Superconductivity in ZrB_{12} and LuB_{12} with Various Boron Isotopes

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Abstract In BCS-type superconductors Zr^NB_{12} ($T_C \approx 6$ K) and Lu^NB_{12} ($T_C \approx 0.42$ K) heat capacity $C(T)$ and magnetization measurements have been carried out on high quality single crystals with various boron isotopes (with $N = 10, 11$, and with natural composition of ^{10}B and ^{11}B). Parameters of the superconducting and normal states have been deduced from this study, allowing comparison between these two dodecaborides. It was shown that ZrB_{12} is a type-II superconductor in which the Ginzburg–Landau parameter varies in the range $\kappa = 0.8\text{--}1.12$. A detailed analysis of specific heat in the normal state of $\text{R}^{10}\text{B}_{12}$, $\text{R}^{11}\text{B}_{12}$ and $\text{R}^{\text{nat}}\text{B}_{12}$ (where $\text{R} = \text{Zr}, \text{Lu}$) has revealed three Einstein type vibration modes of Zr^{4+} -ions in ZrB_{12} with characteristic energies $\theta_{\text{E1}}(\text{Zr}^N\text{B}_{12}) \approx 200$ K and $\theta_{\text{E2,3}}(\text{Zr}^N\text{B}_{12}) \approx 450$ K,

whereas only one quasi-local mode of Lu^{3+} -ions in LuB_{12} with $\theta_{\text{E1}}(\text{Lu}^N\text{B}_{12}) \approx 160\text{--}170$ K was detected. This difference of vibration spectra has been found to be the main reason for the dramatic change of T_C for ZrB_{12} and LuB_{12} . Using strong coupling approximation, moreover, the Coulomb pseudopotential μ^* , electron–phonon interaction constant λ^* and logarithmic average frequency ω_{ln} were determined.

Keywords Cage-glasses · Superconductivity · Einstein mode pairing

The discovery of superconductivity in MgB_2 at $T_C \approx 40$ K has stimulated intensive studies of other superconducting borides, renewing interest to investigation of Lu and Zr dodecaborides with quite moderate T_C values. In changing the metal ion $\text{R}=\text{Lu}, \text{Zr}$ very different T_C values are obtained, and about 15 times' ratio of the critical temperatures ($T_C \approx 6$ K for ZrB_{12} [1, 2] and $T_C \approx 0.4$ K for LuB_{12} [3]) was detected. The origin of this behavior is not cleared up to now for these materials with similar conduction band and crystalline structures belonging to the same cage-glasses class of borides [4]. Inelastic neutron scattering studies of the phonon spectra in LuB_{12} and ZrB_{12} [5] have detected noticeable, but not dramatic changes (15 meV and 17.5 meV) in the position of almost dispersion-less quasi-local mode, which is attributed to vibrations of loosely bounded Lu/Zr ions enclosed in spacious cuboctahedra B_{24} cavities of the rigid covalent boron sublattice of RB_{12} . A moderate difference in electron structure of these two compounds is caused by conduction band filling when Lu^{3+} -ion is changed to Zr^{4+} in the RB_{12} unit cell. As a result, an elevation by about 0.3–0.4 eV of the Fermi level E_F was observed in zirconium dodecaboride in comparison with the E_F position in LuB_{12}

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Fig. 1 Left and right panels: Temperature dependences of the critical field for $\text{Lu}^{10}\text{B}_{12}$ ($\blacktriangle$) and $\text{Lu}^{11}\text{B}_{12}$ ($\blacktriangledown$), $\text{Lu}^{\text{nat}}\text{B}_{12}$ ($\blacksquare$) and $\text{Zr}^{\text{nat}}\text{B}_{12}$ ($\bullet$). Lines in the left panel are guides to the eye and the line at the right panel represents the BCS dependence (1)

Fig. 2 Temperature dependences of the specific heat of $\text{Zr}^{11}\text{B}_{12}$ in the temperature range 1.8–300 K (left panel). In the right panel the range of superconducting phase transition (1.8–7 K) is shown in coordinates $C/T = f(T)$ for several magnetic fields below 1000 Oe (see also [7])

[6], which is accompanied with only a small increase in the electron density of states of ZrB_{12} .

To shed more light on the nature of the T_c difference between ZrB_{12} and LuB_{12} we have studied the heat capacity of these compounds in the temperature range 1.8–300 K in combination with magnetic measurements in the normal and superconducting states. The experiments have been carried out on the high quality single crystals with different boron isotopes— R^NB_{12} ($\text{R}=\text{Zr}, \text{Lu}$; $N=10$, natural and 11) produced by inductive zone melting. The specific heat was measured by Quantum Design PPMS-9 installation, and the diamagnetic response was investigated by AC-modulation technique in HelioxTMVT ^3He variable temperature refrigerator in the range 0.3–4.2 K, and by home-built SQUID-magnetometer at temperatures 4.2–300 K and in magnetic field up to 10 kOe.

Figure 1 shows the H – T magnetic phase diagrams of the superconducting state obtained for Lu^NB_{12} and $\text{Zr}^{\text{nat}}\text{B}_{12}$ from magnetic measurements. The temperature dependences of the critical field presented in Fig. 1 were approxi-

mated by the BCS relation

$$H_c(T)/H_c(0) = 1.7367x[1 - 0.273x - 0.0949x^2],$$

$$x = 1 - T/T_c. \quad (1)$$

The values of the thermodynamic critical field $H_c(0)$ detected from the approximation (1) are shown on the right panel of Fig. 1.

As an example, results of heat capacity measurements of $\text{Zr}^{11}\text{B}_{12}$ are shown in Fig. 2, where the left panel demonstrates $C(T)$ dependences in the temperature range 1.8–300 K for magnetic fields up to 30 kOe. In the right panel the superconducting phase transition is presented for several magnetic fields below 1000 Oe. The temperature dependence of the specific heat in normal and superconducting states has been used to estimate the thermodynamic critical field $H_c(T)$ from the relations

$$1/2\mu_0 V H^2 C(T) = \Delta F(T) = \Delta U(T) - T \Delta S(T) \quad (2)$$

Table 1 Superconducting transition temperature T_C , thermodynamic critical field H_C , upper critical field H_{C2} , superconducting gap Δ , Ginzburg–Landau parameter κ , coherence length $\xi(0)$, and penetration depth $\lambda(0)$ of $Zr^{10}B_{12}$, $Zr^{nat}B_{12}$, and $Zr^{11}B_{12}$ dodecaborides (see also [7])

Composition	T_C , K	$H_C(0)$, Oe	$\Delta(0)$, K	H_{C2} , Oe	$\kappa(0)$	$\xi(0)$, Å	$\lambda(0)$, Å
$Zr^{10}B_{12}$	5.76	361	9.8	584	1.14	751	859
$Zr^{11}B_{12}$	5.96	395	10.2	547	0.98	776	760
$Zr^{nat}B_{12}$	5.98	410	10.4	578	1.00	755	752

Fig. 3 Temperature dependence of the Ginzburg–Landau parameter κ for the $Zr^{10}B_{12}$, $Zr^{nat}B_{12}$, and $Zr^{11}B_{12}$ compositions. The thermodynamic critical field, $H_C(T)/H_C(0)$, determined by integration of relations (2)–(4) (see the text) is shown in the inset. I and II denote types-I and -II superconductivities

$$\Delta U(T) = \int [C_s(T') - C_n(T')] dT' \quad (3)$$

$$\Delta S(T) = \int dT' [C_s(T') - C_n(T')]/T', \quad (4)$$

where F , U , and S denote the free energy, internal energy, and entropy, respectively; V is the molar volume. Subscripts n and s correspond to normal and superconducting phases, and the integration in Eqs. (3)–(4) is performed for the temperature range from T to T_C . The calculated values of $H_C(0)$ are given in Table 1. In the inset of Fig. 3, we also show the normalized plot of $(H_C(T)/H_C(0))$ for the thermodynamic magnetic field for all three $Zr^N B_{12}$ compositions under study.

Then, according to the relations of BCS theory

$$\Delta(0) = [2\pi N(E_F)]^{-1/2} H_C(0) \quad (5)$$

$$\xi(0) = (\Phi_0/2\pi H_{C2})^{1/2} \quad (6)$$

$$\kappa(T) = 2^{-1/2} H_{C2}(T)/H_C(T), \quad (7)$$

where Φ_0 is the flux quantum, we determined the superconducting gap $\Delta(0)$, coherence length $\xi(0)$, and penetration depth $\lambda(0)$ (see Table 1). The electron density of states $N(E_F)$ was estimated from the Sommerfeld coefficient γ , which was determined to be ~ 4.5 mJ/(mole·K²) (Fig. 2) and 3.4 mJ/(mole·K²) [2] for ZrB_{12} and LuB_{12} ,

respectively. Additionally, the electron–phonon interaction constant λ_{ep} was estimated to be $\lambda_{ep} \sim 0.4$ from the electronic contribution. The plotted temperature dependence of the Ginzburg–Landau parameter $\kappa(T)$ is in Fig. 3. The ratio $2\Delta(0)/k_B T_C = 3.41$ – 3.47 determined in this work for $Zr^N B_{12}$ with different N corresponds with reasonable accuracy to the value of 3.52 predicted by the BCS model, and to the value of 3.7 found in [2]. The analysis of the $\kappa(T)$ curves (Fig. 3) indicates that all studied ZrB_{12} samples are type-II superconductors, since the $\kappa(T)$ plots for $Zr^{nat}B_{12}$, $Zr^{10}B_{12}$, and $Zr^{11}B_{12}$ are located above the threshold value $\kappa_C = 2^{-1/2}$. Thus, the conclusion made in [3] about the I–II/I phase transition in ZrB_{12} was not confirmed by our analysis.

A comparative analysis of contributions to specific heat in the normal state of $Zr^N B_{12}$ and $Lu^N B_{12}$ was carried out in framework of the approach developed for cage-glass systems in [4]. Debye temperatures θ_D ($Lu^N B_{12}$) = 1190 K and θ_D ($Zr^N B_{12}$) = 1500 K were used to estimate the contribution from the boron sublattice component C_{ph} to specific heat [2, 4]. After subtracting both of the electron heat capacity $C_{el} = \gamma T$ and Debye component C_{ph} from total heat capacity ($C_{exp} - C_{el} - C_{ph}$), the rest was approximated by the sum of Einstein oscillators

$$\frac{C_E}{T^3} = \frac{3R}{\theta_E^3} \left(\frac{\theta_E}{T} \right)^5 \frac{e^{-\frac{\theta_E}{T}}}{(1 - e^{-\frac{\theta_E}{T}})^2} \quad (8)$$

attributed to Zr/Lu vibrations in oversized B_{24} octahedron cages, and by Schottky type contributions

$$\frac{C_{Shi}}{T^3} = \frac{RN_i g_{0i} g_{1i}}{T^3} \left(\frac{\Delta E_i}{T} \right)^2 \frac{e^{\frac{\Delta E_i}{T}}}{(g_{0i} e^{\frac{\Delta E_i}{T}} + g_{1i})^2} \quad (9)$$

which originate from N_i two-level systems (TLS) of the randomly distributed Zr/Lu ions. The R-ions' disordering results from random distribution of the boron vacancies in the RB_{12} matrix, producing consequently a displacement of Zr/Lu ions from their central positions inside B_{24} cavities in these cage-glass compounds [4] (in Eq. (9) R is the gas constant, g_{0i} and g_{1i} are the degeneracies of $i = 1, 2$, and ΔE_i are the splitting energies). Examples of the data analysis are presented in Fig. 4.

The deduced Einstein temperatures θ_{Ei} (Eq. (8)), splitting energies ΔE_{1i} and ΔE_{2i} and concentrations N_1 and

Fig. 4 Analysis of the rest $(C_{\text{exp}} - C_{\text{el}} - C_{\text{ph}})/T^3 = f(T)$ for R^NB_{12} ($\text{R} = \text{Zr}, \text{Lu}$; $N = 10, \text{nat}$ and 11) with the separation into Einstein (E) and Schottky type (TLS1, TLS2) components (see Eqs. (8)–(9)). The lines are the approximation by Schottky and Einstein contributions and by the resulting curve

N_2 for TLS1 and TLS2 (Eq. (9)) are also shown in panels of Fig. 4. It is worth to note that the most important difference between heat capacities of ZrB_{12} and LuB_{12} consists of the composition of quasi-local modes in these two dodecaborides. Indeed, it is evident from Fig. 4 that two high frequency Einstein oscillators $\theta_{E2} \approx \theta_{E3} = 420\text{--}450$ K were observed additionally to the main Zr^{4+} -ion vibration (with energy $\theta_{E1} \approx 200$ K ≈ 17.5 meV) in the case of ZrB_{12} (see left panel) in comparison with LuB_{12} where only a single Lu^{3+} mode (with $\theta_E \approx 165$ K ≈ 14.2 meV, see right panel) was detected for all Lu^NB_{12} crystals with different boron isotopes. The characteristics of Schottky components TLS1 and TLS2 (Fig. 4) will be discussed elsewhere. Here we will consider in detail only the effect of Einstein modes on superconductivity of ZrB_{12} and LuB_{12} . The isotope effect in ZrB_{12} for zirconium ($\beta \approx -0.32 \pm 0.02$) is much larger than for boron ($\beta \approx -0.09 \pm 0.05$) [8], pointing to a dominant contribution of the Zr/Lu atom quasi-local modes to the electron–phonon coupling responsible for superconductivity in RB_{12} . Our analysis is based on McMillan equations

$$k_B T_C = \frac{\hbar \omega_{\text{ln}}}{1.2} \exp \left[-\frac{1.04(1 + \lambda^*)}{\lambda^* - \mu^*(1 + 0.62\lambda^*)} \right] \quad (10)$$

$$\omega_{\text{ln}} = \exp \left[+\frac{2}{\lambda} \int_0^\infty \ln \omega \frac{\alpha^2 F(\omega)}{\omega} d\omega \right], \quad (11)$$

where μ^* denotes the Coulomb pseudopotential, λ^* the electron–phonon interaction constant and ω_{ln} the logarithmic average frequency. From Eq. (10) for LuB_{12} , in which superconductivity is mediated by the single Einstein mode, we have $\omega_{\text{ln}} = \theta_E \approx 165$ K, and taking into account $\lambda^* =$

$\lambda_{\text{ep}} \approx 0.4$ [2] and $T_C \approx 0.42$ K it is possible to estimate $\mu^* \approx 0.119$. In case of ZrB_{12} , where three quasi-local vibrations are responsible for superconductivity, λ^* may be written as

$$\lambda^* = 2 \int_0^\infty \frac{\alpha^2 F(\omega)}{\omega} d\omega = \frac{1}{3}(\lambda_1 + 2\lambda_{2,3}) \quad (12)$$

(here $\alpha^2 F(\omega)$ is Eliashberg function and λ_i are partial electron–phonon interaction constants for different Einstein modes). In a crude approximation when $\lambda_1 = \lambda_{2,3}$ the $\omega_{\text{ln}}(\text{ZrB}_{12}) \approx 344$ K, the coupling constant becomes $\lambda^*(\text{ZrB}_{12}) \approx 0.59$. If we suppose that $\lambda_1 \approx 0.4$ [2], from Eq. (12) we receive $\lambda_{2,3} \approx 0.685$. Then the correction to ω_{ln} may be obtained as $\omega_{\text{ln}} = \omega_{E1}(\frac{\lambda_1}{\lambda_1 + 2\lambda_2}) \cdot \omega_{E2}(\frac{2\lambda_2}{\lambda_1 + 2\lambda_2}) \approx 368$ K, resulting only in a small reduction of electron–phonon interaction constant: $\lambda^*(\text{ZrB}_{12}) \approx 0.58$. Thus, the dramatic T_C variation in Lu- and Zr-dodecaborides may be naturally explained by an essential (~ 2.2 times) increase of the pre-exponent ω_{ln} between LuB_{12} and ZrB_{12} superconductors in combination with a noticeable (in the range of 0.4–0.58) enhancement of λ^* .

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