SPECIFIC HEAT OF SELECTED RCu_2*

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The temperature dependence of specific heat of selected RCu_2 (R = Sm and Tm) was studied in detail in comparison with that of the nonmagnetic analogues (YCu_2 and $LuCu_2$). The electron and the phonon part of the specific heat was determined for all the investigated compounds as well as the magnetic entropy for the magnetically ordered ones. The density functional calculations were performed for YCu_2 and $LuCu_2$ compounds to obtain an additional information about the electronic structure of the RCu_2 system.

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1. Introduction

The isostructural series of intermetallic compounds RCu_2 (R = rare earth) crystallizes (with the only exception of $LaCu_2$) in the orthorhombic $CeCu_2$-type structure with the space group *Imma* [1]. They become very popular due to unusual physical properties depending on external conditions (*e.g.* giant magnetoelastic effect). Almost all of them order antiferromagnetically (AF) and exhibit a variety of different magnetic phases in the ordered state.

Here we compare the specific heat of $SmCu_2$ and $TmCu_2$ with their non-magnetic analogues YCu_2 and $LuCu_2$. The calculated density of states (DOS) of the non-magnetic compounds allows us to calculate the theoretical Sommerfeld coefficient γ.

2. Methodology, results and discussion

High-quality and well defined samples were necessary for our detailed experimental study. All the compounds were prepared by arc melting from high

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purity constituents under the protective Ar-atmosphere. Polycrystalline samples of YCu_2 and $LuCu_2$ were synthesized in the mono-arc furnace. Top-class single crystals of $SmCu_2$ and $TmCu_2$ were grown by Czochralski technique in the tri-arc furnace from $\sim$ 10 g of melt with $\sim$ 10 mm/h pulling speed. To compensate the several orders higher volatility of both Sm and Tm, five atomic percents of R were added to the starting composition.

Homogeneity and stoichiometry of all prepared compounds were checked by microprobe. Also the powder X-ray diffraction analysis did not revealed any foreign phase and confirmed the $CeCu_2$-type crystal structure. The lattice parameters and the atomic positions yielded by the Rietweld analysis are in a good agreement with the published values [1].

The specific heat measurements were performed on the PPMS (Physical Properties Measurement System) using the relaxation method [2] in the temperature range T = 1.5–300 K. The data were analyzed as a sum of individual contributions.

The specific heat data of nonmagnetic YCu_2 and $LuCu_2$ were analyzed in detail to extract the phonon and electronic parts of specific heat. The analysis of the phonon part includes both the Debye and the Einstein models using the characteristic temperatures θ_{D} (for the acoustic part) and θ_{E} (for the optical branches), respectively, as well as the correction on the anharmonic contribution α to the phonon spectrum (for details see [3]). The inferred values were used as starting parameters in the multi-parameter fit of magnetic samples in the paramagnetic region. The crystal field level schemes were then deduced from the fit as well as the Schottky contribution to the specific heat for both $SmCu_2$ and $TmCu_2$ (like in [4]).

The band structure calculations were performed for YCu_2 and $LuCu_2$ using the general potential linearized augmented plane wave method (WIEN97 code [5]). To solve the many particle problem for the ideal crystal the generalized gradient approximation has been chosen in our calculations. The ground state equilibrium crystal structure of $LuCu_2$ (z_{Ce}, y_{Cu}, z_{Cu}) was found using combined analysis of the X-ray data and minimization of total energy and DFT forces in first principle calculations. The estimation of the mass enhancement factor λ can be obtained from both the specific heat data and the state of art of the DFT electronic structure calculations using the $\gamma_{\mathrm{exp}} = \gamma_{\mathrm{calc}}(1 + \lambda)$ relation.

The specific heat analysis yields the experimental values of the linear coefficient $\gamma = 8.2, 5.7, 6.0$ and 5.7 mJ/molK^2 for YCu_2, $LuCu_2$, $SmCu_2$ and $TmCu_2$, respectively. The γ values of magnetic samples might be influenced by the magnetic order, but the stability of the fit in the whole temperature region does not show such influence.

The analysis of the acoustic phonon contribution gives respective values of $\theta_{\mathrm{D}} = 156$, 145, 148 and 151 K and $\alpha_{\mathrm{D}} = 2.9 \times 10^{-4}$, 0.8×10^{-4}, 2.2×10^{-4}

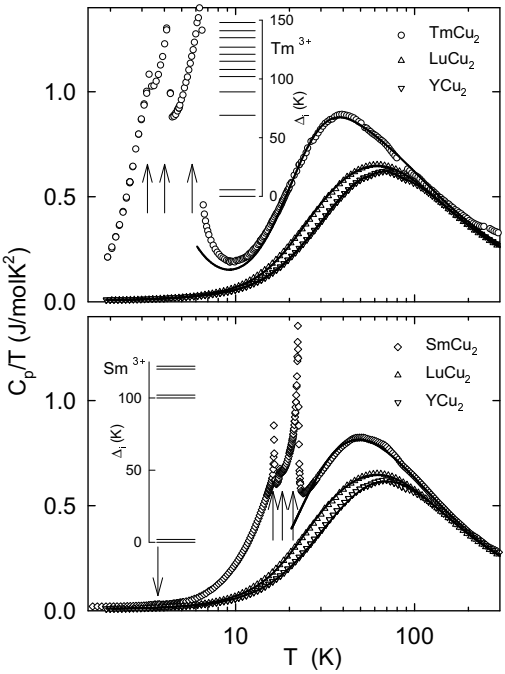

Fig. 1. The temperature dependence of the specific heat of $TmCu_2$ and $SmCu_2$ in comparison with non-magnetic analogues. The insets show the respective CF-level schemes, the arrows mark the magnetic phase transitions.

and 1.2×10^{-4} K^{-1}. To reduce the number of adjustable parameters, the 6 optical branches of the phonon spectrum were described by a superposition of n-times degenerated Einstein modes, denoted by θ_{Ei}. The corresponding values are then: $\theta_{\mathrm{E1}} = 166$ (2), 137 (2), 136 (2) and 132 (2) K with $\alpha_{\mathrm{E1}} = 2.0\times10^{-4}$, 2.0×10^{-4}, 2.1×10^{-4} and 1.6×10^{-4} K^{-1}, $\theta_{\mathrm{E2}} = 250$ (2), 251 (2), 188 (2) and 230 (3) K with $\alpha_{\mathrm{E2}} = 1.5 \times 10^{-4}$, 2.0×10^{-4}, 3.0×10^{-4} and 2.1×10^{-4} K^{-1} and $\theta_{\mathrm{E3}} = 271$ (2), 274 (2), 265 (2) and 295 (1) K with $\alpha_{\mathrm{E3}} = 1.8 \times 10^{-4}$, 2.9×10^{-4}, 2.9×10^{-4} and 13×10^{-4} K^{-1} for YCu_2, $LuCu_2$, $SmCu_2$ and $TmCu_2$, respectively. From the fit we can see that the phonon spectrum does not substantially differ (within the $\approx 5\%$ error) from compound to compound, as expected for the isostructural series.

The crystal-field level scheme is described by the energy gaps Δ_i of the excited levels from the ground state. For the Sm^{3+} ion (3 Kramer's doublets) the fit yields $\Delta_1 = 100$ K and $\Delta_2 = 120$ K. In the case of Tm^{3+} ion (13 non-Kramer's singlets) we found $\Delta_i = 5.6$, 69, 89, 102, 108, 115, 121, 127, 135, 141, 148 and 152 K. The saturated values of magnetic entropy compare well to the respective theoretical values $R\ln 6$ and $R\ln 13$. In comparison

with [4] we have to say, that while the low levels remain roughly the same, the fit to the new data in the wide temperature range from the high-quality single crystal had significantly improved the positions of the higher exited levels.

The comparison of the experimental γ values with the calculated ones allowed us to deduce the mass enhancement factors $\lambda = 1.1$ and 0.78 for YCu_2 and $LuCu_2$, respectively. These values suggest that the medium many particle correlations are present in the valence electron subsystems of the studied nonmagnetic RCu_2 compounds.

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