Electronic structure, phonon spectra and electron-phonon interaction in TiB_2 and ZrB_2

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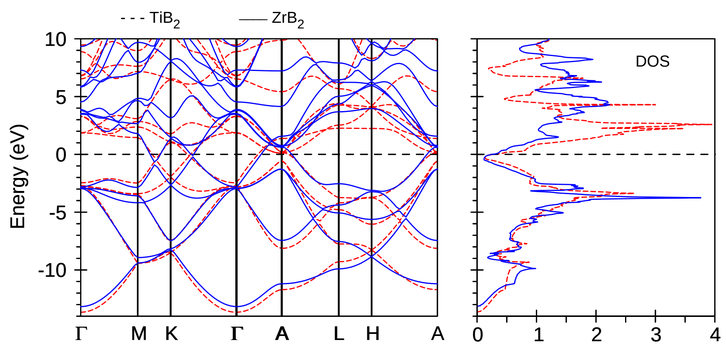
Motivations

- The discovery of superconductivity in MgB_2 at 39 K by Akimitsu [1] has lead to booming activity in the physics community and activated a search for superconductivity in other diborides. Natural candidates for this search are AB_2-type light metal diborides (A = Li, Be, Al). However, up to now superconductivity has not been reported in the majority of these compounds. According to Ref. [2] no superconducting transition down to 0.42 K has been observed in powders of diborides of transition metals (A = Ti, Zr, Hf, V, Ta, Cr, Mo, U). Only NbB_2 is expected to superconduct with a rather low transition temperature (< 1 K). Finally, the reported T_c=7 K in ZrB_2 [3] encourages further studies of these diborides.
- The electronic structure, optical and x-ray absorption spectra, angle dependence of the cyclotron masses and extremal cross sections of the Fermi surface, phonon spectra, electron-phonon Eliashberg and transport spectral functions, temperature dependence of electrical resistivity of the MB_2 (M=Ti and Zr) diborides were investigated from first principles using the fully relativistic and full potential linear muffin-tin orbital methods. The calculations of the dynamic matrix were carried out within the framework of the linear response theory.

Energy band structure



Energy band structure of TiB_2 and ZrB_2

Optical spectra

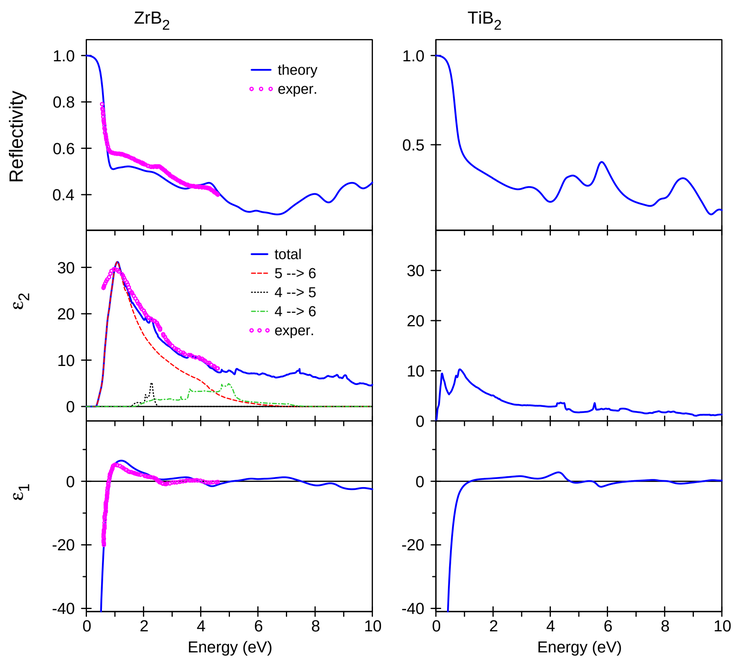
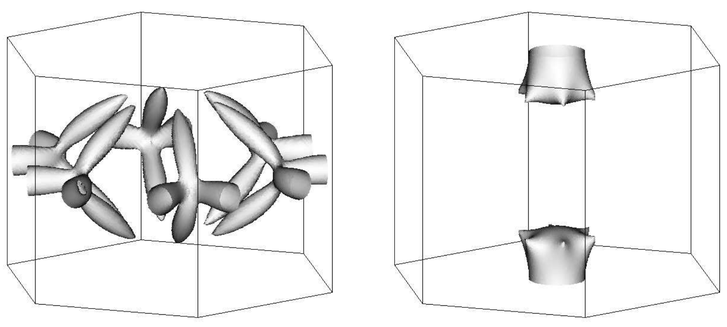


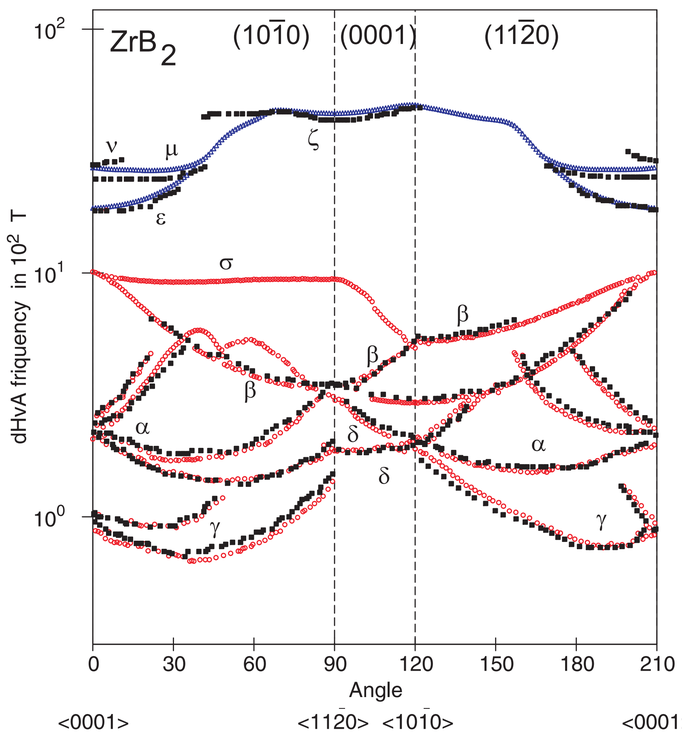
Figure presents the theoretically calculated and experimentally measured [4] optical reflectivity spectra $R(\omega)$ as well as dielectric constants $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ for ZrB_2 and TiB_2. We performed decomposition of the calculated ε_2 spectrum into the contributions arising from separate interband transitions and different places of $\mathbf{k}$ space. We found that the major peak in the $\varepsilon_2(\omega)$ (around 1 eV) is mostly determined by the $5 \rightarrow 6$ interband transitions along the $\Gamma-$A and A$-$L symmetry directions. The shoulder at 2 eV is due to the $4 \rightarrow 5$ interband transitions around A symmetry point.

Fermi surface



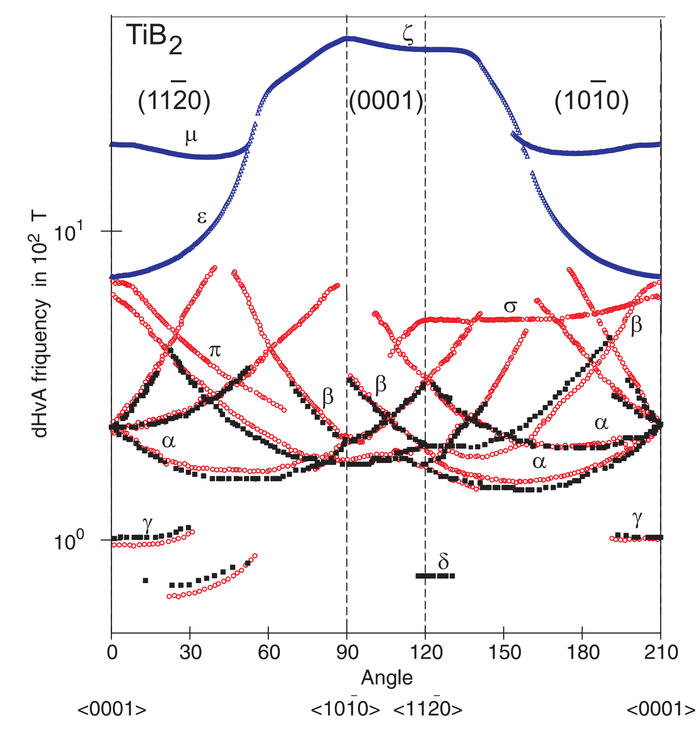
Theoretical calculations show a ring-like electron FS around the K symmetry point (left panel) and of a wrinkled dumbell-like hole FS at the A point (right panel) in ZrB_2 and TiB_2. The electron FS and hole FS have threefold and sixfold symmetries, respectively.

dHvA effect in ZrB_2



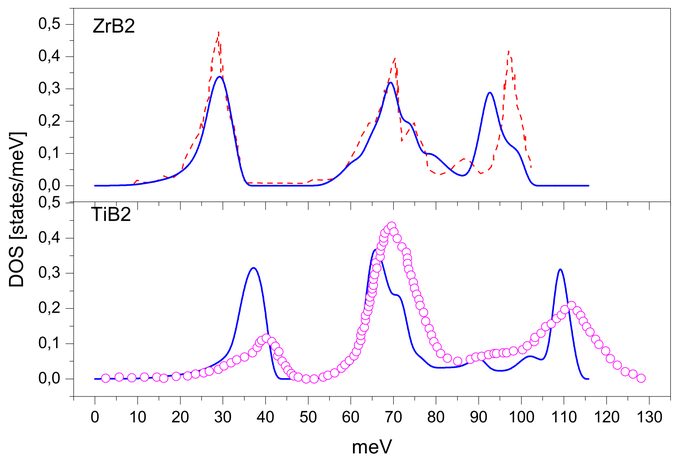
Angular variations of the experimentally measured dHvA frequencies [5] for ZrB_2 (black squares) in comparison with theory (red and blue circles). The observed frequencies of α, β, γ, and δ oscillations belong to electron FS around the K point. The ϵ, ν, μ, and ζ orbits belong to the hole wrinkled dumbbell FS. The theory reasonably well reproduces the frequencies measured experimentally. We discover a new branch σ which belongs to the electron FS around the K point.

dHvA effect in TiB_2



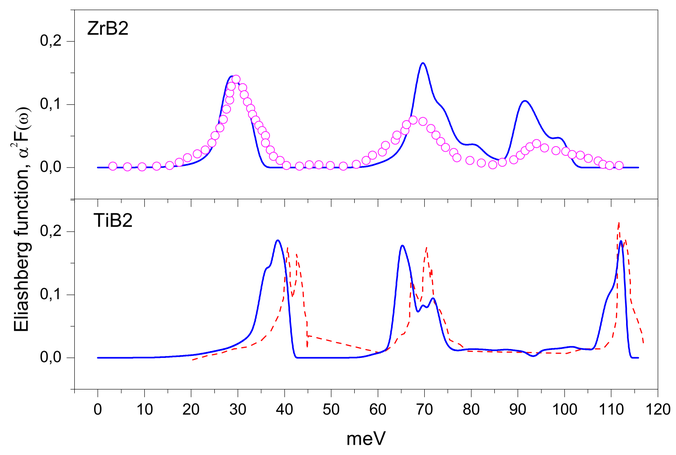
Angular variation of experimentally measured dHvA frequencies in TiB_2 [6] in comparison with theoretical calculations. The theoretical calculations quite well reproduce the angle dependence of the extremal cross sections for low frequency orbits γ, α and β. Similar to ZrB_2 we detected theoretically a new branch σ in TiB_2 which is not observed experimentally. This branch belongs to the electron FS around the K point. We also find an additional orbit π at the (11$\bar{2}$0) plane which is absent in ZrB_2 and did not detected experimentally. For high frequencies we found the ϵ, μ and ζ branches similar to the corresponding orbits in ZrB_2. However, these orbits have not been detected in the dHvA experiment. One of the possible reasons for that is the relatively large cyclotron masses for these orbits. We found that the cyclotron masses for the ϵ, μ, and ζ orbits in TiB_2 are much higher than the corresponding orbits in ZrB_2. The masses for the low-frequency oscillations α, β, γ and δ are less than $0.2m_0$ for ZrB_2.

Phonon DOS



Theoretical phonon density of states (full blue lines) for ZrB_2 and TiB_2 and experimentally measured one for TiB_2 [4] (open circles). Dashed red line presents the calculated phonon DOS of ZrB_2 by Deligoz *et al.* [8].

Electron phonon interaction



The theoretically calculated Eliashberg function $\alpha F(\omega)$ of ZrB_2 and $Ti2B_2$ (full blue lines) and experimentally measured point contact spectral function [9] (open circles) for ZrB_2. Dashed red line presents Eliashberg function of TiB_2 calculated by Heid *et al.* [10].

Electrical resistivity

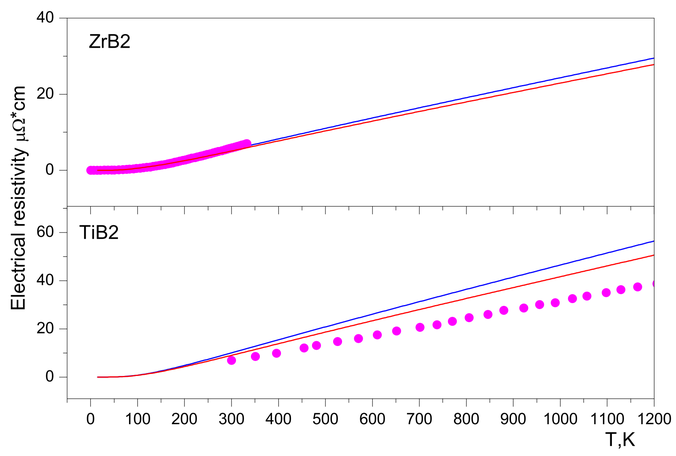


Figure represents the experimental data for mono-crystalline ZrB_2 (upper panel) and TiB_2 (lower panel) [11] as well as our calculations. We found that the anisotropy of the electrical resistivity in TiB_2 (lower panel) is larger than it was in ZrB_2. Our theoretical results slightly exceed experimental data, especially at high temperatures. This is due to using in our calculations the lowest-order variational approximation in solution of the Boltzmann equation which gives upper limit for the electrical resistivity.

Conclusions

- Theory reproduces the experimentally measured dHvA frequencies in both the ZrB_2 and TiB_2 reasonably well. We found that masses for low-frequency oscillations α, β, γ, and δ are less than $0.2m_0$. Masses for high-frequency oscillations ϵ, ν, μ, and ζ are large. The cyclotron masses for these orbits in TiB_2 are much higher than the corresponding orbits in ZrB_2. It could be one of the reasons why they have not been observed in the dHvA measurements.
- Calculated phonon spectra and phonon DOSs for both ZrB_2 and TiB_2 are in good agreement with experimental results as well as previous calculations. The Elishberg function of electron-phonon interaction in ZrB_2 is in good agreement with the experimentally measured point contact spectral function for both the position and the shape of the major peaks. We did not find regions with high electron-phonon interaction or phonon dispersion curves with soft modes in either ZrB_2 or TiB_2. This is in agreement with the fact that no trace of superconductivity was found in these borides. The averaged electron-phonon interaction constant was found to be rather small λ_{e-ph}=0.14 and 0.15 for ZrB_2 and TiB_2, respectively. We calculated the temperature dependence of the electrical resistivity in ZrB_2 and TiB_2 in the lowest-order variational approximation of the Boltzmann equation. We found rather small anisotropical behavior of the electrical resistivity in ZrB_2 to be in good agreement with experimental observation. We found that the anisotropy of electrical resistivity in TiB_2 is larger than it is in ZrB_2.
- The results are published in: S. M. Sichkar, V. N. Antonov, and V. P. Antropov - Phys. Rev. B **87**, 064305 (2013).

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