Study of the Fermi Surface of ZrB$_{12}$ Using the de Haas-van Alphen Effect

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The de Haas-van Alphen (dHvA) effect in the cluster superconductor ZrB$_{12}$ was studied by magnetic torque measurements in magnetic fields up to 28 T at temperatures down to 0.07 K. The dHvA oscillations due to orbits from the neck sections and “cubic box” of the Fermi surface were detected. The dHvA frequencies as well as the cyclotron effective masses were calculated using the full-potential linear muffin-tin orbitals method within the generalized gradient approximation. A comparison of the experimental and calculated cyclotron mass shows unusually large electron-phonon interaction on the neck ($\lambda_{ep} = 0.95$) and box ($\lambda_{ep} = 1.07$) sections of the Fermi surface on the Brillouin zone boundaries.

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The discovery of superconductivity in magnesium diboride [1] led to interest in superconductivity in other borides [2]. It was suggested by Matthias et al. [3] that the superconductivity in YB$_6$ and ZrB$_{12}$ was due to the effect of a cluster of light boron atoms. A 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 [4]. There has been little and controversial effort devoted to studying the basic superconducting and electron transport properties of ZrB$_{12}$ (see discussion in Ref. [5]). There is disagreement with different techniques, and it was recently suggested that the features in the superconducting properties of ZrB$_{12}$ can be explained by the two-band BCS model with not only a different superconducting gap but $T_c$ as well [5]. Recently, the band-structure calculations of ZrB$_{12}$ [6,7] by the self-consistent full-potential linear muffin-tin orbitals (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 the superconducting properties of ZrB$_{12}$. Until now, there have been no direct experimental probes of the FS structure of ZrB$_{12}$. In this Letter, we report the first study of the de Haas-van Alphen (dHvA) effect in ZrB$_{12}$ single crystals and a detailed comparison with the predictions of band-structure calculations. Four branches of dHvA frequencies are clearly resolved in our data and can be assigned to the neck sections and the “cubic box” of the FS. The effective masses corresponding to the neck and box orbits have been measured and compared with our band-structure calculations. Results shows that the electron-phonon enhancement is very large for the FS sections on the Brillouin zone (BZ) boundaries.

Under ambient conditions, dodecaboride ZrB$_{12}$ crystallizes in the fcc structure of the UB$_{12}$ type (space group $Fm\overline{3}m$, $a = 0.74075$ nm [5]), a rocksalt-type structure with Zr on Na and B$_{12}$ clusters on Cl sites. The boron atoms form a B$_{12}$ cubic octahedral unit. All of the dHvA measurements reported here have been performed on the same samples that had been previously studied for the electron transport, magnetic penetration depth, and $H_{c2}(T)$ [5]. The details of the sample preparation and characterization are presented elsewhere [5]. The sample dimensions are $0.5 \times 0.5 \times 2$ and $1 \times 1 \times 0.5$ mm$^3$, with the $\{110\}$ and $\{100\}$ axis parallel to its length and normal, respectively. The critical temperature of the ZrB$_{12}$ samples was found to be $T_c = 6.0$ K, while the resistivity ratio $\rho_{300 K}/\rho_{6.5 K} \approx 10$ was rather low [5].

The dHvA oscillations [Fig. 1(a)] were observed by measuring the torque with a capacitive cantilever technique [8]. The measurements were performed on the M6 and M10, respectively, 23 and 28 T resistive magnets of the Grenoble High Magnetic Field Laboratory. For these measurements, the sample was mounted in a holder equipped with a system allowing the sample to be rotated in situ. The angles were measured to a relative accuracy of at least one tenth of a degree. In the measurements, the $\{110\}$, $\{111\}$, and $\{100\}$ axes of the sample were parallel to the rotation axis; this allowed the magnetic fields to be rotated in the sample basal planes. The measurements were made at different temperatures in the range 0.07–4.2 K with the sample immersed in a pumped $^3$He or $^4$He bath. The sample temperature was measured using a calibrated RuO$_2$ thermometer.

The oscillatory part of torque is given by [8] $T = -(1/F)\bar{M}_i(\partial F/\partial \theta)BV$, where $\bar{M}_i$ is the oscillatory component of the parallel magnetization, $F = S_T h c / 2 \pi e$ is the...
A frequency proportional to the extremal cross-section area \( S_F \) of the FS, \( \theta \) is the orientation of the Fermi surface with respect to the applied field \( B \), and \( V \) is the crystal volume. In a normal metal, \( M_\parallel \) would be given by the usual Lifshitz-Kosevich formula for the dHvA amplitude \( A \) as follows [9]:

\[
A \propto B^{1/2} \left| \frac{\partial^2 S_F}{\partial k^2} \right|^{-1/2} \frac{\alpha m_e T/B}{\sinh(\alpha m_e T/B)} \exp(-\alpha m_e T_D/B),
\]

where \( m_e = \hbar^2(\partial S_F/\partial E)/2\pi \) is the cyclotron effective mass and \( T_D = \hbar/2\pi k_B \tau \) is the Dingle temperature. We can try to estimate the residual quasiparticle lifetime \( \tau \) from the Drude formula for resistivity \( \rho(0) = 3/N_0 \tau \nu_F^2 e^2 \), where we use measured \( \rho(0) = 1.8 \mu\Omega \text{ cm} 

\[\text{[5]}\] to obtain the FS-averaged \( \tau = 1.74 \times 10^{-14} \text{ sec} \). According to the equation of \( T_D \), we thus obtain a very high FS-averaged Dingle temperature of 70 K. Contrary to this estimation, we observed rather large dHvA oscillations.

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

The electronic structure of ZrB\(_{12}\) was calculated using the LMTO method within the generalized gradient approximation. The details of the calculation are presented elsewhere [7]. Our results are in very good agreement with the previously published band-structure calculation [6]. The Fermi surface was computed over a \( 30 \times 30 \times 30 \) mesh in the irreducible part of the first BZ. The corresponding extremal orbits from the Cu-like but hole FS sheet and those from the electron boxlike sheet are shown in Fig. 3. The extremal areas, related to the dHvA frequencies through (1), 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 \( E \) with \( \Delta E = 0.5 \text{ mRy} \).

The angular dependence of the dHvA frequencies (Fig. 2) imposes strong constraints on the possible top-
ologies 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 show 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 $\gamma$ and $\delta$ in the vicinity of 6 kT are the signature of the nearly cubic boxes of the electron sheet. The deviation from the cube is evidenced by the splitting of the $\delta$ branch between the (111) and (100) field directions (Fig. 2). Also, the $\delta$ peak is split into two satellites $\delta$ and $\gamma$ close to the (110) direction. Apparently, this splitting is due to small warping of the cubic box sheet not seen from calculations.

The highest measured frequency of 7.4 kT in the (110) direction, $\epsilon$, does not seem to match any of the calculated orbits. The dHvA frequency of the $\epsilon$ branch, however, is about 15% lower than the results of the 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 hypothesis, we have done a calculation with $E_F$ 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, which does not strongly affect the agreement with experimental points. Also, the size of the necks matches extremely well between the experiment and the calculation, and 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 the $\epsilon$ branch relies on the observation that two FS sheets are nearly or fully degenerate in several points of the BZ. This is evidenced in the inset in Fig. 1(b), which shows 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 orbit shown in the inset in Fig. 1(b) by a dotted line is the closer to the measured $\epsilon$ branch. There are different possibilities of reconnecting these magnetic breakdown orbits combining the two bands of the FS. Thus, the observation of two additional peaks above the $\epsilon$ peak and their disappearance in smaller fields also support this magnetic breakdown conclusion.

While the $\beta$ branch of dHvA frequencies just below 4 kT in the (110) direction may be an additional consequence of the magnetic breakdown of the dog’s-bone orbit, because of the magnetic field sensitivity of this peak, no frequencies below 4 kT could be obtained in reconnecting the orbits. The form of this peak is inverted relative to other ones, indicating a probable artifact. Note also that we observed additional $\epsilon$ and $\beta$ branches close to the (110) direction only, where the dHvA oscillation amplitude is weakest. Therefore, we ruled out the magnetic interaction effect, due to the change in the field orientation with respect to the sample when the last one is oscillating with a large amplitude.

The cyclotron effective masses $m_c$ were measured for the neck and box orbits from the temperature dependence of the dHvA amplitude of the $\alpha$ and $\beta$ branches determined from FFT by performing field sweeps at different temperatures.

According to (1), the $A(T)$ dependence can be approximated as $A(T) = \text{const} / \sinh(m_c T / m_e B)$ at a mean value of the magnetic field $B$. Figure 4 shows the angular dependence of $m_c / m_e$ for neck and box orbits in the (110) plane. We determined $m_c$ equal to $(0.41 \pm 0.01)m_e$ for the neck

![FIG. 3](color online). Theoretical model of the Fermi surface of ZrB$_{12}$: hole and electron sheets considered in the dHvA branch calculation.

![FIG. 4](color online). Experimental (symbols) and calculated (solid lines) cyclotron mass of ZrB$_{12}$. N, DB, B, and R denote the neck, dog’s-bone, belly, and rosette orbits, respectively.
branch for $\vec{B}\parallel(111)$ and $(0.83 \pm 0.09)m_e$ for the box sections at $\vec{B}\parallel(100)$. Calculating the electron-phonon coupling constant $\lambda_{ep}$ from $m_{exp}/m_{calc} = \lambda_{ep} + 1$, we observed the large value of $\lambda_{ep} = 0.9$, on the neck section at $\vec{B}\parallel(111)$, decreasing quickly at larger and smaller angles. The $\lambda_{ep}$ for the box sheet at $\vec{B}\parallel(100)$ is less (0.66) and also sharply decreases at $13^\circ$ from (100).

Actually, a similar large enhancement of the electron-phonon interaction on the BZ boundary was observed for neck sections of the FS of noble metals [10]. In the BZ boundary region, the hybridization of the wave functions and umklapp processes are very important on top of the $k$ dependence of the matrix element of the electron-phonon interaction. Optics also gave large $\lambda_{ep} = 1.0 \pm 0.2$ for ZrB$_{12}$ averaged for the whole FS [7], while very small $\lambda_{ep} = 0.2$ was observed from specific heat data [11]. Based on the McMillan equation for $T_c$ and the Debye temperature $T_D = 300$ K [5], we have found $T_c = 6$ K with $\lambda_{ep} = 0.61$ in good agreement with our data.

The Dingle temperature $T_D$ can be obtained from the plot of $\ln(ABT^{1/2}/\sinh(\alpha m_e T/m_e B))$ versus $1/B$ according to (1). For $\vec{B}\parallel(111)$, $T_D$ is rather large—15.6 K for the neck section and 18.6 K ($\vec{B}\parallel(100)$) for the box sections. From the equation of $T_D$ we estimate the electron scattering time $\tau = 7.4 \times 10^{-14}$ sec for the neck section, almost 4 times larger than the one deduced from residual resistivity. Unfortunately, the dHvA oscillations for the belly section of the FS have not been seen even at lower temperature 70 mK and magnetic fields up to 28 T. One source of this difference could be a large difference in the scattering rate $\tau$.

Figure 2 and Table I show that the values of the extremal areas $S_F$ found from the dHvA effect and band-structure calculations are in very good agreement. The differences between the measured $S_F$ values and calculated ones are not significant in many cases. The remaining discrepancy with the band-structure calculations concerns the absence of big belly, dog’s-bone, and rosette sections of hole sheet dHvA orbits in the present study and the absence of extremal sections corresponding to the $y$ branch in the calculated FS. The nonobservation of these orbits could be due to a relatively short mean-free path $l$ on the hole sheet relative to electron sections. Thus, future experiments with purer samples are essential for observation of belly sections of the hole FS sheet in a first BZ which may clarify the anisotropy of $\lambda_{ep}$.

In summary, we have presented the first experimental study of the Fermi surface of the cluster superconductor ZrB$_{12}$, using the dHvA effect. Experimental data are in good agreement with band-structure calculations of the FS topology of this compound. The cyclotron mass data show unusually large electron-phonon interaction on the neck and box sections of the Fermi surface on the BZ boundaries. The results support the observation of magnetic breakdown between the neck and box sheets in fields above 25 T.

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\begin{table}  
\centering  
\caption{Summary of the FS cross sections together with cyclotron mass along with theoretical prediction.}  
\begin{tabular}{|c|c|c|c|c|c|}  
\hline  
Field & Orbit & $S_{exp}(\AA^2)$ & $S_{calc}(\AA^2)$ & $m_e^i/m_e$ & $m_e^{exp}/m_e$ \  
\hline  
(110) & Neck & 0.195 & 0.1722 & & \  
& Box I & 0.490 & 0.47 & & \  
& Box II & 0.536 & 0.5765 & 0.47 & \  
& DB & 0.712 & 0.7778 & 0.6 & \  
(111) & Neck & 0.147 & 0.1375 & 0.21 & 0.41 \  
& Box I & 0.562 & 0.5677 & 0.44 & \  
& Belly & 1.0799 & 1.0 & & \  
(100) & Box I & 0.478 & 0.4852 & 0.40 & 0.83 \  
& Box II & 0.520 & 0.5272 & 0.40 & 0.67 \  
& Rosette & 0.837 & 0.56 & & \  
\hline  
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