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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 ($\Delta C_{CF} = -k_B T^3$) in Fig. 1). Luong et al. [2] showed that the energy difference between the ground-state doublet and the first excited doublet amount to 76 K. Using the values for the two lowest-order CF parameters, $B_2^0 = -0.35$ K and $B_2^0 = -0.36$ 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, $B_2^0 = -0.22$ K, $B_2^0 = -0.30 \times 10^{-2}$ K, $B_2^0 = -0.14 \times 10^{-2}$ K, $B_2^0 = 0.30 \times 10^{-2}$ K, $B_2^0 = -0.20 \times 10^{-4}$ K, $B_2^0 = -0.47 \times 10^{-4}$ K, $B_2^0 = -0.97 \times 10^{-4}$ K, $B_2^0 = -2.96 \times 10^{-4}$ 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:

$$H_{CF} = B_2^0 O_2^0 + B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_6^0 O_6^0,$$

(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

$$\Delta C = -\frac{3k_B^2 F}{\beta T^2},$$

(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 $\Delta C_1$ 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 $\Delta C_1$), given by this energy scheme, disagrees with our experiments. The curve $\Delta C_2$ in Fig. 1 was obtained by taking into account all eight doublets reported by Gubbens et al. [5].
Fig. 1. Calculated and experimental results for the crystal-field contribution to the specific heat of ErCu$_2$. AC$_1$ and AC$_2$ curves are calculated using CF data in Refs. [1] and [5], respectively. AC$_{exp}$ (from Refs. [2,3]) is obtained from specific heat and thermal expansion measurements.

From this figure it can also be seen that the temperature dependence of AC$_2$ has a similar behaviour with the experimental one but the calculated value of AC$_2$ is larger at high temperature range. This difference between calculated AC$_2$ 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 $\Theta_D$. The electronic contribution to the specific heat of YCu$_2$ is low ($\gamma = 6.7$ mJ/K$^2$ 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 ($T_N = 40$ K for GdCu$_2$), we derived a value of 198 K for $\Theta_D$(GdCu$_2$). The Debye temperature of ErCu$_2$ has been estimated by using the relation

$$\Theta_D(\text{ErCu}_2) = \Theta_D(\text{GdCu}_2) \frac{M^{1/2}_{\text{GdCu}_2}}{M^{1/2}_{\text{ErCu}_2}},$$

where $M$ is the mass per formula unit. A value of 194 K for $\Theta_D$(ErCu$_2$) was derived. The CF contribution AC$_{exp}$ 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 $R_nX_nY_p$ and $R'_nX'_nY'_p$:

$$\Theta_D(R_nX_nY_p) = \Theta_D(R'_nX'_nY'_p) = \left( \frac{m(M_R)^{3/2} + n(M_X)^{3/2} + p(M_Y)^{3/2}}{m(M'_R)^{3/2} + n(M'_X)^{3/2} + p(M'_Y)^{3/2}} \right)^{1/3},$$

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 $\Theta_D$ of YCu$_2$, we derive $\Theta_D$(ErCu$_2$) = 197 K, i.e. very close to the value of 194 K obtained above.

Another possible reason of the discrepancy between the experimental curve AC$_{exp}$ and the calculated curve AC$_2$ 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 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.

References