TUNNELING EFFECT AND MAGNETIC-CRYSTALLOGRAPHIC TRANSITION IN Tb_2O_2S

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Neutron experiments on a single crystal of Tb_2O_2S are reported. Below $T_N = 6$ K a collinear antiferromagnetic ordering takes place and induces a crystallographic distortion. This distortion and the moment orientation relative to the c axis are explained using a crystal field band model.

1. Introduction

Among the rare earth oxysulfides extensively studied in our laboratory, Tb_2O_2S exhibits a particular magnetic behaviour [1]. The high magnetic anisotropy in this uniaxial compound seems inconsistent with the fact that about the same high field moment values are observed along the three crystallographic axes. This unusual property arises because the easy magnetization axis makes an angle with the c axis, as shown by neutron experiments on a powder sample [2]. However, these experiments do not permit us to determine the moment direction unambiguously. To answer this question neutron measurements on a single crystal have been made; they have shown that Tb_2O_2S undergoes changes in crystal structure at the magnetic ordering. This behaviour will be interpreted on the basis of a crystal field band model according to Trammell's theory [3].

2. Experimental

Single crystals were grown by melting the powder at 2500°C and cooling down slowly in a tungsten crucible. A spherical-shaped single crystal of 2 mm in diameter was used for the neutron experiments which were carried out with a double-axis spectrometer operating in the Siloe reactor.

3. Results

The terbium oxysulfide crystallizes in the space group $P\bar{3}m$, the hexagonal unit cell contains one formula unit. Tb^{3+} ions are located at a site of C_{3v} symmetry; the three-fold axis is parallel to the c axis, the three mirror planes are defined by the three orthohexagonal axes (b_1, b_2, b_3) and the c axis (fig. 1). Below T_N a collinear antiferromagnetic order develops in this compound. The orthorhombic magnetic cell is related to the hexagonal cell by the following relationship: $a_M = a$, $b_M = a\sqrt{3}$ and $c_M = 2c$ (fig. 1). There exist then three K domains noted by K_1 (a_1, b_1), K_2 (a_2, b_2) and K_3 (a_3, b_3). The scattering vectors are all indexed on the orthohexagonal cell $(a, b = a\sqrt{3}, c)$.

Moreover, as the A.F. direction makes an angle θ with the c axis each K domain gives rise to two S domains. So there exist six magnetic domains: K_1S_1, K_1S_2, etc. The magnetic and nuclear peak profiles given in fig. 2 have been measured using an ω-scan procedure with the vertically oriented c axis. The magnetic peaks of a K domain are split into two peaks except the $(h0\frac{1}{2}l)$ reflections. It must be noted that for $(hk\frac{1}{2}l)$

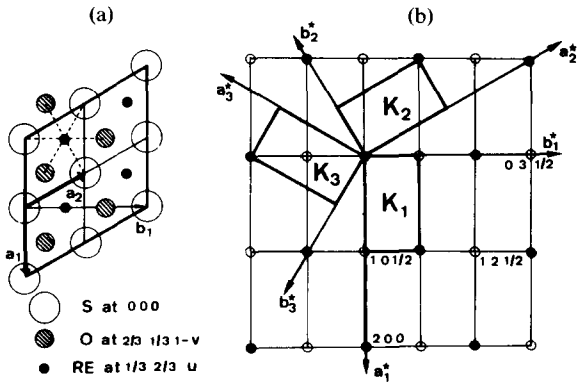

Fig. 1. (a) Projection of the Tb_2O_2S crystallographic structure in the basal plane. Dashed lines represent the three mirror planes. (b) K domains and the orthohexagonal reciprocal lattice: nuclear (●) and magnetic (○) peaks of K_1 domain are represented.

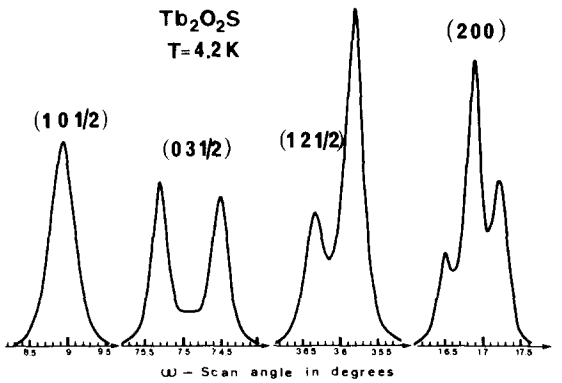

Fig. 2. Profiles of the (2 0 0) nuclear peak and (1 0 $\frac{1}{2}$), (0 3 $\frac{1}{2}$), (1 2 $\frac{1}{2}$) magnetic peaks associated with the K_1 domain at $T = 4.2$ K.

reflections the two peaks do not have the same intensity. These two peaks are associated with the two S domains, they indicate that the magnetic cell is no longer orthorhombic but triclinic. Then the nuclear peaks must give rise to six components though some are superimposed so that only three peaks are observed (fig. 2). Using the observed peak profiles we can deduce that the distortion consists of a basal plane structural change, i.e. the angle between a and b axes decreases by 0.38 degree as well as the ratio b/a from $\sqrt{3}$ to $1.725_5 \pm 0.001$. The thermal variation of the (10$\frac{1}{2}$) reflection intensity (fig. 3) indicates

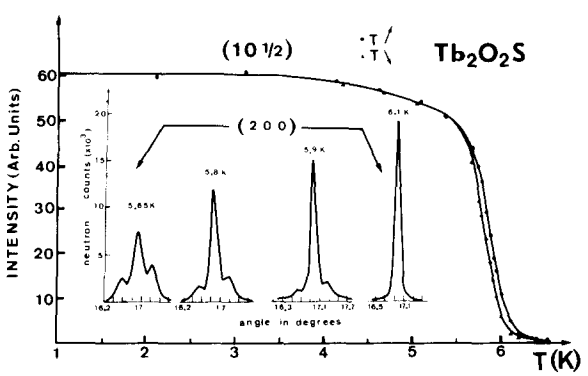

Fig. 3. The thermal variation of the (1 0 $\frac{1}{2}$) intensity and the (2 0 0) nuclear peak splitting at different temperatures.

that the magnetic ordering takes place at $T_N = 6$ K. The abrupt decrease of the intensity and its hysteresis give evidence for a first order transition which is also illustrated by the thermal variation of the (2 0 0) nuclear peak profile (fig. 3). The position of the split peaks is temperature independent while the intensities rise with decreasing temperature indicating a broadening of the transition.

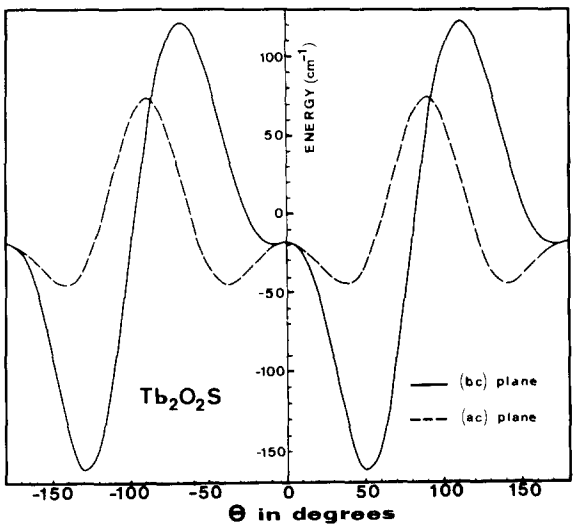

Fig. 4. The angular dependence of the classical CEF potential in (a, c) and (b, c) planes.

To determine the magnetic structure, more than 100 magnetic integrated intensities corresponding to the three K domains have been collected. A program refinement of the structure based on these observations, and especially taking into account the intensity ratio of the S_1 and S_2 domain contributions, have permitted the magnetic structure to be determined unambiguously. It consists of a collinear antiferromagnetic arrangement. Within a given K domain (K_1) the easy A.F. direction lies in the (b_2, c) plane for the K_1S_1 domain and in the (b_3, c) plane for the K_1S_2, the angle with the c axis is $47 \pm 2°$ and the moment value is $7.2 \pm 0.2\ \mu_B$ at $T = 4.2$ K. This structure is consistent with that determined by powder experiments though the moment direction is in an appropriate (b, c) plane and not in an (a, c) plane. This unusual moment direction originates from crystal field effects as will be discussed.

4. Interpretation by a crystal field band model

Using first-order perturbation theory, the crystal electric field (CEF) hamiltonian H_c for a C_{3v} symmetry can be written in terms of Stevens operators as follows:

$$H_c = \alpha V_2^0 O_2^0 + \beta (V_4^0 O_4^0 + V_4^3 O_4^3) + \gamma (V_6^0 O_6^0 + V_6^3 O_6^3 + V_6^6 O_6^6).$$

The multiplet ground state $J = 6$ of Tb^{3+} is split into nine levels (5 singlets and 4 doublets) for such a symmetry. Inspection of the level energies, determined by optical experiments, shows four closely spaced low lying levels (2 singlets and 2 doublets) defining a six-fold CEF band with a large separation from the next levels (0, 6, 15, 26, 110, ... cm^{-1}). The fitted CEF parameter values are (in cm^{-1}) [4]:

$$V_2^0 = 101, \quad V_4^0 = 50, \quad V_4^3 = -2560,$$
$$V_6^0 = 10, \quad V_6^3 = 265, \quad V_6^6 = 232.$$

According to Trammell's theory [3] this CEF band can be accounted for by a semiclassical calculation. The angular momentum $\boldsymbol{J}$ is considered as a classical vector pointing in a direction $\boldsymbol{u}$ and precessing around the bottoms of the classical CEF potential. Using the above CEF parameters, the calculated potentials are plotted in fig. 4 for (a, c) and (b, c) planes. Two energy minima are found in one (b, c) plane, they correspond to two opposite directions making an angle of 50° with the c axis. The ternary symmetry leads then to six minima where the classical moment will lie defining therefore a six-fold CEF band composed of 2 doublets and 2 singlets as determined by optical measurements. However, this cannot be the correct quantum-mechanical description because of tunnelling between the six potential wells which splits the CEF band. To calculate quantitatively this splitting a CEF calculation has been done in the subspace spanned by the six states $|J, u_i\rangle$ such as

$$\boldsymbol{J} \cdot \boldsymbol{u}_i |J, u_i\rangle = J|J, u_i\rangle,$$

where $\boldsymbol{u}_i$ is defined by the polar coordinates θ_i and ϕ_i. As these states are not orthogonal H_c must be replaced by $H' = S^{-1/2} H_c S^{-1/2}$ to calculate the CEF band splitting. The matrix elements $S_{ki} = \langle J, u_k | J, u_i \rangle$ represent the overlaps between the two states. For a given CEF parameter set, the tunneling effect splitting depends only on the angle θ between $\boldsymbol{u}$ and the c axis. The value $\theta = 45°$ together with the above CEF parameters give a good agreement between the calculated (0, 6, 11.5, 32 cm^{-1}) and the observed (0, 6, 15, 26 cm^{-1}) splittings.

This calculation shows that the ground state of a Tb^{3+} ion in Tb_2O_2S corresponds to an angular momentum taking only six directions in (b, c) planes and making an angle of about 45° with the c axis. At high temperature, $\boldsymbol{J}$ tunnels between the six minima whereas at the ordering temperature the moment lies along one direction. Thus the energy of the corresponding minimum is lowered from which may result in a crystallographic distortion. The six minima are related to the six antiferromagnetic domains. A more detailed analysis will be published elsewhere.

References

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