Fermi Surface Measurements on the Low Carrier Density Ferromagnet Ca$_{1-x}$La$_x$B$_6$ and SrB$_6$

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Recently it has been discovered that weak ferromagnetism of a dilute 3D electron gas develops on the energy scale of the Fermi temperature in some of the hexaborides; that is, the Curie temperature approximately equals the Fermi temperature. We report the results of de Haas-van Alphen experiments on two concentrations of La-doped CaB$_6$ as well as Ca-deficient Ca$_{1-x}$B$_6$ and Sr-deficient Sr$_{1-x}$B$_6$. The results show that a Fermi surface exists in each case and that there are significant electron-electron interactions in the low density electron gas.

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The cubic hexaborides of the alkaline and rare earth elements have long attracted interest for their wide variety of physical properties in spite of the simple crystallographic structure. These physical properties include very low work functions leading to the use of LaB$_6$ as a thermionic emitter, dense Kondo behavior and electric quadrupole ordering in CeB$_6$, Kondo insulating properties in SmB$_6$ and interesting low carrier density ferromagnetism in the local moment system EuB$_6$. A new aspect to the rich spectrum of properties found in the hexaborides, high temperature weak ferromagnetism at low carrier concentration (HTFLCC) with no atomic localized moments was added about two years ago.

The host materials for HTFLCC are the divalent alkaline earth hexaborides CaB$_6$, SrB$_6$ and BaB$_6$. The crystal structure of these materials can be thought of as a simple cubic CsCl-type arrangement of B$_6$-octahedra and metal ions. The early electronic structure cluster calculations of Longuet-Higgins and Roberts found that the linked B$_6$-network required 20 electrons for a closed shell electronic configuration, indicating that the alkaline earth hexaborides would be semiconductors. More recent band structure calculations show that divalent hexaborides should be semimetals, with a small direct overlap of a primarily boron derived valence band and with a primarily alkaline earth derived conduction band at the X-point in the Brillouin zone. A study of the low temperature properties of single crystals of SrB$_6$ did find approximately 0.001c/Sr, and indications for the importance of electron-hole Coulomb effects.

The unusual aspect of these La-doped divalent hexaborides is that for certain values of $x$ in Ca$_{1-x}$La$_x$B$_6$ a weak ferromagnetic moment, peaking at 0.1$\mu_B$/La at $x=0.005$ is found, and nearly identical magnetic effects with La-doping of CaB$_6$, SrB$_6$ and BaB$_6$ also are found. In addition, it was recently found that Ca-deficient Ca$_{1-x}$B$_6$ is ferromagnetic, but the moment is distinctly smaller than that found at $x = 0.005$, usually by at least an order of magnitude. In all cases the maximum moment is found at $x = 0.005$. For the largest moment at $x = 0.005$ the data show the loss of magnetization occurs with a Curie temperature near $T_C = 600$ K.

Because no obvious source for a strong coupling between any possible magnetic impurities giving rise to a Curie temperature as high as $T_C = 600$ K presents itself, the coupling of defect d-state moments on this scale seems rather implausible. One candidate for the origin of the magnetic polarization emerges from studies of electronic correlations in the low density electron gas, such as those of Ceperley and Alder. This is a topic of theoretical speculation with a long and interesting history, going back to Bloch and Wigner. The study of Ceperley and Alder is a $T = 0$ K computation, comparing unpolarized and completely polarized states of the electron gas, with ferromagnetism showing up for values of $r_S$, the radius of the sphere containing one conduction electron, of order 80 $a_B$. For $x = 0.005$, we compute $r_S = 15.0$ Å = 28.4 $a_B$, using the Bohr radius, $a_B$ for the free electron. How the ferromagnetic ground state might occur in an ordered lattice is unknown. The natural energy scale in this particular analysis is the Fermi energy, and for free electrons one calculates $E_F = 0.062$ eV = 720 K for $x = 0.005$ in CaB$_6$. This temperature is of order the observed Curie temperature. More recently, this finding has caused several theoretical investigations into possible mechanisms for this new type of magnetism.

In addition there have been two other recent energy band calculations devoted entirely to this subject. The ordered moment is approximately 0.07$\mu_B$/carrier at $x = 0.005$, which corresponds to only a partial polarization of the Fermi sea. The reduction of the moment
per carrier seen as \( x \) increases and \( r_S \) decreases might then be interpreted as a reduction in the net polarization as the electron density increases.

We report here the results of de Haas - van Alphen measurements on \( \text{Ca}_{1-x}\text{La}_x\text{B}_6 \) and \( \text{SrB}_6 \) at mK temperatures and in fields up to 32 T in which we observe quantum oscillations corresponding to several extremal cross-sectional areas of the FS, proving the existence of conduction electrons in these materials. In addition, we have measured the effective mass of the carriers on these orbits.

These measurements were performed at the National High Magnetic Field Laboratory, Tallahassee, FL using a torque cantilever magnetometer designed for operation at low temperatures between 20 and 500 mK in applied fields ranging from 0 to 32 T. Samples of \( \text{CaB}_6 \), \( \text{Ca}_{0.9975}\text{La}_{0.0025}\text{B}_6 \), \( \text{Ca}_{0.995}\text{La}_{0.005}\text{B}_6 \), and \( \text{SrB}_6 \) were grown in an Al flux and etched in a 25\% HNO\(_2\) in H\(_2\)O solution down to a small plate that was mounted on the cantilever with GE Varnish. No evidence of Al inclusion was observed upon magnification, and no evidence of superconductivity from Al was observed upon cooling. The oscillatory part of the sample’s magnetization is measured as a function of field and the resulting signal is periodic in \( 1/B \) with a frequency \( F \). This oscillatory magnetization \( \tilde{M} \) is given by the Lifshitz-Kosevich (LK) equation:

\[
\tilde{M} = R_S R_D R_T \sin \left[ \left( \frac{2\pi p F}{B} \right) - \frac{1}{2} \pm \frac{\pi}{4} \right],
\]

where \( R_S, R_D, \) and \( R_T \) are the spin, Dingle, and temperature signal amplitude reduction factors respectively, and \( p \) is the harmonic number. The frequencies of the dHvA oscillations are proportional to extremal areas of the FS perpendicular to the applied field direction. The effective mass of the carriers is determined from the temperature reduction factor by measuring the oscillatory signal amplitudes as a function of temperature. The measured signal from the torque cantilever is a voltage proportional to the gap between the flexible cantilever plate to which the sample is glued and a fixed (reference) plate. The gap is measured as a capacitance with a precision capacitance bridge. The measured oscillations in the torque, \( \tilde{\tau} \), arise from anisotropy in the Fermi surface, such that

\[
\tilde{\tau} = -\frac{1}{F} \frac{dF}{d\theta} \tilde{M} BV
\]

where \( F \) is the dHvA frequency, \( \theta \) is the angle of the applied field, \( B \), \( \tilde{M} \) is the LK expression above, and \( V \) is the volume of the sample. The \( \frac{dF}{d\theta} \) dependence means that a roughly spherical FS with nearly constant FS areas as a function of angle will have a reduced torque signal from that of a highly elliptical FS. Because the signals are inversely proportional to the measured dHvA frequencies, this technique is particularly sensitive to the low frequencies seen in the present results.

The dHvA results shown in the figures are derived from high field measurements. The La-doped samples (except for \( x = 0.010 \)) showed clear evidence of ferromagnetism as shown in Figure 1. Comparing the magnitude of the magnetization as a function of La-doping is complicated by the low frequency dHvA, clearly seen in the pure \( \text{CaB}_6 \) and the \( x = 0.0025 \) traces. The ferromagnetic moment is maximum for \( x = 0.005 \) and is smallest for the \( x = 0.010 \).

The ferromagnetic background of the \( x = 0.0025 \) and \( 0.005 \) samples of \( \text{CaB}_6 \) was subtracted before Fourier transforming the data. We also looked for dHvA oscillations in an \( x = 0.010 \) sample; however, none were observed. The difficulty of observing dHvA in the \( x = 0.010 \) sample can be attributed to increased scattering.

Our measurements for \( \text{SrB}_6 \) are in reasonable agreement with the theoretically predicted FS and ARPES measurements [11]. The FS of \( \text{SrB}_6 \) is centered around the X point and consists of two pieces, an electron “ring” and a hole “lens” (however, the hole pocket due to the boron bands was not observed in the photoemission measurements by Denlinger et al.). Figure 2 shows the raw data and frequencies for \( \text{SrB}_6 \). The hole “lens” corresponds to the dominant low frequency orbit (\( F \approx 44 \) T). The smaller peak corresponds to a FS sheet which has a cross-sectional area approximately 7 times larger than the “lens”. This is even larger than a magnetic breakdown orbit encompassing both the “ring” and the “lens”. Neither of the observed orbits correspond to the electron “ring” mentioned by Rodriguez et al. [9].

The FS of pure \( \text{CaB}_6 \) is topologically similar as can be seen in Figure 3. The higher frequency was determined by fitting the low frequency and subtracting it from the measured data. The resulting data set showed clear evidence of this 300 T orbit.

It should be noted that the number of holes in either \( \text{CaB}_6 \) or \( \text{SrB}_6 \) is determined by the number of Ca or Sr vacancies in the sample. Thus the dHvA frequencies in these two cases may be sample dependent.

La doped \( \text{CaB}_6 \) lacks the strong low frequency orbit attributed to the hole “lens” in the divalent metal deficient materials; however, the higher frequency orbit persists (see Figures 1 and 3). This higher frequency may be modulated by a frequency too low to detect. If this is the case, then La doped \( \text{CaB}_6 \) might have an extremely small hole pocket. In the \( \text{Ca}_{0.995}\text{La}_{0.005}\text{B}_6 \) sample, a 450 T orbit accompanies the dominant 350 T orbit (Figure 3). As electrons are added to the material, the Fermi level rises leading to a change in the topology of the FS. This is consistent with the hole surface dropping out with increased doping yielding a single ellipsoidal electron sheet. We propose that the 450 T orbit arises from the ellipticity of the FS. The eccentricity of this FS sheet is \( \eta = 450/350 = 1.3 \). From the volume of the FS the number of electrons per unit cell can be calculated [12]. Because the FS is centered at the X point, 3 full FS vol-
umes with 2 spin directions contribute to the electron density. So assuming two states at the FS, the electron density is 0.01 per unit cell. If the FS is completely polarized with only one spin state contributing, then the density is 0.005 per unit cell.

The frequencies and cyclotron masses for each of these materials is summarized in Table I. The remarkable result showed in this table is the mass of the higher frequencies orbits in the CaB$_6$ and its electron doped variants. The cyclotron mass for the charge carriers in SrB$_6$ could not be determined because there was no measurable change in signal amplitude from 25 to 600 mK indicating a lighter mass; higher temperature measurements are required to determine these lighter masses. The larger masses of the calcium materials comes from the strong electron-electron interactions.

Because these samples were grown in an Al flux, we were careful to look for evidence of Al contamination that might produce “false” quantum oscillations [13]. As mentioned above, we selected small samples which were visibly free of Al pockets. Also, we looked for the superconducting phase transition of Al on the cool down. As a final test we looked for dHvA signals in a piece of the Al flux on the cantilever, but the flux showed no quantum oscillations. Additionally, the large cyclotron masses of the higher frequency orbits mitigates against attributing their origin to Al contamination – there are no orbits in Al as heavy as 4.5 m$_e$.

From the results of these measurements it can be seen that in every case of HTFLCC Fermi surfaces of the conduction electrons exist. For the optimally doped Ca$_{1-x}$La$_x$B$_6$ a single electron FS is observed and in the divalent CaB$_6$ and SrB$_6$ an additional hole pocket is observed. Strong electron-electron interactions are observed in each case with the largest values observed in the optimally doped samples. Thus not only must the mechanism giving rise to the band structure be understood, but these inter-electron interactions must be accounted for to understand the true mechanism giving rise to the ferromagnetism.

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![FIG. 1. Comparison of the relative magnetization. The upturn in the magnetization of the pure CaB$_6$ is due to the dHvA effect. The $x = 0.0025$ trace is modulated by a low dHvA frequency. The $x = 0.005$ sample shows the largest moment.](image1)

![FIG. 2. FFT of the dHvA oscillations in SrB$_6$. Inset: torque as a function of inverse field at 600 mK.](image2)

![FIG. 3. Top: FFT and data showing the 50 T orbit CaB$_6$. Bottom: FFT and data showing the 300 T orbit.](image3)
FIG. 4. FFT and data showing the 350 T orbit with modulation.

FIG. 5. FFT and data showing the 350 and 450 T orbits.

TABLE I. Listing of dHvA frequencies and cyclotron masses for the hexaborides studied in this paper.

| Material         | F (T) ± 10 | m*          |
|------------------|------------|-------------|
| SrB₆             | 44         | –           |
|                  | 311        | –           |
| CaB₆             | 50         | 0.63 ± 0.05 |
|                  | 300        | 1.14 ± 0.18 |
| Ca₀.₉⁹₇₅La₀.₀⁰₂⁵B₆ | 350        | 4.6 ± 0.2   |
| Ca₀.₉⁹₅La₀.₀⁰₅B₆  | 350        | 4.5 ± 0.6   |
|                  | 450        | 4.4 ± 0.9   |

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