PHYSICAL REVIEW B VOLUME 4, NUMBER 10 15 NOVEMBER 1971

Minority Carriers in Graphite

John A. Woollam
National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio 44135
(Received 24 June 1971)

Quantum oscillations as a function of magnetic field in the Hall effect and thermoelectric power are studied in two samples of pressure-annealed pyrolytic graphite. Only the oscillations originating from minority-Fermi-surface carriers are discussed. de Haas–van Alphen-type frequencies are measured over a wide range of angles between the magnetic field and the c axis of the Brillouin zone. The major conclusions are as follows: (i) There are at least two minority carriers in graphite; (ii) pyrolytic and natural single crystals have the same minority-Fermi-surface sections; (iii) both minority carriers observed by quantum effects very likely originate from the corners of the Brillouin zone near the H points; and (iv) under the assumption that $\gamma_0 = 3.18$ eV, we estimate that $\Delta = +0.004$ eV.

I. INTRODUCTION

Crystalline hexagonal graphite has two sets of Fermi surfaces. There are two large, or "majority," sections, one electron and one hole, which are fairly well understood.[1–3] There are also at least two very small, or "minority," sections. The nature (electron or hole) and location (in the Brillouin zone) of these carriers are not well understood.

The first evidence for the existence of minority carriers was from Hall-effect studies,[4,5] and one of the first detailed studies of minority carriers was by Soule on natural single crystals using the de Haas–van Alphen (dHvA) effect.[6] Later, Williamson *et al.*[3] reported minority-carrier dHvA frequencies in both pyrolytic and natural single-crystal graphite. Williamson's pyrolytic and Soule's single-crystal results were very different from each other.

Both Soule,[6] and Williamson *et al.*[3] studied the dependence of the dHvA period on the angle between the c axis and the magnetic field $\vec{H}$. Their periods are plotted against angle in Fig. 1. In natural single crystals Soule found a period of 1.35 T^{-1} (1 T = 10 kG) for $\vec{H}$ parallel to c, and 0.15 T^{-1} for $\vec{H}$ perpendicular to c. The ratio of these two periods is the anisotropy ratio and is equal to 9. The observation of these oscillations for $\vec{H}$ perpendicular to c suggested to Soule that the Fermi surface was closed. Anderson *et al.*[7] have confirmed the results of Soule on natural single crystals for $\vec{H}$ parallel to c.

In pyrolytic graphite Williamson found quite different results. For $\vec{H}$ parallel to c the period was approximately 2.94 T^{-1}, as shown in Fig. 1. (The results reported in Ref. 2 were wrong owing to a magnet calibration error, later corrected.) Williamson *et al.* were only able to observe oscillations out to about 70° from c in their pyrolytic sample. It was not at all certain if this was the same carrier as that studied by Soule in a natural single crystal.

Flood[8,9] found a minority period of 0.85 ± 0.20 T^{-1} (see Fig. 1) for $\vec{H}$ parallel to c on a pyrolytic sample. (Sample PG 1, having a 300–4.2-K resistance ratio of about unity. Results on PG 1 to PG 6 are reported elsewhere.[1,2,10]) This period is closer to Soule's single-crystal value (dashed line, Fig. 1) than that found in Williamson's pyrolytic sample.

Since Soule's work[4] on single crystals, the very low magnetic field (non-oscillatory region) Hall effect has been used by Spain to detect the presence of minority carriers in pyrolytic graphite.[11] Spain observes both minority electrons and holes, depending on temperature.

In the present paper, minority carriers are studied by observing the oscillations (as a function of magnetic field) in the Hall voltage and thermoelectric power. Two samples of pressure-annealed pyrolytic graphite are studied. The periods are measured as a function of the angle θ between the magnetic field $\vec{H}$ and the c axis, where $0 \le \theta \le 87°$. These results are compared with all previous data and demonstrate a remarkable similarity between natural single-crystal and pyrolytic-graphite results. The location of minority carriers in the Brillouin zone is discussed, and an estimate of the band parameter Δ is made.

II. THEORY

A. Quantum Oscillations

The theory for quantum oscillations is well established and is discussed in many standard texts.[12] The effect results from the quantization of electron orbital motion in the presence of an applied magnetic field. The resultant energy levels (Landau levels) depend on field strength. As the magnetic field strength changes, the Landau levels move through Fermi-surface boundaries. The familiar oscillations (dHvA) in magnetic susceptibiltiy result, which are periodic in H^{-1}. The effect of the Landau-level crossings of the Fermi energy on the Hall effect and thermoelectric power is not as frequently studied. (See, however, Refs. 1 and 2.)

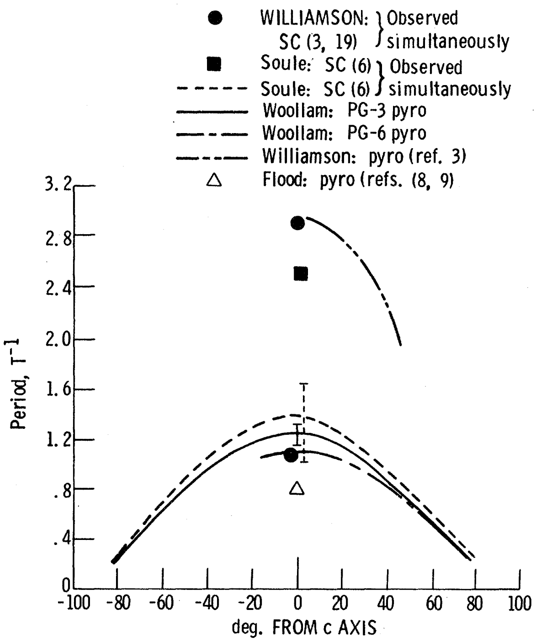

FIG. 1. dHvA periods vs angle between magnetic field and c axis. Some error bars are omitted for clarity. The figure summarizes data on four pyrolytic and two natural single-crystal samples. SC: single crystal; PG: pyrolytic graphite. Results on PG 6 are also shown in Fig. 7.

Yet, these effects are useful since their amplitudes are frequently sensitive to features of the Fermi surface which other oscillating effects are not sensitive to. Other reasons for studying transport effects are discussed in Ref. 1. All effects yield the same period P. It is often desirable to express the results as a frequency F, where

$$F = 1/P. \tag{1}$$

The frequency F is proportional to the extremal cross-sectional area of the Fermi surface perpendicular to the magnetic field direction.

The theory for quantum oscillations in the Hall effect can be found in Ref. 13. Thermoelectric-power quantum effects are discussed in Refs. 1 and 2.

B. Band Structure of Graphite

1. *Majority Carriers*

A frequently used energy-band structure of graphite was calculated by Slonczewski and Weiss[14] and parametrized by McClure.[15] Results of the calculation show that energy levels can be determined when the following parameters in the band-structure theory are found experimentally:

$$\gamma_0 = 3.18 \text{ eV}, \quad \gamma_1 = 0.40 \text{ eV}, \quad \gamma_2 = -0.021 \text{ eV},$$
$$\gamma_3 = 0.29 \text{ eV}, \quad \gamma_4 = 0.18 \text{ eV}, \quad \gamma_5 = -0.0183 \text{ eV}, \tag{2}$$
$$\Delta = 0.009 \text{ eV}, \quad E_F = -0.0237.$$

The values quoted have been principally determined from circularly polarized magnetoreflection and the dHvA-effect measurements.[3,16] McClure[17] has recently made an extensive fitting of a variety of experimental results to the band theory. His results are consistent with the values listed in Eq. (2), but he shows what changes can be made and still be within experimental limits.

The γ's determine the carrier effective mass, the extremal areas, and the dHvA-period anisotropy. Conversely, the γ's are partially determined from experimental measurements of these quantities. The resulting majority-carrier Fermi surfaces are shown in Fig. 2.

2. *Minority Carriers*

There have been several suggestions as to the location of minority carriers in the Brillouin zone. The majority-carrier Fermi surfaces are shown in Fig. 2, along with possible minority carriers. The

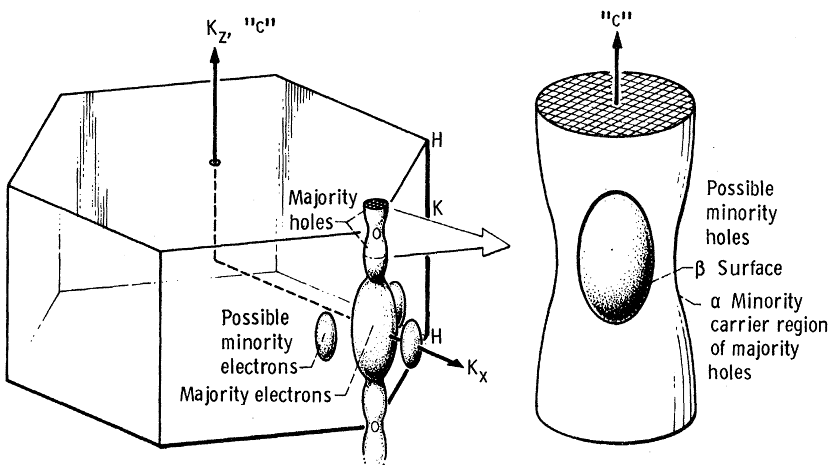

FIG. 2. Majority-, and possible minority-, carrier Fermi surfaces of graphite and Brillouin zone. Identical Fermi surfaces, located along the five other Brillouin-zone edges, are omitted for clarity.

hexagonal "pill-box" Brillouin zone of graphite is shown with Fermi surfaces drawn only on one of the vertical edges. These surfaces would actually be present on all edges. Nozière[18] suggested that minority carriers could be formed by strong trigonal warping of the majority-electron surfaces. This is the origin of the three minority-electron sections pictured in Fig. 2. However, strong trigonal warping implies a large value of γ_3. In order to produce the separate minority carriers shown in Fig. 2, the band parameter γ_3 would have to be at least three times larger than the value listed in Eq. (2). Therefore, the existence of these sections is doubtful.

Williamson *et al.*[3] suggested that the surfaces near the points H (Fig. 2) were the origin of their observations (large period in Fig. 1). At H there are two extremal areas which could give rise to quantum oscillations, denoted by α and β in Fig. 2. The smaller area β, shown as an ellipsoid, would have the larger period. The outer section α is actually part of the majority-carrier holes but the extremal area near the edge of the zone gives rise to minority-carrier effects. Both sections are holes. The cross-sectional areas can be estimated from the Slonczewski-Weiss band model[14] as follows:

$$A_m = 4\pi E_F(E_F - \Delta)\, 3a_0^2\gamma_0^2 , \tag{3}$$

where E_F is the Fermi energy, a_0 is the lattice spacing in the plane perpendicular to c, and A_m is the extremal area perpendicular to the c axis with no spin-orbit interaction. Spin-orbit coupling produces two quantum-oscillation frequencies by changing Eq. (3) by an amount

$$\frac{\delta A_m}{A_m}(\vec{H}\,\|\,c) \simeq \frac{\pm\lambda\Delta}{E_F(E_F-\Delta)} . \tag{4}$$

III. EXPERIMENTAL PROCEDURE

The samples (kindly provided by Dr. A. W. Moore) used in the present experiments were made by stress-annealing pyrolytic graphite. These samples are polycrystalline, but with individual grains aligned with their axes having a 2° half-width about a common direction. The ratio of the 300- to 4-K resistance was 1.5 for PG 3 and approximately 4 for PG 6.

The Hall-effect measurements were made on PG 6 after shaping the sample with a sand-erosion cutter into a long bar with small tabs on the sides for leads. Constant current was provided in the basal plane, and voltage was measured with a nanovolt amplifier, as illustrated in Fig. 3.

The adiabatic thermoelectric power[1] was measured with constant heat input to one end of the sample. A similar tab arrangement was used for attaching leads. Emf's were measured having a typical noise level of 0.1 μV.

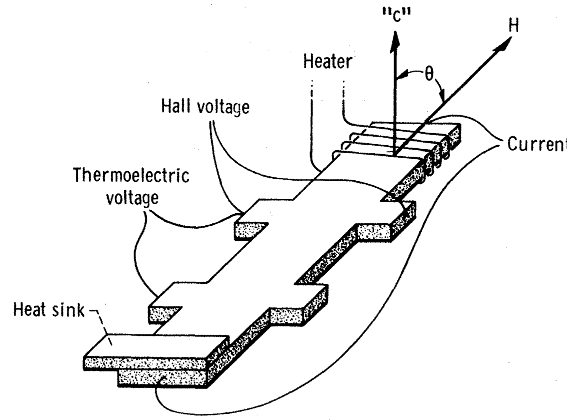

FIG. 3. Sample geometry for Hall effect and thermoelectric-power measurements.

Measurements were made in two magnets. The first magnet used was a superconducting split pair, providing 4.0 T in a transverse configuration. The second magnet was a superconducting solenoid having a maximum field of 10.5 T. An insert Dewar for this magnet permitted pumping helium to 1.0 K in a test region of 0.054-m (2.5-in.) diam. Fields were measured in the solenoid using a magnetoresistor calibrated with NMR. In the split-pair magnet, the field was measured by integrating the induced voltage produced by the sweeping field.

IV. RESULTS

A. Thermoelectric Power in PG 3

In Fig. 4 the thermolectric power in sample PG 3 is plotted as a function of magnetic field at 1.2 K for H 10° from the c axis. The majority-carrier oscillations are superimposed on the lower-frequency minority-carrier oscillations. The majority-carrier thermoelectric-power effects are discussed extensively in Refs. 1 and 2. In Fig. 4 the minority extrema are marked by arrows. The minority-carrier oscillations could easily be followed to large angles between the magnetic field and the c axis because their amplitudes do not die out as rapidly with angle as do the majority-carrier oscillations. For example, at $\theta = 75°$ there are ten minority-carrier extrema observable below 2.0 T, but only two or three majority-carrier oscillations. The thermoelectric-power minority dHvA periods were measured out to $\theta = 80°$ and these are plotted in Fig. 1. Our pyrolytic periods are, within experimental error, the same as Soule's natural-single-crystal periods.

Williamson's results on a pyrolytic sample are plotted in Fig. 1. At $\theta = 0°$ he gets $F = 0.34 \pm 0.015$ T, or a period of approximately 3.0 ± 0.1 T^{-1}. As is visible from Fig. 1, these results are quite different from the results on natural single crystals

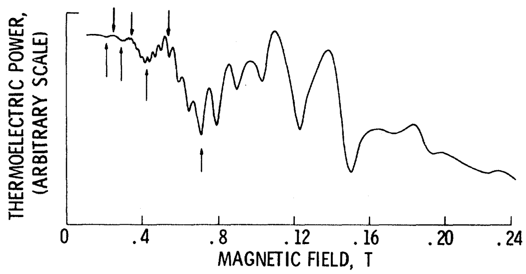

FIG. 4. Thermoelectric power vs magnetic field (1 T = 10 kG) at 1.2 °K in PG 3 for the magnetic field 10° from the c axis. Minority extrema are marked by arrows.

and the pyrolytic results presented in this paper.

B. Hall Effect in PG 6

The Hall effect ρ_{yx} in a second sample PG 6 was studied extensively for minority-carrier effects. It is also a pressure-annealed pyrolytic sample having a resistance ratio $R_{300\ K}$ to $R_{4.2\ K}$ of 3.5. In this sample the minority-carrier effects could be seen to $\theta = 87°$. The magnetoresistance, ρ_{yy}, anisotropy was used to accurately locate the angles close to $\theta = 90°$. In Fig. 5 the magnetoresistance is plotted as a function of angle at a field of 10.2 T. At $\theta = 90°$, there is a sharp minimum which was used to locate $\theta = 90°$ to within $\pm\frac{1}{4}°$.

Examples of the minority oscillations in the Hall resistance as a function of magnetic field are shown in Fig. 6 for $\theta = 77°$. At low fields the minority-carrier oscillations dominated. The majority-carrier oscillations were not visible below about 4 T. For θ greater than 80° there were no majority-carried oscillations present in fields to 10 T.

The Hall-effect results on PG 6 are shown in Fig. 1. For θ between 80° and 90° the quantum-oscillation results as a function of angle are better seen as plots of frequency rather than period. In Fig. 7 the Hall frequencies in PG 6 are plotted as a function of angle. If the originating Fermi surface were a cylinder, then the frequency would follow

$$F = F(0)\ \sec\theta\ . \tag{5}$$

$F(\theta)$ was measured at $\theta = 0°$ to be 0.9 ± 0.1 T. Equation (5) is plotted in Fig. 7 assuming $F(0) = 0.6$ T, $F(0) = 1.2$ T, and $F(0) = 0.9$ T; $F(0) = 0.9$ T appears to fit the data best. Thus the data can be fitted, within experimental error, to the equation

$$F = 0.9\ \sec\theta \tag{6}$$

for θ between 0° and 87°. This suggests that the Fermi surface is an extremely elongated ellipsoid. The ratio

$$F(\theta = 87°)/F(\theta = 0°)$$

equals 13.5, and rapidly increases with increasing θ.

V. INTERPRETATION AND DISCUSSION

In Fig. 1 there is close agreement between the data from two independent natural single crystals and two independent pyrolytic samples. A third pyrolytic (Flood's) gives near agreement. This indicates that both pyrolytic and natural single crystals have the same minority-Fermi-surface pocket of carriers. Since the band structure depends sensitively on minority carriers, this suggests that the two band structures are very nearly the same.

That Williamson's results in a pyrolytic sample are so different indicates that (a) there are two distinct pockets of minority carriers and he is observing the other one, or (b) his pyrolytic sample has dissolved impurities in it. There is evidence for (a) in the results of Soule[6] and in some unpublished single-crystal results of Williamson,[19] where both authors each report seeing two dHvA frequencies simultaneously. Conclusion (b) is possible because a minority-pocket size will change rapidly with doping, as shown by Soule.[4] Soule's doping by boron reduced the period, whereas the period would have to be increased to explain Williamson's results.

The three electron carriers shown opposite the

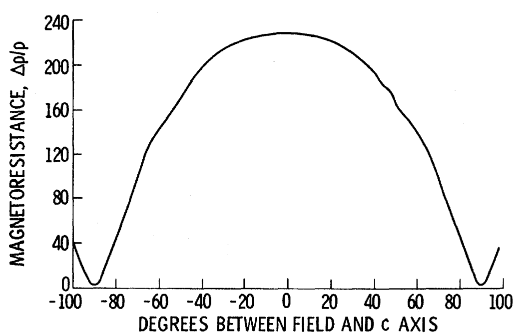

FIG. 5. Magnetoresistance in PG 6 at 10.2 T (1 T = 10 kG) vs angle between the field and the c axis. The plot is used to accurately locate perpendicularity to the c axis.

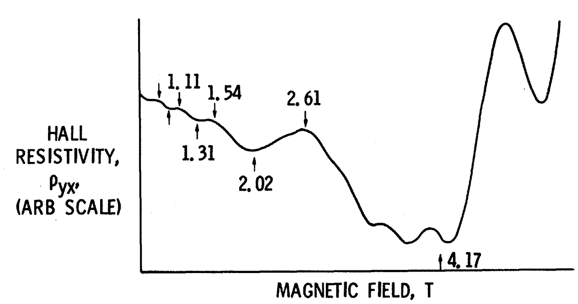

FIG. 6. Hall resistivity ρ_{yx} vs magnetic field at 1.1 K with the magnetic field 77° from the c axis in PG 6 pyrolytic graphite. Minority extrema are marked with arrows and the field values are indicated in teslas (1 T = 10 kG).

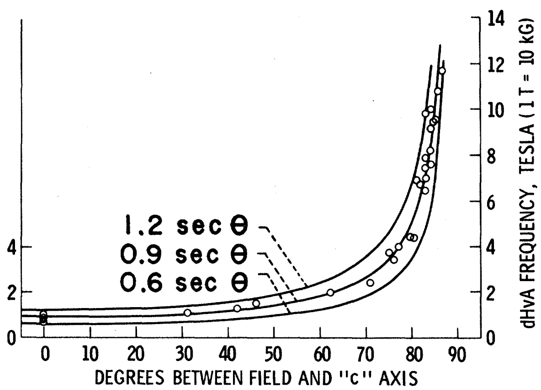

FIG. 7. Minority-carrier quantum-oscillation frequency vs angle between the magnetic field and the c axis for PG 6. These results are also plotted as period vs angle in Fig. 1.

K point in Fig. 2 are probably not being observed in the present experiments for the following reasons: The extreme anisotropy of dHvA frequencies with angle observed in PG 6 is probably too large. It would take $\gamma_3 = 0.9$ eV (see Refs. 6 and 18), which is 3 times larger than magnetoreflection results[16] indicate for this parameter.

The other possible location of minority carriers is near the points H in the Brillouin zone (see Fig. 2). With spin-orbit coupling included, there will be two minority sections near H, as shown and discussed earlier. Since the majority carriers near this point are hole carriers, the minority carriers will both be holes. In fact, one of the minority sections is a narrow part of the majority surface. Being an extremal cross section, it will give rise to a low-frequency oscillation. This section (call it α) will be extremely anisotropic in cross-sectional area. For $\theta = 90°$ this will be a frequency of approximately twice the majority-hole frequency, assuming no magnetic breakdown. From Soule, McClure, and Smith's[20] majority-carrier data, this frequency will be 133 T. From our results on PG 6, the frequency for $\theta = 0°$ is 0.9 T. Thus the anisotropy ratio for the α minority carrier is expected to be approximately

$$F(\theta = 90°)/F(\theta = 0°) = 148$$

with no magnetic breakdown, or 74 with breakdown present.

As discussed by Williamson *et al.*,[3] the expected anisotropy ratio for the small ellipsoid (β) is expected to be 2.3. Since we find that the ratio is greater than 13 and still increasing with angle for PG 6, it is concluded that we have observed the α minority carrier.

We conclude that Williamson's very-low-frequency (greater period) observations in pyrolytic graphite originated from the β surface. His observed anisotropy ratio (corrected for a magnet calibration error) of 2.0 or greater is close to the value of 2.3 predicted for this section. Williamson's dHvA frequency was also small, indicating a smaller cross-sectional area than the α section.

McClure and Yafet[21] estimated the spin-orbit coupling constant to be $\lambda \sim 2\times10^{-4}$ eV, and recent spin-splitting data[10,22,23] show that λ is $-2\pm1\times10^{-4}$ eV. From Eq. (4) the shifts in frequency are less than $\frac{1}{2}\%$ for $|\lambda| = 2\times10^{-4}$ eV. Thus, the factor-of-2 separation in periods shown in Fig. 1 is not due to spin-orbit coupling alone. Tsukada and Uemura[24] have shown that stacking faults in the crystal could have effects similar to, but much larger than, spin-orbit coupling. The effect would be to separate the frequencies, producing two independent branches, as shown in Fig. 1.

The lower-period branch shown in Fig. 1 was the dominant carrier seen by Soule, and his data overlap the PG 3 and PG 6 data in both magnitude and angular dependence out to $\theta = 80°$. This is most likely the α section. His second frequency is roughly the same as observed by Williamson (see Fig. 1) and would be from the β section. The only unexplained feature of this assignment is the anisotropy ratio. In PG 6 the anisotropy ratio was greater than 13 at $\theta = 87°$ and could become very large at $\theta = 90°$. Soule's ratio was 9 at $\theta = 90°$ and this ratio is much smaller than expected for the α surface. This is the only discrepancy we can find in the assignment of the two period branches of Fig. 2 to the α and β sections. Soule has pointed out (private communication) that the discrepancy could be explained by a very small angle between the rotation planes in which θ is measured.

With the α and β assignment, then, the frequency which would result if there were no stacking faults or spin-orbit coupling would be 0.467 T. Using Eq. (3), an estimate of Δ can be made: If $\gamma_0 = 3.18$ eV,[16,17] then $\Delta = +0.004$ eV.

VI. CONCLUSION

We have studied the quantum-oscillation frequencies using the thermoelectric power and Hall effect for two independent samples of pressure-annealed pyrolytic graphite. These frequencies are studied over a wide range of angles between the magnetic field and the c axis.

From the present experiments and from the results of previous workers, there are four major conclusions: (i) There are at least two minority-carrier sections of the Fermi surface in graphite. (ii) Pyrolytic and single-crystal graphite have the *same* minority Fermi-surface sections. (iii) Both minority sections very likely originate from the corners of the Brillouin zone, near the H points. (iv) The band parameter Δ is $+0.004$ eV if we assume[16,17] $\gamma_0 = 3.18$ eV.

[1]J. A. Woollam, Phys. Rev. B 3, 1148 (1971).
[2]J. A. Woollam, NASA Report No. TN D-7037, 1971 (unpublished).
[3]S. J. Williamson, S. Foner, and M. S. Dresselhaus, Phys. Rev. 140, A1429 (1965).
[4]D. E. Soule, Phys. Rev. 112, 698 (1958).
[5]J. W. McClure, Phys. Rev. 112, 715 (1958).
[6]D. E. Soule, IBM J. Res. Develop. 8, 268 (1964).
[7]J. R. Anderson, W. J. O'Sullivan, J. E. Schirber, and D. E Soule, Phys. Rev. 164, 1038 (1967).
[8]D. J. Flood, Phys. Letters 30A, 168 (1969).
[9]D. J. Flood, NASA Report No. TN D-5488, 1969 (unpublished).
[10]J. A. Woollam, Phys. Rev. Letters 25, 810 (1970).
[11]I. L. Spain, D. A. Young, and A. R. Ubbelohde, Phil. Trans. Roy. Soc. London 262, 345 (1967).
[12]D. Shoenberg, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland, Amsterdam, 1957), Vol. II, p. 226.
[13]P. N. Argyres, Phys. Rev. 117, 315 (1960).
[14]J. C. Slonczewski and P. R. Weiss, Phys. Rev. 109, 272 (1958).
[15]J. W. McClure, Phys. Rev. 108, 612 (1957).
[16]P. R. Schroeder, M. S. Dresselhaus, and A. Javan, American Physical Society Conference on the Physics of Semimetals and Narrow Gap Semiconductors, Dallas, Tex., 1970 (unpublished). A more recent listing, based on magnetoreflection experiments, was presented by Heflinger and Dresselhaus at the Tenth Biennial Conference on Carbon, Bethlehem, Pa., 1971 (unpublished), and these values are listed in Eq. (2). (See also Ref. 17.)
[17]J. W. McClure, Tenth Biennial Conference on Carbon, Bethlehem, Pa., 1971 (unpublished).
[18]P. Nozières, Phys. Rev. 109, 1510 (1958).
[19]S. J. Williamson (unpublished).
[20]D. E. Soule, J. W. McClure, and L. B. Smith, Phys. Rev. 134, A453 (1964).
[21]J. W. McClure and Y. Yafet, in *Proceedings of the Fifth Conference on Carbon* (Pergamon, New York, 1962), p. 22.
[22]J. A. Woollam, Bull. Am. Phys. Soc. 16, 63 (1971).
[23]J. W. McClure has made a detailed analysis (including γ_3 effects) of the data of Refs. 10 and 22 and concludes that $\lambda = (-2 \pm 1) \times 10^{-4}$ eV. [Results reported at the Tenth Biennial Conference on Carbon, Bethlehem, Pa., 1971 (unpublished). See Ref. 17.]
[24]M. Tsukada and Y. Uemura, in Proceedings of the Ninth International Semiconductors Conference, Moscow, 1968, Vol. II, p. 1278 (unpublished).

PHYSICAL REVIEW B VOLUME 4, NUMBER 10 15 NOVEMBER 1971

Optical Absorption of Surface States in Ultrahigh Vacuum Cleaved (111) Surfaces of Ge and Si

G. Chiarotti, S. Nannarone, R. Pastore, and P. Chiaradia
Istituto di Fisica, Università degli Studi di Roma, Rome, Italy
and Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche, Sezione di Roma, Rome, Italy
(Received 28 May 1971)

The optical absorption due to surface states on ultrahigh vacuum cleaved Ge and Si surfaces has been directly measured. Results show an absorption extending to energies lower than the edge, which disappears when the cleaved surfaces are oxidized. Possible optical transitions giving rise to this absorption are discussed. It is concluded that the dominant processes are transitions between two bands of surface states located in the gap. Combining the present results with photoelectric data, the energy position of the surface bands in Si is given.

INTRODUCTION

The presence of electronic surface states, localized in the forbidden energy gap of a semiconductor, causes an optical absorption extending to energies lower than the edge.[1,2] In clean surfaces this extra absorption is fairly large and disappears as the surface is slowly oxidized.[3] In a previous paper[3] the effect in Ge has been interpreted as due to optical transitions between two bands located in the gap. The purpose of this paper is to show that similar results hold for Si and to correlate information obtained by optical means to that existing in the literature mainly obtained from electrical and photoelectrical measurements.

Allen and Gobeli[4] studied the influence of surface states on the photoelectric yield of ultrahigh vacuum (UHV) cleaved Ge and Si samples. They show that their results could be interpreted on the basis of a two-band model for the surface states.

The electrical properties of clean surfaces have been investigated by Palmer *et al.*,[5] Handler *et al.*,[6] and others[7] who studied the influence of states on surface conductance of Ge and Si. More recently Mönch[8] studied the effect of Cs coverage on surface conductivity and proposed a two-band model for the surface states. On the other hand Henzler,[9] combining low-energy electron diffraction (LEED) technique and electrical measurements, studied the influence of surface structure on the surface states.

From the theoretical point of view, the problem of the electronic surface states is rather formidable.[10] The principal difficulty is the irregular termination of the lattice near the surface.