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Superconducting Phase Diagrams of LuB_{12} and $Lu_{1-x}Zr_xB_{12}$ ($x \leq 0.45$) down to 50 mK

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Lutetium dodecaboride LuB_{12} is a s-wave weak-coupling BCS superconductor with critical temperature $T_c \approx 0.42$ K. In turn, ZrB_{12} is strong-coupling BCS superconductor with the highest critical temperature $T_c \approx 6.0$ K among this group of materials. In case of lutetium substitution by zirconium ions in LuB_{12} one can study the crossover from weak- to strong-coupling superconductor. We have investigated the evolution of critical temperature T_c and critical field H_c in high-quality single crystalline superconducting samples of $Lu_{1-x}Zr_xB_{12}$ ($0 \leq x \leq 0.45$) by measuring magnetic ac-susceptibility between ≈ 1 K and 50 mK. To obtain this kind of experimental data, a new susceptometer was designed, constructed, and tested, that can work in a wide temperature range of 0.05–3 K in ^{3}He -^{4}He dilution refrigerator. The measurements with this new susceptometer revealed how $T_c(x)$ and $H_c(x)$ increases with increasing concentration of zirconium in $Lu_{1-x}Zr_xB_{12}$ solid solutions, as well as how their superconducting phase diagram develops.

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PACS/topics: superconductivity, magnetic susceptibility, dodecaborides, low temperatures

1. Introduction

Superconductivity in dodecaborides ZrB_{12} and LuB_{12} is well known for more than 40 years. Both superconductors, ZrB_{12} ($T_c \approx 6$ K [1]) and LuB_{12} ($T_c \approx 0.4$ K [2]), are very similar in their conduction band, magnetic and crystalline structure. Despite it is not clear up to now why there is such a big difference in their critical temperatures and fields. Studies of inelastic neutron scattering of the phonon spectra in ZrB_{12} and LuB_{12} [3] have shown only small changes in the position of their almost dispersion-less quasi-local modes. It is referred to vibrations of loosely bounded Zr or Lu atoms in cubooctahedron cavities of the rigid covalent boron sublattice. Regarding electron structure of ZrB_{12} and LuB_{12}, a moderate lowering (about 0.3–0.4 eV) of the Fermi level position was observed for zirconium dodecaboride due to a two-fold decrease in the conduction band filling when Zr ions were replaced by Lu ions [4].

Detailed investigations of superconducting properties of solid solutions $Lu_{1-x}Zr_xB_{12}$ can shed more light on this problem. As the first step of this study we show how the concentration dependence of critical temperature $T_c(x)$, and temperature dependences of the critical magnetic field $H_c(T)$ for various concentration of zirconium develop. Recently, a rather complex experimental research of electrical resistivity, magnetization and specific heat down to 0.4 K was carried out on $Lu_{1-x}Zr_xB_{12}$ samples with concentration of zirconium $0.78 \leq x \leq 1$ [5, 6]. In this paper, we have studied solid solutions with values of concentration $x \leq 0.45$ by precise ac-susceptibility measurements down to 50 mK.

2. Experimental details

High quality single crystalline samples of $Lu_{1-x}Zr_xB_{12}$ with concentration $x = 0.00$, 0.04, 0.10, 0.20, and 0.45, were prepared by vertical crucible-free inductive floating zone melting technique in an inert argon atmosphere. The exact ratio of Zr/Lu ions concentration was determined by scanning electron microscopy. To obtain the superconducting phase diagrams down to very low temperatures, a new ac-susceptometer for homebuilt dilution ^{3}He -^{4}He minirefrigerator was designed, constructed and tested. The primary coil from NbTi superconducting wire ($T_c \approx 9$ K) was used to generate an excitation field of about 0.04 Oe by ac-current $I_P = 10^{-4}$ A and frequency $f = 401$ Hz. Usual values of detected voltage induced in the secondary coil (produced from Cu wire) were $U_i \approx 10^{-6}$ V. All samples had the same dimensions of $2 \times 2 \times 0.5$ mm^3 ($a \times b \times c$). The external magnetic field was applied along the c-axis ([001] direction).

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3. Results and discussion

For each sample tested, the first measurement was to examine the temperature dependence of the induced voltage U_i in zero external magnetic field. The purpose was mainly to determine for each sample the critical temperature $T_c(0)$. After then, measurements of temperature and field dependencies of U_i were carried out. Representative field dependencies of the induced voltage signal $U_i(H)$ for LuB_{12} at various stable temperatures are presented in Fig. 1. The critical fields H_c were defined as the midpoint of very sharp step-like superconducting phase transition of $U_i(H)$ dependence. The observed unusual cusp in this $U_i(H)$ dependence close to and below T_c, seems to be caused by the intermediate state formation which arises in LuB_{12} at the transition between the superconducting and normal state. The similar effect was observed in the case of single crystalline type I superconductor Sn [7]. Thus, the observed conformity implies that LuB_{12} is (as Sn) a type I superconductor. The resulting temperature dependence of critical field $H_c(T)$ for LuB_{12} is displayed in Fig. 2. To our knowledge, it is the first detailed observation of the superconducting phase diagram of LuB_{12} up to such low temperatures. The BCS-type of superconductivity in LuB_{12} is clearly demonstrated (see Fig. 2) by the perfect fit of $H_c(T)$ with BCS formula:

$$H_c(T) = H_c(0)\left[1 - \left(\frac{T}{T_c}\right)^2\right].$$

From this fit we were able to determined the value of critical magnetic field $H_c(0) \approx 20$ Oe, which is in accordance with the previous predictions and measurements down to only 0.35 K [8]. Analogously to case of LuB_{12}, we obtained the phase diagrams of $Lu_{1-x}Zr_xB_{12}$ ($x \leq 0.45$) samples (see Fig. 3) from temperature and field sweeps of U_i. The values of critical fields were determined from BCS fits. The same BCS dependence for all studied samples suggests that there is no evolution

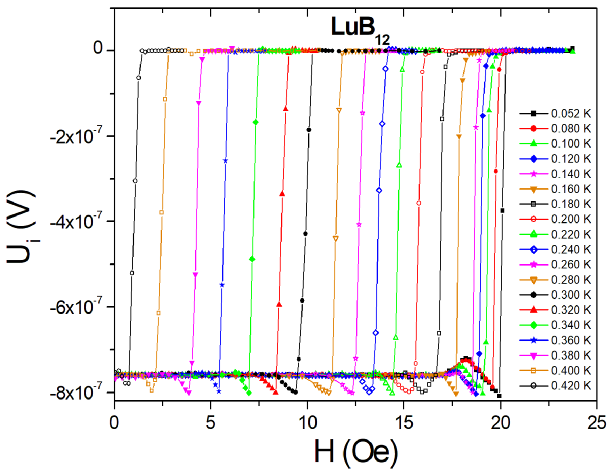

Fig. 1. Field dependences of induced voltage $U_i(H)$ at several constant temperatures for LuB_{12} sample.

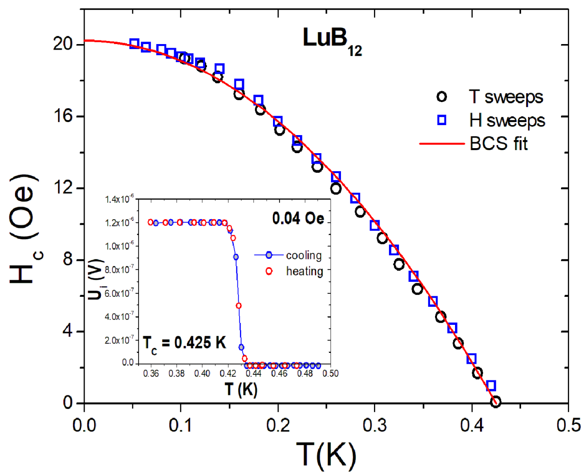

Fig. 2. Superconducting phase diagram $H_c(T)$ for LuB_{12} obtained from temperature and field dependencies of ac-susceptibility, and corresponding BCS fit. Inset includes a virgin curve of induced voltage U_i used for the determination of exact critical temperature $T_c(0)$ values.

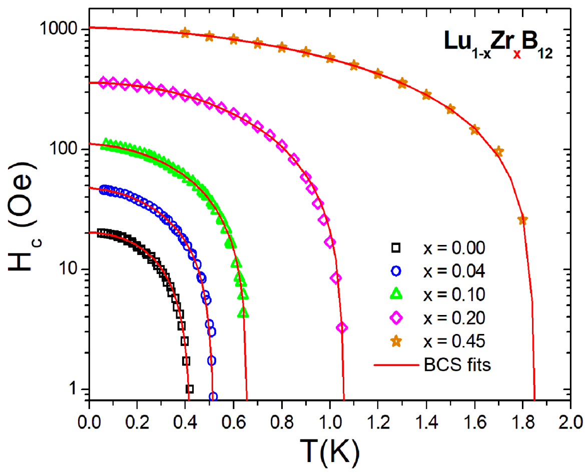

Fig. 3. Phase diagrams of $Lu_{1-x}Zr_xB_{12}$ obtained from ac-susceptibility measurements in ^3He -^4He dilution refrigerator down to 50 mK ($0 \leq x \leq 0.20$) and in ^3He refrigerator down to 0.4 K ($x = 0.45$).

of the coupling strength in inspected Zr concentration window, and that the system remains in the weak-coupling regime. The resulting concentration dependencies of $T_c(x)$ and $H_c(x)$ is displayed in Fig. 4. The best $T_c(x)$ fit for x up to 0.45 was obtained by a linear function with a slope of $dT_c/dx = +32$ mK/at.%. However, the extrapolation of this linear fit up to the maximum value $x = 1$ gives a critical temperature $T_c \approx 3.6$ K which is much lower than the actual value $T_c(ZrB_{12}) = 6$ K [8]. On the contrary, the most suitable quadratic $H_c(x)$ fit provides a critical field value of $H_c = 3.8$ kOe which is considerably higher value than the real one $H_c(ZrB_{12}) = 580$ Oe [8]. Recently, it was shown [6] that for the concentrations $x \geq 0.78$ a higher value

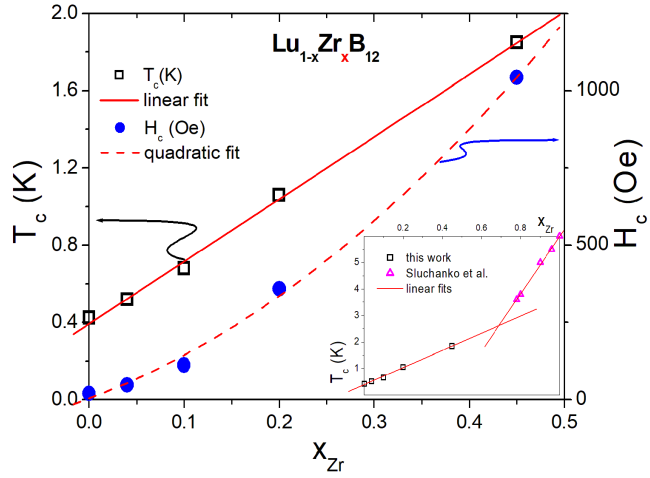

Fig. 4. Variation of critical temperature (left axis) and critical field (right axis) as a function of zirconium concentration ($0 \leq x \leq 0.45$) in Lu$_{1-x}$Zr$_x$B$_{12}$ solid solutions. Evolution of $T_c(x)$ for $0 \leq x \leq 1$ based on data from [6] is presented in the inset.

of $\mathrm{d}T_c/\mathrm{d}x = +120$ mK/at.% was observed. These all indicate that a crossover in the $T_c(x)$ dependence of Lu$_{1-x}$Zr$_x$B$_{12}$ compounds appears between 45% and 78% of Zr (see inset of Fig. 4), a crossover which has to be studied in details in the future.

4. Conclusions

For the first time the superconducting phase diagram of LuB$_{12}$, as well as of Lu$_{1-x}$Zr$_x$B$_{12}$ solid solutions with $x \leq 0.45$, were studied down to very low temperatures. A linear increase of critical temperature and a quadratic increase of critical magnetic field with increasing concentration of zirconium up to 45% were observed. To determine the exact critical concentration at which the crossover from weak to strong coupling occurs, further precise measurements of point contact spectroscopy, magnetization, and specific heat have to be carried out down to very low temperatures.

Acknowledgments

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