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Letter

Electrical resistivity and superconductivity of LaB_6 and LuB_{12}

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Abstract

The electrical resistivity of LaB_6 and LuB_{12} single crystals with high residual resistivity ratios has been measured down to 1.6 K. The temperature dependence below 30 K, caused by phonon scattering, shows for both materials a T^n behaviour with $n = 4.2 \pm 0.1$ for LaB_6 and $n = 5.2 \pm 0.1$ for LuB_{12}. From susceptibility measurements the superconducting transition temperature of LuB_{12} was determined to be 0.44 K, for the LaB_6 sample with residual resistivity ratio of 160 no transition into the superconducting state was observed down to 5 mK.

Keywords: Electrical resistivity; Superconductivity; Susceptibility measurements

1. Introduction

Rare earth hexaborides and dodecaborides have attracted attention because of the variety of their physical properties, providing systems where, e.g., superconductivity (LaB_6, LuB_{12}), valence fluctuations (SmB_6, YbB_{12}) and magnetic ordering (e.g. DyB_6, HoB_{12}) can be found [1].

The hexaborides crystallize in a structure characterized by a three-dimensional skeleton constituted of B_6 octahedra, the interstices of which are filled by metal atoms. In dodecaborides the boron atoms are linked in a rigid three-dimensional network with metal atoms situated in large B_{12} cubooctahedral holes. For a better understanding of the various properties of these borides, often the properties of LaB_6, without 4*f* electrons, and LuB_{12}, with a fully occupied 4*f* shell, are studied.

LaB_6 has a high electrical conductivity, mainly due to the light effective mass of the conduction electrons [2]. It is one of the best thermoelectronic emitters, finding utilization in technical and industrial applications because of its low work function. LuB_{12} is also a good metallic conductor.

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In this paper, electrical resistivity measurements on LaB_6 and LuB_{12} single crystals with high residual resistivity ratios (RRR) down to 1.6 K are reported. The observed temperature dependences are discussed in terms of simple metals. In order to determine the superconducting transition temperatures of these materials, susceptibility measurements down to 5 mK were also performed.

2. Experimental

LaB_6 and LuB_{12} single crystals were prepared by the floating zone method. The RRR of two LaB_6 samples cut in [100] orientation was 80 and 160 and the RRR of both LuB_{12} samples with the same orientation was 70. The electrical resistance was measured potentiometrically using the dc four-terminal method. As current source a Keithley Model 220 was used and for voltage measurements a Keithley Model 181 nanovoltmeter was used. The relative error of resistivity measurements was about 1% at liquid helium temperature and below 0.1% at room temperature. The temperature was determined using Lake Shore Cryotronics calibrated germanium (GR-200A-500) and platinum (Pt-103) thermometers.

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Susceptibility measurements were carried out in an Oxford Instruments dilution refrigerator using a Linear Research LR-400 mutual inductance bridge system.

3. Results and discussion

The electrical resistivity data for LaB_6 (sample with RRR = 160) and LuB_{12} between 1.6 and 300 K are shown in Fig. 1. The electrical resistivity data for LaB_6 (samples with RRR = 80 and 160) and LuB_{12} below 30 K are shown in Fig. 2. The most unexpected feature of the $\rho(T)$ dependences of LaB_6 with metallic behaviour is the increase of resistivity below about 12 K. This increase depends on the RRR of the sample and is less pronounced for a sample with higher RRR, i.e. with higher purity. Such a behaviour can be caused by Kondo scattering of electrons on a small amount of magnetic 4*f* or 3*d* impurity atoms in this material.

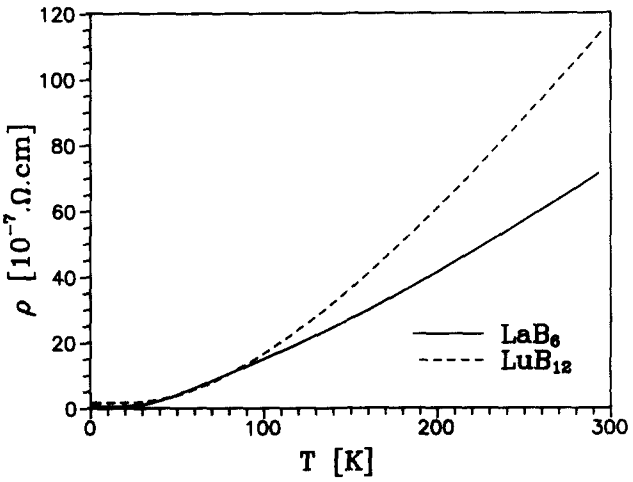

Fig. 1. Electrical resistivities $\rho(T)$ of LaB_6 (RRR = 160) and LuB_{12}.

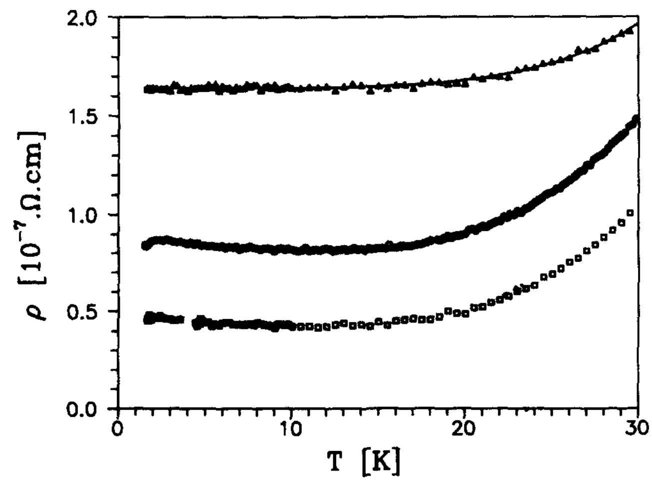

Fig. 2. Electrical resistivities below 30 K of LaB_6 (RRR = 160 (□) and 80 (○)) and LuB_{12} (△) and corresponding fitting lines (see Eqs. (1) and (2) and text).

Assuming that the resistivity increase below 12 K has a Kondo-like behaviour ($\rho \propto \ln T$) and that at low temperatures the residual resistivity (ρ_0) and the electron – phonon scattering ($\rho_{ep} \propto T^n$) determine the transport of conduction electrons, the total resistivity of LaB_6 can be written as

$$\rho(T) = \rho_0 + aT^n + b \ln T \quad (1)$$

where *a*, *b* and *n* do not depend on temperature and temperature *T* is in Kelvin. Fitting the resistivity dependence for the RRR = 80 sample below 30 K (about one tenth of the Debye temperature), the following values were obtained: $\rho_0 = 9.2 \times 10^{-8}$ Ω cm, $a = 4.5 \times 10^{-14}$ Ω cm K^{-n}, $b = -5.1 \times 10^{-9}$ Ω cm and $n = 4.2 \pm 0.1$. For LaB_6 with RRR = 160, owing to its small electrical resistivity at low temperatures resulting in a higher error of the measurement, the parameters of Eq. (1) could not be satisfactorily determined. The above-obtained value of *n* is in agreement with this expected for simple nonmagnetic metals characterized by a Fermi surface that intersects the Brillouin zone boundaries [3].

The small amount of magnetic impurities responsible for the Kondo behaviour in resistivity can also be the reason for the further observed result, that from susceptibility measurements no transition into the superconducting state for the sample with RRR = 160 was detected down to 5 mK. There is, however, an additional explanation for the very low superconducting transition temperature in this material based on the weak interaction of conduction electrons with boron octahedra deforming phonon modes [4,5]. In Ref. [6] the superconducting transition temperature of LaB_6 was reported to be about 0.1 K.

In LuB_{12} prepared by the same technology, no anomalous behaviour at low temperatures (Fig. 2) was observed. The temperature dependence in this case can be fitted using expression

$$\rho(T) = \rho_0 + aT^n \quad (2)$$

where the first term represents the residual resistivity and the second the scattering of electrons by phonons. The obtained fitting values are $\rho_0 = 1.6 \times 10^{-7}$ Ω cm, $a = 7.0 \times 10^{-16}$ Ω cm K^{-n} and $n = 5.2 \pm 0.1$, which is relatively close to the Bloch law dependence ($\rho \propto T^5$) [7], where the phonons are assumed to be adequately described by a Debye model, with a characteristic Debye temperature. The superconducting transition temperature for LuB_{12} was determined to be 0.44 K, which is in good agreement with the value of 0.48 K reported for this material [8].

The values of exponents $n \doteq 5.2$ for LuB_{12} and $n \doteq 4.2$ for LaB_6 may also indicate that the Debye-like phonon spectrum provides a better approximation for dodecaborides than for hexaborides. Note that studies of phonon spectra of LaB_6 [4,5] show a substantial deviation from a Debye-like distribution. However, the confirmation of this statement needs further research, especially on the phonon spectra of dodecaborides.

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