The de Haas – van Alphen effect study of the Fermi surface of ZrB$_{12}$

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Abstract. We present the first experimental study of the Fermi surface of the cluster superconductor ZrB$_{12}$, using the de Haas-van Alphen dHvA effect by magnetic torque measurements in magnetic fields up to 28 T at temperatures down to 0.07 K. The band structure and dHvA frequencies as well as the cyclotron effective masses were calculated using the full potential Linear Muffin-Tin Orbital method within the Generalized Gradient Approximation. We have found that the Fermi surface, FS, of ZrB$_{12}$ consist from one Cu – like but hole open FS sheet and closed electron "Cubic Box" – like sheets. The dHvA oscillations due to orbits from the Neck sections and Cubic Box of the FS were detected, while Belly orbits were not observed. The comparison of the angular dependence of the dHvA frequencies with the band-structure calculations implies overall agreement with theoretical model. The comparison of the experimental and calculated cyclotron mass shows unusually large electron-phonon interaction on Neck ($\lambda_{ep} = 0.95$) and Box ($\lambda_{ep} = 1.07$) sections of the FS on the Brillouin zone boundaries. Results support observation of magnetic breakdown between Neck and Box sheets at B//<110> in fields above 25 T.

1. Introduction
While the superconductivity in ZrB$_{12}$ was discovered long time ago [1], there has been little and controversial efforts devoted to study the electron transport and superconducting properties in these compounds. Matthias et al. [1] suggested that the superconductivity in YB$_6$ and ZrB$_{12}$ was due to the effect of a cluster of light boron atoms. Much smaller isotope effect on $T_c$ for boron in comparison with Zr isotopic substitution suggests that the boron in ZrB$_{12}$ serves as inert background for the Zr driven superconductivity [2]. From the point-contact spectroscopy study [3] and tunneling and magnetic characterization of ZrB$_{12}$ [4], it was concluded that ZrB$_{12}$ is a strong coupling s-wave superconductor with 2$\Delta$(0)/k$_B$T$_c$=4.8. At the same time, it was suggested from the specific heat and thermal expansion measurements [5], that it is a single gap marginal BCS superconductor with 2$\Delta$(0)/k$_B$T$_c$=3.7. Gasparov et al. [6] suggested that unconventional features observed in ZrB$_{12}$ can be explained by two band BCS model scenario with different not only superconducting gap but $T_c$ as well. [5] Recently the optical study and band structure calculations of ZrB$_{12}$ [7] by self-consistent full potential Linear Muffin-Tin Orbital (LMTO) method, have been also reported. It was concluded, that the Fermi surface (FS) of ZrB$_{12}$ is composed of one open and one closed sheet. Knowledge of the experimental Fermi surface in this cluster compound is critical for understanding two-gap model suggested in Ref.6. Until now there have been no direct experimental probes of the FS structure of ZrB$_{12}$. In this paper, we report a detailed study of the dHvA effect in ZrB$_{12}$ single crystals and a comparison with predictions of the band-structure calculations. [8]

2. Experimental Setup
Dodecaboride \( \text{ZrB}_{12} \) crystallizes in the fcc structure of the \( \text{UB}_{12} \) type, a rock salt type structure with \( \text{Zr} \) on \( \text{Na} \) and \( \text{B} \) on \( \text{Cl} \) sites. The boron atoms form \( \text{B}_{12} \) cub octahedral unit clusters. The dHvA measurements reported here have been performed on a samples that had been previously studied for the electron transport, magnetic penetration depth and \( H_{c2}(T) \) [6]. The sample dimensions are \( 0.5 \times 0.5 \times 2 \) mm and \( 1 \times 1 \times 0.5 \) mm, with \( <110> \) and \( <100> \) axis parallel to its length and normal, respectively. The resistivity ratio, \( \rho_{300K}/\rho_{6.5K}=10 \), of these samples, was found to be rather low [6].

The dHvA oscillations were observed by measuring the torque with a capacitive cantilever technique [8]. The measurements of the magnetic torque were performed on M6 and M10 respectively 23 Tesla and 28 Tesla resistive magnets of the Grenoble High Magnetic Field Laboratory. In the measurements, \( <100> \), \( <110> \) and \( <111> \) axis of the sample were parallel to the rotation axis, this allowed the magnetic field to be rotated in the sample basal planes. The measurements were made at different temperatures in the range 0.07 K to 4.2 K with the sample immersed in a pumped \( ^3\text{He} \) or \( ^4\text{He} \) bath. The oscillatory part of the torque is given by

\[
\tilde{T} = -(1 / F) \tilde{M} / (\partial F / \partial \theta) BV \quad [9]
\]

where \( \tilde{M} \) the oscillatory component of the parallel magnetization, \( F \) is the dHvA frequency, \( \theta \) is the orientation of the Fermi surface with respect to the applied field \( B \) and \( V \) is the crystal volume. Here dHvA

![Figure 1](image)

**Fig.1.** (Color online) Typical Fourier spectrum of dHvA oscillations observed with magnetic field applied along \( <110> \) direction. The peaks \( \beta \) and \( \epsilon \) appear for high maximum fields indicating its possible MB origin. Insert shows MB orbits through Dog’s bone and cubic box sheet.

The electronic structure of \( \text{ZrB}_{12} \) was calculated using LMTO method within the Generalized Gradient Approximation. The details of the calculation are presented elsewhere [8]. The Fermi surface was computed over a \( 30 \times 30 \times 30 \) mesh in the irreducible part of the first Brillouin zone (BZ). The corresponding extremal orbits from the first Cu-like but hole FS sheet and those from the second “Box”-like sheet are shown in Fig.3. The extremal areas, related to the dHvA frequencies, were obtained by slicing the calculated FS sheets perpendicular to the field direction, calculating the areas of all closed orbits and searching for the extrema among the slices. The cyclotron band mass for each extremal orbit is obtained by numerical differentiation of \( S_F \) versus \( E \) and are presented in Fig. 4.

3. Results and discussion

We show in Fig. 1 the typical fast Fourier transform (FFT) spectrum of dHvA oscillations for the magnetic field parallel to \( <110> \) direction for two different fields scale. As we can see, only weak harmonics of \( 2\alpha \) are observed for \( B/\langle110\rangle \), while for the other directions of \( B \) up to ten harmonics of \( \alpha \) branch were seen. Fig. 2 shows the angular dependence of the dHvA frequencies (omitting the frequencies assigned as harmonics or combinations). The circles represent the experimental data while the solid and dotted lines show the results of the band-structure calculation described below. The FFT peaks denoted by \( \alpha, \gamma, \delta, \epsilon \) are fundamental.

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FIG.3. Theoretical model of the Fermi surface of ZrB$_{12}$: electron and hole sheets considered in the dHvA branch calculation.

The angular dependence of the dHvA frequencies (Fig.2) imposes strong constraints on the possible topologies of the FS and therefore allows the validity of the calculated FS (solid lines) to be verified. The assignment of the FFT peaks to the ZrB$_{12}$ FS sections was achieved by comparing the values of the frequencies obtained from FFT, and their angular dependencies. The solid lines in Fig.2, shows the excellent agreement between the ab initio electronic structure calculations and the measured one. The lowest frequency $\alpha$ branch between 1.5 and 2 kT corresponds to the Necks of the hole sheet. The branches in the vicinity of 6 kT are the signature of the nearly cubic boxes of electron sheet. The deviation from cube is evidenced by the splitting of the $\delta$ branch between the <111> and <100> field directions (Fig2). Also, the $\delta$ peak is split into two satellites $\delta$ and $\gamma$ close to <110> direction. Apparently, this splitting is due to a small warping of the cubic box sheet not seen from calculations.

The highest measured frequency of 7.4 kT in the <110> direction, $\varepsilon$, does not seem to match any of the calculated orbits. This frequency however is about 15% lower than results of calculated branch due to the “Dog’s bone” orbits. One possible explanation for this discrepancy is that the calculated orbit is too large (by approximately 0.8 kT), i.e. that the distance between the Necks is smaller in the real electronic structure than in the calculation. This could be due to a slight error in the calculation of the Fermi level.

In order to check this problem, we have done a calculation with $E_F$ slightly shifted by -0.16 eV which was the estimated shift to bring the calculated “Dog’s bone” branch over the experimental one in the [110] direction (dotted curves in Fig.2). However, the resulting shift of the Neck branch moves to another direction, while does not very strongly affect the agreement with other experimental points. Also, the size of the Necks which matches extremely well between the experiment and the calculation and that the size of the “Dog’s-bone” orbit is related to the Neck size by the topology of the FS sheet as they both originate from the same hole band sheet.

Another possible explanation for $\varepsilon$ branch relies on the observation that two FS sheets are nearly or fully degenerate in several points of the BZ. This is evidenced in inset in Fig.1 which shows the traces of the two FS sheets in the (110) plane: the Box and the Belly touch at the two high-symmetry points labeled “A” and the Box and the Necks nearly touch at the four “B” points (the calculated energy difference between the two bands at these points is less than 100 meV). With a frequency of 7.6 kT, the magnetic breakdown, MB, orbit shown in inset of Fig.1 by dotted line is the closer to the measured $\varepsilon$-branch. Also, the fact that the observation the frequencies of the $\varepsilon$ -branch and the frequencies above, depends on the applied magnetic field as shown in Fig.1, moved us towards the MB scenario. Observation of two additional peaks (due to different MB orbits) above $\varepsilon$ peak, also support this MB conclusion. While the $\beta$ branch of dHvA frequencies just below 4 kT in the <110> direction may be an additional consequence of the MB of the “Dog’s-bone” orbit, because magnetic field sensitivity of this peak, no frequencies below 4 kT could be obtained in reconnecting the orbits.
The cyclotron effective masses \( m_c \) were measured for the Neck and Box orbits from the temperature dependence of the dHvA amplitude \( A \) of \( \alpha \) and \( \delta \) branches, by performing field sweeps at different temperatures. The \( A(T) \) dependence can be approximated as: \( A/T = \text{const}/\sinh(\alpha m_c T/B) \) (Eq.1) at a mean value of the magnetic field \( B \). Figure 4 show the angular dependence of \( m_c \) for Neck and Box orbits in (110) plane. We determined \( m_c \) equal to 0.41\( m_0 \) for Neck branch for \( B_r//<111> \) and \( m_c=0.68m_0 \) for the Box sections at \( B_r//<100> \).

These values can be compared with the calculated band masses in Fig.4. Calculating the electron-phonon coupling constant \( \lambda_{\text{ep}} \) from \( m_{\text{exp}}/m_{\text{calc}} = \lambda_{\text{ep}} + 1 \) [11], we observed the large value of \( \lambda_{\text{ep}}=0.9, \) on Neck section at \( B//<111> \), decreasing quickly at larger and smaller angles. The \( \lambda_{\text{ep}} \) for Box sheet at \( B//<100> \) is less, 0.66, and also decreases at 13° from \( <100> \). Optics [8] also gave similar large \( \lambda_{\text{ep}} \) (1.0±0.2) averaged for whole Fermi surface, while very small \( \lambda_{\text{ep}}=0.2 \) from specific heat was observed [5]. The Dingle temperature \( T_D \) was obtained from the plot of \( \ln[A/\sinh(zm_cT/B)] \) versus \( 1/B \) according to Eq.1. For the \( B//<111> \), the \( T_D \) is rather large 16.8 K for the Neck section and 19 K (\( B_r//<100> \)), for Box sections. Unfortunately, the dHvA oscillations for Belly section of the FS have not seen even at lower temperature 70mK and magnetic fields up to 28 T. One source of this problem could be a large difference in the \( \tau \).

In summary, we have presented the first experimental study of the Fermi surface of the cluster superconductor \( \text{ZrB}_{12} \), using dHvA effect. Results are in excellent agreement with band structure calculations of the Fermi surface topology of this compound. The comparison of the experimental and calculated cyclotron mass shows unusually large electron-phonon interaction on Neck sections of the hole sheet of the FS. Results support observation of MB from Neck and Box sheets in fields.

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