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TRANSPORT PROPERTIES OF RARE EARTH DODECABORIDES AT LOW TEMPERATURES[1]

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We present results of electrical resistivity measurements on HoB_{12}, ErB_{12} and TmB_{12} single crystalline samples in the temperature range of 1.6 - 30 K and in magnetic field up to 6 T. From the received data, B vs. T phase diagrams of all samples were created. Spin wave scattering of conduction electrons in the antiferromagnetic phase and the scattering of electrons in the paramagnetic phase are analysed and discussed.

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1 Introduction

Rare earth (RE) dodecaborides (REB_{12}) crystallize in the NaCl-based fcc structure, in which the Na^+ ions are replaced by RE ions and the Cl^- ions by B_{12} cubooctahedra. The links within B_{12} clusters and between cubooctahedra are determined by strong covalent bonds, which are responsible for the rigidity and high melting temperatures of these compounds. Theoretical studies of the electronic structure of REB_{12} compounds indicate that two valence electrons of each RE atom compensate the electronic deficiency of the boron sublattice generating an ionic bonding between RE atoms and B_{12} clusters. According to this model, dodecaborides with divalent RE ions are semiconductors, while dodecaborides with trivalent RE ions (e.g., Lu, Dy, Ho, Er and Tm) are metals with one electron per RE atom in the conduction band [1–4].

Rare earth dodecaborides exhibit a variety of physical properties which result predominantly from the 4f shell occupancy of their RE ions. Thus LuB_{12} is diamagnetic and becomes superconducting below 0.4 K, YbB_{12} is an intermediate valence system showing features of van Vleck paramagnetism, and DyB_{12}, HoB_{12}, ErB_{12} and TmB_{12} are metals which order antiferromagnetically at low temperatures, with T_N = 16.5 K for DyB_{12}, T_N = 7.5 K for HoB_{12}, T_N = 6.7 K for ErB_{12} and T_N = 3.4 K for TmB_{12} [4]. These magnetic dodecaborides present very complex magnetic systems. Recent magnetisation and specific heat measurements of HoB_{12} in magnetic

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field up to 8 T [1] suggest three magnetic phases in the B vs. T magnetic phase diagram. Neutron diffraction measurements of powder samples in zero magnetic field exhibit basic reflections (1/2$\pm\delta$, 1/2$\pm\delta$, 1/2$\pm\delta$), where δ=0.035, which reveal an incommensurate amplitude-modulated magnetic structure below T_N. The magnetic behaviour and magnetic phase diagram of this compound can arise from the interplay between the RKKY and dipole-dipole interaction. Moreover, also frustration effects due to the fcc symmetry of the dodecaborides lattice can play a significant role [1].

The aim of this paper is to present results of electrical resistivity measurements on HoB_{12}, ErB_{12} and TmB_{12} in the temperature range of 1.6 - 30 K and in magnetic field up to 6 T, their phase diagrams resulting from $\rho(T)$ measurements and to analyse the scattering mechanism below and above T_N.

2 Experimental details

The investigated compounds were grown by the floating zone method. This method comprises [5] the synthesis of dodecaborides by borothermic reduction of RE oxides in vacuum at 1800 - 2000 K, the compacting of the received powders by slip casting into rods, the sintering in vacuum at 2000 K and the process of inductive zone melting. All samples were grown in a single crystal form. The residual resistivity ratios $R_{300K}/R_{1.6K}$ were about 22, 58 and 25 for HoB_{12}, ErB_{12} and TmB_{12}, respectively.

Electrical resistance measurements were done in a ^{4}He flow cryostat using a standard d.c. four probe method. As current source a Keithley 220 instrument was used. The sample voltage was measured with a Keithley 181 nanovoltmeter. As thermometer a commercially calibrated Lake Shore CERNOX sensor with very small magnetoresistance was used.

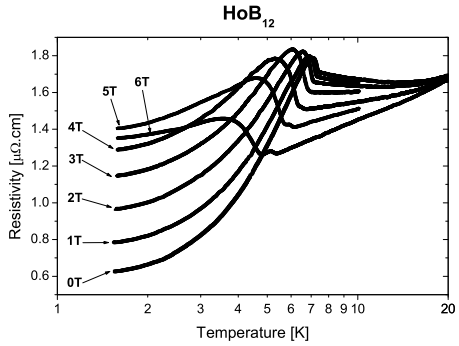
3 Results and discussion

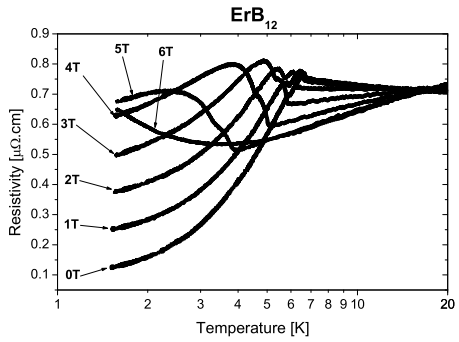
Temperature dependences of the electrical resistivity of HoB_{12}, ErB_{12} and TmB_{12} in various magnetic field are shown in Fig. 1. The antiferromagnetic transitions are observed as sudden changes in the courses of the temperature dependences of resistivities. From the numerical derivative of electrical resistivities with respect to temperature at constant magnetic field and the numerical derivative of electrical resistivities with respect to magnetic field at constant temperature the magnetic phase diagrams of HoB_{12}, ErB_{12} and TmB_{12} were constructed. These diagrams are plotted in Fig. 2. As can be seen from this figure, all diagrams consist of three phases. The phase diagram of HoB_{12} corresponds well with those recently obtained from magnetisation and specific heat measurements [1]. According to ref. [6], the temperature dependence of electrical resistivity in the antiferromagnetic state can be described by equation

$$\rho(T) = \rho_0 + CT^x \mathrm{e}^{\left(-\frac{\Delta E}{k_B T}\right)}, \tag{1}$$

where ρ_0 is the residual resistivity, C a parameter, x an exponent and ΔE the spin wave activation energy usually connected with the anisotropy of the magnetic structure. The entire second term represents the scattering of electrons by spin waves.

The analysis of experimental data in the ordered state was done only for HoB_{12} and ErB_{12}. The evaluation of TmB_{12} was not possible as the Néel temperature of TmB_{12} is very low. In this





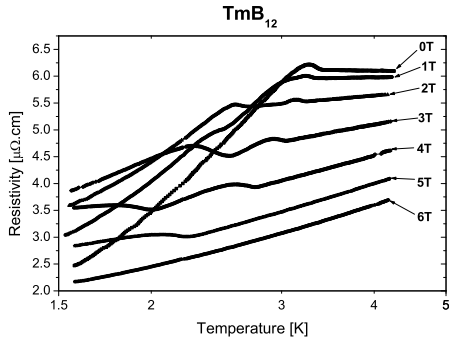
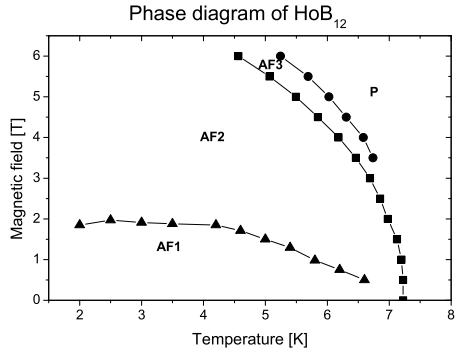
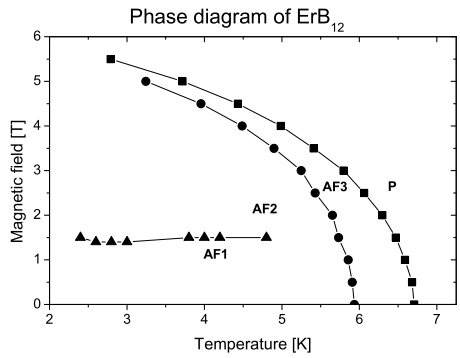


Fig. 1. Temperature dependences of the electrical resistivity of HoB_{12}, ErB_{12} and TmB_{12} in different magnetic fields.





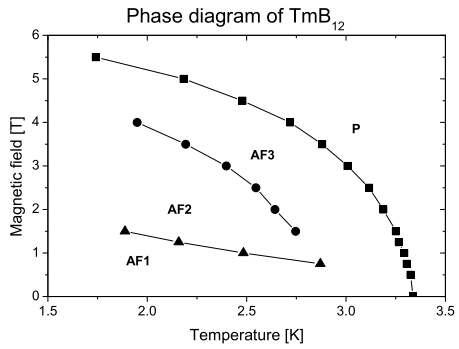


Fig. 2. Magnetic phase diagrams of HoB_{12}, ErB_{12} and TmB_{12}.

case measurements at lowest temperatures are needed. Using eq. (1), for all exponents from the range $2 \leq x \leq 4$ the calculated spin wave activation energy values ΔE of HoB_{12} and ErB_{12} were for all magnetic fields much lower then the available thermal energy $k_B T$. From this follows that in both compounds no energy gap in the spin wave spectrum can be seen in the temperature range of 1.6 - 4.2 K. In this case eq. (1) can be replaced by the relation

$$\rho(T) = \rho_0 + CT^x. \tag{2}$$

The best fits of the experimental data using eq. (2) were received with $x \approx 2$, both for HoB_{12} and for ErB_{12}. The parameter C did not depend on applied magnetic field. On the other hand, the residual resistivity of HoB_{12} and ErB_{12} grows with increasing magnetic field.

Above T_N the electrical resistivity is determined by scattering of electrons on impurities and imperfections (residual resistivity), by scattering on phonons, and by scattering on localized magnetic moments of RE ions (spin-disorder resistivity). Based on these scattering processes [6], a temperature independent behaviour or an increase of $\rho(T)$ with increasing temperature is expected. However, for magnetic fields below 3 T and for temperatures below specific temperatures (these are 20 K for HoB_{12}, 18 K for ErB_{12} and 13 K for TmB_{12}) the electrical resistivity exhibits an opposite dependence. The origin of this dependence is not yet known. A significant role in this behaviour can play crystal electric field effects or short-range magnetic correlations in spin-disorder scattering of conduction electrons.

4 Conclusion

We conclude that HoB_{12}, ErB_{12} and TmB_{12} exhibit complex magnetic phase diagrams with three magnetic phases below T_N. The phase diagram of HoB_{12} corresponds with those recently obtained from magnetisation and specific heat measurements. The resistivity of all samples above T_N exhibits unexpected behaviour, the origin of which is not yet clear. To shed more light on this problem, electrical resistivity measurements at lower temperatures and in higher magnetic field are needed.

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References

[1] A. Kohout, I. Baťko, A. Czopnik, K. Flachbart, S. Maťaš, M. Meissner, Y. Paderno, N. Shitsevalova, K. Siemensmeyer: *Phys. Rev. B* **70** (2004) 224416

[2] I. Baťko, K. Flachbart, A. Kohout, S. Maťaš, M. Meschke, K. Siemensmeyer, N. Shitsevalova, Y. Paderno: *Appl. Phys. A* **74** (2002) 829–830

[3] I. Baťko, K. Flachbart, S. Maťaš, Y. Paderno, N. Shitsevalova: *J. of Alloys and Compounds* **196** (1993) 133–135

[4] S. Gabáni, I. Baťko, K. Flachbart, T. Herrmannsdörfer, R. König, Y. Paderno,: *J. Magn. Magn. Mater.* **207** (1999) 131–136

[5] Y. Paderno, N. Shitsevalova, I. Baťko, K. Flachbart, H. Misiorek, J. Mucha, A. Jezovski: *J. of Alloys and Compounds* **219** (1995) 215–218

[6] K. N. R. Taylor, M. I. Darby: *Physics of Rare Earth Solids*, Chapman & Hall, London 1972