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ELSEVIER

Crystal-field effect in ErCu_2

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Abstract

The crystal-field contribution to the specific heat of the ErCu_2 compound has been calculated using two lowest-order crystal-field parameters derived by Hashimoto et al. and a set of crystal-field parameters determined by Gubbens et al. The calculated results are compared with the experimental ones.

The RCu_2 (R = rare earth) intermetallic compounds have an orthorhombic CeCu_2 structure. Early magnetization and magnetic susceptibility measurements performed by Hashimoto et al. [1] demonstrated the importance of the crystalline electric field (CF) in these compounds. In a previous publication [2] we reported on the specific heat and thermal expansion of RCu_2 compounds and discussed the excess contributions in both quantities arising from magnetic ordering and CF effects. Apart from some sharp features indicating transitions between different types of antiferromagnetic order and apart from a lambda-type of anomaly characteristics for disordering the antiferromagnetic state, broad anomalies were observed for several compounds in the specific heat and thermal expansion. In case of ErCu_2 , Luong et al. [2] and Franse et al. [3] could analyze the excess contributions to the specific heat and thermal expansion by applying Grüneisen relations (see also Ref. [4]), showing that they consist of a ‘long-range’ magnetic and a crystal-field part. The CF term is Schottky-type (ΔC_{exp} curve in Fig. 1). Luong et al. [2] showed that the energy difference between the ground-state doublet and the first excited doublet amounts to 76 K. Using the values for the two lowest-order CF parameters, $B_2^0 = -0.35$ K and $B_2^2 = -0.36$ K, obtained by Hashimoto et al. [1] from an analysis of the paramagnetic susceptibility, Franse et al. [3] have calculated the energy levels in ErCu_2 and derived a splitting of 13 K between the two lowest-order doublets. Apparently, higher-order CF terms have to be taken into account in order to bring the splitting closer to the experimental value of 76 K. Due to the low symmetry in RCu_2 compounds, nine CF parameters are needed to describe the crystal field of the rare earth ion. It is difficult to derive the full set of CF parameters. A combination of different techniques, experimental and theoretical, are used in order to overcome this difficulty.

Gubbens et al. [5] have measured the ErCu_2 compound with ^{166}Er Mössbauer spectroscopy. These authors also reported the results of inelastic neutron scattering, which show a not-yet definitively determined level sequence of doublets above T_N at 0, 61, 78, 88, 124, 142, 148 and 160 K. Gubbens et al. [5] have determined a tentative set of all nine CF parameters. This set is: $B_2^0 = -0.28$ K, $B_2^2 = -0.22$ K, $B_4^0 = -0.30 \times 10^{-2}$ K, $B_4^2 = -0.14 \times 10^{-2}$ K, $B_4^4 = 0.30 \times 10^{-2}$ K, $B_6^0 = -0.20 \times 10^{-4}$ K, $B_6^2 = -0.47 \times 10^{-4}$ K, $B_6^4 = -0.97 \times 10^{-4}$ K, $B_6^6 = -2.96 \times 10^{-4}$ K.

In this contribution we report the results of our calculations of the CF contribution to the specific heat at ErCu_2 compound using CF data obtained by Hashimoto et al. [1] and by Gubbens et al. [5]. The calculated results are compared with the experimental data reported in Refs. [2,3].

The CF Hamiltonian for orthorhombic symmetry is given by:

$$H_{\text{CF}} = B_2^0 O_2^0 + B_2^2 O_2^2 + B_4^0 O_4^0 + B_4^2 O_4^2 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^2 O_6^2 + B_6^4 O_6^4 + B_6^6 O_6^6, \quad (1)$$

where B_n^m are the CF parameters and O_n^m the Stevens equivalent operators. The CF contribution to the specific heat is determined by

$$\Delta C = -T \partial^2 F / \partial T^2, \quad (2)$$

where F is the free energy of the R system over the energy states resulting from a consideration of the Hamiltonian (1) (see, for instance, Ref. [6]). Results of calculations are shown in Fig. 1. In calculating ΔC_1 using two lowest-order CF parameters reported by Hashimoto et al. [1], we derived the following level scheme of doublets: 0, 13, 25, 33, 40, 49, 61 and 75 K. As can be seen from Fig. 1, the CF contribution to the specific heat (curve ΔC_1), given by this energy scheme, disagrees with our experiments. The curve ΔC_2 in Fig. 1 was obtained by taking into account all eight doublets reported by Gubbens et al.

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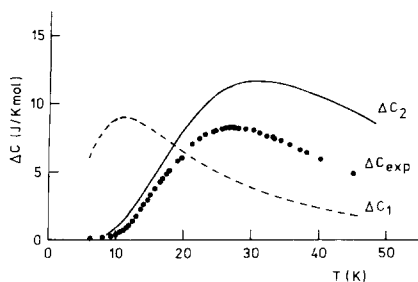


Fig. 1. Calculated and experimental results for the crystal-field contribution to the specific heat of ErCu_2 . ΔC_1 and ΔC_2 curves are calculated using CF data in Refs. [1] and [5], respectively. ΔC_{exp} (from Refs. [2,3]) is obtained from specific heat and thermal expansion measurements.

[5]. From this figure it can also be seen that the temperature dependence of ΔC_2 has a similar behaviour with the experimental one but the calculated value of ΔC_2 is larger at high temperature range. This difference between calculated ΔC_2 and experimental specific heat curves will be discussed in more detail below.

One of the reasons of the above mentioned discrepancy could be an overestimation of the non-magnetic contribution to the specific heat. In order to evaluate the magnetic contribution to the specific heat, non-magnetic (electronic and phonon) contributions have to be subtracted from the total specific heat. It is well known that a proper evaluation of the non-magnetic contribution of magnetic compounds is a difficult problem. Isostructural non-magnetic compounds are usually employed to estimate this non-magnetic contribution. LaCu_2 forms a hexagonal AlB_2 -type of structure and hence is not considered. In case of RCu_2 , we obtained the non-magnetic contribution to the specific heat from measuring the specific heat of YCu_2 [2,7]. The phonon part of the specific heat of YCu_2 follows closely the Debye function, giving a value of 236 K for the Debye temperature Θ_D . The electronic contribution to the specific heat of YCu_2 is low ($\gamma = 6.7 \text{ mJ/K}^2 \text{ mol}$) and was taken the same for the whole series of RCu_2 compounds. Comparing the specific heat data of YCu_2 and GdCu_2 well above the ordering temperature ($T_N = 40 \text{ K}$ for GdCu_2), we derived a value of 198 K for $\Theta_D(\text{GdCu}_2)$. The Debye temperature of ErCu_2 has been estimated by using the relation.

$$\Theta_D(\text{ErCu}_2) = \Theta_D(\text{GdCu}_2) M_{\text{GdCu}_2}^{1/2} M_{\text{ErCu}_2}^{-1/2}, \quad (3)$$

where M is the mass per formula unit. A value of 194 K for $\Theta_D(\text{ErCu}_2)$ was derived. The CF contribution ΔC_{exp} shown in Fig. 1 was obtained after subtracting the non-magnetic part to the specific heat of ErCu_2 . In a more sophisticated approach which accounts for the different molar masses of the components, Bouvier et al. [8] have

deduced the following relation between the corresponding effective Debye temperatures of two compounds $R_m X_n Y_p$ and $R'_m X'_n Y'_p$:

$$\frac{\Theta_D(R_m X_n Y_p)}{\Theta_D(R'_m X'_n Y'_p)} = \left(\frac{m(M_{R'})^{3/2} + n(M_X)^{3/2} + p(M_Y)^{3/2}}{m(M_R)^{3/2} + n(M_X)^{3/2} + p(M_Y)^{3/2}} \right)^{1/3}, \quad (4)$$

where M_R , $M_{R'}$, M_X and M_Y are the molar masses of R, R', X and Y atoms, respectively. Using this renormalization ratio and the value of 236 K for Θ_D of YCu_2 , we derive $\Theta_D(\text{ErCu}_2) = 197 \text{ K}$, i.e. very close to the value of 194 K obtained above.

Another possible reason of the discrepancy between the experimental curve ΔC_{exp} and the calculated curve ΔC_2 could be that higher energy levels do not substantially contribute to the specific heat. We have performed calculations of the CF contribution to the specific heat of ErCu_2 taking into account only the four lowest doublets reported by Gubbens et al. [5] (see above). The calculated curve is in close agreement with the experimental one. This result could suggest (in case of a proper estimate of the phonon contribution to the specific heat) that the energy spectrum in ErCu_2 is divided into two groups. The first group consists of the four lowest doublets located below 88 K. The second group, consisting of four higher doublets, is separated from the first one. We note, as mentioned above, that the energy level scheme in ErCu_2 is not definitively determined and that the set of CF parameters for this compound is not unique at present stage of investigations [5]. Measurements of the specific heat on a single-crystal-line sample in an external magnetic field, among other experiments, would be very useful, since the applied field additionally shifts the energy levels in an anisotropic way.

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