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Fermi surface of the ferromagnetic semimetal, EuB_6

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We report the results of magnetoresistance and magnetization measurements on single crystal EuB_6 for temperatures above and below the ferromagnetic ordering temperatures $T_C^+ = 15.3$ K and $T_C^- = 12.5$ K, in magnetic fields as large as 30 T. Shubnikov–de Haas and de Haas–van Alphen oscillations were observed with four fundamental frequencies. By comparison to band-structure calculations, we ascribe the orbits to small pockets of electrons and holes, centered at the X points. The effective masses and extremal areas of the pockets are in good agreement with the predictions of band-structure calculations. We conclude that EuB_6 is an intrinsic semimetal and not a doped insulator. The intrinsic carrier concentration is 1.2×10^{20} cm^{-3}, although our sample is somewhat uncompensated, with a 65% surplus of holes. There is no appreciable modification to the Fermi-surface dimensions or carrier masses with the onset of ferromagnetism. [S0163-1829(99)01907-4]

Hexaboride compounds have long been studied experimentally and theoretically,[1] and their promise as model compounds lends them a special place in metal physics. The crystal structure is a simple cubic lattice of rare-earth or alkaline-earth ions, with a B_6 octahedron at the cube center. Early tight-binding band-structure calculations[2] proposed a particularly simple view of the electronic structure in which the B_6 octahedra are regarded as anions with charge (-2). In this view, electron transfer from the divalent or trivalent rare-earth or alkaline-earth cations determines whether the compound is a metal or a semiconductor.[3] This picture has lingered, due primarily to its qualitative success in describing the trivalent hexaborides. It has been well established that the trivalent rare-earth hexaborides are simple metals, primarily through the comparison of Fermi surfaces established experimentally from de Haas–van Alphen and Shubnikov–de Haas studies[4–7] to the Fermi surfaces predicted by increasingly sophisticated electronic structure calculations.[8–11] The trivalent hexaborides are rare examples of simple cubic, one electron per unit-cell metals, some ordering antiferromagnetically. The availability of large, high-quality single crystals, the intrinsic stability of the crystal structure, and the broad compositional range of pseudobinary, rare-earth alloys make these materials unparalled as hosts for studies of moment screening and ordering mechanisms,[12] as well as model metallic magnets.[13–16]

This depth of experimental and theoretical understanding does not yet extend to the divalent hexaborides, which have a much more troubled and ambiguous history. Electrical resistivity measurements on EuB_6, SrB_6, and CaB_6 provide evidence for small semiconducting gaps, of order a few tenths of an eV.[3,17,18] Nonetheless, finite resistivity is generally observed at low temperature,[19] as well as clear evidence for gap states from tunneling experiments.[20] This behavior is consistent both with conducting impurity states in a small gap semiconductor, and with the small but intrinsic Fermi surface of a semimetal. The latter view is supported by the most recent electronic structure calculations,[11,21] which proposed that slight dilation of the boron octahedra render the divalent hexaborides semimetallic, with electron and hole concentrations of approximately 10^{20}–10^{21} cm^{-3}, comparable to the lowest carrier concentrations inferred from transport measurements. So far, experimental support for either explanation has been undermined by the crucial role played by sample purity.

EuB_6 is the most extensively studied of the divalent hexaborides, due to its interesting ferromagnetic properties. Figure 1 demonstrates the range of residual resistivities and carrier concentrations measured over the past few decades for a number of nominally stoichiometric samples, as well as several single crystals that have been intentionally doped with La and C. Carrier concentration is determined by Hall effect measurements in the paramagnetic state. We limit our discussion here to EuB_6 samples displaying metallic behav-

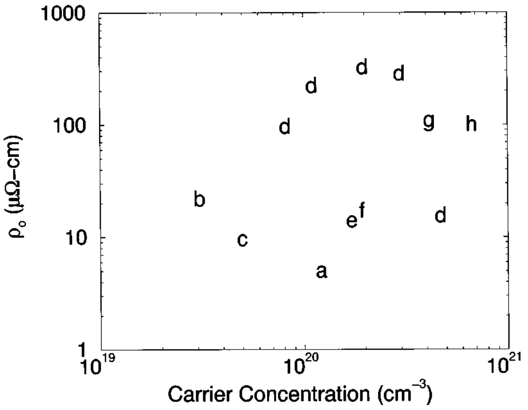

FIG. 1. Residual resistivity ρ_o as a function of carrier concentration n for different EuB_6 samples. n is determined from Hall effect measurements, except for (a), in which de Haas–van Alphen measurements were used. (a) This work. (b) Reference 23. (c) Reference 24. (d) Reference 25, La-doped samples. (e) Reference 26. (f) Reference 22. (g) Reference 27. (h) Reference 28, C-doped sample.

ior with the electrical resistivity decreasing as the temperature is lowered. The observation from Fig. 1 that increases in carrier concentration are generally accompanied by increases in residual resistivity, and presumably sample disorder, is a strong indication that the carriers in most of the samples of Fig. 1 are primarily extrinsic. An alternate explanation, that EuB_6 is an intrinsic semimetal, was suggested on the basis of the large residual resistivity ratio $\rho_{300\ K}/\rho_{4.2\ K}$, and the Hall effect observed in the most highly conducting but lowest carrier-concentration samples.[26] In an intrinsic semimetal, it is possible to lower the residual resistivity by improving the sample perfection without affecting the carrier concentration. However, it is not clear from Fig. 1 whether any of these samples actually approach the limit of predominantly intrinsic carriers.

The primary motivation of the work presented here is to provide an experimental test of the band-structure calculations that propose that pure, stoichiometric EuB_6 is a semimetal, and not a small gap semiconductor. We present here direct evidence for the existence of an intrinsic Fermi suface in divalent EuB_6. We have observed both Shubnikov–de Haas and de Haas–van Alphen oscillations in a high-quality single crystal of EuB_6, whose magnetic and structural properties have been described previously.[29] The Fermi surface consists of both an electron and hole pocket centered at the X point, whose dimensions and carrier masses are in good agreement with the predictions of electronic structure calculations.[21] The success of this comparison proves definitively that the Fermi surface is an intrinsic feature of stoichiometric EuB_6.

We have measured both the magnetoresistance and magnetization of a high-quality single crystal of EuB_6 over a wide range of temperatures and fields. The magnetoresistance measurements were performed in a ^{3}He single-shot refrigerator capable of achieving temperatures as low as 0.4 K in dc fields as large as 30 T, whose angle with respect to the sample principal axes was variable. The sample magnetization was derived from torque measurements for temperatures between 4 and 25 K and fields up to 20 T, performed using a cantilever magnetometer.[30] Our single crystal was grown from an aluminum flux, and its magnetic and structural properties near the upper and lower ferromagnetic transitions $T_C^+ = 15.3$ K and $T_C^- = 12.5$ K have been described in Ref. 29.

The magnetoresistance of our single crystal at 0.4 K is depicted in Fig. 2(a). Here, the field is parallel to the 001 crystalline axis, while the current is transverse, approximately parallel to the sample 100 axis. The magnetoresistance $\Delta\rho/\rho_0$ increases by a factor of almost 150 at 30 T, which is larger than that reported in earlier low-field measurements,[26,31] rivaling in magnitude the negative magnetoresistance observed near the Curie temperatures.[26,32] Several oscillatory components are evident in the magnetoresistance of this high-quality single crystal. The magnetic torque at 4.3 K for H parallel to 001 is displayed in Fig. 2(b), displaying similar oscillations. As shown in the upper panels of Fig. 2, the oscillatory parts of the magnetoresistance and magnetization are periodic functions of inverse field, indicating that they are, respectively, the Shubnikov–de Haas and de Haas–van Alphen oscillations.

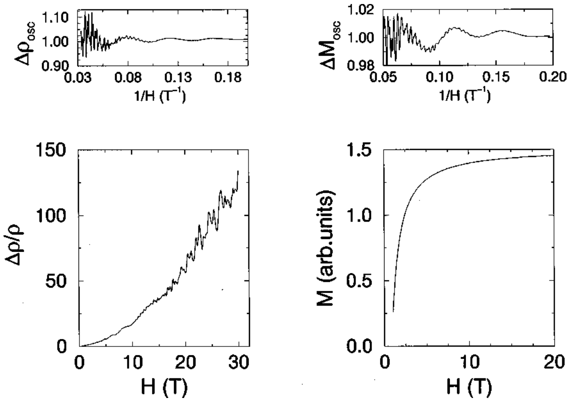

FIG. 2. (a) Magnetoresistance of EuB_6 at 0.4 K. The field is along the 001 axis, while the current flows in the perpendicular plane, approximately along the 100 axis. Top panel: The oscillatory part of the magnetoresistance $\Delta\rho_{osc}$ as a function of inverse field. (b) The magnetic torque, proportional to MH of EuB_6 at 4.3 K, with the field parallel to the 001 axis. Top panel: The oscillatory part of the magnetization ΔM_{osc} as a function of inverse field.

In fact, four fundamental frequencies are found in the Fourier transform of both the 4.3-K magnetization and the 0.4-K magnetoresistance, as well as a number of harmonics and sum and difference frequencies. In all cases, we have restricted our analysis to fields larger than 5 T, for which demagnetization corrections are both reliable and small. Electronic structure calculations[21] propose that the Fermi surface of EuB_6 consists of two elliptical pockets, one electronlike and one holelike, both centered at the X points. Following the electronic structure calculations, we assign k_y to the largest Fermi-surface dimension, while $k_x = k_z$. Since both pockets contain so few carriers, we assume that they are isolated and that no extended orbits are possible. This model of the Fermi surface predicts two oscillation frequencies per ellipsoid for a magnetic field at an arbitrary orientation with respect to the sample principal axes.

The angular dependence of the oscillation frequencies shows that the shape of the Fermi surface for both pockets is close to the ellipsoids predicted by band-structure calculations.[21,33] Figure 3 represents the angular dependences of the fundamental Shubnikov–de Haas frequencies as the sample is rotated through an angle θ about a fixed (010) axis. We note that four distinct frequencies are observed at almost every angle. The angular dependences of the fundamental frequencies allow us to group the four fundamental frequencies into two pairs. As demonstrated by the solid lines in Fig. 3, the complementary angle dependences of the individual frequencies of the pairs agree well with the extremal areas expected for two ellipsoidal Fermi surfaces. The first pocket, described by the frequencies $f_1 = 273$ T and $f_3 = 420$ T, has an asymmetry between the semimajor and semiminor axes of 1.6 ± 0.03, while the second pocket, having $f_2 = 353$ T and $f_4 = 597$ T, has an asymmetry of 1.8 ± 0.03. Pocket one corresponds to a carrier density of 1.2×10^{20} cm^{-3}, while the second pocket contains a slightly larger carrier density, 2.03×10^{20} cm^{-3}. Both the approximate scale for the Fermi-surface dimensions as well as the asymmetry of the electron and hole ellipsoids are in at least qualitative agreement with the electronic structure calculations.[21,33] However, the electron and hole pockets of a stoichiometric semimetal must

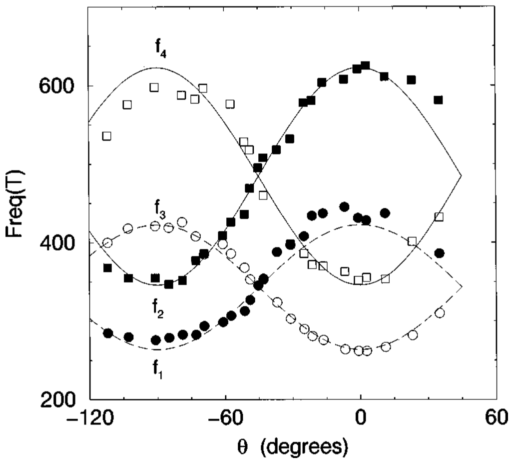

FIG. 3. Variations in the fundamental Shubnikov–de Haas frequencies at 0.4 K with the angle θ between the field and the 100 axis, for rotations about a fixed 010 axis. Solid lines are angle dependences calculated for an ellipsoidal Fermi surface with asymmetry ratio of 1.6, while the dashed lines correspond to an asymmetry ratio of 1.8.

contain identical numbers of carriers, although the shapes of the pockets may differ. We conclude that our sample is somewhat uncompensated, with a 65% difference in the number of electrons and holes. It is most likely that our sample is slightly Eu deficient,[34] suggesting a surplus of holes. For this reason, we assign f_1 and f_3 to the electron pocket and f_2 and f_4 to the hole pocket.

One of the central issues we wish to address with this work is whether the Fermi surface of EuB_6 is strongly affected by the onset of ferromagnetic order, a possible explanation for the giant shift recently observed in the plasma frequency below the Curie temperature T_C.[35] This result could be explained by an approximately threefold increase in carrier concentration or a similar decrease in effective mass as the temperature is reduced from 15 K to 4 K. Neither possibility is consistent with our measurements.

The temperature dependences of the fundamental frequencies for $\theta=0$ are plotted for temperatures from 0.4 K to 25 K in Fig. 4. Each displays a modest and continuous decrease as the temperature is increased, ranging from 8% to 13% over this temperature range. In particular, the temperature dependences of each of the fundamental frequencies are virtually identical above and below the ferromagnetic transitions $T_C^+=15.3$ K and $T_C^-=12.3$ K. This result is in agreement with recent angle-resolved photoemission measurements performed in the paramagnetic state, which find very nearly the same Fermi-surface dimensions as our de Haas–van Alphen and Shubnikov–de Haas oscillation studies.[36]

Similarly, the temperature dependences of the de Haas–van Alphen amplitudes are consistent with effective masses that are temperature independent between 4 and 25 K. The amplitudes of the strongest frequencies from each Fermi-surface pocket, f_1 and f_4, are plotted in Fig. 5. The Lifshitz-Kosevich equation,[37] indicated by the solid lines in Fig. 5, indicates an effective mass of 0.225 ± 0.011 for the electron pocket and 0.313 ± 0.016 for the hole pocket. These low effective masses are consistent with the semimetallic character of EuB_6 and with minimal electronic correlations.

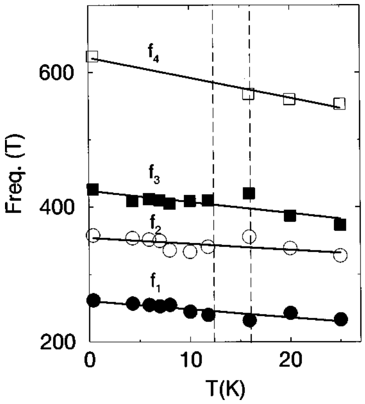

FIG. 4. Fundamental frequencies for $\theta=0$ display a continuous and modest increase with decreasing temperature. The ferromagnetic ordering temperatures, indicated by the vertical dashed lines at $T_C^+=15.3$ K and $T_C^-=12.5$ K are taken from resistance measurements on the same sample (Ref. 29).

Our measurements show that the Fermi surface of EuB_6 is essentially unaffected by the onset of ferromagnetism. Neither the size of the electron and hole pockets, or the carrier effective masses change appreciably in the temperature range in which the plasma frequency increases dramatically. We can offer two possible resolutions to this paradox.

Since the intrinsic Fermi surface in EuB_6 is so small, the conductivity of this material is exquisitely sensitive to small amounts of accidental impurities or variations in stoichiometry, as depicted in Fig. 1. It is possible that the comparison of the Fermi surface and the optical reflectivity results reveals that the extrinsic carriers have much more different properties than the intrinsic carriers. In order to assess the validity of this scenario, it is important that the carrier concentration of the optical reflectivity sample itself be established from its resistivity and Hall effect and compared to that of the sample studied here.

A more exotic possibility is that the Fermi surface of EuB_6 in the ferromagnetic phase is qualitatively modified by magnetic fields. In this view, the high-field de Haas–van Alphen and Shubnikov–de Haas measurements describe a Fermi surface with different properties than that probed by the zero-field reflectivity measurements. To test this idea, we

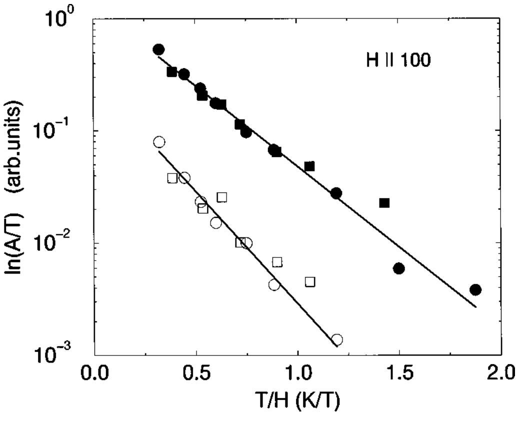

FIG. 5. Temperature dependences of the $\theta=0$ oscillation amplitudes of frequencies f_1 (solid circles) and f_4 (open circles). The solid lines are fits to the Lifshitz-Kosevich equation.

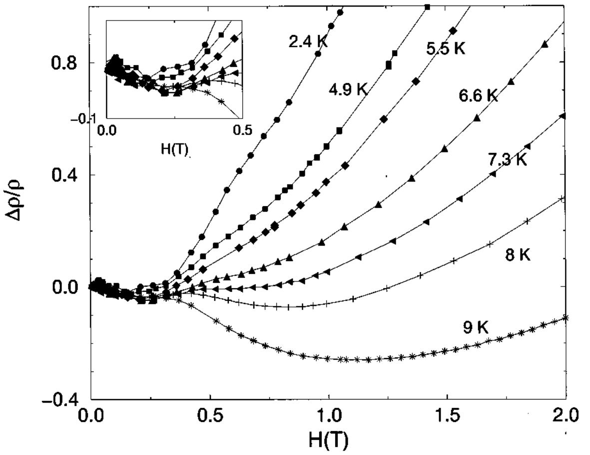

FIG. 6. Magnetoresistance $\Delta\rho/\rho_o$ of EuB_6 for various temperatures. In each case, the field is parallel to the 001 axis, and the current is in the transverse plane, approximately along the 100 axis. Inset: expanded view of low-field region.

have carried out low-field magnetoresistance measurements on the same crystal of EuB_6 used for the de Haas–van Alphen and Shubnikov–de Haas measurements. The results of this study are summarized in Fig. 6. We focus here on the lowest temperatures, away from the region near T_C^+ and T_C^- where the largest negative magnetoresistance is observed. At these low temperatures, the magnetoresistance is negative in very low fields, before becoming positive and increasingly large for fields above ~ 0.2 T. The positive, high-field magnetoresistance can be understood as the normal-metallic magnetoresistance associated with the Fermi surface described by our work. As the temperature is increased, a second minimum in the magnetoresistance is observed at fields that increase with temperature. This higher-field magnetoresistance minimum signals the growing influence of the negative magnetoresistance associated with the ferromagnetic ordering temperatures.[32] At every temperature, the metallic magnetoresistance ultimately dominates at sufficiently high fields.

One explanation for the decrease of the resistivity in low fields might be a field-induced restructuring of the Fermi surface, yielding a smaller number of carriers than is characteristic of the zero-field state. However, the modest decrease in resistivity at low fields suggests that the percentage of total carriers involved in such a reconstruction is likely to be very small, certainly much less than the factor of 3 required to reconcile the temperature dependences of the Fermi surface and reflectivity measurements. Further, the low-field magnetoresistance is remarkably *insensitive* to temperature, unlike the carrier concentration required to explain the optical measurements. Preliminary measurements of the reflectivity in a small magnetic field also indicate that the results are very similar to the zero-field measurements,[38] seemingly ruling out this possibility. What is more, the good agreement between the Fermi-surface dimensions found in our measurements and in the zero-field angle-resolved photemission measurements also argue against this second interpretation.

In summary, we have presented here direct measurements of the Fermi-surface dimension and carrier mass in a divalent hexaboride, EuB_6. We find that there are two Fermi-surface pockets, containing 1.2×10^{20} cm^{-3} intrinsic electrons and holes, although a small departure from stoichiometry affords our sample a hole excess 2.03×10^{20} cm^{-3}. The qualitative agreement with the calculated electronic structure demonstrates that EuB_6 must be considered a semimetal, and not a doped insulator, although the very small carrier concentrations imply that a very high degree of sample purity is required to ascertain that the carriers are primarily intrinsic in origin. We find that the Fermi-surface dimensions and carrier masses are essentially unaffected by the onset of ferromagnetism.

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