Lattice dynamics and electron-phonon coupling in transition metal diborides

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The phonon density of states of transition metal diborides TMB$_2$ with TM = Ti, V, Ta, Nb and Y has been measured using the technique of inelastic neutron scattering. The experimental data are compared with ab initio density functional calculations whereby an excellent agreement is registered. The calculations thus can be used to obtain electron-phonon spectral functions within the isotropic limit. A comparison to similar data for MgB$_2$ and AlB$_2$ which were subject of prior publications as well as parameters important for the superconducting properties are part of the discussion.

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The discovery of superconductivity in MgB$_2$ at the unexpected high temperature of 39 K has renewed the interest in diboride compounds. The well known AlB$_2$ structure (P6/mmmm) is formed with quite a number of transition metals (TM) $^2$. However, a clear proof of superconductivity could not be established for any of these candidates. Obviously the influence of lattice faults on the transport properties is important. A unique feature for MgB$_2$ is the depopulation of B 2p $- \sigma$ bands due to a particular Mg-B interaction $^1$. It has been shown by band structure calculations for the TM-diborides that $E_F$ moves up into the TM 4$d$-states with the consequence that these compounds behave more like normal metals $^3$. Most important for the transport properties is the electron-phonon interaction in these systems. Very recently results from point contact spectroscopy have been reported for TM = Zr, Nb, and Ta. The authors conclude on an only modest electron-phonon interaction parameter for these samples $^4$. A general investigation of the phonon spectra of TM-diborides has so far not been performed. In the present paper we confront measurements of the generalized phonon density of states for selected compounds with TM = Ta, V, Nb, Ti, and Y with ab initio density functional theory (DFT) calculations. Results for electron-phonon spectral functions are derived and placed in context to previous investigations of superconducting MgB$_2$.

All diborides were prepared from stoichiometric mixtures of TM elements and amorphous $^{11}$B. We have chosen the less absorbing $^{11}$B in view of the intended inelastic neutron scattering (INS) experiments. The mixed powders were compacted to pellets and arc melted. The final polycrystalline samples showed metallic brightness and were found to be single phase by x-ray diffraction. All of our samples failed to show superconductivity above 4 K although transition temperatures for the pure elements of Nb and Ta with 9.2 K and 4.39 K are known. Our INS experiments were performed on the IN6 time-of-flight spectrometer at the HFR in Grenoble, France, with an incident neutron energy of 4.75 meV at 300 K in the upscattering mode. A high chopper speed of 201 ms and focusing in the inelastic region was used to improve the resolution. The generalized phonon density of states (G DOS) has been calculated from the recorded intensities integrated over a scattering region from 14 $^\circ$ to 114 $^\circ$. For the data evaluation we have applied multi-phonon corrections in a self-consistent procedure. The GDOS implies a weighting of vibrational modes of by $\sigma/m$ (scattering cross-section over the mass, see Tab. $^1$). For comparison the scattering power of $^{11}$B is 0.525 barn/amu.

Fig. 1 shows a comparison of GDOS spectra for all investigated TM-diborides. Each spectrum is normalized to 1. The most significant common feature is a gap around 40 to 50 meV. When analyzing the respective intensities we find that the high-frequency band is essentially composed of boron vibrations. The gap is thus a consequence of the large mass difference, which leads to a decoupling of transition metal and boron vibrations. A clearly different behavior is observed for MgB$_2$ and AlB$_2$ where due to the smaller mass of the metal atoms a hybridization of metal and boron modes occurs. In the low-frequency band of the transition metal diboride spectra we observe distinct shifts which however do not simply follow a $\sqrt{m}$ relation. This indicates that there are appreciable differences in the B-TM coupling. This conclusion is confirmed by the concomitant variations of interatomic distances (Tab. $^1$). Somewhat more surprising is the fact that significant frequency shifts are equally registered for

| TABLE I: Structural and scattering parameters for selected diborides. Distances are given in Å. The values in brackets apply to optimized geometries found in the DFT calculations after energy optimization. M-B and B-B denote the shortest metal-boron and boron-boron distances, respectively, and $m$ is the TM mass number. $\sigma/m$ is the neutron scattering cross-section over the mass in barn/amu. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $\text{MgB}_2$ | $\text{AlB}_2$ | $\text{TaB}_2$ | $\text{Vb}_2$ | $\text{NbB}_2$ | $\text{TiB}_2$ | $\text{YB}_2$ |
| $\sigma/m$ | 0.151 | 0.056 | 0.033 | 0.098 | 0.067 | 0.085 | 0.087 |
| a | 3.084 | 3.090 | 3.08 | 2.998 | 3.09 | 3.038 | 3.290 |
| (3.056) | (2.965) | (3.08) | (2.979) | (3.093) | (2.998) | (3.254) |
| c | 3.522 | 3.262 | 3.265 | 3.056 | 3.3 | 3.23 | 3.835 |
| (3.622) | (3.232) | (3.272) | (2.995) | (3.337) | (3.188) | (3.830) |
| M-B | 2.504 | 2.383 | 2.421 | 2.297 | 2.477 | 2.409 | 2.716 |
| B-B | 1.781 | 1.737 | 1.799 | 1.772 | 1.794 | 1.773 | 1.914 |
| m | 24.312 | 26.982 | 180.948 | 59.42 | 92.906 | 47.90 | 88.91 |
| $\sqrt{m}$ | 4.934 | 5.413 | 13.459 | 7.686 | 9.675 | 6.972 | 9.428 |
the peak at the high-frequency end of the spectra where the lowest frequency is found in YB₂. The E₂g and B₁g modes, which are important for superconductivity in MgB₂, lie within this region where neighboring boron atoms move against each other. Strong electron-phonon coupling is expected to cause a significant broadening. This broadening is visible in the spectrum of MgB₂ but not in those of the other compounds. The low frequency of the peak in YB₂ alone can, therefore, not be taken as a signature of strong electron-phonon coupling. A simpler explanation is offered by comparatively weak B-B-interactions. As can be seen from Tab.II, the B-B distance is exceptionally large for this compound. If any, then the G(ω) for NbB₂ shows signatures of a stronger electron-phonon coupling, a compound for which some authors report superconductivity.

First principals density-functional calculations give parameter free insight into the electronic structure of all of these compounds. They in addition yield the lattice dynamical properties. Corresponding results are shown in Fig. 2. For the calculations we used the mixed basis pseudopotential method, which is described in some detail in Ref. 5, 6. Norm-conserving pseudopotentials for V, Ta, Nb, Y and Ti were constructed according to the description of Bachelet-Hamann-Schlüter 7, 8, whereas for boron a Vanderbilt-type potential was created 9. The mixed basis scheme uses a combination of local functions together with plane waves for a representation of the valence states. The good agreement between calculated and experimental structural parameters (see Tab. II) as well as between calculated and experimental phonon GDOS (Figs. 1 and 2) proves the validity of our description.

A very unique feature of electron-phonon coupling in MgB₂ is the downshift of the in-plane E₂g mode well below the out-of-plane B₁g mode. Such an inversion of the usual sequence of mode frequencies is not encountered in any of the other diborides as shown in Tab. II, where we compile the calculated Γ-point frequencies of the boron vibrations.

The present calculations prove capable of describing the lattice dynamics of various diborides with quite different electronic transport properties. For the TM diborides, the isotropic character of the d-bands has the consequence that these compounds behave electronically very much like normal 3D metals 3. Although the band structures show strong similarities, the Fermi level E_F moves up and down within the region of the transition metal d-bands. This variable band filling leads to appreciable differences in the various interatomic distances. The E₂g frequencies exhibit an expected inverse correlation with the in-plane lattice constant, which indicates that the B-B covalent bond is electronically rather similar for all these compounds. On the contrast, the out-of-plane boron mode B₁g is very insensitive to changes in

![FIG. 1: The experimental generalized phonon density-of-states for various transition metal diborides. AlB₂ and superconducting MgB₂ are shown for comparison. Very significant changes are related to structural differences. Signature of strong electron-phonon coupling is the dramatic broadening of the highest energy B peak visible for MgB₂ but not for the other candidates.](image1)

![FIG. 2: Calculated GDOS spectra for all diborides shown in Fig. 1. The proper σ/m values have been applied for a direct comparison to the experimental spectra.](image2)

|           | MgB₂ | AlB₂ | TaB₂ | VB₂ | NbB₂ | TiB₂ | YB₂ |
|-----------|------|------|------|-----|------|------|-----|
| E₁u       | 40.5 | 36.6 | 52.6 | 60.6| 52.0 | 65.5 | 44.1|
| A₂u       | 50.2 | 52.1 | 61.9 | 62.1| 60.5 | 66.4 | 45.3|
| E₂g       | 70.8 | 125.0| 100.6| 114.9| 98.4 | 112.8| 75.5|
| B₁g       | 87.0 | 61.3 | 68.8 | 69.6| 69.8 | 70.0 | 75.1|

![TABLE II: Calculated Γ point frequencies in meV.](image3)
Somewhat exceptional in our series of transition metal diborides is only YB$_2$. Peculiarities in the electronic structure lead to a drastic increase of both the a and c lattice constants. As a consequence of the increased B-B bond length, the longitudinal force constant of the B-B bond is strongly reduced, and becomes even smaller than the transverse coupling. This is the reason for the observed softening of the high-frequency B-modes in YB$_2$.

In order to get a more quantitative picture of the electron-phonon coupling within the series of diborides we have calculated the isotropic Eliashberg function $\alpha^2F(\omega)$ which describes the phonon mediated pairing interaction (Fig. 3). Details of the computations are outlined in Ref. [2]. Again MgB$_2$ proves to be singular. The extremely strong coupling at high-phonon frequencies is known to be connected to the E$_{2g}$ boron in-plane mode. It is found as a general trend that the region of strong coupling for TM diborides shifts down to lower energies as found for conventional superconductors thus leaving hope only for modest $T_c$’s. The existence of 2D- and 3D-type Fermi sheets derived mainly from boron $\sigma$ and $\pi$ bands, respectively, has been shown to be important for a quantitative understanding of the transport properties of MgB$_2$ [11]. The 2D Fermi surface is connected to the hole doping of boron $2p$ bands and does not seem to be important for transition metal diborides.

We have also calculated the relevant parameters for the description of the superconducting properties within the Eliashberg formalism. The results are compiled in Tab. III. A common feature unfavorable for superconductivity found in all transition metal diborides is the comparatively low $\omega_{\text{log}}$. This quantity represents the effective average frequency of the coupling modes and sets the energy scale for the pairing interaction. Its small value as compared to MgB$_2$ indicates that the pairing interaction is mainly mediated by the TM vibrations and not by the boron modes. The isotropic coupling constant $\lambda$ shows a variation from weak to intermediate coupling strength. In Tab. III we have also included values for the superconducting transition temperature as obtained by solving the linearized isotropic gap equations. The $T_c$ values depend strongly on the screening properties expressed by $\mu^*$ and drop appreciably for $\mu^* > 0$. The values shown for a typical metallic screening of $\mu^* = 0.13$ thus should only be taken as indicators of the general trend. Furthermore, as mentioned before, for MgB$_2$ it is necessary to go beyond the isotropic limit and take into account the multigap structure introduced by the particular Fermi surface geometry for a proper quantitative description of the pairing state. Anisotropy is expected to play a minor role for the coupling in the low-frequency region of the transition metal vibrations that are dominated by the 3D-metal bands.

The values of $\lambda$ and $\omega_{\text{log}}$ are most favorable for MgB$_2$. The next promising candidates according to the present calculations are TaB$_2$ and NbB$_2$, for which some authors find superconductivity at 9.5 K and 6.4 K, respectively [5]. Differences in stoichiometry might be able to explain different experimental results. As far as a comparison to recent point-contact measurements is possible we can state that the maxima in our $G(\omega)$ correspond well to the peaks found in the second derivative of the $I - V$ characteristic. There is also agreement in a strongly reduced electron-phonon coupling strength for transition metal diborides with respect to MgB$_2$. We, however, want to mention that the reported very small numerical values for $\lambda_{\text{PC}}$ should not be compared directly to our values since point contact experiments do not measure the McMillan $\lambda$.

To summarize, we have presented measurements of the generalized phonon density-of-states for various transition metal diborides. The observed trends in the lattice dynamics can be well ascribed by first principles calculations and do not exhibit indications of strong electron-phonon interaction. This view is supported by theoretical calculations of the electron-phonon coupling. While

**TABLE III: Average coupling constant $\lambda$, effective average phonon frequency $\omega_{\text{log}}$ (in meV), and estimates of $T_c$ from the linearized gap equation. $N(0)$ denotes the density of states at the Fermi energy (per unit cell and spin).**

| Substance | $N(0)$ | $\lambda$ | $\omega_{\text{log}}$ | $T_c (\mu^* = 0.13)$ |
|-----------|--------|-----------|----------------------|----------------------|
| MgB$_2$   | 0.335  | 0.73      | 60.9                 | 21.7                 |
| AlB$_2$   | 0.184  | 0.43      | 49.9                 | 2.3                  |
| TaB$_2$   | 0.452  | 0.79      | 25.8                 | 10.6                 |
| VB$_2$    | 0.592  | 0.28      | 44.1                 | < 1                  |
| NbB$_2$   | 0.520  | 0.67      | 30.5                 | 8.4                  |
| TiB$_2$   | 0.179  | 0.10      | 52.9                 | -                    |
| YB$_2$    | 0.560  | 0.46      | 37.4                 | 2.4                  |
they do not exclude the possibility of superconductivity with low $T_c$ mediated by TM vibrations, they underline the outstanding properties of MgB$_2$ among the class of diborides.

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