortion. The present neutron-diffraction study on a single crystal of DySb was undertaken in order to resolve the problem. Additional results obtained, e.g., the direction of the magnetic moments and the details of the transition, will also be presented.

II. MAGNETIC MODELS

The treatment of the magnetic models follows closely that of the isostructural CoO on which there

exists an extensive body⁶⁻⁹ of work in the past years.

It is convenient to discuss the structure of DySb in terms of the cubic symmetry which it has above the Néel temperature. The crystallographic distortion observed by x rays at T_N introduces tetragonal domains (t domains) in the crystal. If the magnetic structure is indeed type II, magnetic domains of rhombohedral character (r domains) should appear throughout the crystal. The type-II antiferromagnetic structure is represented in Fig. 1(a). The antiferromagnetic sheets are stacked along the [111] direction. The other three r domains are obtained by stacking the antiferromagnetic sheets along another of the equivalent [111] directions.

The magnetic cell can be obtained simply by doubling all the edges of the pseudocubic crystal cell. In this expanded cell, the allowed magnetic lines have the index relations presented in Table I. A characteristic of the type-II structure is that within one t domain each magnetic reflection belongs to one and only one r domain. As a result the relative orientation of the magnetic reflections is very sensitive to a rhombohedral distortion that might accompany the magnetic ordering. On the other hand the nuclear reflections, each composed of four r domains, are rather insensitive to such a distortion. If no distortions were detectable, but

the populations of the r domains were different, the magnetic model would still be confirmed from the intensities of the magnetic reflections. However, if the r domains were equally populated, and no rhombohedral distortion was observable, the neutron-diffraction measurements could not distinguish between the magnetic model hitherto discussed and an alternate one, consistent with the tetragonal symmetry. The latter model that is graphically presented in Fig. 1(b) has been extensively discussed by Van Laar.⁶

III. EXPERIMENTAL

The single crystal used for the experiment was chosen among several grown at IBM Research Laboratory. The crystals were grown from the melt by the Bridgeman method. A prereacted ingot of the compound, prepared from Dy sponge (99.9% purity) and Sb shot (99.999% purity) was melted in a closed tungsten crucible in a rf-heated furnace in a protective atmosphere of UHP-grade argon. The tungsten crucible was positioned in the rf coil so as to produce a temperature gradient of approximately 50 °C/cm along its length. The melt was cooled at a rate of 10 °C/h by means of a proportional controller. The ingots could be broken away from the crucible wall cleanly and were easily cleaved to yield a number of parallelepiped-shaped crystals.

The DySb crystal is hard and it cleaves easily like common rock salt along the cube edges. The sample dimensions were, in reference to the crystal axes, 2.5 mm along [100], 0.5 mm along [010], and 0.5 mm along [001]. The crystal was clamped in the (001) plane between two aluminum plates, held together with brass screws. Cooling down the crystal, the differential expansion of the brass versus DySb ensures enough pressure along the [001] direction to generate at T_N a single t domain. The crystal-clamp system was mounted in a variable-temperature cryostat, and this was set on the rotating table of a conventional two-axes diffractometer at the CP-5 reactor at Argonne National Laboratory. All the neutron-diffraction measurements were taken for the reflections in ($1\bar{1}0$) zone of the crystal. Intensities and line positions were measured for all equivalent peaks in the four quadrants of the zone.

The experimental data obtained above 11 K con-

TABLE I. Magnetic lines allowed in the type-II antiferromagnetic structure. Indices in the expanded ($2 \times 2 \times 2$) cubic cell. General condition: h, k, l all odd.

Domain	(111)	($\bar{1}\bar{1}\bar{1}$)	($\bar{1}\bar{1}1$)	($11\bar{1}$)
	$h+k=4n+2$	$h+k=4n$	$h+k=4n$	$h+k=4n+2$
	$h+l=4n+2$	$h+l=4n$	$h+l=4n+2$	$h+l=4n$
	$k+l=4n+2$	$k+l=4n+2$	$k+l=4n$	$k+l=4n$

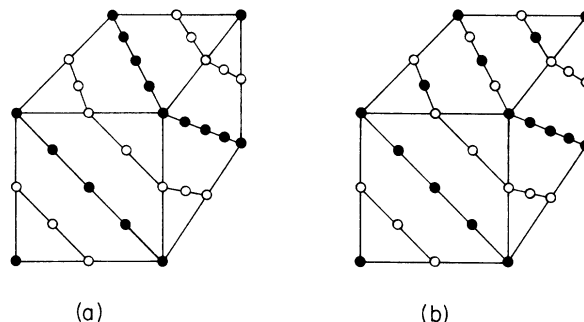


FIG. 1. Possible arrangement of dysprosium spins. Black and white points correspond to spins parallel and antiparallel to the z axis. (a) The type-II antiferromagnetic structure, (b) the tetragonal magnetic structure proposed by Van Laar.

firmed that the sample was a single crystal and no magnetic order was present. Below 9 K, antiferromagnetic lines were present. Between 9 and 11 K, the diffraction data were more complex. This temperature region in the vicinity of the transition will be discussed later.

IV. LINE POSITIONS

At 11 K and above, the crystal appeared almost cubic, with $a=6.143$ Å. A slight contraction was noticed along the [001] axis (0.1%) and attributed to the strain introduced by the clamping. At 9 K and below the positions of the nuclear peaks were in agreement with a tetragonal distortion. Most of the crystal appeared to have transformed into one tetragonal domain, only 4% having become tetragonal with the c axis normal to the direction of the clamping. The sharpness of the peaks allowed a simple experimental correction for the other t domains.

For both the nuclear and magnetic lines the equivalent hkl reflections were measured consecutively. In this way it was possible to obtain very accurate values for the angles between the (hkl) and ($hh\bar{l}$) planes. The measured values of ($\varphi_{hh\bar{l}} - \varphi_{hkl}$) at 5.8 K are reported in Table II. The nuclear lines fit very well in a tetragonal structure with $c/a=0.9933 \pm 0.0004$, in excellent agreement with the data reported in the literature.² However, the agreement is not very good for the magnetic reflections and does not improve by changing the c/a ratio.

Following the arguments in Sec. II, the positions of the magnetic lines were analyzed assuming (i) the type-II antiferromagnetic structure and (ii) a small monoclinic distortion superimposed on the main tetragonal distortion. The angles reported in Table II are then measured between reflections belonging to two different r domains. The monoclinic structure is conveniently expressed in terms of a

TABLE II. Position of nuclear and magnetic reflections at 5.8 K.

Nuclear (<i>hhl</i>)	Observed	$\varphi_{hh\bar{l}} - \varphi_{hhl}$ tetragonal (<i>c/a</i> = 0.9933)		
(111)	70.89 ± 0.01	70.89		
(222)	70.90 ± 0.01	70.89		
(444)	70.88 ± 0.01	70.89		
(224)	109.84 ± 0.01	109.83		
(226)	129.83 ± 0.01	129.82		
(442)	39.19 ± 0.01	39.19		
Magnetic (<i>hhl</i>) ^a	Observed	Tetragonal (<i>c/a</i> = 0.9933)		Monoclinic
(111)	70.87 ± 0.01	70.89	70.88	
(112)	129.77 ± 0.01	129.82	129.76	
(331)	26.74 ± 0.01	26.70	26.74	
(335)	99.71 ± 0.01	99.75	99.72	
(551)	16.16 ± 0.01	16.21	16.16	
(553)	46.30 ± 0.01	46.26	46.28	

^aIndices in the expanded cubic cell.

deformed NaCl structure with the lattice parameters $a = b$, c and $\alpha = \frac{1}{2}\pi - e_2$, $\beta = \frac{1}{2}\pi - e_2$, and $\gamma = \frac{1}{2}\pi - e_1$, where e_1 is equal to the elastic strain e_{xy} and $e_2 = e_{xx} = e_{yy}$. The last column in Table II shows that a much improved fit can be obtained for a monoclinic structure. Using the value of $c/a = 0.9933$ the strains e_1 and e_2 were determined to be 0.0000 ± 0.0004 and 0.0008 ± 0.0004 , respectively.

The nuclear and magnetic reflections obtained at 9.0 K were also analyzed. The positions of nuclear lines were again in good agreement with a tetragonal unit cell. The c/a ratio was found to be 0.9939 ± 0.0004 . For the magnetic lines at 9.0 K a much better fit can be obtained, like at 5.8 K, for a monoclinic rather than a tetragonal unit cell. Using a c/a ratio of 0.9939 the values of e_1 and e_2 were determined to be 0.0001 ± 0.0004 and 0.0007 ± 0.0004 , respectively.

Unfortunately, in the analysis of the monoclinic distortion the c/a ratio and the strain e_1 are strongly correlated. By varying the c/a ratio within the standard error, the strain e_1 can lie anywhere in the range between -0.001 and $+0.001$.

Calculations including the small monoclinic distortion show that the orientation of the nuclear reflections, the average of the four monoclinic domains, remains that predicted by the tetragonal structure.

The width of the experimental peaks in the present experiment is too large to observe any broadening of the nuclear peaks due to the monoclinic distortion. This could be observable in backscattering of x rays, on some choice reflection.

In conclusion, it can be stated that DySb in the antiferromagnetic region has a monoclinic crystal

structure. The monoclinic cell that has the highest symmetry compatible with the observations has the space group $C2/m$, in which the Dy occupies the $2a$ positions and Sb the $2d$ positions.

The type-II antiferromagnetic structure is described naturally in the monoclinic system as a C_{2c} Bravais lattice. The face-centered planes of the monoclinic cell are antiferromagnetic along the c axis (see Fig. 2). The symmetry at the positions of the magnetic atoms ($2/m$) indicates that the magnetic moments either point along the $[1\bar{1}0]$ axis of the distorted cube, or in the plane normal to this axis.

V. LINE INTENSITIES

The preceding discussion leads to the conclusion that DySb orders in the type-II antiferromagnetic structure. Four magnetic domains are present in the tetragonally distorted single crystal, and of these, only two are visible in the $[1\bar{1}0]$ zone. Measurement of the intensities of one domain should make it possible to evaluate the direction of the collinear magnetic moments and the form factor for Dy. The size of the magnetic moments of Dy can be evaluated only with some assumption on the distribution of the magnetic domains, since it is determined from the ratio of the intensities of the magnetic reflections (relative to two domains) and the intensities of the nuclear reflections (sum of all four domains).

Magnetic and nuclear intensities were measured conventionally by taking rocking curves around the relevant lattice points. The integrated intensities for the magnetic peaks can be written in a magnetic cell obtained by doubling all edges of the pseudocubic crystalline cell:

$$I_{hkl} = P \left(\frac{V_M}{V_0} \right) \frac{EAT}{\sin 2\theta} \left(\frac{0.539}{2} \mu_{Dy} f \right)^2 \sin^2 \varphi \\ \times \{ [1 - e^{2\pi i(h+k)/4} - e^{2\pi i(h+1)/4} - e^{2\pi i(k+1)/4}] \}$$

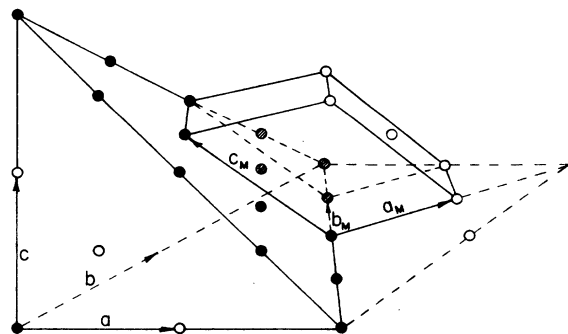


FIG. 2. Positions of the magnetic atoms in the pseudocubic NaCl structure and in the monoclinic C_{2c} Bravais lattice. The axes of the cubic cell are marked a , b , and c and the axes of the monoclinic cell a_M , b_M , and c_M .

$$\times [(1 + e^{2\pi i(h+k)/2} + e^{2\pi i(h+l)/2} + e^{2\pi i(k+l)/2}) \times (1 - e^{2\pi i(h+k+l)/2})]. \quad (1)$$

Here, P is a scaling constant obtained from the nuclear intensities using scattering amplitudes taken from the literature. V_M/V_0 is the relative volume of a magnetic domain to the full volume of the sample. Since the intensities of the two observed domains were equal, it was assumed that all domains were equally populated, $V_M/V_0 = \frac{1}{4}$. E is the extinction correction that was evaluated for the nuclear reflections with the help of Zachariasen's¹⁰ formula. The extinction parameter was assumed to be the same for the nuclear and magnetic reflections. The correction was 10% for the highest magnetic peak. The absorption (A) is rather severe in the sample, owing to the large cross section of dysprosium. The transmission is of the order of 60%, and its detailed angular dependence was calculated from the shape and size of the crystal. The thermal coefficient T was calculated from the intensities of the nuclear lines. The isotropic Debye coefficient thus found below the transition was $W = 0.17 \pm 0.02$. μ_{Dy} is the magnetic moment of dysprosium and f is the form factor; $\sin 2\theta$ is the Lorentz factor. φ is the angle between the scattering vector and the common direction of the sublattice moments of the collinear structure. The second factor in square brackets indicates the selection rules for a class of structures, and specifies that the only magnetic peaks allowed are those for which h, k, l are all odd. No other peaks were found experimentally. The first factor in square brackets indicates the additional selection rules inherent to the type-II antiferromagnetic structure (see Table I). The choice of this particular model, in the class of possible structures, is limited to the terms V_M/V_0 , $\sin^2\varphi$, and the first factor in square brackets. Once that is accepted, the experimental data can be cast in the simple form

$$|F|_{hkl}^2 = \left(\frac{0.539}{2} \mu_{Dy} f \right)^2 \sin^2\varphi. \quad (2)$$

The measured and the calculated $|F|^2$ are presented in Table III. The best agreement is obtained when the magnetic moment tilts away from the $[001]$ axis in the $(1\bar{1}0)$ plane toward the $[11\bar{2}]$ direction. The tilt is increasing with the temperature, as shown in Fig. 3(a). The calculated form factor is that given by Blume, Freeman, and Watson¹¹ for Dy^{+3} in the state $J_g = \frac{15}{2}$. The over-all agreement of the calculated and measured intensities is quite good. In Fig. 4 the experimental values of the form factor have been plotted as obtained from the data at 5.8 K, with the best-fit magnetic moment and tilt angle. The experimental form factor does not seem to deviate significantly from the calculated one.

TABLE III. Comparison between measured and calculated magnetic $|F|^2$. The experimental errors are obtained by comparing the intensities in different quadrants, and in subsequent runs. The calculated values are for the Freeman-Watson form factor with anisotropy coefficients for $J_g = \frac{15}{2}$.

Magnetic (hkl)	At 5.8 K		At 9.0 K	
	$ F _{obs}^2$	$ F _{calc}^2$ ^a	$ F _{obs}^2$	$ F _{calc}^2$ ^b
(111)	4.07 ± 0.06	4.06	3.56 ± 0.14	3.56
(11 $\bar{3}$)	0.94 ± 0.03	0.92	0.61 ± 0.01	0.64
(33 $\bar{1}$)	4.63 ± 0.09	4.61	3.83 ± 0.11	3.75
(333)	3.07 ± 0.09	2.93	2.70 ± 0.16	2.58
(11 $\bar{5}$)	0.32 ± 0.05	0.33	0.29 ± 0.06	0.36
(33 $\bar{5}$)	1.34 ± 0.09	1.42	0.98 ± 0.04	1.07
(551)	3.21 ± 0.07	3.27	2.69 ± 0.12	2.75
(11 $\bar{7}$)	0.12 ± 0.01	0.11	0.03 ± 0.01	0.06
(55 $\bar{3}$)	2.42 ± 0.11	2.54	2.00 ± 0.10	2.03
(337)	0.71 ± 0.02	0.71	0.63 ± 0.03	0.67
(555)	1.60 ± 0.10	1.68	1.49 ± 0.10	1.48
(119)	0.07 ± 0.01	0.06		
(77 $\bar{1}$)	1.78 ± 0.09	2.01	1.59 ± 0.09	1.65
(55 $\bar{7}$)	0.88 ± 0.08	0.92	0.70 ± 0.07	0.70
(339)	0.39 ± 0.08	0.31	0.22 ± 0.11	0.21
(991)	0.99 ± 0.01	1.11		

^a $\mu_{Dy} = 9.30\mu_B$; $\delta = 0.5^\circ$.

^b $\mu_{Dy} = 8.48\mu_B$; $\delta = 2.8^\circ$.

Assuming that the calculated form factor is correct, the values for the magnetic moment of dysprosium at different temperatures were obtained and plotted in Fig. 3(b). The extrapolated value of the magnetic moment at 0 K is $(9.8 \pm 0.2)\mu_B$.

VI. TRANSITION REGION

Between 9 and 11 K the experimental data were rather complex. The intensities of the magnetic lines were observed to decrease sharply with the temperature, while their positions were unchanged. The position of the nuclear peaks changed with temperature and their shape indicated splitting into two peaks, one at the position retained below the transition, the other at the position observed above the transition. Most of the data have already been published¹² and the conclusion was reached that DySb undergoes a sharp (first-order) magnetic and crystallographic transition. This, however, is smeared out by the state of strain of the crystal in a temperature range in which two phases appear: one antiferromagnetic and monoclinic, the second paramagnetic and cubic.

From the relative intensities of the two components of the nuclear doublets it is possible to evaluate the relative volume of the two phases, and to scale up the apparent magnetic moment calculated from the magnetic lines [Fig. 3(b)] by the portion of the volume that remains monoclinic and antiferromagnetic at each temperature. Unfortunately, the results of such analysis are only approximate

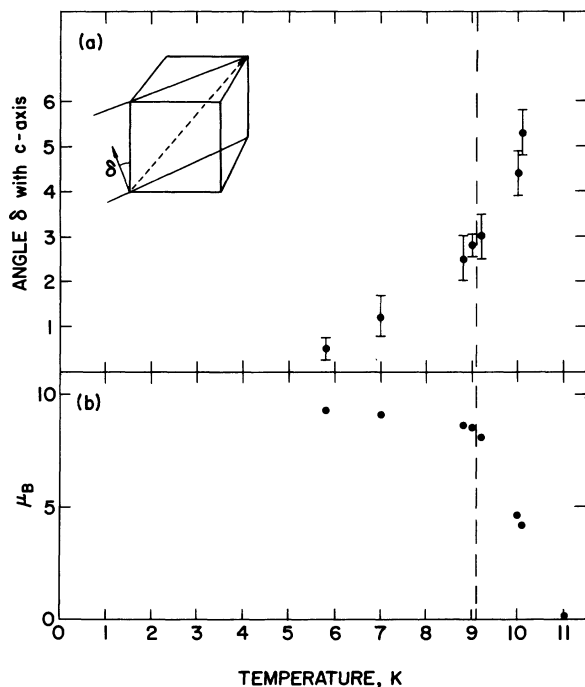


FIG. 3. (a) Angle δ between the direction of the Dy magnetic moments and the c axis as a function of temperature; (b) magnitude of the apparent Dy magnetic moment as a function of temperature.

since the two peaks of the nuclear doublets are themselves broader than above or below the transition region. The values of the scaled magnetic moments thus obtained are not in disagreement with those obtained by extrapolating a Brillouin-type function from the data below the transition region. Both the magnitude of the scaled-up magnetic moment and the angle of the moment relative to the c axis are the average for an assembly of crystallites that become paramagnetic at slightly different temperatures.

In the transition region the integrated intensities of the magnetic reflections belonging to different domains remain approximately the same. However, the lines are appreciably broader, each of the domains taking a characteristic shape and width. At 11 K the magnetic lines are completely absent, with no indication of the short-range order typical of second-order transitions.

VII. DISCUSSION

Aside from nature of the transition discussed in Ref. 12, the present experiments have shown in the magnetically ordered region the presence of a small monoclinic distortion in agreement with a type-II antiferromagnetic structure, and a tilt of the magnetic moments away from the tetragonal axis. Both data have more qualitative than quanti-

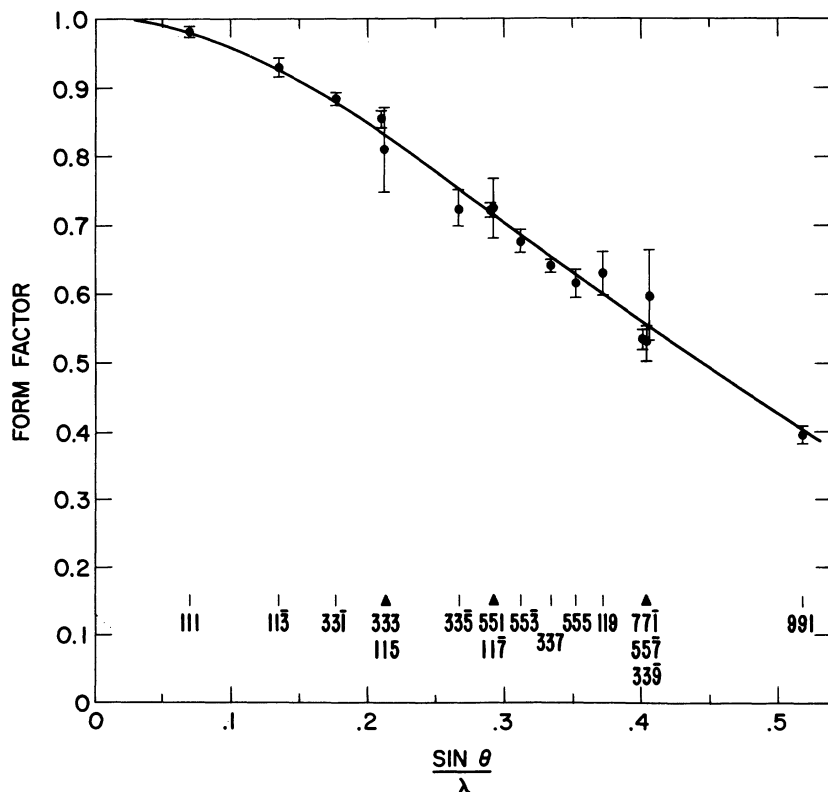


FIG. 4. Experimental magnetic form factor of the Dy ion in DySb. The full line represents the isotropic form factor calculated (Ref. 11) for the tripositive ion.

tative character. However, it has been shown that the distortion from cubic symmetry remains roughly constant with temperature below the transition, whereas the direction of the magnetic moment varies drastically. If the tilt angle δ is correlated with the temperature, an expression of the type

$$\delta = e^{-27/T} \quad (3)$$

(T in Kelvin) gives a good fit to the observed "average" tilt up to 9 K. The question is to what extent such experimental observations contribute to the understanding the nature of the forces in DySb. A number of theoretical papers have appeared in the literature on this and related systems¹³⁻¹⁶ and have attempted to explain the mechanism of correlation between magnetic and elastic forces that drive the system through a sharp magnetic and crystallographic transition. However, in the expressions for the energy, the estimated size of the magnetic terms (isotropic exchange, quadrupole, dipole dipole) and of the elastic terms due to the crystal distortion, are all comparable, so as to make an evaluation of the individual terms from the scarce experimental data extremely difficult. A force that could move the magnetic moments from the tetragonal axis toward the $[\bar{1}\bar{1}2]$ direction is the mag-

netic dipole-dipole interaction¹⁷ that can be expressed for the type-II antiferromagnetic structure by

$$E_D = T_D(\alpha_x\alpha_y + \alpha_y\alpha_z + \alpha_z\alpha_x), \quad (4)$$

where α_x , α_y , α_z are the direction cosines of the sublattice magnetization in respect to the cubic axes and $T_D = 3.9$ K for DySb. If such interaction was working against other energy terms that favor a direction of magnetization along the $[001]$ axis, the direction of magnetization should not have varied dramatically with temperature. If the energy of the system is presented in an approximate form as a set of exchange split crystal-field levels for the single dysprosium ion, the tilt of the moment shows that over the temperature range considered, the system does not behave like a Kramers doublet. The temperature dependence given in expression (3) can be explained if two levels have to be considered, the ground-state doublet in which the magnetic moments point along the $[001]$ axis and an excited state at 27 K in which the moments point along the $[\bar{1}\bar{1}0]$ axis. In order to have a more physical picture of the system below the transition, other experiments are needed, capable of determining the elastic constants, the phonon spectrum, and the crystal levels.

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¹G. Bush, P. Junod, O. Vogt, and F. Hulliger, Phys. Lett. **6**, 79 (1963).

²F. Lévy and O. Vogt, Phys. Lett. A **24**, 444 (1967).

³N. Nereson and V. Struebing, AIP Conf. Proc. **5**, 1385 (1972).

⁴G. Bush and O. Vogt, J. Appl. Phys. **39**, 1334 (1968).

⁵V. D. Gorobchenko, I. I. Lukashevich, V. G. Stankevich, N. I. Filippov, V. I. Chukalin, and E. I. Yarembash, Fiz. Tverd. Tela **13**, 1085 (1971) [Sov. Phys.-Solid State **13**, 901 (1971)].

⁶B. Van Laar, Phys. Rev. **138**, A584 (1965).

⁷B. Van Laar, J. Schweizer, and R. Lemaire, Phys. Rev. **141**, 538 (1966).

⁸D. C. Khan and R. A. Erickson, Phys. Rev. B **1**, 2243

(1970), and references therein.

⁹S. Saito, K. Nakahigashi, and Y. Shimomura, J. Phys. Soc. Jap. **21**, 850 (1966).

¹⁰W. H. Zachariasen, Acta Crystallogr. **23**, 558 (1967).

¹¹M. Blume, A. J. Freeman, and R. E. Watson, J. Chem. Phys. **37**, 1245 (1962).

¹²E. Bucher, R. J. Birgeneau, J. P. Maita, G. P. Felcher, and T. O. Brun, Phys. Rev. Lett. **28**, 746 (1972).

¹³G. T. Trammell, Phys. Rev. **131**, 932 (1963).

¹⁴F. Lévy, Phys. Kondens. Mater. **10**, 85 (1967).

¹⁵H. H. Chen and P. M. Levy, Phys. Rev. Lett. **27**, 1383 (1971).

¹⁶E. Pytte and K. W. H. Stevens, Phys. Rev. Lett. **27**, 862 (1962).

¹⁷J. Kanamori, Prog. Theor. Phys. **17**, 197 (1958).