Spectroscopic Study of Magnetic Phenomena in $DyAsO_4$ and $DyVO_4$ †

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The magnetic properties of $DyAsO_4$ and $DyVO_4$ have been studied by high-resolution optical spectroscopy. The strength of the nearest-neighbor interaction in $DyAsO_4$ has been found from the observed line splittings. The spectral behavior in a magnetic field indicates that $DyAsO_4$ has the same magnetic properties previously observed in $DyVO_4$. In addition, an unexpected third phase is reported to exist in the transition region. The ordered magnetic structure is also determined from the high-field behavior.

INTRODUCTION

There has been a great deal of recent interest in the magnetic properties of the isostructural series: $DyPO_4$, $DyAsO_4$, and $DyVO_4$. $DyPO_4$ has been found to be a particularly simple example of an Ising antiferromagnet whose moments are constrained along the tetragonal axis.[1-3] The magnetic properties of $DyAsO_4$ and $DyVO_4$ are more complex, however. Spectroscopic measurements have shown that both of these crystals order magnetically and that their ground states are highly anisotropic.[4] In contrast to $DyPO_4$, the anisotropy constrains the moments to the plane perpendicular to the tetragonal axis. The difference in the anisotropy between $DyAsO_4$, $DyVO_4$, and $DyPO_4$ is caused by a reversal in the sign of the $A_2^0V_2^0$ term of the crystal field. The sign reversal results in two states having predominately $J_z = \pm\frac{1}{2}$ and $\pm\frac{3}{2}$ character, respectively, lying lowest in $DyVO_4$ and $DyAsO_4$ instead of the predominately $J_z = \pm\frac{15}{2}$ state in $DyPO_4$.[5] This sign change may be the result of small changes in the angles which the Dy-O bond axis makes with the tetragonal axis as one goes through the $DyPO_4$, $DyAsO_4$, $DyVO_4$ series.[6] Recently, spectroscopic and specific-heat measurements have shown that $DyVO_4$ undergoes a crystallographic phase transition at 13.8 K.[7,8] The distortion from tetragonal symmetry results in a mixing of the $J_z = \pm\frac{1}{2}$ and $J_z = \pm\frac{3}{2}$ states to produce the highly anisotropic ground state actually observed in $DyVO_4$. It is thought that the phase transition is induced by Jahn-Teller distortions which break the near degeneracy of the two low-lying states. In addition, magnetic-moment and magnetic-susceptibility measurements indicate that a metamagnetic "spin-flip" transition occurs at 2.1 kG and 0.5 K when a magnetic field is applied along the ordering direction in the basal plane.[7,8] It was also observed that the direction of distortion, and therefore the direction of magnetic moment, could be rotated by rotating the magnetic field in the basal plane since it is energetically more stable to have the large moment aligned with the field.

In this paper, we present new spectroscopic observations of $DyAsO_4$, $DyVO_4$, $YAsO_4$: 5% Dy, and YVO_4: 5% Dy. The spectrum of the dilute crystals clearly shows the existence of the two low-lying states needed for a Jahn-Teller distortion and the large magnetic anisotropy observed. The spectra of the concentrated salts in a field applied in the basal plane indicate that $DyAsO_4$ and $DyVO_4$ have almost identical magnetic properties. It is therefore expected that a crystallographic distortion also occurs in $DyAsO_4$. In addition, there appears to be an unexpected third magnetic phase that appears in the transition region of both crystals as one passes from the antiferromagnetic to the "spin-flip" phase by application of a magnetic field. The character of this third phase is not known but it is distinctly different from the "spin-flip" phase previously observed. It is also shown from the high-field and temperature spectrum that the ordering pattern in $DyVO_4$ is that favored by magnetic dipole interactions (see Fig. 1).

EXPERIMENTAL

The crystals used in this study were grown by a flux method developed by Feigelson.[9,10] The crystal structure is shown in Fig. 1.[11] The dimensions of the crystals were typically $4\times\frac{1}{2}\times\frac{1}{2}$ mm with the tetragonal axis lying in the long direction. Thus, fields applied perpendicular to the tetragonal axis resulted in very large demagnetizing effects. A given value of the magnetic field was always reached by lowering the field from a much higher value. The crystal was therefore forced by the high magnetic field into a single magnetic domain. The optical absorption spectra of the crystals were then recorded both photographically and photoelectrically at high resolution. The details of the measurements have been given elsewhere.[1]

OBSERVATIONS AND DISCUSSION

In rare-earth crystals having very anisotropic near-neighbor magnetic interactions, the different

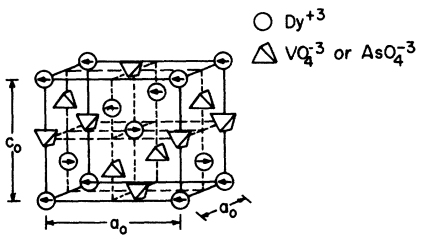

FIG. 1. Crystal structure of $DyAsO_4$ and $DyVO_4$. Arrows have been drawn to show the suggested spin structure (Ref. 13).

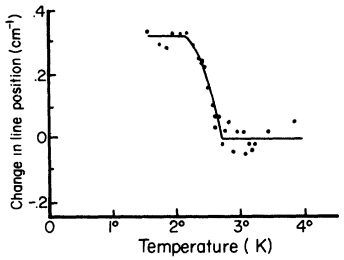

FIG. 2. Relative change in the zero-field line position of the antiferromagnetic line of the $DyAsO_4$ $Z_1 \rightarrow G_1$ transition in π polarization as a function of temperature.

possible configurations of a given ionic moment with respect to its nearest neighbors (nn) give rise to a set of evenly spaced lines in each electronic transition.[12] If the interaction between ions can be written as $\sum_{nn} J S_{0\alpha} S_{i\alpha}$ when all ions are in the ground state and as $\sum_{nn} J' S_{0\alpha} S_{i\alpha}$ when the ion 0 is in an excited state, the spacings between each of the evenly spaced lines is either $\frac{1}{2}(J+J')$ or $\frac{1}{2}|J-J'|$.[1] Since $DyAsO_4$ and $DyVO_4$ have four nearest neighbors, one would expect a series of five evenly spaced lines in the place of each electronic transition. In fact, only one transition in $DyAsO_4$ and $DyVO_4$ has a discernible five-line pattern; the remaining transitions are broad and without structure. The spacings between each of the five lines have been listed in Table I for those transitions with discernible five-line patterns. A value for J and J' could only be obtained for $DyAsO_4$ since the spacing corresponding to $\frac{1}{2}|J-J'|$ could not be seen in $DyVO_4$.

When these crystals order magnetically, there are two changes in the spectral lines. At the ordering temperature, there is a sudden increase in the intensity of the highest energy of the five lines which corresponds to the ordered configuration of an ion and its nearest neighbors. At low temperatures, this line is the only one which survives. Its increase in intensity was, in fact, used initially to measure the ordering temperatures of 2.5 K for $DyAsO_4$ and 3.0 K for $DyVO_4$.[4] The second change that occurs below the ordering temperature is a shift in the zero-field line position. It is caused by the additional longer-range interactions present in the ordered phase. The shift for $DyAsO_4$ is shown in Fig. 2. The shift for $DyVO_4$ was too small to measure.

The five-line pattern can also be observed at fields of ~ 20 kG and temperatures of ~ 15 K in $DyVO_4$. The strongest of the five lines under these conditions is the middle one. A slight increase in field leads to an additional increase in the middle line intensity and a decrease in the intensity of the other four lines. The middle line must therefore correspond to a ferromagnetic alignment of an ion and its four nearest neighbors. Since the middle line also corresponds to an ion whose Kramer's levels are not split, the interactions between an ion and two of its neighbors must be ferromagnetic while the interactions with the other two neighbors must be equal and antiferromagnetic. At zero field, such interactions would lead to the ordered state shown in Fig. 1. This ordered state has been confirmed by neutron-diffraction measurements.[13] It is the state which would be predicted on the basis of magnetic dipole interactions alone. However, if only magnetic dipole interactions were present, one would also expect to see a nine-line pattern since the magnetic dipole interactions are not equal in magnitude for all four neighbors. This large number of lines may, in fact, be responsible for some of the breadth of the lines observed. However, since five equally spaced (although poorly resolved) lines are observed, there must be an additional antiferromagnetic interaction present in addition to the magnetic dipole interactions which will tend to equalize the magnitudes of the four neighbors.

The most interesting and significant changes in the spectrum occur when a magnetic field is applied in the basal plane and the crystal is in the ordered state. The Z_1-F_1 transition of $DyAsO_4$ in π polarization is shown in Fig. 3 for a temperature of 1.5 K and various fields. The line present at zero field is the highest-energy line of the initial five lines.

TABLE I. Separation between each of five lines.

	π polarization	σ polarization	J	J'
$DyAsO_4$ $Z_1 \rightarrow G_1$	0.64 ± 0.10 cm^{-1}	1.60 ± 0.17 cm^{-1}	2.24 ± 0.27 cm^{-1}	0.96 ± 0.27 cm^{-1}
$DyVO_4$ $Z_1 \rightarrow F_1$	2.32 ± 0.12 cm^{-1}	2.32 ± 0.12 cm^{-1}	...	...

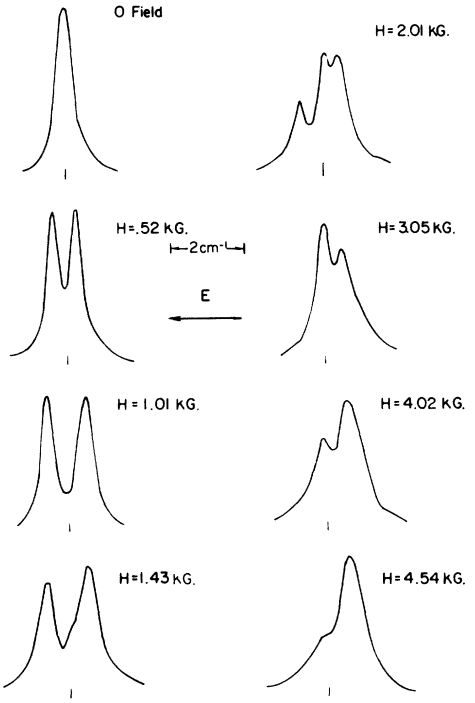

FIG. 3. Photoelectric traces of the $DyAsO_4$ $Z_1 \rightarrow F_1$ transition in π polarization for different magnetic fields. The crystal temperature is 1.5 K for all cases. The zero-field line position of the original line is indicated by the mark below each trace.

When a field is applied in the basal plane, this line splits linearly into two lines. The two lines correspond to ions whose moments point in opposite directions along the magnetic field. At 1 kOe, the lines stop shifting and the highest-energy line begins to disappear. Another line now begins to appear at the position of the original zero-field line. This new line reaches a maximum and then decreases in intensity as the lowest-energy line increases in intensity. No further movement in line position occurs until the newest line has vanished. The remaining low-energy line then moves linearly with field. The total intensity of all three lines does not change throughout this region indicating the transition probabilities are not affected by the field. The line positions in Fig. 3 have been plotted in Fig. 4. The Z_1-F_1 transition of $DyVO_4$ has exactly the same behavior, as shown in Fig. 5. The middle line in the transition region is much more difficult to observe for $DyVO_4$ because of the larger linewidths. The onset of the magnetic transition in $DyVO_4$ is observed at 2 kG (see Fig. 5) in agreement with magnetic moment measurements.[7] The unexpected feature is the existence of the middle line at intermediate fields. Bearing in mind that each line represents the energy of a single ion, two of the lines can be identified with a definite magnetic phase from the

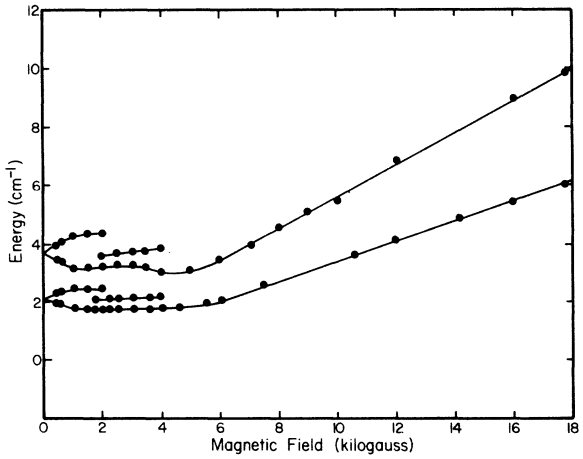

FIG. 4. Zeeman splitting of the $DyAsO_4$ $Z_1 \rightarrow F_1$ transition at 1.5 K.

behavior of the lines at high and low fields. The lowest-energy line persists at high fields and therefore must correspond to the "spin-flop" (or metamagnetic) phase. The simple Zeeman splitting at very low fields simply corresponds to the two possible directions of the moments in the initial antiferromagnetic state. The middle line cannot be associated with either of these two phases nor can it be assigned to a "spin-flop" phase since it does not transform continuously into the "spin-flip" phase (see Fig. 3). The nature of this third phase is not known at this time although it may be speculated that it corresponds to a more complex spin structure such as a distorted helix. Determination of the nature of this phase must probably await neutron-diffraction experiments.

Since the demagnetizing effects in these crystals are so large, the spectra of two additional $DyVO_4$ crystals were taken under the same conditions to

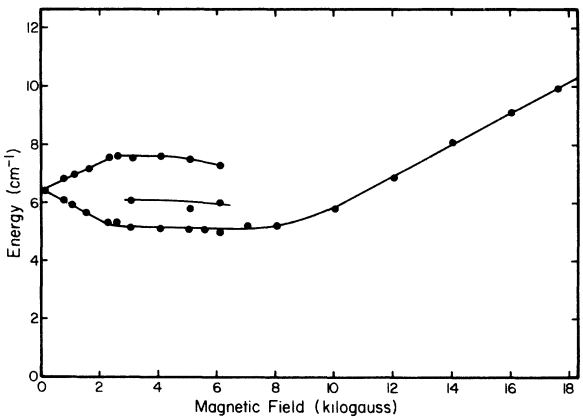

FIG. 5. Zeeman splitting of the $DyVO_4$ $Z_1 \rightarrow F_1$ transition in π polarization at 1.5 K.

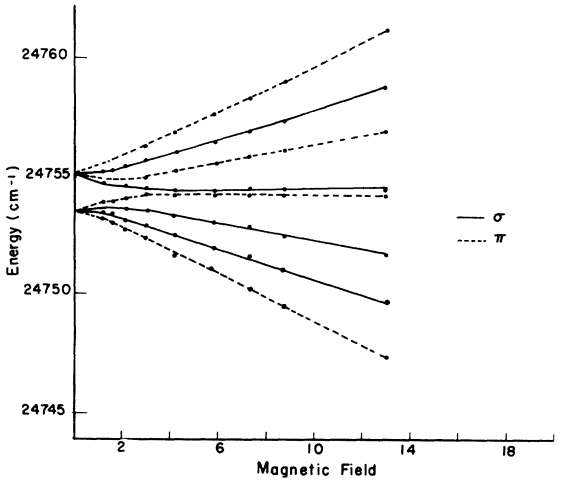

FIG. 6. Zeeman splitting of the $YAsO_4$:5% Dy Z_1 and $Z_2 \rightarrow D_2$ transitions.

determine the effect of shape. The dimensions of the three crystals used were $4\times1\times1$, $4\times0.5\times0.25$, and $0.5\times0.5\times0.25$ mm and all were in the shape of rectangular parallelepipeds. Despite such differences in shape, the spectra of all three crystals were almost identical differing only slightly in line shape at the higher field values (5.7kG). Although one cannot calculate demagnetizing factors for crystals of this shape, it is quite surprising that no large changes occurred in the spectra of crystals with such different sizes.

The large slopes in Figs. 4 and 5 cannot be explained in terms of a single isolated Kramer's level in a tetragonal crystal. For this reason, dilute crystals of $YAsO_4$:Dy and YVO_4:Dy were grown to determine the character of these levels. The spectrum of $YAsO_4$:Dy showed, in fact, two levels separated by only 1.5 ± 0.2 cm^{-1}. The levels mixed very strongly in a perpendicular field to give the same large Zeeman slopes observed in $DyAsO_4$. The behavior in a perpendicular field is shown in Fig. 6. The large slope is only possible if one of the levels contained a large admixture of $J_z=\pm\frac{1}{2}$ and the other a large admixture of $J_z=\pm\frac{3}{2}$. Two levels were also observed in YVO_4:Dy, which were separated by only 5.13 ± 0.1 cm^{-1}. These levels also mixed strongly in a perpendicular field. In pure $DyVO_4$, the levels are mixed with each other by the crystallographic distortions instead of a magnetic field to give the large magnetic moments observed. Since we have found $DyAsO_4$ has an equally large moment at low fields, there must also be a distortion in this crystal. It is interesting to note that the same large Zeeman splittings at very low fields were not observed in the dilute salt, which indicates the same crystallographic distortion is not present in the dilute crystal at low temperatures. This suggests that the distortion is a property of only the concentrated salts and may possibly be the result of the magnetic interactions. Although magnetic interactions are very weak for the rare earths, the crystal field splittings in the XPO_4, $XAsO_4$, XVO_4 series (where X is a rare earth) seem particularly sensitive to small changes in ion position.[6,14] It may therefore be possible to change the magnetic properties by small external strains or applied electric fields.

It has become evident that there are many interesting properties of $DyAsO_4$ and $DyVO_4$ which are yet to be understood. It has been established that a crystallographic phase transition occurs[7] which profoundly affects the magnetic properties by mixing the two low-lying crystal field states. The nature of the field-induced magnetic transition is still not understood. The existence of the middle line in the transition region is not consistent with a simple "spin-flip" phase transition since the line disappears at high fields. Further experiments by other techniques must be performed to determine the origin of this line.

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