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SPECTROSCOPIC PROPERTIES OF DYSPROSIIUM VANADATE

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Résumé. — Le vanadate de dysprosium subit vers 14 °K un changement de phase d'une symétrie tétragonale à une symétrie inférieure, très probablement orthorhombique. On pense que cette distorsion est causée par le dédoublement Jahn Teller d'une paire de doublets dégénérés de base énergie du Dy^{3+}. La direction de cette distorsion est liée à l'orientation du tenseur g et peut être influencée par l'application d'un champ magnétique. Dans sa phase orthorhombique DyVO_4 est ordonné antiferromagnétiquement avec une température de Néel égale à 3 °K. Les moments sont alignés dans le plan de base.

Abstract. — Absorption spectra of Dy^{3+} in DyVO_4 yield evidence that this material undergoes a crystallographic phase transition near 14 °K and a magnetic phase transition near 3 °K. The former is believed to be due to a Jahn Teller type of distortion which removes an accidental degeneracy in the Dy^{3+} ground state. At 4.2 °K and below the effects associated with the magnetic transition have been studied in detail. Zeeman spectra in high fields show the ground state to be anisotropic, with g_a = 19, g_b < 1, g_c ≈ 0.5 (a and b correspond to the original a, a' of the tetragonal cell).

Introduction. — As has been briefly reported elsewhere [1] Dysprosium Vanadate, DyVO_4, is a unique material in many respects. At high temperatures it has a tetragonal structure (space group D_{4h} = 14/mmm) in which each Dy^{3+} ion has four neighbouring Dy^{3+} ions.

Visual observation of an a-b plane crystal (***) of DyVO_4 at 4.2 °K using crossed polaroids revealed domain-like regions. This was interpreted as a crystallographic distortion to a lower symmetry, the direction of the distortion being different in neighbouring domains. A large anomaly in the heat capacity gave the distortion temperature as T_D = 13.8 °K.

The size and shape of the domains at 4.2 °K could be changed by the application of a magnetic field. Optical absorption lines shifted by 13-21 cm^{-1} between 20.4 and 4.2 °K, and an absorption line was observed in the far infra-red at 27.5 cm^{-1}. These observations suggested that the distortion is of the Jahn Teller type. Figure I shows the proposed system, where for T > T_D, the ground state is a quartet and for T < T_D this splits into two Kramers' doublets.

Heat capacity and magnetic moment measurements below 4.2 °K showed the existence of an antiferromagnetic transition at T_N = 3.0 °K. The ground state of the Dy^{3+} ion (T < T_D) is Ising-like with g_a = 19, g_b < 1, and g_c = 0.5. In the ordered state the moments lie along the a-axis and there is a spin flip transition to a ferromagnetic state at H = 2.1 kOe (T < T_D).

Both the magnetic moment experiments and the optical experiments confirmed that for T < T_D this material in an external magnetic field finds it energetically favourable to interchange the a and b axes so as to ensure that the large g value remains as nearly parallel to the field as possible. This magnetic polarisation makes it difficult to perform any experiment with H along the b axis.

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(**) We adhere to the previous convention [1] with crystal directions a, b and c corresponding approximately to the original a, a' and c axes of the tetragonal (high temperature) form.

![Fig. 1. — Energy level diagram for Dy^{3+} in DyVO_4 showing effects of crystallographic distortion and magnetic order. T_D = 14 °K and T_N = 3.0 °K.](image)

Further experiments. — I. TEMPERATURE VARIATION OF OPTICAL SPECTRA. — Spectra have been recorded between 20.4 and 9 °K. With decreasing temperature, line splitting begins around 14 °K and increases to ~ 24 cm^{-1} by 10 °K. This is a direct observation of the Jahn Teller splitting.

II. FAR INFRA-RED SPECTRA. — At 4.2 °K the absorption line at 27.5 ± 0.5 cm^{-1} has a full width at...
half height of 7 cm\(^{-1}\). At 1.5 K the line shifts to 30.1 \(\pm 0.1\) cm\(^{-1}\) with a width of 2 cm\(^{-1}\). This puts a lower limit of 5 cm\(^{-1}\) on the ground state splitting of the antiferromagnetic state. The application of a magnetic field yielded for the ground state

\[ g_a = 20.5 \pm 1.5, \]

\[ g_e \leq 0.5, \] and for the 30 cm\(^{-1}\) state \( g_a \leq 2, \) \( g_e \leq 2. \)

III. Optical Zeeman Spectra at 20.4 \,K. — At 20.4 \,K. the application of a large magnetic field \((H > 50 \,kOe)\) yields a Zeeman pattern all components of which can be observed. The centre of gravity of this pattern moves to higher energy with increasing field, indicating that the field continuously induces the crystallographic distortion even though \( T > T_D. \)

IV. Zeeman Spectra at 1.4 \,K, Polarised Crystal. — Zeeman spectra with the field along the ordering direction displayed splitting appropriate to the \( g = 19 \) ground state. Zeeman spectra were also obtained with the field perpendicular to the ordering direction by using the following trick. The crystal was magnetically polarised by a large field along the c-axis and the field was then reduced to zero. The crystal was rotated through 90° about the c-axis and spectra were recorded rapidly in fields up to 4 kOe. It was possible to obtain spectra showing that \( g_e \leq 1 \) and in which no \( g = 19 \) behaviour was seen. There is thus a direction in the a-b plane which is perpendicular to all Dy\(^{3+}\) moments simultaneously and this precludes some complex systems of magnetic order.

V. Line Structure for \( T < T_D \) and \( H = 0. \) — One line in the optical absorption spectrum shows a well defined structure. For \( \sim 0.5 \,T_D < T < T_D \) this line (ground state to \(^4\text{F}_{9/2}\)) is split into five equally spaced components, the relative intensities of which are strongly temperature dependent. Other workers [2] have interpreted similar structure in terms of nearest neighbour dominated magnetic interactions, where the discrete lines are due to distinct internal field values arising from particular nearest neighbour magnetic configurations. We make the same interpretation here. In DyVO\(_4\) the intensities also vary from sample to sample and with different mounting of the same sample. This is attributed to strain of the magnetoelastic DyVO\(_4\). The positions of the lines were, however, accurately reproducible and the total splitting of the five components was 9.2 cm\(^{-1}\) at 4.2 K and 8.5 cm\(^{-1}\) at 1.4 K. The smaller splitting for \( T < T_N \) is due to contributions from the distant, ordered magnetic ions. We identify the 8.5 cm\(^{-1}\) splitting as the ground state splitting (and note that all other lines have a width \( \geq 8.5 \,cm^{-1}\)).

Our earlier calculation [1] which was based on the value of the spin flip field and assumed the simplest two sublattice antiferromagnetic structure with all four neighbours anti-parallel gave a total (dipole plus exchange) internal field of 4.1 kOe. This produces a splitting of only 3.6 cm\(^{-1}\). There is however an alternative antiferromagnetic structure [3] consisting of ferromagnetic sheets in the a-c plane, which is energetically more favourable in that the dipole field is much greater, \( \approx 7 \,kOe \). Analysis of the spin flip field data on this basis gives an exchange field of 1.4 kOe, making a total internal field of 8.3 kOe. This produces a splitting of 7.4 cm\(^{-1}\), in much better agreement with experiment. With these interactions alone, all n. n. ions interact equally with a given origin ion, a necessary requirement for a five line pattern. One might hope to be able to confirm the interaction constants by extrapolation of the high field Zeeman pattern [4]. In this material this gives results which are internally inconsistent (from line to line). This could be due to further crystallographic distortion in fields above the spin flip field. Confirmation of the magnetic structure proposed here must, therefore, await the results of neutron diffraction experiments.

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