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Specific heat and magnetic ordering of ErBi studied with crystal-field theory in the mean-field approach

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ABSTRACT

The low-temperature specific heat of ErBi is evaluated quantitatively with crystal-field (CF) theory in the mean-field approach by using a set of crystal-field parameters (CFPs) proposed by previous authors. The calculated temperature dependence of the heat capacity exhibits a sharp peak at the magnetic-transition temperature, and shows good agreement with the experimental results over the whole temperature region. To further investigate the mechanism of the magnetic ordering of the material, we have calculated the spontaneous magnetization for the case that only the ground-state CF level is considered and also for the case that the two lowest CF levels are considered, to compare with the results obtained with the full set of CF states of the $J=\frac{15}{2}$ multiplet. The results suggest that the two lowest CF levels play a dominant role in the magnetic ordering below T_N.

1. Introduction

ErBi crystallizes in fcc NaCl-type structure. The temperature dependence of the specific heat of this material exhibits two distinct anomalies: a sharp peak below 4 K due to the transition between the high-temperature paramagnetic state and the antiferromagnetism at low temperatures, and a broad peak around 15 K, which is a Schottky contribution attributed to the crystal-field (CF) splitting [1]. To study the CF effects quantitatively, Wada et al. [1] calculated the magnetic specific heat of ErBi in *paramagnetic* phase with the cubic CF Hamiltonian [2]

$$\mathscr{H}_{\mathrm{CF}} = w\left(\frac{x}{F(4)}O_4 + \frac{(1-|x|)}{F(6)}O_6\right). \quad (1)$$

Two pairs of w and x were found to allow reproducing the Schottky specific heat of the material above T_N, and solutions yield the $\Gamma_8^{(3)}$ quartet as the ground-state CF level.

In this paper, we re-evaluated the magnetic specific heat of ErBi in the whole low temperature range with the two pairs of the CFPs, and found that only one pair, namely $w=-0.14$ K and $x=0.55$, reproduces the experimental results below T_N. In order to understand the mechanism of the antiferromagnetic ordering below T_N, we computed the magnetization of ErBi with the ground-state CF level, with the two lowest CF levels, and also with the full set of CF levels of $J=\frac{15}{2}$ multiplet respectively to make a comparison. The calculated results suggest that the magnetic phenomena in ErBi are governed by the two lowest CF levels in low temperature region.

2. Theoretical model and computational results

In rare-earth materials, the localized 4f electrons are subjected to CF interactions, and the spins of neighboring rare-earth ions are coupled by exchange interaction (RKKY type mediated by conduction electrons and other indirect exchange interactions mediated by valence electrons—in ErBi by 5d electrons of Er and 6p electrons of Bi), which gives rise to magnetic ordering below a magnetic-transition temperature T_{M}. Therefore, to describe the magnetic and thermodynamic properties of a rare-earth magnet below T_{M}, the exchange interaction must be included in the Hamiltonian [3–5]. Otherwise, no magnetic ordering occurs and the sharp peak at T_{M} in the specific heat curve cannot be reproduced theoretically [6,7].

ErBi orders antiferromagnetically below $T_N=3.8$ K. However, its macroscopic properties, such as specific heat, susceptibility and magnetization in a sufficiently high external field, can be described rather nicely with a ferromagnetic-like model since the magnetic moments of the material align collinearly below T_N. The validity of this approach has been justified and explained in detail

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in our previous article [8]. In the mean-field approximation, the Hamiltonian of the system can be rewritten as

$$\mathscr{H} = w\left(\frac{x}{F(4)}O_4 + \frac{(1-|x|)}{F(6)}O_6\right) - \mathscr{J}\vec{J}\cdot\langle\vec{J}\rangle + \frac{1}{2}\mathscr{J}\langle\vec{J}\rangle^2, \quad (2)$$

where the second term represents the exchange interaction between neighboring rare-earth magnetic ions, and the last one is a correction for the double counting of the ion-pairs. The exchange-coupling parameter $\mathscr{J}$ can be determined by fitting T_N of the magnet in computations.

In a simple antiferromagnet, two neighboring magnetic moments align in opposite directions below T_N. In the single-ion ferromagnetic-like Hamiltonian, it is the thermally averaged total angular momentum $\langle\vec{J}\rangle$ of the considered ion that is evaluated in the computing process. To denote the corresponding value of a neighboring ion, a negative sign has to be added. Additionally, $\mathscr{J}$ should be negative for an antiferromagnetic system to have lower energy. Thus, if the calculated $\langle\vec{J}\rangle$ is fed to the code to represent the corresponding value of the neighboring ion, $\mathscr{J}$ becomes positive as seen below.

ErBi crystallizes in a cubic structure, the exchange coupling constant $\mathscr{J}$ should be isotropic as assumed in Eq. (2), so that the last two terms of the Hamiltonian can be expanded as

$$\mathscr{H}_{EX} = -\frac{\mathscr{J}}{2}(J_+\langle J_-\rangle + J_-\langle J_+\rangle - \langle J_+\rangle\langle J_-\rangle - \langle J_z\rangle^2) - \mathscr{J}J_z\langle J_z\rangle. \quad (3)$$

With this special form we are able to evaluate $\langle J_z\rangle$, $\langle J_+\rangle$ and $\langle J_-\rangle$ simultaneously, so as to determine the orientation of the magnetic moment in low-temperature region as explained below. Firstly, the CFPs, $w = -0.14$ K and $x = 0.55$, were used to calculate the specific heat and magnetization of ErBi numerically, in which the exchange parameter $\mathscr{J}$ was determined to be 0.215 K by fitting the magnetic-transition temperature $T_N = 3.8$ K. As shown in Fig. 1, the broad Schottky-type peak in the paramagnetic range due to the CF splitting, and the sharp peak just below T_N attributed to the antiferromagnetic transition, are all nicely reproduced with the above model, showing good agreement with the experimental results. In the whole temperature range, our calculations always gave $\langle J_+\rangle = \langle J_-\rangle = 0$ in the absence of the external field, meaning that the system orders spontaneously along the quantized z-direction below T_N. The calculations do not reproduce the small peak below 3 K in the specific heat curve. This indicates that other

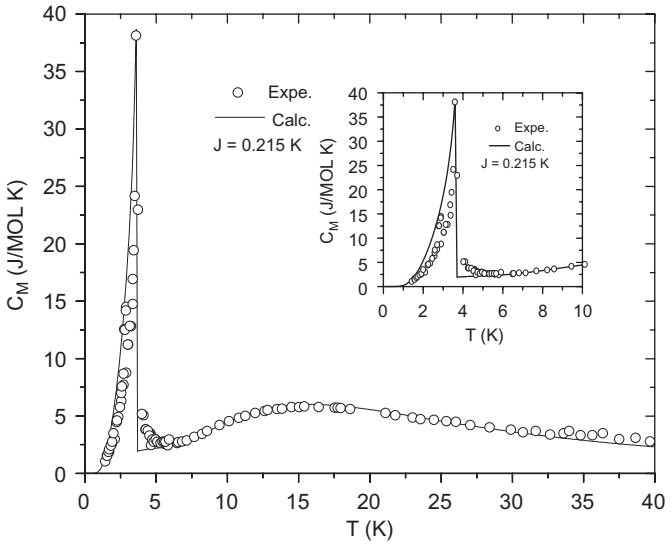

Fig. 1. Magnetic specific heat of ErBi calculated with $w = -0.14, x = 0.55$ K and $\mathscr{J} = 0.215$ K in comparison with experimental results.

mechanisms, such as the magneto-elastic effect and quadrupolar interaction, which usually exist in materials containing heavy rare-earth elements, may have appreciable influence on the magnetic processes below 4 K [9,10]. Anyhow, our single-ion ferromagnetic-like model has indeed produced the main features of the physical properties for the material and we will use it in further theoretical analysis. With the above CFPs, the ground-state CF level is found to be $\Gamma_8^{(3)}$, a quartet given by

$$|\psi_{1,2}^{(0)}\rangle = a|\pm 11/2\rangle + b|\pm 3/2\rangle + c|\mp 5/2\rangle + d|\mp 13/2\rangle,$$
$$|\psi_{3,4}^{(0)}\rangle = r|\pm 9/2\rangle + s|\pm 1/2\rangle + u|\mp 7/2\rangle + v|\mp 15/2\rangle, \quad (4)$$

where $a = -0.017$, $b = 0.720$, $c = 0.683$, $d = -0.122$, $r = -0.084$, $s = -0.416$, $u = -0.440$, $v = 0.791$. The first excited CF level is found to be the doublet

$$\Gamma_6 = 0.191|\pm 9/2\rangle + 0.718|\pm 1/2\rangle + 0.331|\mp 7/2\rangle + 0.582|\mp 15/2\rangle, \quad (5)$$

which is 9.9 K above $\Gamma_8^{(3)}$. The other CF levels are well separated, at more than 40 K above the ground-state. Therefore, we believe that the magnetic properties of the material in the ordered phase are mainly determined by these two lowest CF levels. Especially, because the four states of $\Gamma_8^{(3)}$ are all magnetic in the z-direction, we expect this level plays crucial role in the spontaneous ordering below T_N. To test this idea, we considered the ground-state CF level only, and then the two lowest CF levels as base vectors to calculate the spontaneous magnetization in low temperature region.

When only the ground-state CF level is considered, the matrix elements of J_z, J_+ and J_- have to be evaluated in the vector space spanned by the four states $|\psi_i^{(0)}\rangle$ ($i = 1, 2, 3, 4$). These are found to be

$$J_z = \begin{pmatrix} \alpha & 0 & 0 & 0 \\ 0 & -\alpha & 0 & 0 \\ 0 & 0 & \beta & 0 \\ 0 & 0 & 0 & -\beta \end{pmatrix}, \quad J_+ = \begin{pmatrix} 0 & 0 & \zeta & 0 \\ \eta & 0 & 0 & 0 \\ 0 & 0 & 0 & \delta \\ 0 & \zeta & 0 & 0 \end{pmatrix},$$
$$J_- = \begin{pmatrix} 0 & \eta & 0 & 0 \\ 0 & 0 & 0 & \zeta \\ \zeta & 0 & 0 & 0 \\ 0 & 0 & \delta & 0 \end{pmatrix}, \quad (6)$$

where

$$\alpha = 5.5a^2 + 1.5b^2 - 2.5c^2 - 6.5d^2,$$
$$\beta = 4.5r^2 + 0.5s^2 - 3.5u^2 - 7.5v^2,$$
$$\zeta = ar\sqrt{39} + bs\sqrt{63} + cu\sqrt{55} + dv\sqrt{15},$$
$$\eta = 4(ad\sqrt{7} + bc\sqrt{15}),$$
$$\delta = 8(ur\sqrt{3} + s^2). \quad (7)$$

Obviously, all matrix elements of $\mathscr{H}_{CF}$ are zero in this vector space. These new matrices are substituted into Eq. (2) to compute the thermally averaged values of J_z, J_+ and J_- simultaneously. To very good accuracy, $\langle J_+\rangle$ and $\langle J_-\rangle$ are found to be zero in the whole temperature range considered, i.e., the magnetic moments align only in the quantized z-direction. As expected, such obtained magnetization is weaker in magnitude than that computed with the full CF levels of $J = \frac{15}{2}$ multiplet, and sustains only to 3 K as displayed in Fig. 2.

To further investigate the magnetic-ordering mechanism, the first excited CF level has been taken into account in the computations in addition to the ground-state level. As shown in Fig. 2, the calculated magnetization now shows comparable magnitude and very similar tendency with increasing temperature