MAGNETIC AND THERMAL PROPERTIES OF DYSPROSIUM VANADATE
A. Cooke, D. Martin, M. Wells

To cite this version:

HAL Id: jpa-00213981
https://hal.archives-ouvertes.fr/jpa-00213981
Submitted on 1 Jan 1971

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
MAGNETIC AND THERMAL PROPERTIES OF DYSPROSIUM VANADATE

A. H. COOKE, D. M. MARTIN and M. R. WELLS
Clarendon Laboratory, Parks Road, Oxford, England

Résumé. — Le vanadate de dysprosium est ordonné d'une façon antiferromagnétique avec une température de Néel égale à 3.05 °K. On a étudié l'état antiferromagnétique par des mesures de la susceptibilité et de l'aimantation. On discute les couplages d'échange entre les ions Dy\(^{3+}\), et la structure antiferromagnétique.

Abstract. — Dysprosium vanadate orders antiferromagnetically with a Néel point of 3.05 °K. The antiferromagnetic state has been investigated by magnetic moment and magnetic susceptibility measurements. The exchange interactions and possible ordering patterns of the Dy\(^{3+}\) ions are discussed.

The rare earth vanadates, RVO\(_4\) crystallize in a tetragonal zircon structure, space group I4\(_1\)/amd, in which the rare earth configuration is well described by a four nearest-neighbour diamond-like array. We have investigated the magnetic properties of several members of the series. GdVO\(_4\) behaves as a simple two-sublattice antiferromagnet, ordering along the tetragonal c-axis at 2.5 °K [1]. Preliminary work on TbVO\(_4\) and ErVO\(_4\) indicates that these order antiferromagnetically below 1 °K. HoVO\(_4\) displays a temperature-independent susceptibility below 4.2 °K. As already briefly reported by Cooke et al. [2], DyVO\(_4\) orders antiferromagnetically at 3.0 °K with the ordering axis in the basal plane a-a' of the tetragonal cell. Ordering in this plane is permitted only if the compound has undergone a crystallographic distortion to a symmetry lower than that of the room temperature structure. Optical and spectroscopic observations on a single crystal cooled to 4.2 °K confirmed the change of symmetry, and specific heat measurements showed an anomaly at 14.0 °K attributed to the crystallographic transition as well as a lambda-anomaly at 3.07 °K, the Néel point. Further spectroscopic work which has since been reported by Ellis et al. [3] supports the view that the structural distortion is of the Jahn-Teller type, associated with a splitting of a quartet state of the Dy\(^{3+}\) ions into two Kramers doublets.

In this paper we discuss the exchange and magnetic dipole interactions between the Dy\(^{3+}\) ions, and the possible patterns of ordering. Without detailed X-ray analysis on a crystal cooled to liquid helium temperatures, we are unable to ascertain the low temperature structure, but we shall assume that it is orthorhombic, since all the results can be indexed within this framework, and when we refer to the [010], [001] and [001] axes of the crystal, these correspond to the a, a' and c axes of the original tetragonal cell. We have made magnetic moment and magnetic susceptibility measurements on single crystal specimens at temperatures below 4.2 °K. At these temperatures we may assume that only the ground doublet state of the Dy\(^{3+}\) ion is appreciably populated, since the splitting between this state and the excited doublet is estimated to be 27 cm\(^{-1}\) [2]. Measurements have been made in fields applied along the [001] axis, and in fields applied along directions in the basal plane perpendicular to this axis. For fields applied along the [001] axis, the magnetic susceptibility is small and almost independent of temperature, corresponding to a g-value < 1. Although the crystalline distortion in the basal plane must be quite small, the magnetic properties in this plane are extremely anisotropic, with one principal g-value much higher than the other. Measurements on a crystal whose axes had been determined by X-ray measurements at room temperature showed that the axis of high g-value could be either the [001] or the [010] axis. As already reported [2], this anisotropy is likely to be obscured in measurements of bulk magnetic properties, since a crystal cooled below the transition temperature in zero magnetic field is found to be divided into domain-like regions having different magnetic axes. By applying a sufficiently high magnetic field along say the [010] axis, the crystal can be converted into a single domain, with all the ions having their high g-value along this axis.

Our estimates of the principal g-value in the basal plane are based on magnetic moment measurements on a single crystal in fields up to 25 kOe at 0.5 °K, at which temperature the system may be considered to be fully ordered into sublattices. By applying the maximum field along the [010] direction the crystal was converted into a single domain, and magnetic moment measurements were made as the field was increased to zero. A metamagnetic \textit{spin-flip} transition was observed at a critical field \(H_c = 2.1\ kOe\). At this field the magnetic moment changed abruptly from a very small value in low fields to a saturation moment \(M_s = 52,700\ \text{e. m. u. per mole, corresponding to a g-value of 18.9.}\) Since the maximum possible g-value for a doublet belonging to the \(6\Sigma_{15/2}\) state of the Dy\(^{3+}\) ion is 20, corresponding to \(J = \pm 15/2,\ g_z = 4/3\), the g-values perpendicular to the magnetic axis can be expected to be small, so that the assembly of Dy\(^{3+}\) ions will behave as an Ising-like system. It is difficult to make magnetic measurements in the basal plane in fields perpendicular to the magnetic axis, since application of a field tends to switch this axis to the direction of the field. We therefore made another moment measurement with field along the [100] direction. For an Ising system with magnetic moments confined to the [010] direction, one would expect a metamagnetic transition at a field of \(\sqrt{2} H_s\) to a saturation moment of \(M_s/\sqrt{2}\), and this was observed.

Figure 1 shows two possible patterns of ordering for the Dy\(^{3+}\) ions, based on the assumption that the magnetic and crystalline unit cells are the same, Pattern I, in which all nearest neighbours are antiparallel, is favoured if antiferromagnetic exchange
between nearest neighbours is dominant. Pattern II is favoured if magnetic dipole interaction predominates, since in this pattern the magnetic dipole field at an ion is 6.85 kOe in the favourable direction, while in pattern I it is 1.03 kOe in the unfavourable direction.

From this we find that the exchange field at ion 1 due to ions of types 2 and 4 is 1.43 kOe. Since ions 1 and 4 are not nearest neighbours, it is plausible to attribute the whole of this exchange field to the two ions of type 2. If we write the interaction energy between two ions i and j as $W_{ij} = -2J_{ij}S_i S_j$, this gives an exchange constant $J_{12}/k = -0.91$. If the ordering is of type II, the spin-flip field gives no information as to the exchange interaction between ions 1 and 3, since their relative orientation is unaltered by the flip. (There is no reason to expect that it is the same as between ions 1 and 2.) We can however put an upper limit on it, since strong antiferromagnetic exchange between ions 1 and 3 would make pattern II unstable; this limit is 3.94 kOe, corresponding to $J_{13}/k = -2.5^\circ$. A further estimate can be made as follows: From the total energy change associated with the specific heat anomaly at 3.0 K due to the antiferromagnetic transition, we estimate that at absolute zero each sublattice is subject to an effective field of 8.0 kOe. Under pattern II ordering, magnetic dipole interaction accounts for 6.85 kOe, leaving an exchange field of 1.15 kOe. Since we estimate that the exchange field at ion 1 due to the type 2 ions is 1.43 kOe, this suggests that the exchange field due to the type 3 ions is small, of the order of 0.3 kOe. No great weight can be placed on this figure however, since it is reached as the difference of much larger quantities.

Our measurements do not suffice to decide between the two patterns of ordering. Neutron diffraction work should readily settle the question.

References

