

EFFECTS OF UNIAXIAL STRESS ON THE OPTICAL SPECTRUM OF DyVO_4

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Abstract—Optical absorption spectroscopy is used to investigate the low lying energy levels of DyVO_4 under uniaxial stress and magnetic fields at temperatures above and below the co-operative Jahn-Teller transition. The results agree with the molecular field theory of the previous paper using the parameter $\sigma_0 = 64 \pm 4 \text{ kg/mm}^2$ (which represents the stress of $e_{aa} - e_{bb}$ type required to split the ground state energy levels by 27 cm^{-1} at high temperatures). The behaviour of dilute Dy^{3+} in YVO_4 is studied and predicted from the theory. Deviations from the molecular field theory are found and discussed. Comparison of the results with known elastic constants of DyVO_4 indicates that strain coupling dominates the optic mode coupling.

1. INTRODUCTION

IN THIS paper we present an experimental study of the low lying energy levels of trivalent Dy in DyVO_4 observed by optical spectroscopy. The results are compared to the theory derived in the accompanying paper [1] which we refer to as I. There are very few studies in the literature on the effects of uniaxial stress on trivalent rare earth energy levels in insulators, e.g. [2, 3]. Trivalent rare earth ions are known to interact very weakly with their environment and therefore the levels are expected to shift very little under stress. In this study, for example, we report results on dilute Dy^{3+} in YVO_4 which appear to be typical. Isolated energy levels move less than 1 cm^{-1} in stresses up to 70 kg/mm^2 , whereas a near accidental degeneracy can be split apart

to $\sim 15 \text{ cm}^{-1}$ at the same stresses. Such effects are certainly measurable by optical spectroscopy but are of no particular interest in themselves; they represent the combined effects of elastic constants, internal spring constants and crystal field matrix elements, which cannot be separated in general.

Uniaxial stress experiments in materials which exhibit Jahn-Teller distortions are far more interesting, for such experiments can differentiate between the possible physical mechanisms which could cause the distortions. In most previously studied cases, the distortion temperature is so high that the stress-induced shifts in the energy levels are small compared to the Jahn-Teller stabilization energies, and therefore stress has little effect on the system. By contrast, the recently discovered Jahn-Teller effects in a series of isomorphous crystals, DyVO_4 [4], TbVO_4 [5, 6], DyAsO_4 [7, 8], and TmAsO_4 [9], occur in the range of tens of degrees Kelvin, almost an order of magnitude lower than any previously observed co-operative Jahn-Teller effect. For DyVO_4 and TbVO_4 we have found that stress can interact with and strongly

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influence the Jahn–Teller distortion and the resulting optical line shifts are among the largest ever observed in rare earth insulators.

This paper is divided as follows: in Section 2, we describe experimental techniques; in Section 3, the experimental results; in Section 4 fits of these results to the theory of the previous paper and a summary of our conclusions. A list of the different kinds of experiments reported in this paper is given in Table 1.

2. EXPERIMENTAL TECHNIQUES

Uniaxial stress experiments on single crystals of DyVO_4 were performed at a variety of temperatures by immersing the crystals in liquid helium, hydrogen, or nitrogen. The experiments at 77 K in liquid nitrogen made it possible to study DyVO_4 in a temperature range where the effects of crystallographic or magnetic ordering were negligible. The experiments from 20.4 to 14.1 K in pumped liquid hydrogen were convenient for studying the especially interesting range just above the distortion temperature of 14.0 K. Experiments at 4.2 to 1.4 K in pumped liquid helium made it possible to investigate the crystal in its fully Jahn–Teller ordered state, both above and below its magnetic Neel temperature of 3.0 K. TbVO_4 , which undergoes a Jahn–Teller transition at 33 K, is much less convenient to study in its corresponding temperature ranges.

The Jahn–Teller active distortion of DyVO_4 is ($e_{aa} - e_{bb}$), where a and b are axes perpendicular to the tetragonal c -axis and happen to be parallel to natural growth faces of the material; b is indistinguishable from a in the absence of distortion. DyVO_4 tends to grow in needles along the c -axis, and to prepare the crystals for optical absorption experiments under uniaxial stress, they were cut in slices perpendicular to the c -axis and polished. A uniaxial stress was applied along the a -axis, and a magnetic field could be applied along the b -axis, while light was propagated along the c -axis, as shown in Fig. 1. The natural growth faces along a and b are very even and permit a

reasonably homogeneous stress of up to 70 kg/mm^2 to be applied without cracking the crystals.

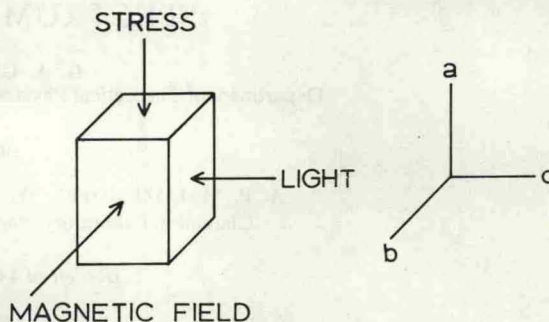


Fig. 1. Typical arrangement of stress and magnetic field for optical absorption experiments on pseudospin flop in DyVO_4 .

By contrast, TbVO_4 distorts with e_{ab} strain; to couple to such a strain, a uniaxial stress would have to be applied at 45° to the natural growth faces. Therefore it is necessary to cut these crystals both in the c -direction and in the basal plane. The difficulty of obtaining truly flat surfaces and hence a homogeneous stress in the crystal is the main reason that we have chosen to study DyVO_4 rather than TbVO_4 .

The stress was applied by means of a piston device developed for these experiments and illustrated in Fig. 2. It has the particular advantages of fitting directly in existing immersion cryostats so that temperature control is easy and a large magnetic field can simultaneously be applied, and also of permitting accurate low stresses to be applied to the crystal without elaborate counterweight arrangements. A moving piston, pulled upwards by an inner stainless steel wire, pressed the sample from below against the fixed piston. Bellows with compressed air of variable pressure are set on top of the cryostat to provide the necessary force for the pistons. Forces due to bellows distortion can be reduced to less than 100 g by adjusting the bellows to the zero position for any given air pressure. Friction in the packed grease seal and in the pistons is less than 20 g in the low

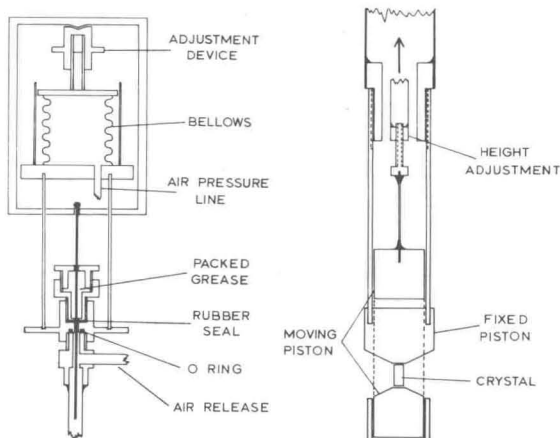


Fig. 2. Piston and bellows device for application of uniaxial stress in optical absorption experiments on DyVO_4 .

pressure region; this is less than the weight of the moving piston plus inner steel rod and has negligible effects compared with the linewidths of the observed optical absorptions.

The optical absorption spectra corresponding to Dy^{3+} absorptions from the ground ${}^6\text{H}_{15/2}$ to the excited ${}^4\text{F}_{9/2}$ and ${}^4\text{I}_{15/2}$ multiplets were recorded photographically with a 3.4 m Ebert spectrograph. The absorption intensities were traced on a Joyce-Loebl densitometer.

The spectra were taken with light polarized along the a and b axes, and very strong polarization effects were observed whenever there was a significant amount of crystallographic distortion, whether spontaneous or induced by an applied stress or magnetic field. Such polarization effects cannot be explained by group theory; for the symmetry of Dy^{3+} in the distorted structure has been shown to be C_{2v} [5], which has no selection rules for Kramers systems [10]. Nevertheless the effects can be understood in terms of transition probabilities derived from the dipole matrix elements. When no distortion is present, both ground and excited states have tetragonal symmetry and no differences in polarization along a or b can exist. But in the distorted structure, the two ground doublets are to a good approximation pure $|J_a = \pm \frac{15}{2}\rangle$ and $|J_b = \pm \frac{15}{2}\rangle$ states, which are highly aniso-

tropic and oriented along the two orthorhombic axes, and therefore the dipole matrix elements can be very different along a and b . For small distortions, in fact, the resulting polarization changes are an even more sensitive measure of the level mixing than the actual splitting of the lines. Even in measuring only splittings, it is essential to use polarized light because many of the optical absorption lines are so broad that they overlap considerably in the unpolarized spectrum.

Further care must be taken in experiments at low stresses or fields because of the fact that when a crystal is first cooled below its distortion temperature, the spectrum appears unpolarized. We attribute this effect to domains of different distortion, which have been observed by Raman spectroscopy [11] and also directly with crossed polaroids [4, 12]. We have found that the crystal can be single-domained in a field of several kilogauss or under a uniaxial stress of fractions of 1 kg/mm^2 , for when such fields or stresses are applied and then removed, the spectrum becomes strongly polarized in the way expected of a 'single-domained' sample. We have taken care to use such single-domained samples in all the experiments we describe.

3. EXPERIMENTAL RESULTS

At temperatures above the distortion temperature, there is generally a sufficient thermal population of the higher-lying of the two ground Kramers doublets to observe transitions from both levels and thus to measure the splitting directly. In zero stress we found a crystal field splitting Δ_∞ of $9 \pm 0.5 \text{ cm}^{-1}$ at 14 to 20.4 K, which decreased to 7.5 cm^{-1} at 77 K, as shown in Table 1; this is an important modification of previously reported results which were obtained without polarized light and in which the splitting had not been resolved [4]. As uniaxial stress was applied, the two levels were observed to split apart in much the same way as when the sample is lowered through its distortion temperature in zero stress [13]. Some typical densitometer

tracings are shown in Fig. 3. The absorption lines in the range 20,950–21,050 cm^{-1} represent transitions from the two ground doublets

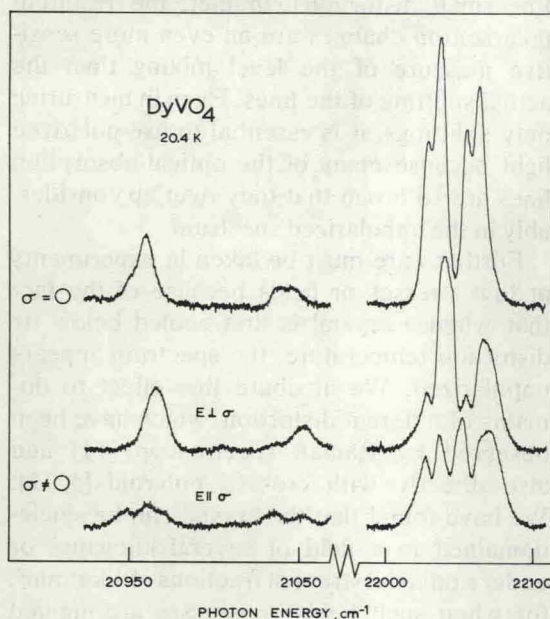


Fig. 3. Densitometer traces of optical absorption lines representing ${}^6\text{H}_{15/2}$ to ${}^4\text{F}_{9/2}$ and ${}^4\text{I}_{15/2}$ transitions in DyVO_4 at 20.4 K, and at uniaxial stresses of 0 and 19 kg/mm^2 .

of the ${}^6\text{H}_{15/2}$ multiplet to the two lowest lying doublets of the ${}^4\text{F}_{9/2}$; those between 22000 and 22100 cm^{-1} represent transitions to the two lowest lying doublets of the ${}^4\text{I}_{15/2}$. These particular transitions were the only ones both sharp enough and far enough from other interfering absorptions to provide a convenient measure of the ground state splitting.

Nevertheless there were significant problems in deducing the splitting from such data. First of all, even in these cases the lines are up to 10 cm^{-1} wide. Secondly, at high stresses the lines look asymmetric, presumably because of nonuniform stress distributions in the crystals. We have always chosen the maximum of the intensity as the centre of an asymmetric line on the assumption that it represents the most prevalent stress value. A third and more severe problem is that the peaks do not coincide in the two polarizations, especially

for the ${}^4\text{I}_{15/2}$ transition of Fig. 3. In most cases, when a line appears strongly in one polarization and weakly in another, the weaker line appears to 'lag' behind the movement of the stronger as the stress is increased. One explanation for this effect arises from the polarization properties described in the previous section. If because of nonuniformity part of the crystal is strained less than the average, this part will give absorption lines which are both closer together and less strongly polarized than the average; therefore such absorption will show through more strongly in the weaker polarization. This interpretation suggests that, to obtain the most representative value for the level splitting in the crystal, one should choose the line position from the stronger rather than the weaker polarization.

This method leads to reasonable agreement in the four measured splittings at low stresses, and some results for the temperature range 14.1–20.4 K are plotted in Fig. 4. At larger

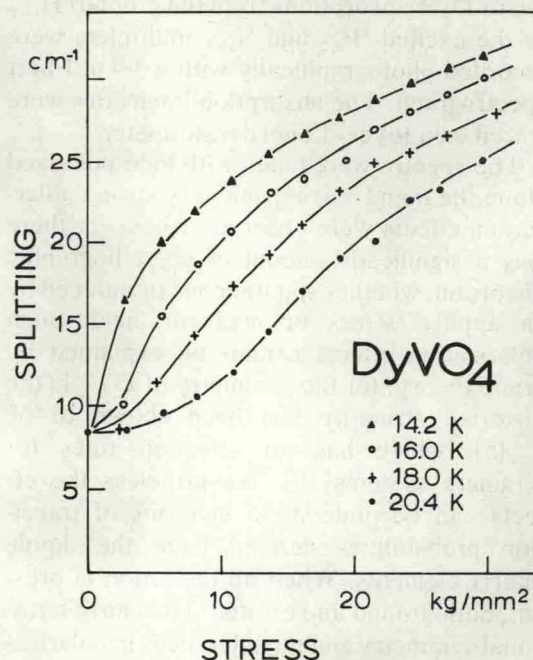


Fig. 4. Ground state splitting of DyVO_4 as a function of uniaxial stress along the a -direction at temperatures between 14.2 and 20.4 K. The curves are drawn smoothly through the experimental points.

stresses in this temperature range, however, discrepancies develop within the two splittings of the ${}^4I_{15/2}$ transitions and between these values and those of the ${}^4F_{9/2}$ transitions. We assume that these discrepancies arise because of the fact that the two lowest lying levels of the excited ${}^4I_{15/2}$ multiplet are close enough together to interact in the same way as the ground levels. For example in the absence of stress it is observed that these two levels are 26 cm^{-1} apart above T_D , but below T_D this splitting increases to 34 cm^{-1} . Likewise an applied stress above T_D mixes these two excited state eigenfunctions and drives the levels apart. At low stress the mixing is very small, but at higher stresses significant changes in the polarization properties can occur because of it. The combination of effects due to nonuniformity, to mixing in both the ground and excited multiplets, and also to thermal depopulation, makes this group of lines especially difficult to analyze. By contrast the two splittings of the ${}^6H_{15/2}$ to ${}^4F_{9/2}$ absorptions are in reasonable agreement with each other, and some of these values are plotted in Fig. 5.

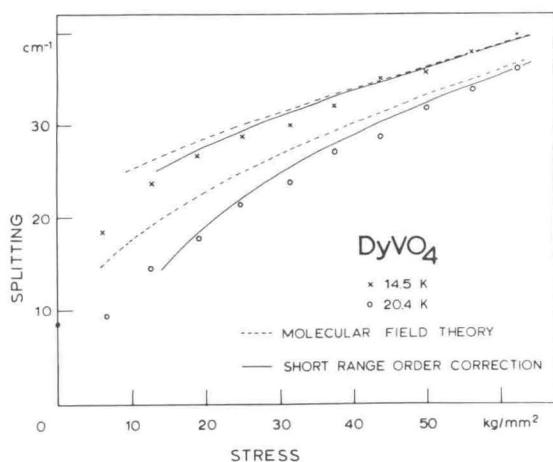


Fig. 5. Ground state splitting of DyVO_4 as a function of stress at 14.5 and 20.4 K. The molecular field theory curve is based on equation (4.2) with $\sigma_0 = 66\text{ kg/mm}^2$; the curve corrected for short range order is based on equation (1.3.22) with $\Gamma = 4$.

The data was found to be quite reproducible for different crystals. The errors in relative splitting at different temperatures are only of order 0.25 cm^{-1} , but the absolute error is of the order of 2 cm^{-1} because of the difficulties mentioned above. At 77 K these difficulties were substantially reduced because the stress-induced splittings were much smaller. This data is plotted in Fig. 6. Data similar in appearance to that of Fig. 6 was also taken on dilute $\text{Dy}_{0.05}\text{Y}_{0.95}\text{VO}_4$, both at 77 K and at 20.4 K, as shown in Fig. 7. In this case the lines were considerably sharper and the data is accurate to 0.25 cm^{-1} .

Experiments were also done as a function of stress between 4.2 and 1.4 K. At these temperatures the higher lying state of the ground multiplet is completely depopulated, and it is no longer possible to measure the splitting directly. Nevertheless all absorption lines shifted to higher energies as a function of stress; those due to transitions to the ${}^4F_{9/2}$ multiplet both moved linearly at the same rate

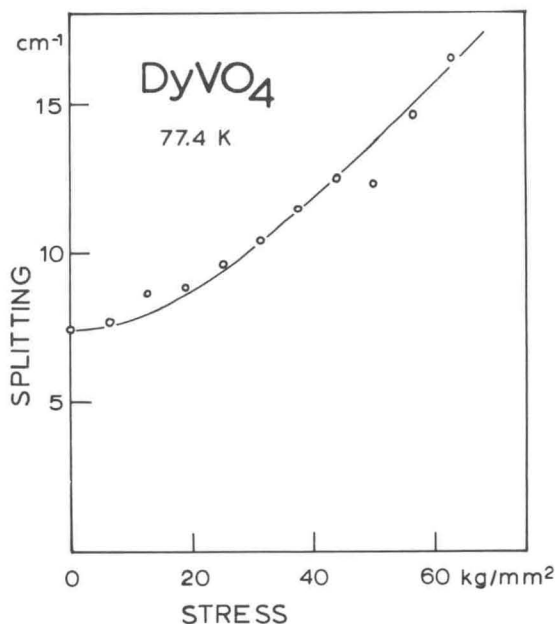


Fig. 6. Ground state splitting of DyVO_4 as a function of uniaxial stress along the a -direction at 77.4 K. The theoretical curve is that of equation (4.3) with the values of Δ_∞ and σ_0 given in Table 1.

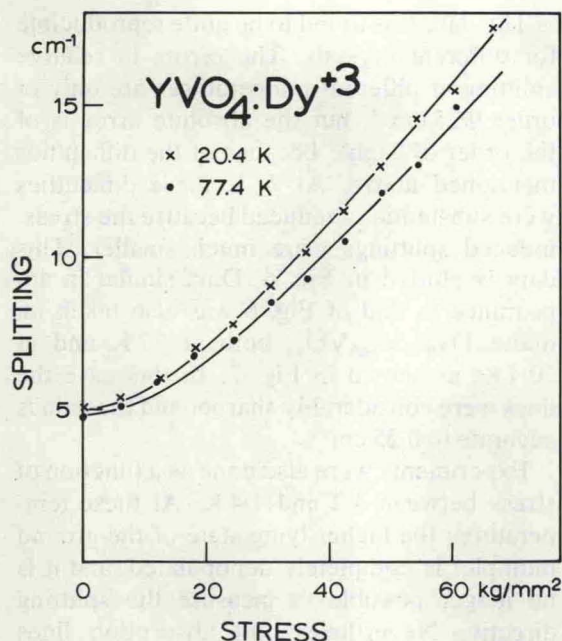


Fig. 7. Ground state splitting of 5 per cent Dy^{3+} in YVO_4 as a function of uniaxial stress along the a -direction at 20.4 and 77 K. The theoretical curves are those of equation (4.5) with the respective values of Δ_∞ and σ_0 given in Table 1.

of $0.126 \text{ cm}^{-1}/\text{kg mm}^{-2}$. These shifts are plotted in Fig. 8. The ${}^4\text{I}_{15/2}$ transitions, however, moved in a more complicated fashion which was attributed to the quadratic repulsion of the two lowest lying ${}^4\text{I}_{15/2}$ levels and to some repulsion of these levels from higher lying ${}^4\text{I}_{15/2}$ levels. For this reason we felt that the ${}^4\text{F}_{9/2}$ transitions provided a more reliable measure of the increased splitting in the ground state.

As will be discussed in the next section, Γ_1^+ type strain can cause a linear centre of gravity shift for two transitions from the two ground Kramers doublets which will provide a correction to the splittings deduced from the line shifts at 4.2 K. Such centre of gravity shifts were measured in DyVO_4 at 77 K, and in dilute Dy^{3+} in YVO_4 at 20.4 and 77 K, and were in all cases linear with a slope of $0.014 \pm 0.003 \text{ cm}^{-1}/\text{kg mm}^{-2}$ to higher energies.

Another series of experiments was performed in applied magnetic fields to determine

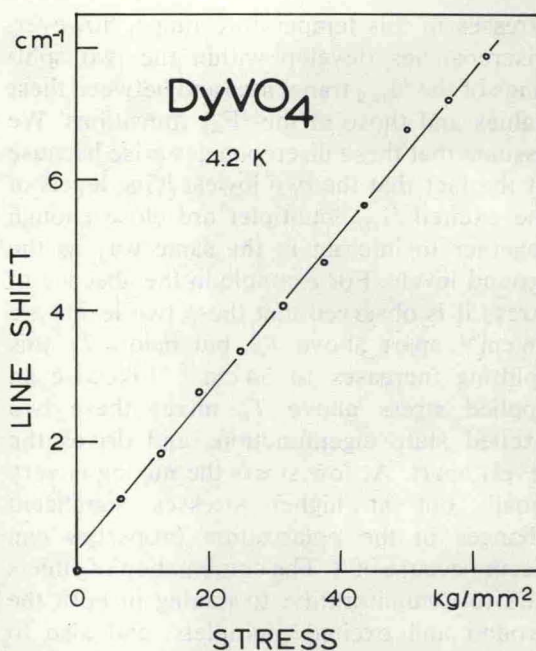


Fig. 8. Shift in energy of ${}^6\text{H}_{15/2}$ to ${}^4\text{F}_{9/2}$ absorption lines of DyVO_4 as a function of stress at 4.2 K.

the pseudospin flop phase diagram (I). It was found that in DyVO_4 a field perpendicular to the stress gave pseudospin flop behaviour, whereas in TbVO_4 the field had to be parallel to the stress. This indicates that the ground state g -factors of the two crystals point in different directions relative to their distortions. The experimental arrangement for DyVO_4 is shown in Fig. 1. The procedure was to apply a certain stress at a given temperature and to increase and then decrease the field in steps of the order of 0.5 kG through the transition. The spectrum was photographed on Polaroid film at each step with light polarized along either of the two principal directions in the basal plane. A typical result is shown in Fig. 9. Since the image of the sample was focussed on the spectrograph slit, the height of each band represents a vertical section of the actual crystal. As mentioned earlier, the two different distortions are characterized by very different polarization patterns, and the change in the pattern as a function of field in Fig. 9 is interpreted as evidence of a pseudo-

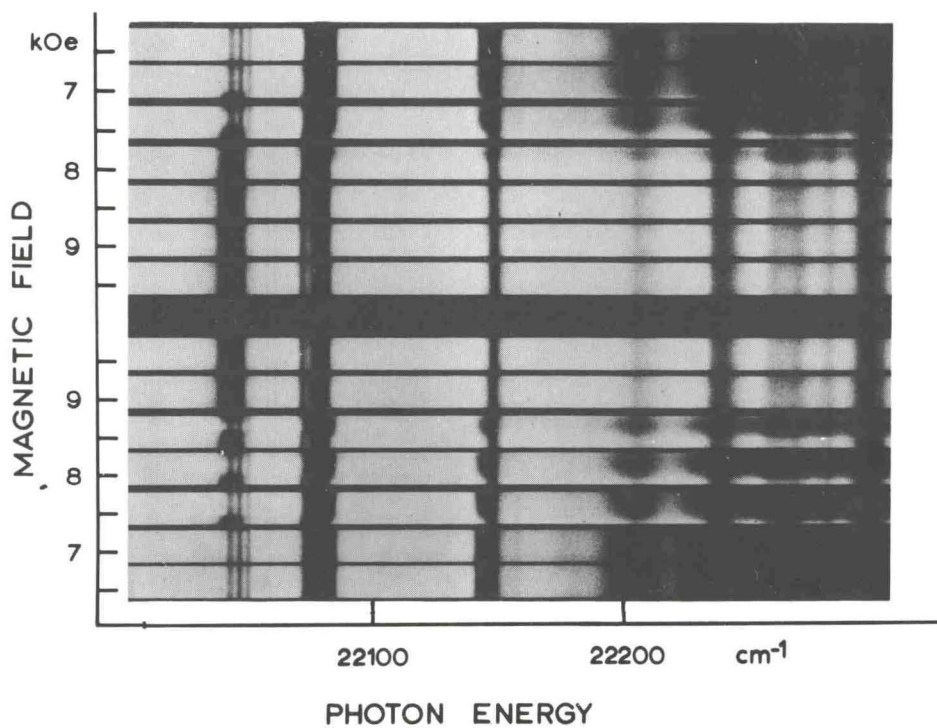


Fig. 9. Polaroid picture of the optical absorption lines of ${}^6\text{H}_{15/2}$ to ${}^4\text{I}_{15/2}$ transitions of DyVO_4 , at 4.2 K and under a stress of 5.85 kg/mm^2 . The magnetic field was first increased and then decreased through the pseudospin flop transition in 0.5 kOe steps. The light was polarized parallel to the stress.

spin flop. The change is gradual over roughly 2 kG, and close examination shows that different sections of the crystal flop before others; this is consistent with the domains expected from the demagnetization effect. The width of the transition is in reasonable agreement with a demagnetization correction of 2.9 kG for this particular sample. Experiments on samples with large demagnetization factors gave consistently broader transitions. It is clearly difficult to determine the beginning or the end point of a transition because of the fact that it might start in an area of the crystal not sampled in the photograph. Instead, the centre of the transition was estimated directly from the photograph by eye. This admittedly subjective procedure nevertheless gave results which were quite reproducible and accurate to within ± 0.5 kG, which was sufficient in view of the stress and demagnetization nonuniformities in the crystal. Values for the critical field H_c obtained by increasing the field through the transition were consistently larger than those obtained by decreasing the field. This effect was attributed to a hysteresis which arises because of the energy barrier between the metastable and stable potential minima of the system, as can be derived from the theory given in I. Experimental results on several different crystals at 4.2 and 1.4 K are plotted in Figs. 10 and 11, with a line connecting the two points which measure the hysteresis.

4. DISCUSSION

Symmetry considerations

Theoretical equations have been derived in I to account for the effects of stress and magnetic field on DyVO_4 . To apply this theory to the experimental results of the last section, it is necessary to relate σ , e and c of the theory to the true stresses, strains and elastic constants of the crystal. There are two conventions in the literature for describing these quantities in a tetragonal crystal, for there are two possible definitions of the tetragonal axes at 45° to each other in the basal plane [14]. We

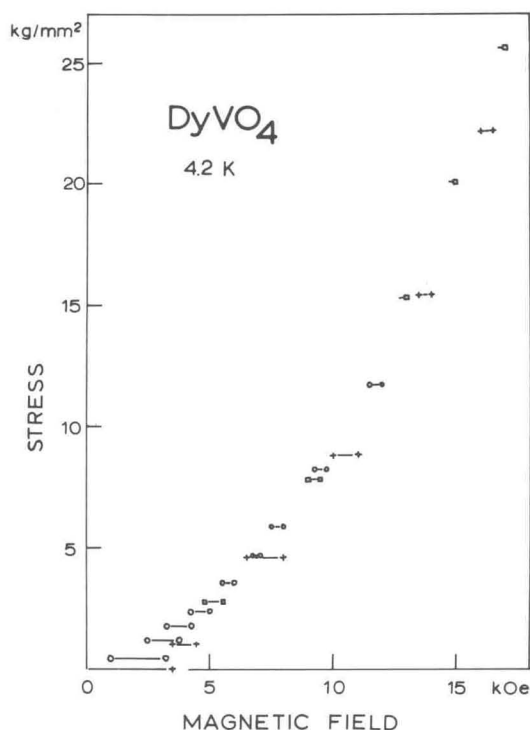


Fig. 10. Pseudospin flop fields in DyVO_4 at 4.2 K for various stresses and crystals with demagnetization factors of 3.14 (\circ), 3.72 (\square) and 4.15 ($+$). Lines connecting two points represent hysteresis between increasing and decreasing fields, as explained in the text.

adopt a set of axes abc which are parallel to the natural growth faces of DyVO_4 , and it has been shown that these axes coincide with those of the X-ray crystallographic unit cell. Taking the six elastic constants of a tetragonal crystal to be defined in this way, we may write the elastic energy of DyVO_4 as

$$\begin{aligned}
 U = & \frac{1}{4}(c_{11} + c_{12})(e_{aa} + e_{bb})^2 + c_{13}(e_{aa} + e_{bb})e_{cc} \\
 & + \frac{1}{2}c_{33}e_{cc}^2 + \frac{1}{2}c_{66}e_{ab}^2 + \frac{1}{4}(c_{11} - c_{12})(e_{aa} - e_{bb})^2 \\
 & + \frac{1}{4}c_{44}(e_{ac}^2 + e_{bc}^2) \quad (4.1)
 \end{aligned}$$

where the e 's are the strain components as defined, for example, by Kittel [15]. Each of these terms characterize distortions of a different symmetry type in the point group D_{4h} of the crystal; the first three are of type Γ_1^+ ; the others are Γ_3^+ , Γ_4^+ , and Γ_5^+ respec-

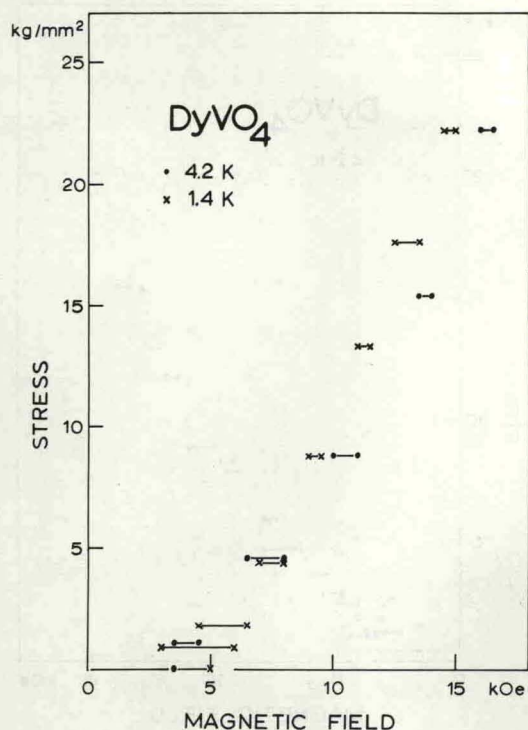


Fig. 11. Pseudospin flop fields in DyVO_4 at 4.2 and 1.4 K for a crystal with a demagnetization factor of $D = 4.15$. Lines connecting two points represent hysteresis as in Fig. 10.

tively (Koster *et al.*[10]; their xyz axes are at 45° in the basal plane to our abc axes).

The Jahn-Teller distortion in DyVO_4 is known to be of $(e_{aa} - e_{bb})$ or Γ_4^+ type, such that the reflection planes of the rare earth site group are preserved[5]. By contrast the TbVO_4 distortion is of an e_{ab} or Γ_3^+ type, such that the two-fold rotations in the basal plane are preserved. From the above equation it is clear that such strains do not couple to strains of any other symmetry, except in the presence of anharmonic forces. Assuming that e of the theory is defined precisely by $(e_{aa} - e_{bb})$ for DyVO_4 , the elastic constant c is $(c_{11} - c_{12})/2$.

The stress-strain equations of a tetragonal crystal show that $(e_{aa} - e_{bb})$ -type distortion can also be induced by uniaxial stress applied along a , or equivalently along b , that is, along the natural tetragonal crystal faces of DyVO_4 .

Such a stress σ_{aa} can be written $\frac{1}{2}(\sigma_{aa} - \sigma_{bb}) + \frac{1}{2}(\sigma_{aa} + \sigma_{bb})$, so that only one half of the measured stress is of a Γ_4^+ type. Therefore, in fitting to the theoretical equations of the previous theory, the experimental stress values must be divided by a factor of 2. The other half of the applied stress induces distortions of a Γ_1^+ type, which include both $(e_{aa} + e_{bb})$ and e_{cc} components because of the coupling terms in (4.1). In the absence of anharmonic forces, such strains will not modify the Γ_4^+ couplings at all, and therefore the theoretical equations derived earlier remain valid. Nevertheless these strains, which are of course linear in the applied stress and which have on-diagonal matrix elements, can also induce linear shifts in the energy levels. We interpret in this way the observed linear shift in the centre of gravity of the two absorption lines which represent transitions from the two ground levels to any given excited state. The fact that all the observed shifts are roughly the same suggests that the dominant shift comes from the ground rather than the excited states.

Molecular field theory

The basic equation relating the applied stress σ to the observed optical splitting Δ is (I-3-15):

$$\frac{\sigma}{\sigma_0} = \sqrt{\frac{\Delta^2 - \Delta_\infty^2}{\Delta^2}} \left(\frac{\Delta}{\Delta_0} - \tanh \frac{\Delta}{2kT} \right) \quad (4.2)$$

Δ_∞ , as given in Table 1, is determined directly from the optical spectrum above T_D , and Δ_0 has been determined by far-infrared and Raman spectroscopy to be $\sim 27 \text{ cm}^{-1}$ [6, 13]. Using this data, (4.2) predicts a co-operative ordering at $T_D = 18.9 \text{ K}$, whereas the observed value is only $14.00 \pm 0.05 \text{ K}$ [16]. This fact, suggests that there are large deviations from molecular field behaviour such as might be expected for a true Ising system with a small number of effective nearest neighbours[17]. Although molecular field theory accounts poorly for the critical behaviour in the vicinity

of T_D , it can still be quite accurate in regions of very large pseudospin alignment. For example, in fitting (4.2) to the data of Fig. 4, we found that if Δ_0 were adjusted to make the $\Delta(\sigma)$ curves fall to 9 cm^{-1} at $\sigma = 0$, then the slopes at high stresses were always too large. Instead, we have fitted the equation to the high stress region as shown in Fig. 5 by fixing Δ_0 at 27 cm^{-1} and varying σ_0 : the resulting value of σ_0 is given in Table 1. As will be seen, the deviations in this fit can be accounted for in terms of short range order.

Table 1. Summary of experimental results for σ_0 and Δ_∞ determined by several methods. $\Delta(\sigma)$ indicates a fit of the stress equation (1.4.22) to the experimental stress results of Section 2. $\sigma_c(H_c)$ indicates a fit to the pseudospin flop phase boundary formulae of the previous paper (I). e indicates a fit to the X-ray and neutron diffraction data of Will[19] and Forsyth and Sampson [20]

Sample	Temp.	Method	σ_0 (kg/mm ²)	Δ_∞ (cm ⁻¹)
DyVO ₄	77.4 K	$\Delta(\sigma)$	79 ± 2	7.5 ± 0.5
	20.4-14.1	$\Delta(\sigma)$	66 ± 2	9.0 ± 0.5
	4.2	$\Delta(\sigma)$	61 ± 4	—
	4.2-1.4	$\sigma_c(H_c)$	69 ± 7	—
	4.2	e	64 ± 6	—
YVO ₄ :Dy	77.4	$\Delta(\sigma)$	60 ± 1	4.85 ± 0.1
	20.4	$\Delta(\sigma)$	55 ± 1	5.05 ± 0.1

The data at 77K shown in Fig. 6, may be fitted to the high temperature limit of (4.2):

$$\Delta = \sqrt{\Delta_\infty^2 + \left(\frac{1}{\Delta_0 - \frac{1}{2kT}}\right)^2 \left(\frac{\sigma}{\sigma_0}\right)^2} \quad (4.3)$$

The values for Δ_∞ and σ_0 , recorded in Table 1, have shifted considerably from their values in the low temperature range. Similar results are found from the data on the lightly doped samples, shown in Fig. 7. The effect of dilution is to introduce a factor ξ , defined as the

fraction of Jahn-Teller active ions, in the stress equation (4.2):

$$\frac{\sigma}{\sigma_0} = \sqrt{\frac{\Delta^2 - \Delta_\infty^2}{\Delta_0^2}} \left(\frac{\Delta}{\Delta_0} - \xi \tanh \frac{\Delta}{2kT} \right) \quad (4.4)$$

where the definitions of σ_0 and Δ_0 are unchanged. T_D and the observed zero temperature splitting now vary linearly with ξ . In the limit $\xi \rightarrow 0$,

$$\Delta = \sqrt{\Delta_\infty^2 + \Delta_0^2 \left(\frac{\sigma}{\sigma_0}\right)^2} \quad (4.5)$$

This equation has been fitted to the data of Fig. 7, assuming $\Delta_0 = 27 \text{ cm}^{-1}$, and the results for Δ_∞ and σ_0 , shown in Table 1, are remarkably similar to those of the concentrated material, indicating that in fact the internal force constants are also very similar. The fact that Δ_∞ and σ_0 behave in the same way with temperature as in the concentrated material suggests that by 77 K a significant amount of thermal expansion due to anharmonic forces is present in both crystals and that therefore the discrepancies in Δ_∞ and σ_0 are not necessarily due to any failure of the molecular field equations.

The line shifts as a function of stress at 4.2K can be used to deduce the splitting if a correction for the centre of gravity shifts due to Γ_1^+ distortion is made. Equation (4.2) predicts a linear dependence of splitting on stress, which is in fact observed in the data of Fig. 8. σ_0 , given in Table 1, is in excellent agreement with the value obtained at 14.1 to 20.4 K, especially considering the 5 per cent error arising from the uncertainty in the centre of gravity correction.

To interpret the data of Figs. 10 and 11 on the pseudospin flop boundary, we assumed that the true thermodynamic phase boundary lay half way between the two hysteresis points. At such low stresses that the sample remains in the field-favoured distortion even when the field is reduced to zero, we assumed that the low field point of the hysteresis lies

at 'negative' values so that the phase boundary is taken to pass through the origin. With this interpretation, the theoretical curve (I.4.14) is in good agreement with the observed results at 4.2 K. But at 1.4 K the predicted phase boundary (I.4.19) is linear down to zero stress, whereas the data is not, although the trend is in the right direction, as can be seen in Fig. 11. We interpret these deviations at 1.4 K as arising from incomplete magnetic ordering or the existence of a not perfectly Ising g -value, both of which would tend to "round out the corner" at low stresses.

σ_0 may be extracted from the data by evaluating the slope of the asymptote at fields above 10 kG where the magnetization is saturated. The result is shown in Table 1 and has a 10 per cent error arising from the difficulty of drawing a reliable slope through the hysteresis points; nevertheless it is once again in remarkable agreement with other

values. The field intercepts of the asymptotes have been predicted in (I.4.18) and (I.4.19). They can be evaluated in terms of the internal ferromagnetic and antiferromagnetic fields of DyVO_4 , which are known from other measurements and calculations [7, 16], and are given in Table 2. Demagnetization factors for the crystal were estimated from the measured a , b and c dimensions on the crude assumption that it was ellipsoidal in shape. Comparison of the observed and predicted intercepts is given in Table 3.

The macroscopic distortion of DyVO_4 has been measured by X-ray and neutron diffraction at low temperatures. The earliest results by Sayetat *et al.* [18], on powdered samples are 30 per cent lower than later results on both powders [19] and single crystals [20]. We use these latter values to calculate σ_0 from the formula

$$e(T=0) = \sqrt{\Delta_0^2 - \Delta_\infty^2} / 2\Omega\sigma_0 = 0.505 \pm 0.05\% \quad (4.6)$$

Table 2. Ferromagnetic and antiferromagnetic internal fields in DyVO_4 at $T=0$, from [7, 16]

	$\text{DyVO}_4, T \ll T_N$ Internal magnetic fields (kOe)			
	Lorentz	Dipole	Exchange	Total
Ferromagnetic	4.6	0.92 ± 0.2	-1.9 ± 0.4	3.6 ± 0.6
Antiferromagnetic	0	6.9 ± 0.2	0.9 ± 0.5	7.8 ± 0.7

which may be derived from (I.3.10) and (I.3.13). The striking agreement between this value of σ_0 and the others of Table 1, which were determined at a wide variety of temperatures and by physically different kinds of experiments, leaves little doubt that the molecular field theory provides an accurate framework for understanding the basic behaviour of DyVO_4 .

Table 3. Comparison of predicted and observed field intercepts, in kOe, of the asymptotes of the pseudospin flop phase boundary in DyVO_4 at 4.2 and 1.4 K

Temp.	$\text{DyVO}_4, T_N \geq T \ll T_D$ Pseudo-spin flop: field intercept of asymptote (kOe)			
	Intercept	Demagnetization correction	Total	Observed
4.2 K	$\left(\frac{2kT \ln 2}{g\beta} - \frac{1}{2}H_F\right) = 2.8 \pm 0.3$	2.3 ± 0.5	5.1 ± 0.8	7 ± 1
1.4 K	$\frac{1}{2}(H_{AF} - H_F) = 2.1 \pm 0.6$	2.3 ± 0.5	4.4 ± 1.2	5.5 ± 1

We now make an estimate of the ratio λ/η (I), from equation (I.3.19), which relates the high temperature elastic constant to our experimentally determined values of σ_0 and Δ_0 . Using typical values of these parameters from Table 1, we find

$$\frac{1}{2}(c_{11} - c_{12}) = 12.5 \times 10^{11} \left(\frac{1}{1 + \frac{\lambda}{\eta}} \right) \text{dyn/cm}^2. \quad (4.7)$$

Recent measurements on the elastic constant $c_{11} - c_{12}$ of DyVO_4 by Melcher and Scott[21] and by Sandercock[22] show the anomaly at T_d predicted in paper I, and obtain a value at high temperatures of $c_{11} - c_{12}/2 = 9.3 \pm 0.4 \times 10^{11}$ dynes/cm². Using this value in equation (4.7) gives $\lambda/\eta \approx \frac{1}{3}$ and since $\Delta_0 = \lambda + \eta = 27 \text{ cm}^{-1}$ we obtain $\lambda \approx 7 \text{ cm}^{-1}$ and $\eta \approx 20 \text{ cm}^{-1}$. This result would indicate that the coupling via strain is the dominant interaction driving the transition.

Short range order

As is clear from Fig. 5, the stress data at temperatures near T_D deviates significantly from the molecular field curve even at high stress. We have attributed these deviations to short range order and have obtained a fit using the corrected stress equation (I.3.22). A value of $\Gamma = 4$ gives remarkable agreement with the data, especially considering that it accounts properly for both the temperature-dependence and the stress dependence of the deviations, provided the splitting is sufficiently large.

The observed transition temperature also deviates from the result predicted by molecular field theory [16, 23],

$$\frac{T_d(\text{observed})}{T_d(\text{molecular field})} = 0.74 \pm 0.02.$$

The simple theory discussed in I which takes account of the first order effects of fluctuation predicts

$$\frac{T_d(\text{calculated})}{T_d(\text{molecular field})} = \frac{\Gamma}{1 + \Gamma}$$

which is again in agreement with experiment for $\Gamma = 4$. The specific heat is strongly affected by the high temperature tail of the Schottky anomaly associated with the splitting $\Delta_\infty = 9 \text{ cm}^{-1}$. It is thus difficult to obtain meaningful results from the specific heat curve on the short range order.

We defined Γ in (I 3.23) as

$$\Gamma = \left[\sum_m J'(n-m) \right]^2 / \left[\sum_m (J'(n-m))^2 \right].$$

A low value of Γ can occur if either all the interactions are short range (in this case $\Gamma = z$ the number of neighbours) or if there are interactions whose sign changes as a function of angle or distance (such as dipolar forces). The dominant interaction has been shown to be coupling via the strain which is long range. This rules out the first interpretation for Γ and suggests that a spatially oscillating interaction occurs. We showed in I that dipole and higher order multipole interactions are associated with the same coupling coefficient as that which gives rise to the coupling to uniform strain. It is possible that coupling via the optic phonons as well as these multipole interactions are responsible for the fluctuation effects. An independent test of the importance of long range couplings may be obtained from measurements of the ordering temperature as a function of dilution; such measurements are in progress.

The success of the simple molecular field theory and the first order theory for short range order in accounting for the cooperative Jahn-Teller transition in DyVO_4 make this system a model one for the study of such phenomena. An understanding of the accidental degeneracy and of the unusually large electron-lattice coupling which are responsible for the transition must await further study of the crystal field and of the actual internal structure of DyVO_4 .

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