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Electron-phonon interaction in transition-metal diborides TB_2 (T=Zr,Nb,Ta) studied by point-contact spectroscopy

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The electron-phonon interaction (EPI) in transition-metal diborides TB_2 (T=Zr,Nb,Ta) is investigated by point-contact (PC) spectroscopy. The PC EPI functions were recovered and the EPI parameters $\lambda \lesssim 0.1$ were estimated for all three compounds. Common and distinctive features between the EPI functions for those diborides are discussed also in connection with superconductivity in MgB_2.

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I. INTRODUCTION

The recent discovery of superconductivity in MgB_2 at 39 K by Akimitsu (see Nagamatsu *et al.*[1]) renewed the interest in electron transport measurements and activated a search for superconductivity in other diborides. According to a recent review[2] no superconducting transition has been observed so far in diborides of transition metals TB_2 (T=Ti, Zr, Hf, V, Cr, Mo). Only NbB_2 is expected to superconduct with a rather low transition temperature $T_c < 1$ K, and contradictory reports about superconductivity up to $T_c = 9.5$ K in TaB_2 can be found in the literature (see, e.g., Refs. 2 and 3 and further references therein). Finally, the reported $T_c = 7$ K in ZrB_2 (Ref. 3) encourages further studies of these three diborides.

The goal of this paper is to determine the electron-phonon interaction (EPI) function for selected diborides by means of point-contact (PC) spectroscopy in order to address the above-mentioned issues about superconductivity in these compounds. The measurement of the nonlinear conductivity of PC's between two metals allows us, in a direct way,[4] to recover the PC EPI function $\alpha^2F(\omega)$. The knowledge of $\alpha^2F(\omega)$ for conducting systems provides a consistent check for the possibility of a phonon-mediated pairing mechanism, e.g., by an estimation of the electron-phonon-coupling strength characterized by the EPI parameter $\lambda = 2\int \alpha^2F(\omega)\omega^{-1}d\omega$. From a comparison of the experimentally determined $\alpha^2F(\omega)$ with theoretical calculations, different models and approaches can be discriminated. Thus the PC spectroscopy could be helpful to understand details of the EPI in the diborides under consideration, and to evaluate contradictory reports about possible superconductivity within this family.

II. EXPERIMENTAL DETAILS

We have used single crystals of TB_2 (T=Zr,Nb,Ta) grown by the rf-heated floating-zone method.[5] Samples were prepared using a diamond wire saw. The residual resistivity ρ_0 and the residual resistance ratio (RRR) of TB_2 are shown in Table I.

The experimental cell with the sample holders, which allows mechanical movements of electrodes by differential screw mechanism, was placed directly in liquid ^{4}He to ensure good thermal coupling. The PC's were established *in situ* at low temperatures by a touching of the cleaved surface of TB_2 by the edge of another single crystal. We did not control the mutual orientation of electrodes; therefore, the contact axis was not determined with respect to the definite crystallographic direction. However, we did not observe an appreciable variation of the maxima position (see additional remarks for NbB_2 at the end of the discussion below) and their relative intensity in the spectra for different contacts. Therefore, we believe the anisotropy is not crucial. Both the differential resistance dV/dI and the second derivative of the I-V characteristic $d^2V/dI^2(V)$ vs V were registered using a standard lock-in technique. The zero-bias resistance R_0 of investigated contacts ranged from a few ohms up to several tens of ohms at 4.2 K.

III. RESULTS AND DISCUSSION

The voltage V applied to the ballistic contact defines the excess energy eV of electrons; therefore, for some of them backscattering processes caused by the creation of phonons can take place. This results in a decrease of the net current through the contact and leads to a nonlinear I-V characteristic. According to the theory of Kulik, Omelyanchouk, and Shekhter[6] in this case the second derivative $-d^2I/dV^2(V)$ of

TABLE I. Parameters of investigated TB_2 single crystals.

Samples [a]	$\rho_0 \times 10^9$, Ωm	RRR	$n^b \cdot 10^{-28}$, m^{-3}
ZrB_2	3.31	24	13
NbB_2	–	–	18.2
TaB_2	220	1.2	18.6

[a]For NbB_2, the estimated ρ was two orders of magnitude larger compared to the other diborides, probably due to the presence of inner cracks. Therefore, corresponding cells in the Table I are empty.

[b]The density of carriers n was estimated by the number of valence electrons (four for ZrB_2, five for NbB_2 and TaB_2) per volume of the corresponding unit cell.

the I-V curve at low temperatures is proportional to $\alpha^2_{\rm PC}F(\omega)$. In the free electron approximation[7]

$$-\frac{d^2I}{dV^2}\propto R^{-1}\frac{dR}{dV}=\frac{8\,ed}{3\,\hbar v_{\rm F}}\alpha^2_{\rm PC}(\epsilon)F(\epsilon)|_{\epsilon=eV}, \qquad (1)$$

where $R=dV/dI$, $\alpha_{\rm PC}$, roughly speaking, measures the interaction of an electron with one or another phonon branch. The kinematic restriction of electron scattering processes in a PC is taken into account by the factor $K=1/2(1-\theta/\tan\theta)$, where θ is the angle between initial and final momenta of scattered electrons [for transport and Eliashberg EPI functions the corresponding factors are: $K=(1-\cos\theta)$ and $K=1$, respectively]. Therefore in PC spectra the large angle $\theta\rightarrow\pi$ scattering (backscattering) processes of electrons dominate.

From Eq. (1) the EPI function $\alpha^2_{\rm PC}(\epsilon)\,F(\epsilon)$ can be expressed via the measured rms signal of the first V_1 and second V_2 harmonics of a small alternating voltage superimposed on the ramped dc voltage V:

$$\alpha^2_{PC}(\epsilon)\,F(\epsilon)=\frac{3\sqrt{2}}{4}\frac{\hbar v_{\rm F}}{ed}\frac{V_2}{V_1^2}. \qquad (2)$$

The PC diameter d, appearing in Eqs. (1) and (2), determines the constriction resistance which consists of a sum of the ballistic Sharvin and the diffusive Maxwell terms according to the simple formula

$$R_{\rm PC}(T)\simeq\frac{16\rho l}{3\pi d^2}+\frac{\rho(T)}{d} \qquad (3)$$

derived by Wexler,[8] which is commonly used to estimate the PC diameter d. Here $\rho l=p_F/ne^2$, where p_F is the Fermi momentum, n is the density of charge carriers. Representative examples of measured $d^2V/dI^2(V)$ dependencies are shown in Fig. 1. Among tens of curves, which show reproducible phonon structures for each compound, we selected $d^2V/dI^2(V)$ characteristics with the most pronounced and intensive maxima. A common feature for all crystals is the presence of the main low energy maximum placed at about 30, 28, and 20 mV for ZrB_2, NbB_2, and TaB_2, respectively. This is in line with the common consideration that at fixed spring constants the phonon frequency decreases with increasing atomic mass (see Fig. 2). Such a behavior suggests that the first peak corresponds to the vibration of transition metal. Curiously, on the one hand, the aforementioned peaks appear just above the maximal phonon energy on PC spectra of the corresponding clean metals: Zr,[9] and Nb and Ta from Ref. 10 (see Table II). On the other hand, the neutron data peak position for MgB_2 on Fig. 2, at about 36 meV,[12] is far below the straight line connecting the TB_2 compounds. This might be considered a consequence of a softening of the corresponding spring constants, i.e., metallic bonds in MgB_2 instead of relatively strong TdB2p covalent bonds in the TB_2 series. Notice that the recent data[11] recovered maxima in the PC spectra of MgB_2, even at lower energies of about 30 and 20 meV. This cannot be occasional. It points either to

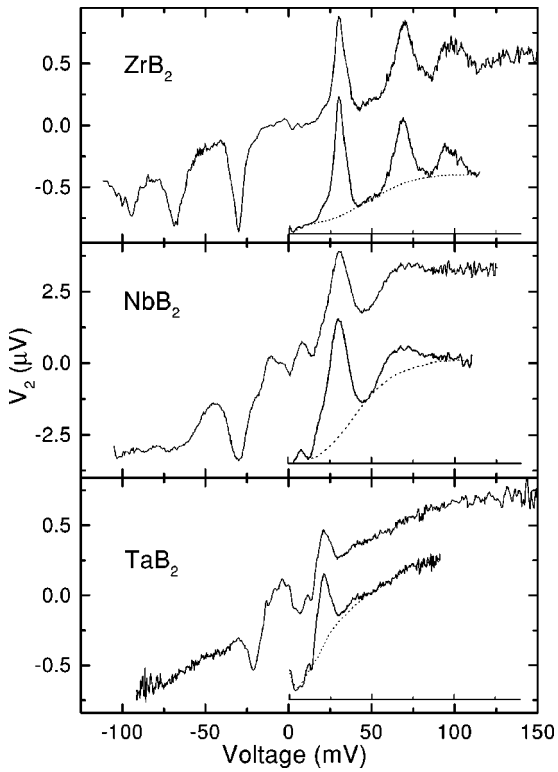

FIG. 1. Raw PC spectra $d^2V/dI^2(V)$ for investigated compounds at $T=4.2$ K. The phonon structure is clearly resolved with pronounced maxima up to 100 mV (see ZrB_2), while for TaB_2 only the low energy peak at 20 mV is seen. The spectra exhibit also a zero-bias anomaly, better pronounced in NbB_2 and TaB_2. The zero-bias resistance and modulation signal for ZrB_2 are $R_0=5.5\,\Omega$ and $V_1(0)=0.8$ mV, for NbB_2 they are $R_0=50\,\Omega$, $V_1(0)=2.8$ mV, and for TaB_2 they are $R_0=25\,\Omega$, $V_1(0)=1.3$ mV. The inset in each panel shows the second derivative $-d^2I/dV^2\propto(d^2V/dI^2)\times(dV/dI)^{-3}$ averaged for both polarities. Dotted lines present the behavior of the background.

peculiarities in the lattice dynamics of MgB_2 since such peaks are missing in standard first-principles phonon calculations[13,14] or to the presence of other, nonphononic, low-frequency bosonic excitations.[15] It is noteworthy that the presence of such anomalous low-energy modes has also been noticed by other experimental techniques: Raman scattering[16] and tunneling measurements.[17] Their relationship to its high critical temperature remains unclear at present.

Because of the large mass difference between the transition metal and the boron atoms the boron derived modes are expected to occur at much higher energy. Indeed, for ZrB_2 two additional maxima at 70 and 100 mV (Ref. 18) are well resolved, while for NbB_2 the high energy part of the spectrum presents a broad maximum around 60 mV. For TaB_2 the high energy phonon peaks were difficult to resolve, although according to a rough estimation[19] the boron in-plane and out-of-plane displacement modes should have energies of 98 and 85 meV, respectively. No spectral features were found for the above-mentioned compounds above 100 meV. This is in line with the measured surface phonons[20] for ZrB_2 and NbB_2. There all phonon frequencies are below 100 meV. Moreover, for both compounds, a phonon dispersion study[20]

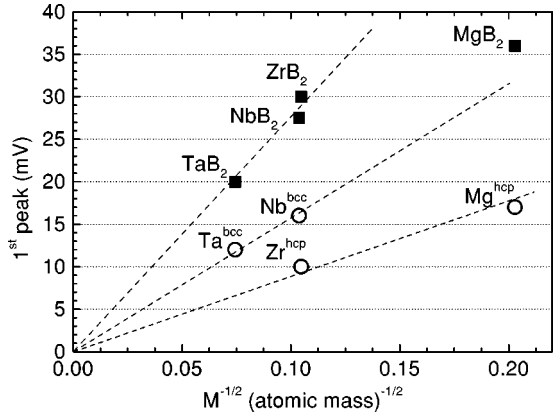

FIG. 2. The position of the first peak (squares) in the measured PC spectra for ZrB_2, NbB_2, and TaB_2 vs the inverse square root of atomic mass of the corresponding transition metal. For MgB_2 the peak position is according to the inelastic neutron scattering data (Ref. 12). Open circles show the position of the first peak in the PC spectra for the corresponding metals (Refs. 9 and 10). Straight dashed lines are to guide the eye.

demonstrated a gap between 30 and 50 meV which separates acoustic and optic branches. In this energy region a minimum in our PC spectra occurs. Comparing the high energy parts of the ZrB_2 and NbB_2 PC spectra, we may support the statement[20] that, for NbB_2 the boron surface phonon modes are softer and more complex than in the case of ZrB_2. Possibly for this reason in the PC spectra of NbB_2 all boron derived modes form broad structureless maxima around 60–70 meV (see Fig. 3).

To recover the spectral EPI function according to Eq. (2), at first $d^2V/dI^2(V)$ has been transformed into $-d^2I/dV^2(V)$, and thereafter the background (see Fig. 1, insets) was subtracted. There are a few models, both theoretical and empirical, for the background behavior. Using our experience with PC spectra of different metals and compounds we have drawn the background simply by eye with a dependence like $\exp(-1/x^2)$, as shown in Fig. 1, insets. During this procedure we paid attention to the following: (i) zero-bias anomalies were disregarded; (ii) the background curve is made to touch the measured one at the minimum above the first peak, where a gap between acoustic and optical phonons is expected; and (iii) above 100 mV or below in the case of lacking visible maxima the background coincides with the data. Figure 3 presents the recovered PC EPI function for the investigated diborides calculated by Eq. (2)

TABLE II. The phonon maxima and the EPI constant λ in TB_2 compounds measured by PC spectroscopy. The fifth column shows the maximal energy for phonon features in the PC spectrum (Refs. 9 and 10) for the corresponding transition metals: T=Zr, Nb, Ta.

Samples	First peak meV	Second peak meV	Third peak meV	$\hbar\omega^T_{max}$ meV	λ_{PC}
ZrB_2	30±0.5	68±1	95±2	25	0.06
NbB_2	28±2	60±5	–	28	0.08
TaB_2	20±1	40?	–	20	0.025

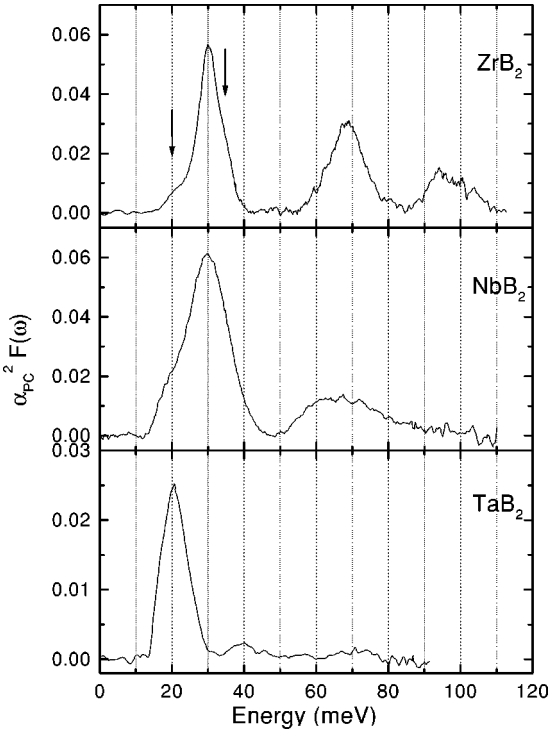

FIG. 3. The PC EPI function for ZrB_2, NbB_2, and TaB_2, recovered from the spectra in Fig. 1. The vertical arrows mark reproducible fine features as a bump and a shoulder for ZrB_2.

with a Fermi velocity $v_F=1\times10^6$ m/s. To obtain the PC diameter d we used the Sharvin part of the PC resistance from Eq. (3) and the calculated value $\rho l=p_F/ne^2=(3\pi^2)^{1/3}\hbar e^{-2}n^{-2/3}$ with n from Table I. By virtue of the fact that $d\propto(\rho l)^{1/2}\propto n^{-1/3}$ the simplicity of the evaluation of n (see Table I, footnote) is not crucial for the calculation of d and afterward for estimation of the EPI parameter λ.

It is also seen from Fig. 3 that the upper boundaries of the ZrB_2 and NbB_2 spectra are at about 110 and 90 meV (see Fig. 3), which is much larger than their Debye temperatures of 280 and 460 K, respectively, estimated from the Bloch-Grüneisen temperature dependence of the resistivity.[3]

With the EPI function we have calculated the EPI parameter $\lambda=2\int\alpha^2F(\omega)\omega^{-1}d\omega$. We should emphasize that, in general, due to presence of the K factor, $\lambda_{PC}\neq\lambda_{Eliashberg}$; however, for many superconductors it was found[10] that $\lambda_{PC}\simeq\lambda_{Eliashberg}$. As we can see from Table II, λ_{PC} is rather low for the diborides.[21] We remark that a small $\lambda_{PC}\simeq0.02$ was also reported for PC studies of the transition metal silicides $NbSi_2$ and $TaSi_2$.[22] The reason for this can be the deviation from the ballistic electron flow and the establishment of a regime with $l_i\ll d$ in PC (here l_i is the elastic mean free path of electrons), which adds a prefactor[23] of the order of l_i/d in Eq. (1). The large background level and the absence of the high energy peaks, e.g., for the PC spectra of TaB_2, may have the same origin: the lack of a ballistic regime in our PC's. Also note, that the TaB_2 samples are of relative low quality (their RRR's amounts to only 1.2) (see Table I); that is, a small l_i value is already expected in the bulk. Therefore, for TaB_2 we assume that λ is underestimated. However, in

the case of ZrB_2, where the PC spectra present distinct peaks up to the maximal energy, and even at the first peak such details as a bump at 20 mV and a shoulder at 35 mV are seen, we believe that our parameter λ_{PC} corresponds here to a real state of the art. Our results also show that NbB_2 has the largest λ_{PC} among the studied compounds. Thus the search for superconductivity in NbB_2 is more interesting. We should note that, among the studied diborides, for NbB_2 we observed the largest variation in the position of the first peak. For some PC spectra the peak shifted down to 22–23 mV. In this case any high energy maxima, e.g., at 60 mV, was difficult to resolve. Most likely this is due to disturbed metal structure in the PC area caused by low temperature deformation at the contact formation. In any case the effect of the anisotropy has to be studied. Of course, to draw a more weighty conclusion about details of the EPI and the λ value in the presented TB_2 family, a theoretical calculation of $\alpha^2_{PC}F(\omega)$ with the above-mentioned K factor, and a comparison with experimental data, any desirable.

Finally, we should stress that by investigation of MgB_2 thin films[11] the EPI inelastic contribution to the PC spectrum was estimated only in a few percent of the total PC resistance, which is nearly an order of magnitude lower than for the TB_2 under consideration. Why the EPI features on PC spectra of MgB_2 are shallow and hardly reproducible is still unclear at the moment. Possibly this is due to a weak EPI for a three-dimensional band of the Fermi surface sheet, which determines the PC conductivity of thin films,[24] along with a small l_i/d ratio.

IV. CONCLUSION

We have measured the PC spectra in transition metal diborides: ZrB_2, NbB_2 and TaB_2. The spectra exhibit structures up to an energy of about 100 meV, which is unequivocally caused by phonons. For all compounds the PC EPI function was established and the EPI parameter λ was calculated. The obtained small λ values strongly question the reported bulk superconductivity in these compounds. The PC EPI spectra of the above-mentioned diborides differs even qualitatively from that measured earlier for superconducting MgB_2.

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