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Phonon Drag and Magnetic Anomalies of Thermopower in RB_{12} (R = Ho, Er, Tm, Lu)

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High precision measurements of the Seebeck coefficient $S(T)$ were carried out on the single crystals of RB_{12} (R = Ho, Er, Tm, Lu) at temperatures 2–300 K. It was shown that the effects of phonon drag result from vibrations of rare earth ions ($\hbar\omega_E \approx$ 10–33 meV) in the rigid framework structure of the B_{12} clusters and determine the main contribution to thermopower at intermediate temperatures (30–300 K). The correlated behavior of transport parameters favors the appreciable enhancement of spin fluctuations in the sequence of magnetic compounds (HoB_{12}–TmB_{12}) when approaching to the valence instability state in YbB_{12}. The giant increase in $S(T)$ detected in the vicinity of the Néel temperature T_N for HoB_{12}, ErB_{12}, and TmB_{12} seems to result from the density of states renormalization caused by antiferromagnetic ordering.

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1. Introduction

Rare earth and transition metals dodecaborides with framework structural units — boron nanoclusters B_{12} — demonstrate an amazing variety of ground states depending on cubic crystal structure parameters, the number of $4f$-electrons in the inner shell and the valence state of rare-earth ion (see, e.g., [1]). In particular, the dielectric non-magnetic ground state of intermediate valence compound

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$Yb^{2.9+}B_{12}$ drastically differs from that of metallic ($R^{3+}B_{12}$) compounds with superconducting (ZrB_{12}, LuB_{12}) and antiferromagnetic (AFM) (TbB_{12}, DyB_{12}, HoB_{12}, ErB_{12}, TmB_{12}) low temperature phases. In this respect rare-earth dodecaborides could be treated as perspective model objects for studying the interplay between the electronic structure, phonon spectra and magnetic properties in these 3D fcc systems with nanoclusters and localized magnetic moments.

To shed more light on the peculiarities of charge transport and ground state formation in RB_{12}, a comprehensive study of thermoelectric properties has been performed for HoB_{12}, ErB_{12}, TmB_{12}, and LuB_{12} at temperatures 2–300 K. The high quality single crystals of RB_{12} were grown by the crucible-less inductive zone melting in argon gas atmosphere [2]. The Seebeck coefficient was measured by the original four-probe technique [3]. The temperature gradient on the sample was applied in the (110) plane along ⟨001⟩ direction.

2. Results and discussion

The temperature dependences of the Seebeck coefficient $S(T)$ measured for magnetic and non-magnetic compounds RB_{12} (R = Ho, Er, Tm, Lu) are shown in Fig. 1. The experimental data demonstrate a pronounced decrease in the absolute values of the Seebeck coefficient down to 10 K, the amplitude of the negative minimum of $S(T)$ being the largest one for non-magnetic LuB_{12} (Fig. 1). A similar behavior of the Seebeck coefficient earlier observed on ZrB_{12} at intermediate temperatures was explained in terms of phonon drag thermopower resulting from vibrations of rare-earth ions in the rigid framework structure of the B_{12} clusters [4]. Following the arguments of [4] the relaxation time approach was applied to describe the phonon drag contribution with the help of relation

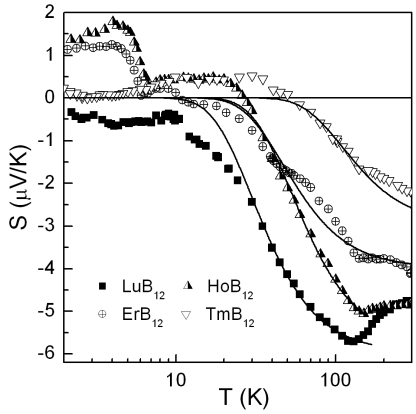

Fig. 1. Temperature dependences of the Seebeck coefficient $S(T)$ for RB_{12} compounds (R = Ho, Er, Tm, Lu). The phonon drag thermopower $S_{\rm ph}$ estimated within the time relaxation approach of Eq. (1) is for each compound shown by a solid line.

$$S_{\rm ph}(T) = S^0_{\rm ph}\left(\frac{\Theta_{\rm E}}{T}\right)^2 \frac{\exp(\Theta_{\rm E}/T)}{[\exp(\Theta_{\rm E}/T)-1]^2}, \tag{1}$$

where $S^0_{\rm ph}$ is the amplitude of phonon drag thermopower and $\Theta_{\rm E}$ is the characteristic frequency of the Einstein phonons in temperature units. The good agreement between experimental data and fitting results established in this study (Fig. 1) proves the dominant role of electron interaction with the Einstein modes. Besides, it is clearly seen from the upper part of Fig. 2 that approaching to the valence instability state in YbB_{12} in the sequence HoB_{12}–ErB_{12}–TmB_{12} is accompanied by hardening of the Einstein modes from ≈ 15 meV to ≈ 30 meV. Moreover, the simultaneous decrease in $|S^0_{\rm ph}|$ (Fig. 2) and the Hall mobility [5] contradicts obviously to the reduction of the free ion de Gennes factor $(g-1)^2J(J+1)$ (g and J are g-factor and angular momentum of $4f$-shell, respectively), which is commonly used as a measure of magnetic scattering of charge carriers. This observation allows us to conclude in favor of the enhancement of spin (and charge — for YbB_{12}) fluctuations in the set of RB_{12} compounds.

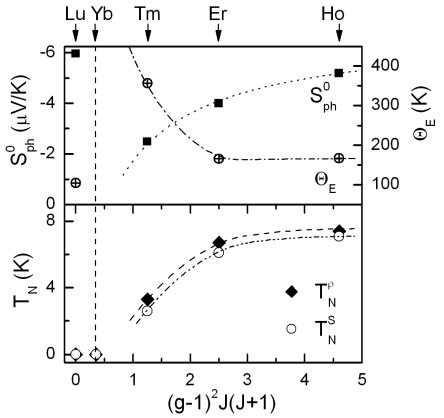

Fig. 2. The phonon drag thermopower $S^0_{\rm ph}$ and the characteristic frequency of the Einstein mode $\Theta_{\rm E}$ derived from Eq. (1) (upper part), as well as the Néel temperatures determined from resistivity ($T^\rho_{\rm N}$) and thermopower ($T^{\rm S}_{\rm N}$) data (lower part) of RB_{12} compounds (R = Ho, Er, Tm, Lu) depending on the free ion values of the de Gennes factor $(g-1)^2J(J-1)$ (see text). The drawn lines are quide for eyes.

Lowering temperature results in the transition to positive thermopower for all magnetic dodecaborides under investigation (Fig. 1). The magnetic contribution to the Seebeck coefficient was analyzed by subtracting the phonon drag thermopower from the experimental $S(T)$ curves. Data of Fig. 3 show that in paramagnetic state the position and the amplitude of the positive maximum for ErB_{12} are noticeably lower than these ones for HoB_{12} and TmB_{12}. Moreover, the transition into AFM state in RB_{12} is accompanied by a giant increase in $S(T)$ (Fig. 3). This huge

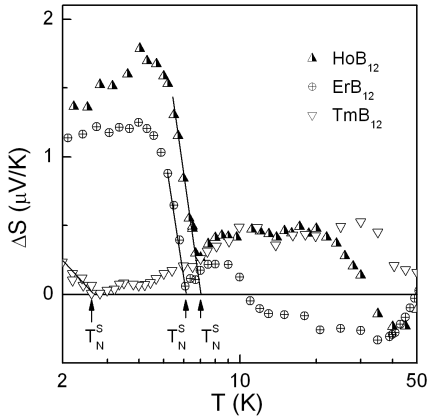

Fig. 3. The magnetic contribution to thermopower $\Delta S = S - S_{\rm ph}$ estimated for magnetic dodecaborides RB_{12} (R = Ho, Er, Tm).

enhancement of thermopower seems to indicate a strong asymmetry of the electron density-of-states (DOS), which appears due to the DOS renormalization caused by AFM ordering. It is also interesting to note that the values of the Néel temperature estimated for ErB_{12}, HoB_{12}, and TmB_{12} by linear extrapolation of $S(T)$ curves in the AFM phase to temperature axis (Fig. 3) are noticeably lower than these obtained from resistivity measurements [5] (see the lower part in Fig. 2). The observed discrepancy as well as the magnetic anomalies of thermopower require more detailed investigation of transport, thermal, and magnetic properties in AFM state of these magnetic compounds.

Acknowledgments

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