Fermi-Surface Measurements in Normal and Superconducting $2H$-$NbSe_2$

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Landau quantum oscillations are observed for the first time in the layered, superconducting, incommensurate-charge-density-wave compound $2H$-$NbSe_2$. The oscillations are observed clearly above H_{c2} but also *below* H_{c2}, with somewhat increased scattering. This is interpreted as scattering of the orbiting normal electrons from the flux lattice. The observed sheet of Fermi surface can be explained if Mattheiss's augmented-plane-wave band structure is modified slightly.

The electronic anomalies observed in various layer dichalcogenides have recently been attributed[1] to the formation of charge-density waves (CDW). The wavelength and strength of the CDW are thought to depend critically on certain aspects of the Fermi surface (FS)—either on the existence of nesting surfaces, as is the case for the *spin*-density wave in pure chromium,[2-4] or on the existence of saddle points in a two-dimensional band structure.[5] Direct measurements of the FS would be highly desirable for comparison with the calculated band structures.[6-10] We present here the first FS measurements in a layer compound exhibiting a CDW.[11] The CDW appears below 32 K with a periodicity which is incommensurate with the lattice.[12] The part of the FS reported here can be fitted into Mattheiss's augmented-plane-wave (APW) band calculation[8] if one of the energy bands near the point Γ is shifted a small amount.

In addition to exhibiting a CDW, $2H$-$NbSe_2$ is a high-field, very anisotropic superconductor with $T_c = 7.2$ K and upper critical field as high as $H_{c2\parallel} = 130$ kG and $H_{c2\perp} = 32$ kG for $\vec{H}$ parallel and perpendicular to the layers.[13-15] Our observation of de Haas–van Alphen (dHvA) and magnetothermal oscillations in the superconducting mixed state well below H_{c2} constitutes the first observation of these effects in *any* superconductor. This rather surprising result allows us to characterize the scattering of normal electrons by the lattice of vortices.

Oscillations as a function of magnetic field strength and direction[16] were observed in both the magnetization (dHvA effect) and in the temperature (magnetothermal oscillations), in the field range 20–106 kG and temperature range 1.5–3.5 K. The sample was held by a rotatable sample holder and a modulation field of up to 200 Oe peak-to-peak amplitude and either 11 or 50 Hz frequency was superimposed parallel to the main field. Crystals of $NbSe_2$ were grown from prepared polycrystalline material (starting with 99.999% Nb and Se) by chemical transport. Transport was carried out in a sealed quartz tube 25 cm long with a thermal gradient of 1000 to 900°C, using 0.75 atm iodine as the carrier. The sample was of flat hexagonal shape, 0.4 mm thick and 2.1 mm from one tip to the opposite tip. The superconducting transition was observed at 7.0 K. The $2H$ phase was confirmed by powder x-ray diffraction on other crystals from the same batch.

A typical trace of magnetothermal oscillations is shown in Fig. 1, giving $dT/dH|_S$ versus H, for $\vec{H}$ rotated 25° out of the plane of the sample.

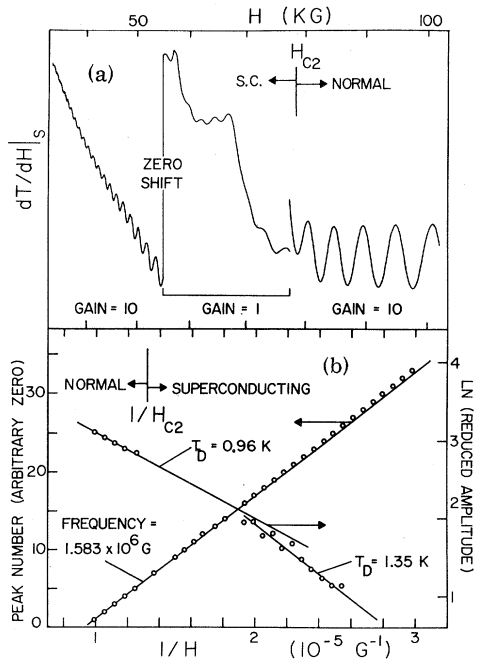

FIG. 1. (a) Magnetothermal oscillations versus magnetic field strength above and below H_{c2}. Note gain change near H_{c2}. (b) Peak number and reduced amplitude versus $1/H$ for the data of (a).

Clear oscillations are observed for both high and low fields. We associate the anomaly at intermediate fields with a broad transition to the superconducting mixed state. The field strength at which the anomaly occurs depends strongly on the direction of the applied field, following the previously measured[13-15] angular dependence of H_{c2}. To determine whether the low-field oscillations connect smoothly with the high-field oscillations, we plot peak number (with arbitrary zero) against $1/H$ in Fig. 1(b). We see that the connection is quite smooth but with a slight increase in frequency of $(3 \pm 1)\%$ at the lower fields, well below H_{c2} which at this orientation is 78 kG. The slope of the standard Dingle plot[16] of reduced amplitude versus $1/H$ indicates the effective scattering (Dingle) temperature T_D, which is proportional to the broadening of the Landau levels. In the normal state at high fields, $T_D = 0.96$ K, while in the mixed state,[17] $T_D = 1.35$ K. Similar results are obtained with the dHvA oscillations. Thus, the electrons (or holes) on this sheet of Fermi surface undergo an enhanced scattering when the sample is in the mixed state compared with the scattering rate in the normal state. The enhanced scattering is equivalent to the thermal broadening at a temperature of 0.40 ± 0.05 K.

Both field-sweep data and field-rotation data are shown in Fig. 2. The frequency of oscillation (i.e., cross-sectional area of FS perpendicular to the applied field) shows hexagonal symmetry with less than 3% variation in the basal plane and very close to $\sec\theta$ variation in the perpendicular plane. The effective mass was measured in the normal state from the temperature dependence of the dHvA-oscillation amplitude and was found to be $0.78 m_0$ for the field lying 27° out of the basal plane.

The data of Fig. 2 indicate that the Fermi surface we observe is of a nearly circular pancake shape with its largest dimensions lying the the basal plane. Since the data disappear in noise 15° from the c axis, it is not possible to invert the data to obtain the shape exactly. However, if we fit an ellipsoid of revolution to the data we obtain an average diameter of 0.344 $Å^{-1}$ and thickness of 0.054 $Å^{-1}$.

In Fig. 3 we show the relevant energy bands and the FS resulting from Mattheiss's APW–tight-binding band calculation,[8] performed for the *absence* of a CDW. One would expect that FS to be cut up by the introduction of energy gaps at those states on the FS separated by the wave vector $\vec{Q}$ of the CDW, namely,[12] $(0.98)(\frac{2}{3})\Gamma M$, in much the same manner that the paramagnetic FS of chromium is cut up by the wave vector of the incommensurate *spin*-density wave.[4] We have applied this technique, which is equivalent to folding the band structure into a smaller Brillouin zone, to Mattheiss's FS but have not found any resulting surfaces that correspond to the experimental data. On the other hand, we notice that

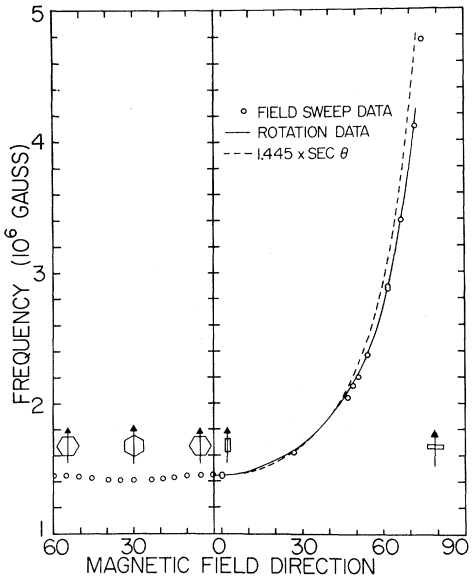

FIG. 2. Frequency versus magnetic-field orientation.

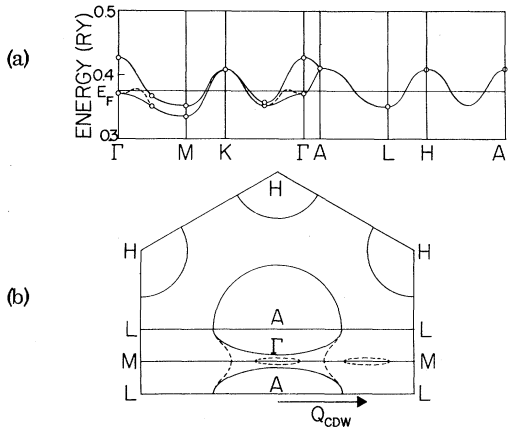

FIG. 3. (a) Solid lines, APW–tight-binding energy bands (Ref. 8) near the Fermi level; dashed lines, proposed modifications to explain the present data. (b) Corresponding Fermi surface and proposed modifications. Translation of the pancake at Γ by $\vec{Q}_{CDW}$ is also shown.

if the band structure is modified[18] in the vicinity of Γ as indicated by the dashed lines in Fig. 3, an electron surface of just the right dimensions can easily be formed to match the experimental data. We note further that the proposed electron pocket would probably survive the presence of a CDW, since translation by $\pm Q_{CDW}$ does not connect the surface with any other parts of the FS.

Naively, one might have expected the dHvA and magnetothermal oscillations to disappear completely in a type-II superconductor as one reduces the field past H_{c2}. A normal electron traveling through the forest of fluxoids might experience an extremely inhomogeneous B field inside the material and suffer heavy scattering from the fluxoids. However, if we use experimentally determined parameters[14] to calculate the field distribution we find that for a material like $NbSe_2$ with a very large value of the Ginsburg-Landau parameter κ (approximately the ratio of the penetration depth λ to the coherence length ξ), the internal field distribution varies only slightly between fluxoids for applied fields on the order of $H_{c2}/2$. For $NbSe_2$, λ and ξ are highly anisotropic. Figure 4 compares the flux pattern and orbit size at 50 kG. Most of the electron orbit is seen to consist of travel perpendicular to the layers and in that direction the field variation is certainly no greater than $\sim \xi_\perp/\lambda_\perp = 1\%$. More detailed calculations[19] suggest a value as small as 0.05%. Furthermore, the deBroglie wavelength is 3–4 times the spacing of the lattice of flux lines, so that one might not expect the electron to respond to the spatial field perturbation very strongly.

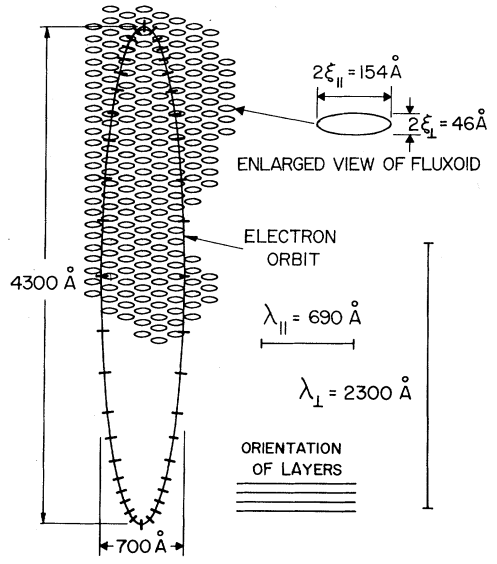

FIG. 4. Comparison of the fluxoid pattern and the observed orbit, for $\vec{H} = 50$ kOe parallel to layers. Tick marks around the orbit indicate the semiclassical de Broglie wavelength of the orbiting normal electron.

One might analyze the situation in terms of a smearing of the phase of the orbiting electrons as they experience a complicated variation in Fermi level, and thus in area.[20] The variation in E_F from the normal core to the intermediate regions is just Δ, one-half the superconducting energy gap. At $H = 0$, $\Delta/k_B = 1.76T_c = 12.6$ K; at $H = 50$ kOe it might not be unreasonable to expect an orbitally averaged value 1/10 as large, or 1.3 K. This value is comparable with our measured broadening Γ of the Landau levels,[16] where $\Gamma/k_B = \pi T_D = 1.2$ K. A detailed calculation would be difficult but the order of magnitude seems reasonable.

The shift toward higher frequency in the superconducting state observed in Fig. 1 is to be expected if the electron orbit is actually located in the superconducting material. The Landau quantum oscillations are periodic in $1/B$, but B in a superconductor is decreasing toward zero more rapidly than is H, for $H_{c1} < H < H_{c2}$, so that the oscillations come more rapidly (higher apparent frequency) than they would if B and H were equal. The magnitude of the effect is approximately correct but numerical comparisons are difficult because of the uncertain demagnetization factor.

In conclusion, we have observed Landau quantum oscillations in a superconductor at fields below H_{c2} for the first time. These are also the first Fermi-surface measurements in a CDW layer compound. The piece of Fermi surface observed is attributed to an electron pocket formed by a proposed modification of Mattheiss's band structure. It is believed that the piece is small enough and well enough separated from other parts of the calculated FS that the wave vector of the CDW does not alter it. From the field dependence of the amplitude we can argue that the *number* of electrons contributing to the signal does not change significantly upon lowering H through H_{c2} but their *scattering rate* does. The increased scattering temperature is $T_D = 0.40$ K in the field range 40–80 kG. Such increased broadening of the Landau levels is not at all unreasonable when one investigates the internal field profile.

These observations should encourage one to look for Landau quantum oscillations in other high-κ superconductors where little hope was

held for Fermi-surface measurements, such as V_3Si, V_3Ga, and Nb_3Sn. Measurements on other layer compounds should also be very interesting, to study further the effects of the Fermi surface and charge-density wave on one another.

We thank L. F. Mattheiss, F. J. Di Salvo, L. R. Testardi, J. J. Hauser, W. A. Reed, J. A. Wilson, and T. M. Rice for a number of stimulating conversations.

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[15]S. Foner and E. J. McNiff, Jr., Phys. Lett. 45A, 429 (1973).
[16]For an excellent review of Fermi-surface measurements, see A. V. Gold, in *Solid State Physics*, edited by J. F. Cochran and R. R. Haering (Gordon and Breach, New York, 1968), Vol. 1, p. 39.
[17]The steeper slope at low fields could also be explained by incomplete penetration of the modulation field in the mixed state. Measurements of the total oscillating (50 Hz) moment of the sample, however, indicate better than ~90% penetration down to the lowest fields where dHvA data were observed (~20 kG). Likewise, the amplitude of the dHvA signal seemed to follow the expected Bessel function fairly well. Another explanation of the steeper slope might involve two extremal areas giving a long beat. The similarity of data at neighboring angles and at lower magnetic fields, especially in the dHvA data, make this explanation seem doubtful to us. Other explanations, such as fortuitous magnetic breakdown, seem less likely, but we must await a much more complete picture of the FS before ruling them out completely.
[18]L. F. Mattheiss has brought to our attention similarities between our proposed modification and the corresponding band in the layer-method calculation for MoS_2 (Ref. 9).
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[20]We thank L. R. Testardi for pointing out this argument.

Band Structure and Optical Properties of Silicon Dioxide*

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The mixed-basis method has been used to compute the energy bands of an idealized β-cristobalite form of silicon dioxide. A direct-forbidden optical-absorption edge is predicted. Peaks in observed x-ray emission and optical-absorption spectra identified with critical points in the densities of states.

We report the results of mixed-basis calculations of the energy bands of silicon dioxide in the form of idealized β-cristobalite, a diamond structure with an oxygen lying midway between each pair of nearest-neighbor silicons.[1] This is the first detailed band-structure calculation for any form of SiO_2, and complements earlier molecular-cluster calculations[2,3] and semiempirical calculations[4] of the valence bands. Many properties of SiO_2 do not appear to depend strongly on long-range symmetry, as, for example, the optical reflectivity spectrum[5,6] from 8 to 20 eV and x-ray-emission spectra.[7] Consequently, our results provide considerable insight into the analyses of experiments on various forms.

The mixed-basis method[8] utilizes Bloch sums