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Strong-Coupling Features in YB_6 and ZrB_{12} Studied by Point-Contact Spectroscopy

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Point-contact spectroscopy studies of the superconducting energy gap and the electron–phonon coupling mechanism are performed on the boron rich YB_6 and ZrB_{12} single crystals. The obtained values of the superconducting energy gaps suggest the strong coupling with $2\Delta/k_BT_c \approx 4.2$ for YB_6 and $2\Delta/k_BT_c \approx 4.15$ for ZrB_{12}. We have observed the dominant soft phonon modes mediating superconductivity in the both samples at energy ≈ 8 meV for YB_6 and ≈ 11 meV in ZrB_{12}, respectively.

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1. Introduction

Discovery of two-gap superconductivity in MgB_2 at $T_c \approx 40$ K provoked a renewed interest in studies of physical properties of the "already well known" superconducting borides. Such systems are also YB_6 (with superconducting transition at $T_c \leq 8.4$ K) and ZrB_{12} ($T_c = 6$ K) [1]. The both boron-rich compounds are hard cubic materials with low frequency phonon modes and low DOS at the Fermi level. Our previous point-contact spectroscopy measurements [2] and the specific heat results of Lortz et al. [3] suggest strong-coupling superconductivity of YB_6 characterized by the reduced superconducting gap $2\Delta/k_BT_c \approx 4.1$ and the dominant Einstein-like phonon mode at $E \approx 8$ meV. In ZrB_{12} more contradicting results have been published. The specific heat measurements show a medium coupling strength of superconductivity with $2\Delta/k_BT_c \approx 3.7$ and a dominant phonon mode at 15 meV [4]. On the other hand, the direct measurements of the energy gap by point-contact spectroscopy [5] indicate very strong coupling for ZrB_{12} with $2\Delta/k_BT_c \approx 4.4$.

In this paper we present our preliminary results on the study of strong coupling features revealed in the point-contact spectra measured on YB_6 and ZrB_{12} in the superconducting state. The superconducting energy gap and the characteristic phonon mode mediating superconductivity are presented for the both borides.

2. Model

Point-contact (PC) spectroscopy enables direct experimental study of the electron–phonon interaction (EPI) in normal metals. The current–voltage (I–V) characteristics measured through a ballistic microconstriction between two metals in the normal state (N–N) due to inelastic quasiparticle scattering on phonons reveal small nonlinearities at characteristic phonon energies of both metals. The second derivatives of the I–V curves $\mathrm{d}^2V/\mathrm{d}I^2(V)$ are related to the EPI function $\alpha^2F(\omega)$. When a PC is formed between a normal metal and a superconductor (N–S) also the superconducting energy gap can be revealed in the $\mathrm{d}I/\mathrm{d}V(V)$ spectrum. In this case the Blonder–Tinkham–Klapwijk (BTK) theory describes PC spectrum incorporating the parameter of the barrier strength Z, the value of the energy gap Δ, and a parameter Γ for the quasi-particle lifetime broadening [6]. This model is capable to describe spectra obtained on different PC interfaces, spanning from a pure metallic one (with $Z = 0$ and PC conductance twice higher inside the gap voltage region $V \leq \Delta/e$) to a Giaver-like tunneling case (with $Z \gg 0$ and a peak at the gap voltage). PC spectroscopy is also applicable for the study the EPI in superconductors. The I–V curves measured on N–S contacts can show nonlinearities at energies higher than Δ either due to inelastic quasiparticle scattering on phonons (similarly to the classical PC spectroscopy on normal metals), or due to an energy dependent gap present in the elastic component of the PC spectra of the superconductors with strong coupling. In the both mechanisms the $\mathrm{d}^2V/\mathrm{d}I^2(V)$ derivative is proportional to the EPI function $\alpha^2F(\omega)$. The first mechanism leads to about the same nonlinearities in the spectrum at the phonon energies independently if the superconducting electrode of the junction is in the normal or superconducting state. On the other hand, in the case of strongly coupled superconductors the elastic component in the spectrum due to energy dependent gap reveals significantly stronger nonlinearities which fade out when the junction is driven into the normal state with $\Delta = 0$. This case is analogous

to the superconducting tunnelling spectroscopy. Yet another effect of the energy dependent superconducting gap is an energy shift of the strongly coupled phonon anomalies to the higher energies by the size of the gap [7].

3. Experimental

PC spectroscopy measurements have been performed on the high quality single crystalline YB_6 ($T_c = 7.4$ K) and ZrB_{12} ($T_c = 6$ K) samples [8]. The bulk T_c is determined from resistive transitions which have been approved by the local PC spectroscopy measurements. The point contacts have been formed *in situ* by pressing a metallic tip (Pt or W) on the fresh surface of a superconductor using a differential screw mechanism.

4. Results

Figure 1 shows the representative PC spectra of the both samples (solid lines) measured at $T = 1.6$ K (upper curves) and 4.2 K (lower curves). The open symbols plot the fitting curves from the BTK model. The energy gap values obtained from fits at the lowest temperature $T = 1.6$ K, which are $\Delta_{YB6} = 1.35 \mp 0.02$ meV and $\Delta_{ZrB12} = 1.07 \mp 0.03$ meV confirm strong coupling superconductivity in the both systems with coupling strengths $2\Delta/k_BT_c \approx 4.2$ for YB_6 and $2\Delta/k_BT_c \approx 4.15$ for ZrB_{12}. For the spectra measured at $T = 4.2$ K the gap values $\Delta_{YB6}(4.2\text{ K}) = 1.1 \mp 0.03$ meV and $\Delta_{ZrB12}(4.2\text{ K}) = 0.85 \mp 0.02$ meV have been obtained.

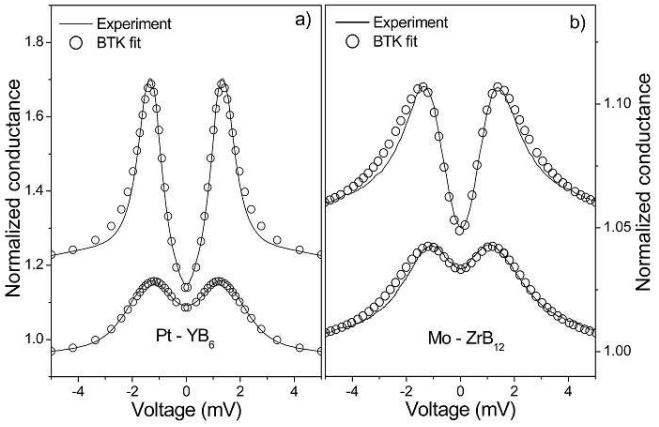

Fig. 1. Typical normalized PC spectra (solid lines) of Pt–YB6 (a) and Mo–ZrB_{12} (b) measured at $T = 1.6$ K — upper curves and $T = 4.2$ K — lower curves. BTK fitting results are plotted by open circles. Curves are shifted for the clarity.

Figure 2 plots the second derivatives of the PC spectra of YB_6 (Fig. 2a) and ZrB_{12} (Fig. 2b) in the superconducting state (solid line). The Pt and W tips as counterelectrodes in PC have been chosen, because their characteristic phonon energies do not cover the range where the

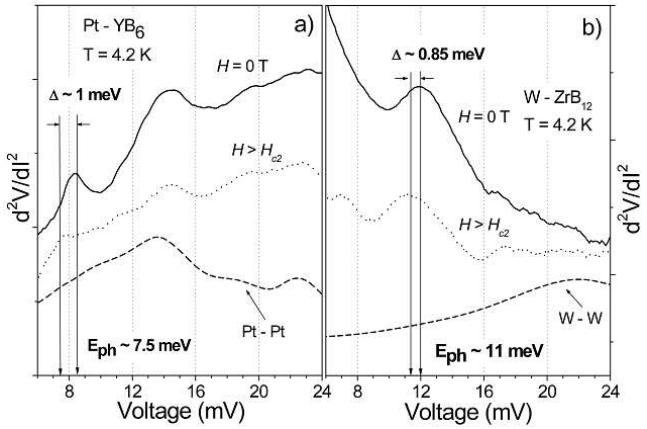

Fig. 2. Second derivatives of the I–V characteristics of Pt–YB_6 (a) and W–ZrB_{12} (b) measured in superconducting ($T = 4.2$ K, $H = 0$ T, solid line) and normal state ($T = 4.2$ K, $H > H_{c2}$, doted line). The dashed lines are the EPI spectra of Pt (a) and W (b). The long arrows emphasize the shift of the low energy phonon modes by the value of the superconducting energy gap $\Delta_{YB6}(4.2\text{ K}) \approx 1$ mV and $\Delta_{ZrB12}(4.2\text{ K}) \approx 0.85$ mV.

strong coupling phonon modes in YB_6 and ZrB_{12} are expected [8]. The dashed lines in Fig. 2 show the PC spectra of the electron–phonon interaction of Pt and W, respectively. The PC spectra have been measured also with YB_6 and ZrB_{12} in the normal state — above the upper critical field $H > H_{c2}$. The values of H_{c2} have been determined directly in our experiments at the fields, where the superconducting gap structure of the PC spectra has disappeared. Their values $H_{c2} = 0.28$ T for YB_6 and $H_{c2} = 0.045$ T for ZrB_{12} are in a good agreement with the data published by another groups [3, 4]. The majority of the $\mathrm{d}^2V/\mathrm{d}I^2(V)$ spectra revealed well defined nonlinearities up to 30 mV. In the case of Pt–YB_6 (Fig. 2a) at the zero field a sharp peak visible at the energy 8.5 mV is followed by two maxima at the voltages around 14–15 mV and 18–25 mV. Comparing this spectrum with the EPI spectrum of Pt (dashed line) determined in Ref. [9] one can see that the maxima observed in our spectra above 10 mV are positioned at the characteristic phonon energies of Pt. Importantly, the low energy sharp peak observed in the superconducting state at 8.5 mV is reduced in the increased magnetic field and a shift of its position is visible from 8.5 mV to ≈ 7.5 mV in the normal state. The same behavior is observed in W–ZrB_{12} point-contacts (Fig. 2b). The zero field maximum of $\mathrm{d}^2V/\mathrm{d}I^2(V)$ at 12 mV is slightly reduced and shifted to value near 11 mV at a field $H = 0.1$ T $> H_{c2}$. Then, in the both borides the low-energy phonon peak position is reduced by the value of the superconducting energy gap $\Delta_{YB6}(4.2\text{ K}) \approx 1$ meV and $\Delta_{ZrB12}(4.2\text{ K}) \approx 0.85$ meV and its intensity is suppressed when the sample is driven from the superconducting to the normal state. These two features are typical for the PC spectra of strongly coupled superconductors.

5. Conclusions

We can conclude, that the strong coupling superconductivity of YB_6 with $2\Delta/k_BT_c \approx 4.2$ is mediated by the phonon mode of Y atoms located at ≈ 7.5 meV [4]. Similarly, the Zr atom vibrations at ≈ 11 meV enclosed in the boron cage [4] are responsible for the strong coupling in ZrB_{12} with $2\Delta/k_BT_c \approx 4.15$.

Acknowledgments

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