

Spectroscopic Study of Magnetic Behavior and Jahn-Teller Distortions in the Even-Electron System TbPO_4^\dagger

J. N. Lee* and H. W. Moos

The Johns Hopkins University, Physics Department, Baltimore, Maryland 21218

(Received 18 October 1971)

The high-resolution optical spectra of TbPO_4 show that there is antiferromagnetic ordering in the vicinity of 2.25 K, but that there must also be a Jahn-Teller distortion. Evidence that the distortion behavior couples strongly to the magnetic behavior is provided by optical experiments which show that (i) the distortion behavior must occur simultaneously with either magnetic ordering or the application of a large magnetic field and that (ii) the distortion is rotatable by an external magnetic field. It is possible to deduce from the distortion behavior the possible directions for the easy axis. A model is presented to explain the magnetic and distortion behavior. A variety of spectral features, including metamagnetic behavior, are observed but are not fully understood.

I. INTRODUCTION

Studies on the zircon-structure rare-earth phosphates, arsenates, and vanadates have shown these crystals to exhibit a variety of magnetic phenomena.¹⁻⁴ In addition, some of these studies provide evidence that this particular crystal structure may be quite susceptible to cooperative Jahn-Teller-type distortions lowering the symmetry of the crystal.²⁻⁵ The cause of such distortions and their relation to magnetic phase transitions is not well understood. (One other instance in which a rare-earth crystal exhibits Jahn-Teller distortions is the case of PrAlO_3 .⁶) It has already been found that the Jahn-Teller distortions in² DyVO_4 and³ DyAsO_4 define the direction for the easy axis in a subsequent magnetic-ordering process at lower temperatures. Dy^{3+} , however, is an odd-electron system. The situation can be quite different for even-electron systems. A degenerate ground state in such a system implies a magnetic moment for the rare-earth ion; but this degeneracy might also tend to be lifted by a cooperative Jahn-Teller distortion. Hence, it is possible that the coupling between the magnetic and crystal field interactions will be quite complicated, depending on the relative magnitudes of the two interactions. TbPO_4 may be a rather general example of an even-electron system where both magnetic and Jahn-Teller effects occur and sometimes compete. This crystal orders antiferromagnetically and shows strong evidence for crystal field effects on the magnetic behavior. This paper will be concerned with the interpretation of the high-resolution optical spectra of TbPO_4 . This interpretation will be carried out in the light of the neutron-diffraction results on powdered TbPO_4 ,⁷ which show that the crystal magnetically orders into two collinear sublattices 40° off the c axis of the tetragonal unit cell. After preliminary comments on the experimental techniques (Sec. II), we

shall present the main features of the TbPO_4 spectra and their immediate implications (Sec. III). In Sec. IV, we discuss models that will consistently explain the data, as well as description of additional experiments that support these models.

II. EXPERIMENTAL TECHNIQUES

The TbPO_4 crystals were grown from the flux according to Feigelson,⁸ using 99.9%- and 99.999%-pure terbium oxide. X-ray backscatter Laue photographs taken at room temperature confirm that crystals grown in this manner possess tetragonal symmetry. (It is also possible to grow a monoclinic modification of TbPO_4 .⁹) The tetragonal form of TbPO_4 has $D_{4h}^{19} - I4_1/amd$ space-group symmetry with D_{2d} rare-earth-site symmetry.¹⁰ The unit cell is shown in Fig. 1 of Ref. 1. For TbPO_4 , the reported room-temperature lattice parameters are $a_0 = 6.941 \text{ \AA}$ and $c_0 = 6.070 \text{ \AA}$. The Laue photographs also showed that the c axis of the unit cell is along the long dimension of the crystal and that the edges of the crystal correspond to edges of the unit cell. The crystals were generally needlelike, and the largest were parallelepipeds about $5 \times 0.5 \times 0.25 \text{ mm}$. For the parallel Zeeman effect (i.e., magnetic field parallel to the c axis of the crystal), several crystals were mounted together in parallel. Single crystals were used for the perpendicular Zeeman effect.

The absorption spectra were recorded photographically on a 6.4-m Paschen with a dispersion of 1.2 \AA/mm in first order, and photoelectrically with a 1.8-m Ebert spectrometer with a resolving power of 2.5×10^5 at 5461 \AA . A 3.4-m Jarrel-Ash grating spectrometer with first-order dispersion of 5 \AA/mm was used to record the fluorescence spectra photographically. Absorption work was limited to the 5D_4 manifold and the lowest (sharpest) levels of the 5D_3 and higher manifolds in Tb.

Absolute orientation was obtained by placing a

laser beam along the optic axis of the spectrometer and reflecting it off the face of the crystal back on to itself. Reproducibility was estimated to be $\pm 2^\circ$. The crystal could be rotated in either of two directions (labeled CCW or CW) about an axis perpendicular to both the optic axis and the direction of the external magnetic field.

III. EXPERIMENTAL RESULTS FOR TbPO₄

The spectra of TbPO₄ taken with and without an applied magnetic field will be considered separately. The behavior at the zero-field spectra with temperature indicates that a second-order phase transition occurs in the vicinity of 2.25 K. The spectra in an applied magnetic field shows that the ground state of TbPO₄ is degenerate and hence possesses a magnetic moment. Some of these results have been reported briefly.^{7,11} We include them for completeness.

A. Spectra in Zero Field

Spectra taken in zero field as a function of temperature showed a temperature-dependent line shift to the blue as the temperature was lowered (see Fig. 1). This shift has been interpreted as due to splitting of the ground state by internal magnetic (and possibly crystalline electric) fields that arise as the crystal magnetically orders with decreasing temperature.¹¹ At the low temperatures involved, only the lower of the split levels is populated so only a shifting of line position to higher wave numbers is observed. Near 2.2 K the lines had an unusual shape. Since according to Fig. 1 the ground levels should be split by only a small amount, the line shape could have been caused by the upper level being appreciably depopulated with respect to the lower level. Large uncertainties in the temperature (± 0.1 K) near 2.2 K, plus the broadness of the lines, prevented a fitting to the line shape. The splitting of the ground state was also inferred from the appearance of a weak sideband on the long-wavelength (or low-energy) side of a very strong line at 20455.8 cm⁻¹, with an intensity of 10⁻²–10⁻³ the main-line intensity. The strong main line was found to appear weakly in the opposite polarization. Here it is not overabsorbed, permitting a very accurate determination of its center. Measurements of the positions of this weak line and the sideband to the strong line gave a splitting of $\Delta = (7.0 \pm 0.2)$ cm⁻¹ at 1.1 K, which is approximately twice the lineshift shown in Fig. 1. This splitting Δ predicts the sideband-to-main-line intensity to be $I/I_0 = 0.0012$, due to the depopulation of the upper level (with respect to the lower) by the factor $e^{-\Delta/kT}$. This is consistent with the relative intensity estimated above.

If the line shift in TbPO₄ is associated with a symmetrical splitting of the ground state by magnetic ordering, one may make comparisons with similarly

produced line shiftings observed in other rare-earth systems. A line shift (or splitting) with a detailed temperature dependence very similar to the one in TbPO₄ has been observed by dysprosium aluminum garnet (DAG) and demonstrated by means of a Monte Carlo calculation to be proportional to the magnetic energy of the crystal.¹² Thus, the temperature at the inflection point of the line shift should correspond to a local maximum in the specific heat. If a magnetic phase transition occurs, this maximum is at the Néel temperature (T_N). Since TbPO₄ is a non-Kramers's system, the ground doublet may be split by both magnetic and crystal field effects. If, in spite of this, the interpretation for DAG is applied to TbPO₄, from Fig. 1, T_N is (2.25 ± 0.15) K. The uncertainty is due in part to the temperature determination and in part to the line breadth. This value is in good agreement with heat-capacity results which give $T_N = 2.17$ K.¹¹

Another striking feature of the absorption spectra at 1.5 K in zero field was the appearance of a satellite line on the high-energy side of all the main lines. Photoelectric traces of the lines on the 1.8-m Ebert showed that these satellites are 10⁻¹–10⁻² of the main-line intensity and that there is a qualitative correlation of the satellite intensity with that of the main line. The trace for the 20478.5 cm⁻¹ line in zero field is shown in Fig. 4 (trace *f*). The separation from the main line is (2.80 ± 0.10) cm⁻¹ for the ⁵D₄ manifold levels and is (3.0 ± 0.1) cm⁻¹ for the ⁵D₃ levels. Changing the temperature from 1.1 to 1.7 K produces no change in the satellite intensity and its position relative to the main lines (which do shift about 0.2 cm⁻¹). Above 1.7 K, the satellite becomes broad and diffuse and is unobservable by 1.9 K. Crystals grown from different

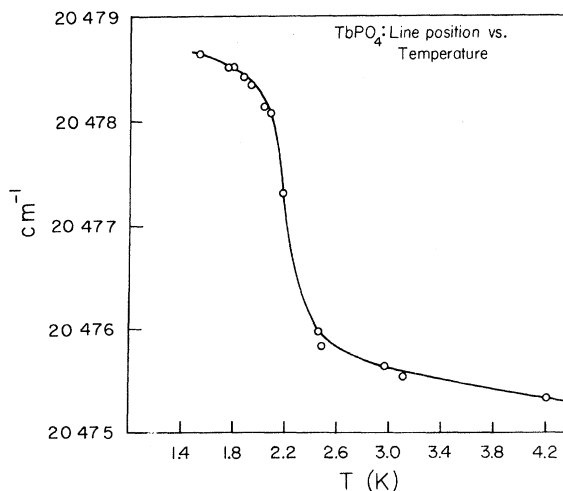


FIG. 1. Line position as a function of temperature for a typical optical transition in TbPO₄. The line shift from 1.5 to 1.1 K is less than 0.2 cm⁻¹ (Ref. 11).

percentage purity terbium oxide (99.9 and 99.999% pure) showed no variation in satellite intensity or position. This feature, which is not completely understood, will be discussed further in Sec. IV.

B. Spectra in a Magnetic Field

The Zeeman behavior for typical lines (at 20 512.7 and 20 478.5 cm^{-1} in the 5D_4 manifold) at 1.5 K is shown in Fig. 2 for the parallel effect (i. e., external field parallel to the c axis). The upper levels for these lines are singlets, so except for second-order mixing with nearby upper levels, these lines should reflect the ground-state behavior, particularly for very low fields. All the lines are split, or pseudosplit, into two levels of equal intensity at low fields. Since the two components of this parallel-effect splitting were observed to be of equal intensity, it was concluded that this was not a single-ion splitting, as one would have then observed the thermal depopulation of the upper of these two levels as a reduction in the intensity of the optical transitions originating from this level at 1.5 K. What was observed must be the removal of the degeneracy arising from the existence of more than one magnetic sublattice. In fact, the number of pseudosplit components (two) would be expected to equal the number of sublattices. Neutron diffraction confirms that there are two sublattices.⁷

The pseudosplitting observed here, however, differs from the usual pseudosplitting in that here the

splittings are nonlinear and asymmetric towards smaller wave numbers (see Fig. 2). The shift of the small-wave-number component at 4 kG is typically 40% greater than the large-wave-number component with respect to the zero-field line position, and the degree of asymmetry is found to vary from level to level. This asymmetry cannot be due entirely to interactions between upper levels, since the asymmetry is too large and is always toward small wave numbers. The straight lines drawn in the low-field region in Fig. 2 emphasize the data at fields just below 5 kG; splitting factors were estimated from these lines, and the average taken for the two components. However, this average is less than the ground-state splitting factor above 25 kG by about 30% (see below).

The low-field ground-state behavior may also be obtained from the average of the pseudosplittings of an optical transition to an upper-state doublet (at 26 254.6 cm^{-1}). The ground-state pseudosplit energy levels so deduced are shown in Fig. 3, compared with the results derived from the isolated singlet at 20 478.5 cm^{-1} . The agreement is good, implying the asymmetric behavior is a general property of the ground state.

The ground-state magnetic moment was obtained from the high-field parallel effect. The ground-state splitting factor s_g was obtained from transitions to three upper-state doublets around 26 500 cm^{-1} in the range 20–36 kG. The ground moment

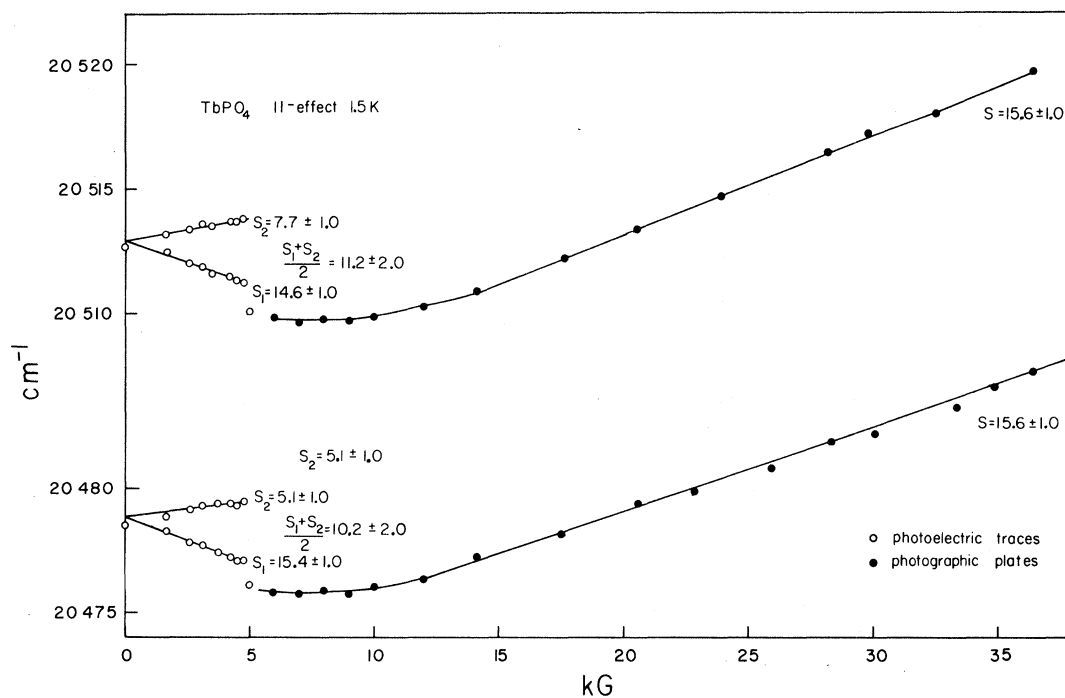


FIG. 2. Parallel Zeeman effect for optical transitions to 5D_4 in TbPO_4 at 1.5 K. S denotes the splitting factor.

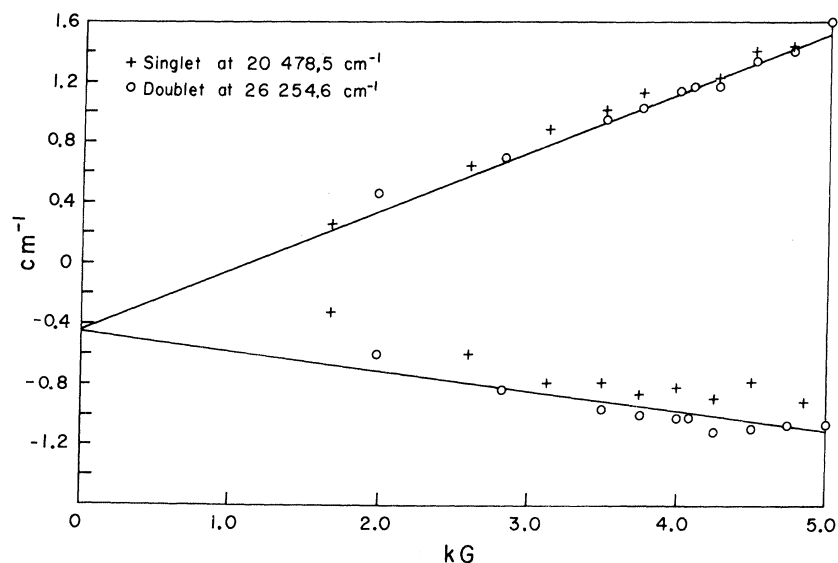


FIG. 3. Low-field ground-state parallel pseudo-Zeeman behavior in TbPO_4 at 1.5 K. 0 cm^{-1} denotes the zero-field position of the ground level.

μ_g was determined according to

$$\mu_g = s_g S \mu_B, \quad (1)$$

where S is the fictitious spin of the ground state ($=\frac{1}{2}$) and μ_B is the Bohr magneton. At 1.5 K, it was found that

$$\mu_g = (8.0 \pm 0.2) \mu_B.$$

The same value for μ_g was found at 4.2 K, with a somewhat larger uncertainty ($\pm 1.0 \mu_B$).

In the parallel effect the average of the ground-state pseudosplittings gives a splitting factor (see Fig. 2) that is smaller than the high-field ground splitting factor ($s_g = 16.0$). This is strong evidence that the ordered-moment configuration is not completely aligned along the c axis. Such a spin arrangement might be the result of a distortion away from tetragonal symmetry—the distortion defining the direction of the easy axis.

With a field perpendicular to the c axis, a similar low-field pseudosplitting occurred but about five times smaller in magnitude than in the parallel effect. This is best seen from photoelectric traces which are reproduced in Fig. 4. No splitting factors could be determined for the components in this case, since the components are clearly resolved only at the highest fields just before a phase transition occurs. There was also an asymmetry toward smaller wave numbers in this splitting.

Sharp discontinuities in the Zeeman pattern, implying phase transitions, were observed at 1.5 K at $(4.8 \pm 0.1) \text{ kG}$ for the parallel effect (see Fig. 2) and at approximately 11.0 kG for the perpendicular effect. (The transition fields were taken to be those fields where the pseudosplit components have disappeared.) In the perpendicular case, the transition region is not sharp—extending over a region of

3–4 kG—as can be seen in Fig. 4, where the paramagnetic line first appears at 7 kG and is present for the higher-field traces. Figure 4 also illustrates

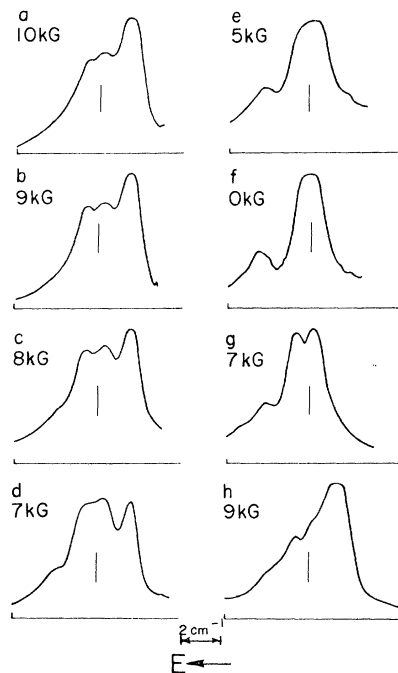


FIG. 4. Photoelectric traces showing perpendicular Zeeman behavior for the transition to the singlet level at $20\,478.5 \text{ cm}^{-1}$. Traces a – f were obtained with a crystal $7.0 \times 0.77 \times 0.27 \text{ mm}$, and traces g and h were obtained with a crystal $4.5 \times 0.87 \times 0.25 \text{ mm}$, illustrating the variation of the behavior with crystal dimensions. The mark underneath the traces denotes the zero-field line position. E denotes the wave number of the line. The feature on the left-hand side of the main line is the satellite discussed in Sec. III A.

the variation in the transition field with crystal dimensions.

If a crystal possesses tetragonal symmetry, one should obtain a splitting factor that is isotropic in the basal plane. Perpendicular-effect experiments were performed at high fields at 1.5 and 4.2 K for various orientations of the external field (H) in the basal plane. The crystal was rotated about the c axis to several fixed positions with respect to the field, and the splitting factors of the Tb levels obtained from Paschen spectra taken between 20.60 and 34.87 kG. The ground-state splitting factor was obtained from the behavior of a narrow doublet at approximately $26\,250\text{ cm}^{-1}$.

The ground-state splitting-factor variation with field direction in the basal plane is shown in Fig. 5, along with the identification of the orientation axes.¹¹ The variation is somewhat analogous to that found in² DyVO₄ and immediately indicates that the symmetry is lower than tetragonal both above and below T_N . Additional measurements show that this splitting-factor variation has a $\frac{1}{2}\pi$ periodicity in the basal plane, which indicates that the distortion is rotatable by an external field. Rotatable distortions have previously been found in⁶ PrAlO₃ and DyVO₄.² The cusplike behavior about the 0° position means that the field at the 0° position is at equal angles to possible easy-axis directions, and small deviations of the field from 0° causes the system to favor one easy-axis direction over the other. Hence, the easy axis is taken to lie in either the (110) or ($\bar{1}\bar{1}0$) plane.

The distortion behavior described above allows one to deduce the precise directions of the moments in ordered TbPO₄. The neutron diffraction on a powdered sample permits determination of only the number of sublattices (two) and the angle the easy

axis makes with the c axis of the tetragonal unit cell (40°). Figure 5 indicates that there is a maximum in the splitting-factor variation in the 45° direction. Presumably ordering will occur along the easy axis. Hence, the easy axis should lie 40° off the c axis in either the (110) or the ($\bar{1}\bar{1}0$) plane. However, the results shown in Fig. 5 were obtained at high fields, so there is a possibility for interaction between the distortion and magnetic behavior. For example, there is evidence the distortions in DyVO₄ and DyAsO₄ can be induced by a magnetic field.^{13, 14} One would therefore like to have more confirming optical experiments for the determination of the easy-axis direction. A study of the ground-state splitting-factor variation in the (110) or ($\bar{1}\bar{1}0$) plane would be useful, but this experiment was impractical in view of the needlelike morphology of the TbPO₄ crystals.

Another feature of the spectra was the appearance of some very striking line-broadening phenomena in high fields, for both the parallel and perpendicular effects. In the high-field perpendicular effect at 4.2 K, the lines were quite broad around the 0° position, having about a 5–8 cm⁻¹ half-width, but rotation through an angle of only 10° in either direction results in a sharpening of the lines to about a 1.0–1.5-cm⁻¹ half-width (in addition to changing the splitting factor—see Fig. 5). No similar line broadening occurred in the perpendicular effect at 1.5 K. The linewidth at the 0° position in a field of 34.87 kG narrowed rapidly between 4.2 and 3.4 K. The perpendicular-effect line broadening also had a $\frac{1}{2}\pi$ periodicity.

In the parallel effect at 1.5 and 4.2 K a very similar line broadening occurred with the field exactly parallel to the c axis. At 1.5 K, deviating

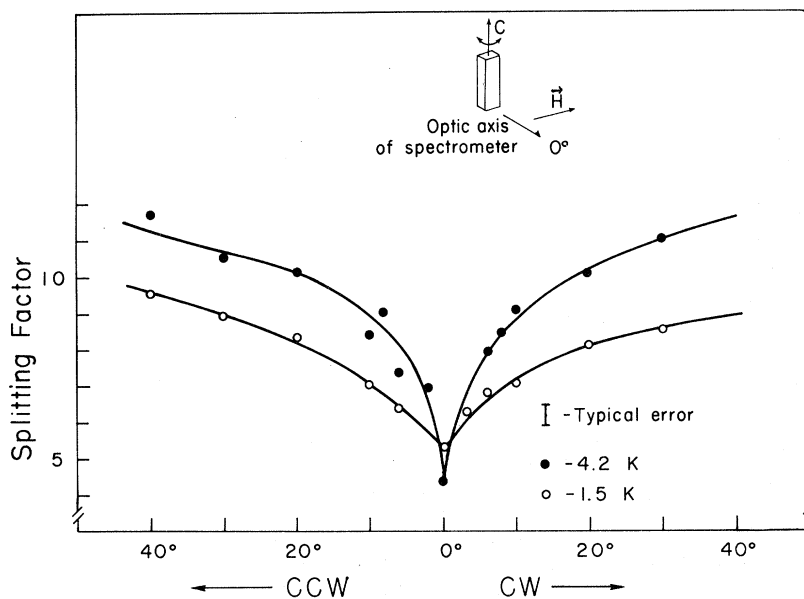


FIG. 5. Ground-state splitting factor as a function of field orientation in the basal plane. Optic axis of the spectrometer perpendicular to the crystal face [(100) plane] denotes the 0° position. \vec{H} , c , and the optic axis are orthogonal. The error shown is the absolute, rather than relative, error (Ref. 11).

the field 15° from the c axis again sharpened the lines to a 1.0-cm^{-1} half-width. At 4.2 K a deviation of about 30° was necessary to sharpen the lines equivalently. These line broadenings will be discussed further in Sec. IV C.

A final feature of the TbPO_4 spectra is the changes in the zero- and low-field spectra after crystals were exposed to large magnetic fields (~ 30 kG). After exposure, each of the zero-field lines at 1.5 and 1.1 K was replaced by two lines—one at the ordered and one near the disordered line position [see Fig. 6(b)]. In some samples the ordered line was replaced by narrow doublets (separation $\sim 0.8\text{ cm}^{-1}$). The perpendicular-effect splitting in low fields is suppressed. The parallel-effect pseudosplitting appeared unaffected, although there was a reduction in the intensity of the pseudosplit components. The disordered line showed no Zeeman behavior in low fields. Heating the crystals up to room temperature and then cooling down again to 1.5 K still resulted in the altered zero-field spectra. Experiments at high fields on these crystals at 1.5 K reproduced the results previously obtained with unaltered crystals. These induced changes in the spectra, and how they may be related to similar spectral features in $\text{TbPO}_4:1\text{-at.}\% \text{ Ho}$ will be discussed in Sec. IV C.

IV. DISCUSSION AND FURTHER EXPERIMENTS

The data presented in Sec. III pose a number of questions. First, the presence of a Jahn-Teller distortion mechanism (both above and below T_N) was inferred from the behavior of the perpendicular Zeeman-effect spectra. Hence, there is the question as to the origin of the distortion. Second, the phase transitions which occur at critical fields below T_N were not explained. Finally, a number of features in both the zero-field spectra and the spectra in an applied field were noted without further explanation; one would like to ascertain the relationship between these features and the magnetic and/or crystal field properties of TbPO_4 .

A. Crystallographic Distortion in TbPO_4

The possibility that TbPO_4 does not possess tetragonal symmetry above magnetic-ordering temperature ($T_N = 2.17$ K) is implied by the variation in the ground-state splitting factor in the basal plane at 4.2 (see Fig. 5); it has been ascertained from x-ray Laue photographs that these TbPO_4 crystals have tetragonal symmetry at room temperature. If indeed there is a distortion, one would particularly like to know at what temperature the distortion occurs and the new symmetry of the system below the distortion temperature.

To see if a distortion does occur, the spectra of TbPO_4 were taken as a function of temperature in zero magnetic field. No relative shifting or

change in the number of Tb^{3+} lines was observed in the range 4.2–23 K and the spectra at 77 K were the same as that at 4.2 K.

If TbPO_4 underwent a spontaneous distortion at some as yet undetermined temperature it may be possible to observe either strains or domainlike regions when viewing the crystal between crossed polaroids. This was done at 4.2 and at 77 K. No strains or domains were observed in either case.

The spectra of $\text{TbPO}_4:1\text{-}$ and $\text{TbPO}_4:5\text{-at.}\% \text{ Ho}$ were also investigated for information about TbPO_4 . The Ho^{3+} ion was used as a probe in this case, since in D_{2d} symmetry there should be some degenerate Ho^{3+} levels which should be sensitive to both magnetic and crystal field effects. Further, the ionic radius of Ho^{3+} (0.894 \AA) is quite close to that of Tb^{3+} (0.923 \AA). Between 4.2 and 23 K and at 77 K, in both the 1 and the 5% samples, the Tb^{3+} spectra are identical to the 100% TbPO_4 spectra at 4.2 K, and the Ho^{3+} lines did not exhibit any shiftings or splittings. However, some of the Ho^{3+} lines in both crystals showed small splittings at 1.5 K (typically $\sim 1\text{ cm}^{-1}$).

In view of the results of all the above experiments, it thus appears that the structure of TbPO_4 does not change in the range 4.2 to at least 77 K. However, the perpendicular-effect results at 4.2 K (Fig. 6) show a large variation in the ground-state splitting factor with field direction in the basal plane. Hence, the distortion must be induced by the magnetic field. Further evidence for this may be deduced from the results of an ap-

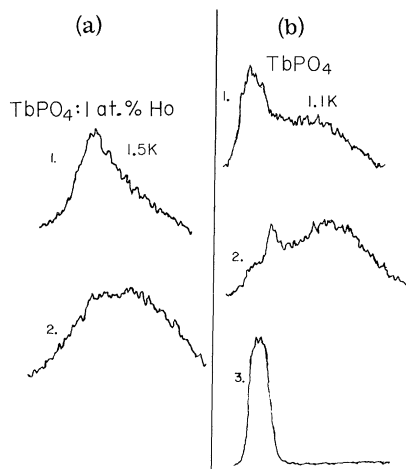


FIG. 6. (a) Densitometer traces of the $20\,478.5\text{-cm}^{-1}$ Tb^{3+} line in $\text{TbPO}_4:1\text{-at.}\% \text{ Ho}$ at 1.5 K. Traces 1 and 2 are for different crystals from the same growth. (b) Densitometer traces of $20\,478.5\text{-cm}^{-1}$ Tb^{3+} line at 1.1 K. Traces 1 and 2 are for crystals that have been previously exposed to high magnetic fields at 1.1 K. The crystal for trace 3 had not been exposed to magnetic fields and shows the normal zero-field linewidth.

proximate crystal field calculation and from a comparison of the high-field parallel-effect results at 4.2 and 77 K.

As there is no evidence for a crystal distortion above the Néel temperature, the tetragonal symmetry of TbPO_4 was approximated by the crystal field parameters for a similar symmetry crystal $\text{YPO}_4:\text{Er}$.¹⁵ Comparison of the so-calculated 7F_6 ground manifold levels with the 7F_6 levels deduced from fluorescence spectra taken at 77 K shows that there is reasonable agreement between the observed and calculated spread of the manifold, and groupings of levels are observed within the manifold at approximately the positions where groupings occur in the calculation.¹⁶ The most important result of this rough agreement is that it allows for an identification of the ground state level of TbPO_4 as a $\mu = 1$ level associated with the doubly degenerate Γ_5 representation in D_{2d} .¹⁷ A similar calculation using $\text{YPO}_4:\text{Eu}$ parameters¹⁸ also gave a $\mu = 1$ ground state.

The crystal field parameters used here are only an approximation in the case of TbPO_4 so one cannot reasonably expect an accurate prediction for the magnetic moment of the ground level. However, one does know that only M_J 's differing by four are mixed in a tetragonal field. A $\mu = 1$ level will be a mixture of $M_J = \pm 1, \pm 5$, and ± 3 , so the magnetic moment of the ground level is expected to correspond to an $|M_J|$ less than 6 (or a splitting factor of less than 18).¹⁹ However, it has already been noted (Sec. III B) that s_g in the parallel effect at 4.2 K is 16.0 ± 2.0 , and it was also inferred that a field along the c axis may not give the maximum for the g tensor because of the easy-axis direction. Hence, the ground state M_J at 4.2 K must be very close to ± 6 . On the other hand, measurement of s_g in the parallel effect at 77 K gave $s_g = 9.64 \pm 0.20$, which is in much better agreement with the ground splitting factor calculated using $\text{YPO}_4:\text{Er}$ crystal field parameters ($= 11.2$). However, this difference in the observed high-field behavior at 77 and 4.2 K is in disagreement with the zero-field results, which shows that the structure of the spectra at these two temperatures is the same and hence there should be no change in symmetry between 77 and 4.2 K.

We may resolve the apparent discrepancy between the high-field and zero-field results by arguing that a distortion occurs in TbPO_4 upon the application of a large magnetic field at relatively low temperatures. In the same way, it is possible that a distortion will accompany the onset of magnetic order, i. e., it accompanies the buildup in the internal magnetic fields. In short, the crystal may behave in this manner because the distortion will increase the effective M_J value of the ground state and hence decrease the Zeeman en-

ergy of the system if only the lower of the Zeeman components is appreciably populated (i. e., the temperature is low). The total free energy of the system will be lowered if the decrease in Zeeman energy is not offset by an increase in elastic energy due to the distortion.

The minimum field in which the proposed magnetically induced distortion would occur (at say 4.2 K) could not be determined: The broadness of the lines at 4.2 K and the nonlinear Zeeman behavior at lower fields (< 20 kG) prevented a determination of the splitting-factor variation with field direction in the basal plane at low fields.

It is of interest to note that the agreement between the observed 7F_6 levels and those calculated from $\text{YPO}_4:\text{Er}$ parameters may well be due to the overwhelming importance of the B_2^0 term which splits the 7F_6 levels into doublets arranged according to $|M_J|$.²⁰ This is apparently the reason many terbium compounds have a ground state consisting of $M_J = \pm 6$ degenerate. The sign of B_2^0 in these compounds makes ± 6 (rather than ± 1) lie low. It may therefore be easy for a magnetic field to induce a distortion with the result that M_J in the ground state is increased to nearly ± 6 .

B. Phase Transitions in an External Field

In Sec. III B it was noted that phase transitions occurred when an external magnetic field exceeded certain critical values for both the parallel and perpendicular effects in TbPO_4 . These phase transitions can be associated with either the metamagnetic "spin-flip" or "spin-flop" transition.²¹ The spectra observed resemble those associated with an antiferromagnetic-to-spin-flop-type transition. There is a discontinuity in the Zeeman pattern at or around the critical field, and there is a region above the critical field where there is very little Zeeman behavior (see Figs. 2 and 4). The value of J_0 , the isotropic exchange parameter, and the value and variation of the anisotropy energy as a function of spin direction within the crystal are not known. Therefore, it is not possible to perform verifying calculations on the basis of a spin-flop process. It is not possible to explicitly prove or disprove that the observed phase transitions correspond to spin flop, but there are two facts that together would tend to question the spin-flop hypothesis. First, it has been shown that, ignoring anisotropic exchange between sublattices, the maximum angle between the external field and the easy axis that will still result in a spin-flop transition is²²

$$\psi = 28.6^\circ (H_A/H_E), \quad (2)$$

where H_A is the anisotropy field and H_E is the isotropic exchange field. Since the moment configuration in TbPO_4 consists of two collinear sub-

lattices at an angle of 40° to the c axis, if there is a spin flop in the parallel effect, the implication would be that

$$H_A/H_E \geq 40/28.6 = 1.4. \quad (3)$$

This must be considered a fairly large value (see below.) For the perpendicular effect this ratio will be even larger, as the easy axis in TbPO_4 is at an angle of 63° to one of the a axes of the tetragonal unit cell. The second point to consider is that there may well be a limit to the size of H_A/H_E that will permit spin flop. Although one does not know the value for any such limit in a system such as TbPO_4 , it has been shown that if one applies a magnetic field along the easy axis of a uniaxial system which has an anisotropy energy variation of $\cos^2\phi$, where ϕ is the angle away from the easy axis, spin flop becomes impossible if²¹

$$H_A/H_E \geq 1. \quad (4)$$

If, on the other hand, one assumes that the observed phase transitions in TbPO_4 correspond to spin flip, we can approximate the ratio of the critical fields for the parallel and perpendicular effects to be

$$\frac{H_{c\parallel}}{H_{c\perp}} = \frac{H_{c0} \cos \theta_{\perp}}{H_{c0} \cos \theta_{\parallel}} = \frac{\cos 63^\circ}{\cos 40^\circ} = 0.593, \quad (5)$$

where H_{c0} is the critical field if the field is applied exactly along the axis of alignment, and θ_{\parallel} and θ_{\perp} are the angles the field makes with the easy axis in the parallel and perpendicular effect, respectively. Experimentally, we obtain

$$\frac{H_{c\parallel}}{H_{c\perp}} = \frac{(4.8 \pm 0.1) \text{ kG}}{(9.0 \pm 2.0) \text{ kG}} = 0.543 \pm 0.140, \quad (6)$$

which is in quite reasonable agreement with the prediction in Eq. (5).

In assuming spin flip, one will have to also assume several properties about the system in order to account for all the observations. The discontinuity of the Zeeman pattern at the critical field must be explained. For instance, the anisotropic interactions could change magnitude above the critical field, causing the spins in the paramagnetic state to lie in a direction different from the easy axis. Second, the Zeeman behavior above the critical field would have to be accounted for by domain and shape effects. In a spin flip, one would have expected linear Zeeman behavior immediately above the critical field.

C. Additional Spectral Features

1. Satellites to Main Lines in TbPO_4

The origin of the satellite line that occurs to the high-energy side of all the main lines at low tem-

peratures (≤ 1.6 K) is not understood. It broadened out with the application of a magnetic field and disappeared above 2–3 kG (see Fig. 4). It did not show pseudosplitting, as did the sideband on the low-energy side of the strongest Tb line (see Sec. IIIB).

In the perpendicular effect at 1.5 K, a similar higher-energy satellite reappeared for the strong 20455.8-cm^{-1} transition to 5D_4 at a field of approximately 18 kG. Since the main transition is very overabsorbed, splitting factors could not be measured very accurately. However, there is no indication that the separation between main line and satellite changed over the range 18–36 kG. This separation was approximately the same as for the zero-field satellite. Faulhaber and Hufner²³ argue that satellites having the same splitting factor as the main line strongly indicate the presence of impurity ions on nearby regular lattice sites, but the behavior here was the same for crystals grown from different purity terbium oxide. Rotation away from the 0° position at high fields reduced the intensity of this satellite, until it disappeared at around 30° ; the intensity at the 0° position was constant up to 36 kG. The reason for this behavior is also not known. An angular dependence of intensities has been noted in a low-temperature high-field study of satellite lines in erbium aluminum garnet,²⁴ but the satellites in that study showed, in addition, an intensity variation with field for a fixed position of the crystal. This high-field satellite in TbPO_4 may or may not be related to the zero-field one.

In the case of the zero-field satellite lines, the most probable explanation is that these lines are associated with a distortion of the crystal field, i. e., some of the terbium ions may have distorted site symmetry compared to the other Tb ions. The absence of any differences in the photoelectric intensities of the satellite line relative to the main lines for crystals grown from different purity terbium oxide would seem to rule out impurities. A distortion of the site symmetry might be caused by factors such as imperfections in the crystal, terbium ions in special interstitial sites, or domainlike cooperative distortions.

2. Line Broadenings

In Sec. III it was found that the easy axis in TbPO_4 should lie in either the (110) or $(1\bar{1}0)$ plane. Also, it was noted that line broadenings occurred at the 0° position, for various temperatures, in both the parallel and perpendicular Zeeman effects. In the 0° position neither of two equivalent directions in the above-mentioned planes will be energetically favored over the other. The resultant degeneracy in the direction might possibly be manifested then as a broadening of the spectral lines.

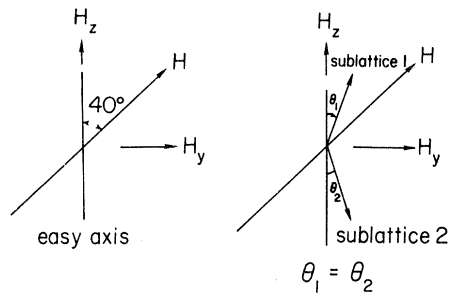


FIG. 7. Possible sublattice orientation in TbPO_4 at low fields. H denotes the external magnetic field, with H_x in the direction of the easy axis.

For example, spins in adjacent unit cells may point in different, though equivalent, directions.

3. Asymmetry in Pseudosplittings

The asymmetric and nonlinear low-field behavior observed in TbPO_4 is not due to the fact that the external field may be comparable in magnitude to the internal fields (~ 10 kG). If the external field were sufficiently strong, the spins might be pulled towards the field, as is illustrated in Fig. 7 for the parallel effect. By symmetry, $\theta_1 = \theta_2$. On the basis of Zeeman energy alone, one would expect the ground-state asymmetry to be towards lower energy, as sublattice 1 corresponds to the lower of the two pseudosplit levels. But, this is *not* what is observed; the ground-state pseudosplitting is asymmetric towards higher energy (see Fig. 3).

At present, it appears that a complex source of anisotropy is required to reproduce the observed low-field splitting. Crystalline field anisotropy is a likely source, as it may also be responsible for

the unusual direction of ordering with respect to the tetragonal axes.

4. Comparison of TbPO_4 and $\text{TbPO}_4:1\text{-at.}\% \text{ Ho}$

Experiments conducted at 1.1 K and in high fields on TbPO_4 appear to result in damage to or permanent alteration in the crystals (see Sec. IIIB). The zero-field spectra at 1.5 and 1.1 K of altered TbPO_4 crystals resemble those of $\text{TbPO}_4:1\text{-at.}\% \text{ Ho}$ at the same temperatures. In both these crystals, each Tb^{3+} line is replaced by two lines—one at the ordered and one near the disordered line position [see Figs. 6(a) and 6(b)].

One possible interpretation of the 1.1-K results is that the application of a high magnetic field at this temperature induces a permanent distortion in TbPO_4 . There are four equivalent ordering directions (when referred to the axes of the tetragonal unit cell) for the moment configuration deduced in Sec. IIIB; any permanent distortion will remove the equivalency. If this permanent distortion occurs only in microscopic domains, say over only a few unit cells, it may be possible that the long-range order in TbPO_4 below T_N will be broken up, giving rise to the disordered line. Similarly, the Ho^{3+} ions in $\text{TbPO}_4:1\text{-at.}\% \text{ Ho}$ may break up the long-range order.

More work will be required in order to provide definitive interpretations for the features discussed in this section.

It would be worthwhile to attempt calculations to reproduce features of the TbPO_4 spectra. A tunneling model has been proposed to account for only the crystallographic phase transitions observed in DyVO_4 and TbVO_4 ,²⁵ but calculations for TbPO_4 might involve a generalization of this model to account for magnetic effects on the distortion behavior.

[†]Work partially supported by U. S. Army Research Office, Durham, N. C.

^{*}Work based in part on the thesis submitted by J. N. Lee in partial fulfillment of the requirements for the Ph. D. degree at The Johns Hopkins University (1971) (unpublished). Present address: Harry Diamond Laboratories, Washington, D. C. 20438.

¹J. C. Wright, H. W. Moos, J. H. Colwell, B. W. Mangum, and D. D. Thornton, *Phys. Rev. B* **3**, 843 (1971).

²A. H. Cooke, C. J. Ellis, K. A. Gehring, M. J. M. Leask, D. M. Martin, B. M. Wanklyn, M. R. Wells, and R. L. White, *Solid State Commun.* **8**, 689 (1970).

³J. C. Wright and H. W. Moos, *Phys. Rev. B* **4**, 163 (1971).

⁴B. W. Mangum, J. N. Lee, and H. W. Moos, *Phys. Rev. Letters* **27**, 1517 (1971).

⁵K. A. Gehring, A. P. Malozemoff, W. Staude, and R. N. Tyte, *Solid State Commun.* **9**, 511 (1971).

⁶L. A. Riseberg, E. Cohen, W. A. Nordland, and

L. G. Van Uitert, *Phys. Letters* **30A**, 4 (1969).

⁷S. Spooner, J. N. Lee, and H. W. Moos, *Solid State Commun.* **9**, 1143 (1971).

⁸R. S. Feigelson, *J. Am. Ceram. Soc.* **47**, 257 (1964).

⁹M. K. Carron, M. E. Mrose, and K. J. Murata, *Am. Mineralogist* **43**, 985 (1958).

¹⁰R. W. G. Wyckoff, *Crystal Structures*, 2nd ed. (Interscience, New York, 1965), Chap. VIII.

¹¹J. N. Lee, H. W. Moos, and B. W. Mangum, *Solid State Commun.* **9**, 1139 (1971).

¹²A. H. Cooke, K. A. Gehring, M. J. M. Leask, D. Smith, and J. H. M. Thornley, *Phys. Rev. Letters* **14**, 685 (1965); K. A. Gehring, M. J. M. Leask, and J. H. M. Thornley, *J. Phys. C* **2**, 484 (1969).

¹³C. J. Ellis, K. A. Gehring, M. J. M. Leask, and R. L. White, *J. Phys.* (to be published).

¹⁴R. P. Hudson and B. W. Mangum, *Phys. Letters* **36A**, 157 (1971).

¹⁵D. Kuse, *Z. Physik* **203**, 49 (1967).

¹⁶J. N. Lee, Ph.D. dissertation (Johns Hopkins University, 1971) (unpublished).

¹⁷George F. Koster, John O. Dimmock, Robert G. Wheeler, and Herman Statz, *Properties of the Thirty-Two Point Groups* (MIT Press, Cambridge, 1963).

¹⁸C. Brecher, H. Samelson, R. Riley, and A. Lempicki, *Phys. Rev.* **49**, 3303 (1968).

¹⁹G. S. Ofelt, *J. Chem. Phys.* **38**, 2171 (1963).

²⁰Gerhard H. Dieke, *Spectra and Energy Level of Rare Earth Ions in Crystals* (Interscience, New York, 1968).

²¹F. Keffer, in *Handbuch der Physik*, edited by H. P. J.

Wijn (Springer-Verlag, Berlin, 1966), Sec. 50.

²²H. Rohrer and H. Thomas, *J. Appl. Phys.* **40**, 1025 (1969).

²³R. S. Faulhaber and S. Hüfner, *Z. Physik* **228**, 235 (1969).

²⁴E. Belorizky, M. J. M. Leask, and K. J. Maxwell, *Colloq. Intern. Centre Natl. Rech. Sci. Les Elements de Terres Rares* **2**, 435 (1969).

²⁵E. Pytte and K. W. H. Stevens, *Phys. Rev. Letters* **27**, 862 (1971).

PHYSICAL REVIEW B

VOLUME 5, NUMBER 9

1 MAY 1972

Magnetic-Susceptibility, Optical-Absorption, and Crystal-Field Energies for $\text{SrCl}_2:\text{Yb}^{3+}$

Raymond W. Mires, Donald J. Arnold, and William K. Dean
Department of Physics, Texas Tech University, Lubbock, Texas 79409
 (Received 3 December 1971)

Magnetic-susceptibility measurements have been used to locate the low-lying crystal-field levels of $\text{SrCl}_2:\text{Yb}^{3+}$. The two upper levels arising from the crystal-field-split $^2F_{5/2}$ manifold were located by optical-absorption spectra. The five crystal-field levels were found to lie at 0, 155, 650, 10 193, and 10 612 cm^{-1} . A theoretical analysis showed that the magnetic-susceptibility, optical-absorption, and electron-spin-resonance data could not be correlated without the use of second-order crystal-field mixing. In spite of the reasonably good correlation among the three experiments, the analysis, which was based on an electrostatic model, did give some unexpected results for some of the more important physical quantities. This may indicate the importance of covalency and overlap in this crystal system similar to that already found for $\text{CaF}_2:\text{Tm}^{2+}$.

I. INTRODUCTION

The trivalent ytterbium ion has a $(4f)^{13}$ electron configuration which gives rise to a rather simple energy-level diagram when placed in a crystal field of cubic symmetry. In such a field the ground-spin-orbit manifold $^2F_{7/2}$ is split into the three levels Γ_7 , Γ_8 , Γ_6 , while the $^2F_{5/2}$ manifold is split into Γ_7 and Γ_8 levels which are of the order of 10 000 cm^{-1} above the other three. In lower-symmetry fields, only the two Γ_8 levels are split into two Kramers doublets. Only trivalent cerium and divalent thulium compare in simplicity with Yb^{3+} . It is not surprising that considerable work has been done already in understanding the optical and magnetic properties of this ion in several different host crystals.

A number of the garnets have been used as a host crystal for Yb^{3+} . In these, the previous research has included the measurement of magnetic susceptibility,¹ paramagnetic relaxation,² ferromagnetic resonance,³ and optical spectra.⁴⁻⁸ Similar studies have been made where Yb^{3+} has been incorporated into various scheelite lattices^{9,10} as well as some of the ethyl sulfates.¹¹ Also, YCl_3 ,¹² LuCl_3 ,¹² and ZnS ¹³ have been used as host

crystals for Yb^{3+} . However, in all of these crystals the ytterbium ion is always found in noncubic sites, resulting in anisotropic ground-state g factors and Kramers doublets for all of the crystal-field levels. When the alkaline-earth fluorides are used for host crystals, the Yb^{3+} ion has been found in cubic as well as noncubic sites. Again, considerable study has been made of the optical spectra,¹⁴⁻¹⁸ paramagnetic resonance,¹⁵⁻¹⁷ spin-lattice relaxation,^{19,20} and electron-nuclear double resonance (ENDOR) measurements.²¹ With one exception,¹⁶ the host crystals used in all of these studies were CaF_2 , SrF_2 , and BaF_2 , with CaF_2 receiving the most attention. In spite of all this work, Yb^{3+} in these host crystals is still not completely understood.

The crystal system which appears to hold the most for understanding Yb^{3+} in cubic sites is $\text{SrCl}_2:\text{Yb}^{3+}$. SrCl_2 has the fluorite structure but its lattice is about 28% larger than CaF_2 and 13% larger than BaF_2 , thus minimizing the effect of the various types of charge compensation mechanisms. In fact, Boatner, Reynolds, and Abraham²² have studied the electron spin resonance in this system and found that resonance lines arising from ions in lower-symmetry sites could