Study of the electron-phonon interaction in metal diborides MeB$_2$ (Me=Zr, Nb, Ta, Mg) by point-contact spectroscopy

I. K. Yanson$^1$, Yu. G. Naidyuk$^1$, O. E. Kvitsinskaya$^1$, V. V. Fisun$^1$, N. L. Bobrov$^1$, P. N. Chubov$^1$, V. V. Ryabovoi$^1$, G. Behr$^2$, W. N. Kang$^3$, E.-M. Choi$^3$, H.-J. Kim$^3$, S.-I. Lee$^3$, T. Aizawa$^4$, S. Otani$^4$, and S.-L. Drechsler$^2$

$^1$ B. Verkin Institute for Low Temperature Physics and Engineering, National Academy of Sciences of Ukraine, 47 Lenin Ave., 61103, Kharkiv, Ukraine
$^2$ Leibniz-Institut für Festkörper- und Werkstofforschung Dresden e.V., Postfach 270116, D-01171 Dresden, Germany
$^3$ Pohang University of Science and Technology, Pohang 790-784, South Korea and
$^4$ Advanced Materials Lab., National Institute for Materials Sciences, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

(Dated: March 22, 2022)

We review investigations of the electron-phonon interaction (EPI) in metal diborides MeB$_2$ (Me=Zr, Nb, Ta, Mg) by point-contact (PC) spectroscopy. For transition metal compounds the PC EPI functions were recovered and EPI parameter $\lambda \lesssim 0.1$ were estimated. The data are consistent with the measured surface phonon dispersion curves. The low $\lambda$ value questions some reports about superconductivity in these compounds. Contrary, EPI in superconducting MgB$_2$ films manifests also in the PC spectra itself by virtue of an elastic EPI contribution to the excess current determined by the energy dependence of the superconducting order parameter. To analyse the phonon features in the PC spectra of MgB$_2$ a two-band model is exploited and the proximity effect in the k-space is suggested.

PACS numbers: 63.20.Kr, 74.80.Fp, 73.40.Jn

Introduction. Recently discovered superconductivity in the sp compound MgB$_2$ attracts much attention mainly due to relatively high $T_c \simeq 39$ K, which is the highest as for two-component systems. Probably a specific feature of this compound appears to be a rare example of two disconnected bands of the Fermi surface with quite different dynamical properties. One of those bands is two-dimensional (2D), with extremely strong electron-phonon interaction (EPI), while the other is 3D with a weak EPI.

The overwhelming majority of the community anticipated an electron-phonon mechanism in MgB$_2$. Thus, the preferable reason of the formation of Cooper pairs is EPI, and its investigation to understand the nature and peculiarities of superconductivity in MgB$_2$ is vastly desirable.

In the wake of the finding of superconductivity in MgB$_2$, scientific activity was applied to its search in other diborides (all having a hexagonal layered crystal structure of an AlB$_2$ type) along with the further study of their properties. According to a recent review, no superconducting transition has been observed so far in the diborides of transition metals MeB$_2$ (Me=Ti, Zr, Hf, V, Cr, Mo). As to the superconductivity in NbB$_2$, TaB$_2$ and ZrB$_2$ the controversial reports can be found.

In this article we would like to summarize our findings in the determination of the EPI function for the above mentioned diborides from the point-contact (PC) spectra. The attractive feature of the PC spectroscopy is that the measurement at low temperatures of the voltage derivative of the PC resistance allows a straightforward determination of the PC EPI function $\alpha^2 F(\omega)$. The knowledge of $\alpha^2 F(\omega)$ for conducting systems provides a consistent check for the possibility of a phonon-mediated pairing mechanism, e.g., by estimation of the electron-phonon-coupling strength characterized by the EPI parameter $\lambda = 2 \int \alpha^2 F(\omega) \omega^{-1} d\omega$. From the comparison of the experimentally determined $\alpha^2 F(\omega)$ with theoretical calculations different models and approaches can be discriminated.

Experimental details. The samples are c-axis oriented films of MgB$_2$, whose characteristics are described in Ref $^1$ and single crystals of MeB$_2$ (Me=Zr, Nb, Ta). The residual resistivity $\rho_0$ and the residual resistivity ratio (RRR) of all investigated diborides are shown in Table 1.

Different PC’s were established in situ by touching of the MgB$_2$ film or the cleaved surface of a transition metal single crystal by a sharpened edge of an Ag counter electrode. This geometry corresponds to a current flowing preferably along the c-axis of the film, a number of contacts was measured by touching the film edge after breaking Al$_2$O$_3$ substrate. By this means, the current flows preferably along the ab plane. As to PC’s on another diborides, the orientation of electrodes was not controlled with respect to the crystallographic axis. The zero-bias resistance $R_0$ of the investigated contacts ranged from a few ohms up to several tens of ohms at 4.2 K.

Both the differential resistance $dV/dI$ and the second derivative of I−V characteristic $d^2V/dI^2$ vs V were registered using a standard lock-in technique.

Results and discussion. According to the Kulik, Omelyanchouk and Shekhter theory $^8$ the second derivative $-d^2 I/dV^2$ of the I−V curve of a ballistic PC at low temperatures due to EPI is proportional to $\alpha_{PC}^2 F(\omega)$. In the free electron approximation $^9$

$$-\frac{d^2 I}{dV^2} \times R^{-1} \frac{dR}{dV} = \frac{8 e^2}{3 h v_F} \alpha_{PC}^2 F(\omega)|_{\omega \approx \omega_0},$$

where $R = dV/dI$. The factor $K = 1/2(1 - \theta/\tan \theta)$, entering in $\alpha_{PC}^2$, takes into account the kinematic restric-
Table I: Parameters of investigated diborides.

| Compound | Sample | $\rho_0 \cdot 10^3$, $\Omega$ m | RRR | $n^2 \cdot 10^{-28}$, m$^{-3}$ |
|----------|--------|-------------------------------|-----|-------------------------------|
| MgB$_2$  | film   | 60                           | 2.3 | 6.9                           |
| ZrB$_2$  | sgl. cry. | 3.3                       | 24  | 13                            |
| NbB$_2$  | sgl. cry. | -                           | -   | 18.2                          |
| TaB$_2$  | sgl. cry. | 220                         | 1.2 | 18.6                          |

* The density of carriers $n$ was estimated by the number of valence electrons (2 for MgB$_2$, 4 for ZrB$_2$, 5 for NbB$_2$ and TaB$_2$) per volume of the corresponding unit cell.

...ion of electron scattering processes in PC (for transport and Eliashberg EPI functions the corresponding factors are: $K = (1 - \cos \theta)$ and $K = 1$, respectively, with $\theta$ is the angle between initial and final momenta of scattered electrons). Respectively, the large angle $\theta \to \pi$ scattering (back-scattering) processes of electrons dominate in $\alpha^2_{PC}$.

According to Eq. (1) 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 $V$ defines the EPI function $\alpha^2_{PC}(\epsilon) F(\epsilon)$:

$$\alpha^2_{PC}(\epsilon) F(\epsilon) = \frac{3\sqrt{2}}{4} \frac{h v_F}{e d} \frac{V_2}{V^2}.$$ 

(2)

To estimate the PC diameter $d$, which enters in Eqs. (1) and (2), the relation $R_{PC}(T) \approx \frac{16\rho l}{3\pi^2} + \frac{\rho_T(T)}{\lambda^2}$ derived by Wexler is commonly used, which consists of a sum of the ballistic, Sharvin, and the diffusive, Maxwell, terms. Here $\rho l = p_F/n e^2$, where $p_F$ is the Fermi momentum, $n$ is the density of charge carriers.

**A. Transition metal diborides**

Representative examples of the $d^2I/dV^2(V)$ dependencies for each compound averaged over both voltage polarities are shown in Fig. 1 (left panel). Reproducible phonon maxima are clearly resolved up to 100 mV (see ZrB$_2$), while for TaB$_2$ only low energy peak at 20 mV is seen. The spectra exhibit also a zero-bias anomaly, especially remarkable in NbB$_2$ and TaB$_2$. A common feature for all spectra 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 general consideration that at fixed spring constants the phonon frequency decreases with increasing of atomic mass (see Fig. 1, right panel). Such a behavior suggests that the first peak corresponds to the vibration of the transition metal. On the other hand the neutron data peak position for MgB$_2$ on Fig. 1 (right panel) at about 35 meV is far below the straight line connecting the MeB$_2$ compounds. This might be considered as the consequence of a softening of the corresponding spring constants (i.e. metallic bonds in MgB$_2$ instead of relatively strong Me/Be covalent bonds in the MeB$_2$ series).

Table II: The phonon maxima and the EPI constant $\lambda$ in MeB$_2$ compounds measured by PC spectroscopy. The fifth column shows the maximal energy for phonon features in the PC spectrum for the corresponding transition metals: $\lambda_{PC}$.

| Samples | 1$^{st}$ peak meV | 2$^{nd}$ peak meV | 3$^{rd}$ peak meV | $h \omega_{max}$ meV | $\lambda_{PC}$ meV |
|---------|-----------------|-----------------|-----------------|-----------------|-----------------|
| MgB$_2$ | 30(?)           | ~ 60            | ~ 90            | 30              | -               |
| ZrB$_2$ | 30 ± 0.5        | 68 ± 1          | 94 ± 2          | 25              | 0.06            |
| NbB$_2$ | 28 ± 2          | 60 ± 5          | -               | 28              | 0.08            |
| TaB$_2$ | 20 ± 1          | 40(?)           | -               | 20              | 0.025           |
FIG. 2: The PC EPI function for ZrB$_2$ and NbB$_2$ recovered from the spectra in Fig. 1 (top panel) as compared to the HREELS data for these compounds (bottom panel).

60 mV. For TaB$_2$ the high energy phonon peaks were difficult to resolve, where according to a rough estimation 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 mentioned compounds above 100 meV. Our spectra are in line with the measured surface phonons for ZrB$_2$ and NbB$_2$ although the surface phonons, in general, are softer. For both compounds phonon dispersion study (Fig. 2, bottom panel) demonstrates a gap between 30-50 meV which separates acoustic and optic branches. Close to this energy region a acoustic and optic branches. Close to this energy region a gap feature is seen for ZrB$_2$ giving rise to structureless maxima around 60-70 mV (see Fig. 1). Note that the upper boundaries of the ZrB$_2$ and NbB$_2$ PC spectra are at about 110 mV and 90 mV (see Fig. 1), what is much larger than their Debye temperatures of 280 K and 460 K, respectively, estimated from the Bloch-Gruneisen temperature dependence of the resistivity [19].

With the use of the EPI function the parameter $\lambda = 2 \int \alpha^2 F(\omega)\omega^{-1}d\omega$ was calculated. For many superconductors it was found [3] that $\lambda_{PC} \approx \lambda_{Eliashberg}$. Table 2 shows that $\lambda_{PC}$ is rather low for the investigated diborides what is in line with the small $\lambda$ values reported for PC studies of the transition metal silicides NbSi$_2$ and TaSi$_2$ [34] ($\lambda_{PC} \approx 0.02$). The possible reasons for a small $\lambda$ value are discussed in Ref. [3]. Our results show that NbB$_2$ has the largest $\lambda_{PC}$ among the studied compounds, therefore existence of superconductivity in NbB$_2$ with observable $T_c$ is more likely.

FIG. 3: Averaged for both polarities spectrum $V_2 \propto d^2V/dI^2$ after subtracting of a linear background of MgB$_2$-Ag PC ($R_0 = 35 \Omega$, $T=4.2 K$, $V_{20} = 2.52 mV$) in comparison to the neutron PDOS of MgB$_2$ [5]. Inset: differential resistance $R = dV/dI(V)$ of the same PC.

B. MgB$_2$

In Fig. 3 the $V_2(eV) \propto d^2V/dI^2 (eV)$ and $dV/dI(V)$ (in the inset) characteristics are shown in the superconducting state at zero field. In the energy-gap region the two gap features are clearly seen with $\Delta_1 = 2.4$ and $\Delta_2 = 5.7$ meV (see inset). Further on, we simply denote by $\Delta$ the position of a $dV/dI$ minimum. In Fig. 3 the $V_2(V) \propto d^2V/dI^2$ dependence after subtracting of linear background in comparison to the phonon density of states (PDOS) is shown. Some accordance is seen between the positions of PDOS peaks and maxima in $V_2(V)$ dependence.

The reproducibility of this kind of PC spectrum for different contacts is seen in Fig. 3(b). Here, the contact resistance varies from 43 to 111 Ω with gap minima at $\Delta = 2.1$, 2.6, and 4.9 meV, respectively. The larger gap for curve 3 equals 7.0 meV. All the PC spectra (b) correlate with PDOS. The slight variation is probably due to the anisotropy and different scattering rates in the contacts. Compared with the theoretical EPI function for an isotropic one-band model (see, for example, Ref. [23]), the peak at $eV=60 \div 70$ meV of $E_{2g}$ boron mode is not too much higher in intensity, in accord with our earlier observation [24]. For the two-band model in clean limit, we expect an information mostly from the 3D band keeping in mind that we measure the c-axis oriented films. In this case, the theory predicts, that the EPI spectral function has the $E_{2g}$-peak intensity of the same order of magnitude as the other peaks of PDOS (see Fig. 1 in Ref. [24]).

According to our classification of the energy gap structure [24], it is due to the random orientation of the contact axis and scattering of charge carriers between two-band of Fermi surface, having gaps $\Delta_1$ and $\Delta_2$.
mixed. With an increase of interband scattering the magnitude of $\Delta_1$ ($\Delta_2$) moves to the higher (lower) value, respectively. For dirty contacts, where the admixture of the 2D band is essential, only one gap maximum remains with a broad distribution around $\approx 3.5 \text{ meV}$.

In this case $l$ is smaller than $d$ (where $l$ and $d$ are the electron mean free path and the size of the contact, respectively), and the inelastic backscattering contribution to the phonon structure, proportional to $l/d^2$ is small. Therefore, in the superconducting state, the observed phonon structure presents mainly the elastic contribution to the excess current.

The elastic term is proportional to the energy dependent part of the excess current $I_{exc}(eV)$, similar to the phonon structure in the quasiparticle DOS for tunneling spectroscopy:

$$ \frac{dI_{exc}}{dV}(eV) = \frac{1}{R_0} \left( \frac{\Delta_{in}(eV)}{eV + \sqrt{(eV)^2 - \Delta_{in}^2(eV)}} \right)^2, \quad (3) $$

where $\Delta_{in}(eV)$ is the gap parameter in the 3D band, induced by the 2D-band EPI. As seen in Fig. 3(a), if the $\Delta$ value increases (curves 1-3), then the intensity of the phonon structure in the units of $d(ln R)/dV = 2\sqrt{2}V_2/V_1^2$ increases too (Fig. 3(b)). That is because the modulation voltage $V_1$ decreases, whereas the amplitudes in $V_2(eV)$-units remain approximately the same. Note, that for curve 3 in Fig. 3(a) one has to take the lower gap $\Delta_1$, because the current is mainly determined by 3D band, as mentioned above.

In Fig. 4, the normal state spectrum above $T_c$ is displayed together with the differential resistances in the superconducting state (see inset), showing the energy gap structure. In spite of an increase of the temperature smearing above $20\text{ mV}$ at $41\text{ K}$ the residual phonon structure is still visible (curve 1 in Fig. 5). The smeared phonon features are superimposed on the rising linear background. For curve 2, we see an increase in scattering at $\approx 35\text{ mV}$, where the acoustic phonon peak occurs, and the saturation around $100\text{ mV}$, where the phonon spectrum ends. In the normal state, only those nonlinearities remain, which are due to the inelastic processes.

We stress that judging from the larger superconducting gap value ($\approx 3.5 \text{ meV}$ for curve 2 in the inset) the essential contribution is expected from the $\Delta_2(E)$ of 2D band for normal-state spectrum No. 2. This spectrum should contrast with curve 6 in Fig. 5 (see below), where the direct contribution from the 2D band is small, due to lower value of $\Delta$. Thus, the backscattering processes from the 3D band are mostly essential for spectrum 6 and the phonon features are not resolved at high energies. The shape of spectrum 1 in Fig. 5 presents the behavior intermediate between these two extremes, although its energy gap is approximately equal to curve 6 in Fig. 5. Beside the visible phonon features in the range $30 \div 100\text{ mV}$, it possesses a low energy bump at about $20\text{ mV}$.

The phonon spectra of PC with a small value of energy gaps are characterized by the presence of low frequency phonon peaks. The small peak at energy of about $25\text{ mV}$ (Fig. 5, curves 1, 2) is visible, where a tiny knee exists on the PDOS (see PDOS in Fig. 5). In the normal state (at $T > T_c$), these low frequency peaks transform into the S-shape structure in $d^2V/dI^2(V)$ spectra (curve 6), corresponding to the wide minimum of $dV/dI(V)$ near zero bias. This low-frequency structure is hardly due to the remnants of superconducting quasigap at $T > T_c$, since it is absent in junction No. 2, whose characteristic is
shown in Fig. 6. Rather, it could be thought of as strong interaction in the 3D band with very low-frequency excitations, whose origin is not clear yet. On increasing the temperature, the low frequency peak broadens further like common spectral features do in the normal state. Fig. 6 shows (compare curves 1 and 2) that the field smears out the intensity of the high energy peaks, which are induced in the 3D band by EPI of the 2D band. The disappearance of phonon peaks at field and temperature rise proves that they do not belong to the inelastic backscattering processes, which should have the same intensity both in the superconducting and in normal states. It seems more plausible that the high energy phonon peaks are due to the elastic contribution in the

FIG. 6: Second harmonic dependences on field and temperature averaged for both voltage polarities. The temperature and magnetic field are: 4.2 K, 0 T; 4.2 K, 4 T; 10 K, 4 T; 20 K, 4 T; 30 K, 4 T; 40 K, 4 T, for curves 1-6, respectively. The modulation voltage $V_m(0)$ is 2.2 mV. $\Delta=2.7$ meV. Curves are shifted vertically for clarity.

excess current induced by EPI from the 2D band, as was already stated above.

**Conclusion.** We have measured the PC spectra in transition metal diborides: ZrB$_2$, NbB$_2$ and TaB$_2$. For all compounds the main phonon peak position was established, the PC EPI function was recovered, and the EPI parameter $\lambda$ was determined. The obtained small $\lambda$ values question strongly the reported bulk superconductivity in these compounds with remarkable $T_c$. To draw a more weighty conclusion about details of EPI and the $\lambda$ values in the presented MeB$_2$ family, a theoretical calculation of $\alpha^2F(\omega)$ with the mentioned $K$-factor and their comparison with experimental data is very desirable.

The PC EPI spectra of the superconducting MgB$_2$ differ even qualitatively from those measured for the mentioned transition-metals diborides. For MgB$_2$ the reproducible peaks on $d^2V/dI^2(V)$ are seen in the superconducting state, which disappear in the normal state. It proves that they are due to the energy dependence of the superconducting order parameter. The superconductivity here is presumably due to the 2D-band EPI, which induces the $\Delta(E)$ structure in the 3D band. At a small value of the superconducting gap the phonon structure is weak, and its intensity begins to increase with growing $\Delta$. The robustness against the magnetic field also grows notably with increasing $\Delta$.

In the normal state the intensity of the inelastic spectrum also correlates with the value of the superconducting gap. The tendency is observed that the high energy phonon contribution to the PC spectra becomes more prominent for a larger gap. This is supported also by our recent data on MgB$_2$ single crystals. For a smaller gap, the low-frequency bump appears in the spectra. It might be due to EPI with some unknown low-frequency excitation, but further work is needed to exclude that it is not caused simply by phonon peaks of the normal-metal counter electrode.

---

1. J. Nagamatsu et al., Nature (London) 410, 63 (2001).
2. S.V. Shulga et al., cond-mat/0103154
3. J. Kortus et al., Phys. Rev. Lett 86, 4656 (2001).
4. A.Y. Liu, I.I. Mazin, and J. Kortus, Phys. Rev. Lett. 87, 087005 (2001).
5. Y. Kong et al., Phys. Rev. B 64, 020501(R) (2001).
6. T. Yildirim et al., Phys. Rev. Lett. 87, 037001 (2001).
7. H.J. Choi et al., Phys. Rev B. 66, 020513(R) (2002).
8. K.-P. Bohnen, R. Heid, and B. Renker, Phys. Rev. Lett. 86, 5771 (2001).
9. C.Buzea and T.Yamashita, Superconductors, Science & Technology, 14, R115-R146 (2001).
10. V. A. Gasparov et al, JETP Lett. 73, 532 (2001).
11. I. K. Yanson, Sov. J. Low Temp. Phys. 9, 343 (1983).
12. W. N. Kang et al., Science 292, 1521 (2001); W.N. Kang et al., Phys. Rev. Lett. 87, 087002 (2001)
13. I. O. Kulik, A. N. Omelyanchouk and R. I. Shekhter, Sov. J. Low Temp. Phys. 3 840 (1977).
14. I. O. Kulik, Sov. J. Low Temp. Phys. 18, 302 (1992).
15. A. Wexler, Proc. Phys. Soc. (London) 89, 927 (1966).
16. B. Renker et al., Phys. Rev. Lett 88, 067001 (2002).
17. PC spectra of Zr were measured by N. L. Bobrov and V. V. Fisun (unpublished data).
18. A. V. Khotkevich and I. K. Yanson, Atlas of Point Contact Spectra of Electron-Phonon Interaction in Metals (Kluwer Academic Publisher, Boston, 1995).
19. T. Aizawa, W. Hayami, and S. Otani, Phys. Rev. B 65, 024303 (2002).
20. Yu. G. Naidyuk et al, Phys.Rev. B 66 140301(R) (2002).
21. H. Rosner et al., Phys. Rev. B 64, 144516 (2001).
22. O. P. Balkashin et al., Sol. State Commun. 100, 293 (1996).
23. N. L. Bobrov et al., in New Trends in Superconductivity, Vol.67 of NATO Advanced Studies Institute, Series B: Physics and Chemistry, edited by J.F. Annett and S. Kru-
A. A. Golubov et al., J. Phys.: Condens. Matter, 14, 1353 (2002).

Yu. G. Naidyuk et al., JETP Letter 75, 238 (2002).

I. O. Kulik and I. K. Yanson, Sov. J. Low Temp. Phys. 4, 596 (1978).

I.K. Yanson, in Quantum Mesoscopic Phenomena and Mesoscopic Devices in Microelectronics, Vol.559 of NATO Science Series, Series C: Mathematical and Physical Sciences, edited by I.O. Kulik and R.Ellialtioglu, (Kluwer, Dordrecht, 2000), p. 61-77.

A.N. Omel’yanchuk, S.I. Belobrod’ko and I.O. Kulik, Sov. J. Low Temp. Phys. 14, 630 (1988).

Yu. G. Naidyuk et al., cond-mat/0211134.

D. Lampakis et al., cond-mat/0105447.