Magnetoreflection study of graphite under pressure

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The magnetoreflection technique is applied to study Landau-level transitions in graphite under pressures up to 2 kbar to provide detailed information on the pressure dependence of the graphite electronic structure. In this pressure range the magnetoreflection spectra can be explained in terms of the Slonczewski-Weiss-McClure (SWMcC) band model with small changes in the band parameters that describe the graphite dispersion relations at atmospheric pressure. Using the SWMcC model and neglecting γ_3, a two-band model is developed to describe the K-point Landau levels and changes in these Landau levels produced by external perturbations. From this analysis a value for $\partial \ln\gamma_1/\partial p = 0.024 \pm 0.004$ (kbar)$^{-1}$ is determined from the magnetoreflection spectra, in good agreement with recent pressure-dependent optical studies. Information on the pressure dependence of γ_0 and γ_4 is also presented. The implications of the present magnetoreflection results on previous pressure-dependent Fermi-surface studies are explored.

I. INTRODUCTION

The effects of pressure on the electronic properties of graphite have been investigated through Fermi-surface[1,2] and transport measurements[3] and very recently through near-infrared reflectivity measurements[4] using hydrostatic pressures. These experiments have been analyzed in terms of the Slonczewski-Weiss-McClure (SWMcC) model[5,6] which gives an analytic expression for the electronic states near E_F for graphite both with and without pressure, since pressure does not change the crystal structure of graphite and the SWMcC model is based on crystal symmetry. This model expresses the electron dispersion relation in terms of seven parameters (Δ, γ_i, $i=0,1,\ldots,5$) that may be related to tight-binding parameters and in practice are determined experimentally. Thus, it is possible to describe the effect of pressure on the electronic band structure of graphite in terms of the pressure dependence of the various band parameters.

While all the reported values agree qualitatively, there is a quantitative discrepancy in the band parameter pressure derivatives obtained from either Fermi-surface and transport measurements[1-3] or optical measurements.[4] Here we report values for the pressure derivatives of selected band parameters obtained from magnetoreflection measurements at a photon energy of 117 meV and magnetic fields up to 10 T.

For the analysis of experimental results based on Fermi-surface and transport experiments,[1-3] plausible relations between various undetermined pressure coefficients of band parameters were assumed because these experiments do not determine these parameters independently. Anderson *et al.*[1] measured the pressure dependence of Fermi-surface extremal cross sectional areas associated with both majority (electrons and holes) and minority carriers, while Itskevich and Fisher reported only measurements on the electron Fermi surface.[2] Analysis of Fermi-surface and transport measurements yielded values for the dependence on pressure p of the band parameters γ_1, γ_2, and Δ based on the simplifications

$$\frac{\partial \gamma_0}{\partial p}=0\,, \tag{1}$$

$$\frac{\partial \ln\gamma_2}{\partial p}=2\frac{\partial \ln \gamma_1}{\partial p}\,, \tag{2}$$

$$\gamma_3=\gamma_4=\gamma_5=0\,. \tag{3}$$

The pressure derivative of the number of carriers at 4.2 K has been determined by Kechin *et al.*[3] from galvanomagnetic data. Using all these results,[1-3] Noto and Tsuzuku[7,8] obtained a set of values for the logarithmic pressure derivatives of the parameters $\gamma_1, \gamma_2, \Delta$, based on the assumption of Eq. (1) but circumventing the condition of Eq. (2) by using the experimental result of Likhter and Kechin[9] that $\partial \ln\tau/\partial p \sim 0$, where τ is the carrier relaxation time at room temperature. Spain[10] has made an analysis of the effect of pressure on the conductivity of graphite at low temperatures and concluded that the experimental knowledge, at the time his analysis was carried out, did not allow the pressure derivatives of the band parameters to be calculated with any accuracy.

A recent computer analysis of all the available pressure-dependent data has been carried out by Dillon *et al.*[11] They concluded that the results for the pressure variation of the band parameters are sensitive to the set of assumptions used in the analysis. They further concluded that the constraint that gives reasonable relative magnitudes for the logarithmic pressure derivatives of the different band parameters is

$$\frac{\partial \ln|\gamma_2|}{\partial p}=\frac{\partial \ln|\gamma_5|}{\partial p}=2\frac{\partial \ln|\gamma_1|}{\partial p}=2\frac{\partial \ln\gamma_3}{\partial p}=2\frac{\partial \ln\gamma_4}{\partial p} \quad (4)$$

together with Eq. (1).

These relations are physically reasonable because they assume that the pressure dependence of second-order parameters (γ_2, γ_5) is the same and equal to twice that of the first-order parameters. This analysis assumed that because of the large anisotropy of the compressibility of graphite,[12] the in-plane parameter γ_0 changes negligibly with pressure, compared to the corresponding change of the out-of-plane parameters $(\Delta, \gamma_i, i=1, \ldots, 5)$. The results of their analysis[11] yield wide error limits for the logarithmic pressure derivatives of the band parameters [e.g., $0.012 < \partial \ln\gamma_1/\partial p < 0.022$ (kbar)$^{-1}$], due mainly to the large error limits for the experimental quantities $\partial \ln S_k/\partial p$, where S_k represents any of the extremal Fermi-surface cross sectional areas.

Nagayoshi[13] has evaluated the pressure coefficients of all the band parameters from an energy-band calculation and has found that Eqs. (1) and (4) are relatively well satisfied. He, however, obtained significantly different values for $\partial \ln\gamma_1/\partial p$ and $\partial \ln|\Delta|/\partial p$ than had been previously reported.[1-3,8]

On the other hand, very recent near-infrared reflectivity measurements[4] of graphite under pressure up to 2.8 kbar, have yielded directly the pressure dependences: $\partial \ln\gamma_1/\partial p = 0.028 \pm 0.003$ (kbar)$^{-1}$ and $\partial \ln\gamma_5/\partial p = 0.055 \pm 0.016$ (kbar)$^{-1}$, without additional assumptions such as Eqs. (1)–(4). These values confirm that $\partial \ln\gamma_5/\partial p \simeq 2\partial \ln\gamma_1/\partial p$ and are in good agreement with the theoretical estimates of Nagayoshi but disagree with determinations based on Fermi-surface measurements.[1-3]

The magnetoreflection experiments reported here provide a direct determination of selected band parameters that control the effective mass parameters of graphite. It should be noted that in the magnetoreflection experiment, the band-parameter determination is based on measurement of resonant magnetic fields and is therefore more direct than the near infrared measurements where the band-parameter determination is based on a lineshape analysis. In particular we find that γ_0 is almost independent of pressure and that $\partial \ln\gamma_1/\partial p = 0.024 \pm 0.004$ (kbar)$^{-1}$, in very good agreement with the results of the zero-field reflectivity measurements. A summary of values for $\partial \ln\gamma_1/\partial p$ is given in Table I. For the analysis of our magnetoreflection results for K-point transitions, we have derived a two-band approximation (summarized in Sec. II of this paper) from the SWMcC magnetic effective-mass Hamiltonian.[14] The details of the experimental measurements under pressure are given in Sec. III, and the results and analysis are considered in Sec. IV. Finally, Sec. V discusses the applicability of the two-band approximation for the analysis of magnetoreflection experiments at atmospheric pressure and high pressure, and the relation of the present results to other studies of the pressure dependence of the graphite electronic structure.

II. THE TWO-BAND APPROXIMATION

Most of the experimental work that has led to the accurate determination of the band parameters of the SWMcC model has been carried out at high magnetic fields where the electronic states are quantized into Landau levels. The effective-mass Hamiltonian for graphite in the presence of a magnetic field with $\vec{H} \parallel \vec{c}_0$ has been developed from the SWMcC model by McClure[14] and others.[15-18] In the approximation where $\gamma_3 = 0$, the effective magnetic Hamiltonian for a state N can be written simply as[19]

$$H(\xi, N)=\begin{bmatrix} E_1(N) & 0 & -\left(\frac{B}{2}\right)^{1/2}(1-\nu)N^{1/2} & -\left(\frac{B}{2}\right)^{1/2}(1-\nu)(N+1)^{1/2} \\ 0 & E_2(N) & \left(\frac{B}{2}\right)^{1/2}(1+\nu)N^{1/2} & -\left(\frac{B}{2}\right)^{1/2}(1+\nu)(N+1)^{1/2} \\ -\left(\frac{B}{2}\right)^{1/2}(1-\nu)N^{1/2} & \left(\frac{B}{2}\right)^{1/2}(1+\nu)N^{1/2} & E_3(N)-\mu H & 0 \\ -\left(\frac{B}{2}\right)^{1/2}(1-\nu)(N+1)^{1/2} & -\left(\frac{B}{2}\right)^{1/2}(1+\nu)(N+1)^{1/2} & 0 & E_3(N)+\mu H \end{bmatrix} \quad (5)$$

in which the diagonal energy terms are given by

$$E_1(N) = \Delta + \gamma_1\Gamma + \tfrac{1}{2}\gamma_5\Gamma^2 + (N+\tfrac{1}{2})\mu H, \quad (6)$$

$$E_2(N) = \Delta - \gamma_1\Gamma + \tfrac{1}{2}\gamma_5\Gamma^2 + (N+\tfrac{1}{2})\mu H, \quad (7)$$

$$E_3(N) = \tfrac{1}{2}\gamma_2\Gamma^2 + (N+\tfrac{1}{2})\mu H, \quad (8)$$

the quantities Γ and B by

$$\Gamma = 2\cos(\pi\xi), \quad (9)$$

TABLE I. Values for logarithmic pressure dependence of band parameter γ_1.

Method	$\partial \ln\gamma_1/\partial p$ (kbar)$^{-1}$	Reference
de Haas–van Alphen	0.012 [a]	1
Shubnikov–de Haas	0.012 [a]	2
Galvanomagnetic data	0.012 [a]	3
Reflectivity	0.028	4
Theory	0.020	13
Magnetoreflection	0.024 [b]	present work

[a] It was assumed that $\partial \ln\gamma_0/\partial p = 0$, that $\partial \ln\gamma_2/\partial p = 2\,\partial \ln\gamma_1/\partial p$, and that $\gamma_3 = \gamma_4 = \gamma_5 = 0$.
[b] The value $\partial \ln\gamma_0/\partial p = -0.0016$ (kbar)$^{-1}$ from Ref. 13 was used in the analysis.

$$B = \gamma_0^2 \frac{3a_0^2}{2}\left(\frac{eH}{\hbar c}\right), \tag{10}$$

μ is twice the Bohr magneton $\mu_B = e\hbar/mc$, and a_0 is the in-plane lattice constant. The dimensionless wave vector along the c axis is denoted by ξ and is related to the wave vector k_z, measured from the K point, $\xi = k_z c_0/2\pi$.

The secular equation for the magnetic energy eigenvalues which derives from Eq. (5) is a quartic equation in E. For the H-point Landau levels, an exact solution can be found which depends only on the two band parameters γ_0 and Δ, even when $\gamma_3 \neq 0$ is considered explicitly.

The effect of γ_3 on the magnetic energy levels has been considered by Inoue,[16] Schroeder,[19] and recently by Dresselhaus[17] and Nakao.[18] Their results indicate that γ_3 has a strong influence on the energy of the low-quantum-number Landau levels as well as on the selection rules. The $\gamma_3 = 0$ approximation is, however, useful in the high quantum limit for the analysis of small changes due to perturbations, because the γ_3 terms produce a similar shift for all levels in this limit.

The exact determination of the magnetic energy levels in graphite requires, in principle, the diagonalization of an infinite matrix and, in practice, the diagonalization of at least a 36×36 matrix.[19] This is a long procedure which is not always convenient to follow, especially in situations where a small change in the zero-temperature, atmospheric-pressure band parameter values is to be determined. Based on the 4×4 Hamiltonian given by Eq. (5), we have derived a two-band model approximation for the Landau-energy levels about the Fermi level at the K point of the Brillouin zone which we here apply to the analysis of pressure-induced changes in the K-point magnetoreflection spectra. This model is in principle applicable to the interpretation of any experiments involving perturbations to the magnetic energy-level structure, including perturbations caused by the introduction of intercalants.

The procedure used follows the one employed by McClure,[14] but goes a step further in the order of the approximation, so that our model can account for the band parameter combinations γ_0^2/γ_1 and $\eta = (\gamma_4/\gamma_0) - (2\gamma_2 - 2\gamma_5 - \Delta)/8\gamma_1$. (McClure's model assumes $\gamma_4 = \Delta = 0$ and $\gamma_2 = \gamma_5$.) These combinations of band parameters are physically related to the sum and difference of the Landau-level separations of the valence and conduction bands about the K point.

The secular equation resulting from Eq. (5) when the paramagnetic terms are neglected is

$$B^2 N(N+1) - (N+\tfrac{1}{2})B\left(\frac{E-E_1}{(1-\nu)^2} + \frac{E-E_2}{(1+\nu)^2}\right)(E-E_3) + \frac{(E-E_3)^2(E-E_1)(E-E_2)}{(1-\nu^2)^2} = 0, \tag{11}$$

where the zone edge energies E_1, E_2, and E_3 are given by

$$E_1 = \Delta + \gamma_1\Gamma + \tfrac{1}{2}\gamma_5\Gamma^2, \tag{12}$$

$$E_2 = \Delta - \gamma_1\Gamma + \tfrac{1}{2}\gamma_5\Gamma^2, \tag{13}$$

$$E_3 = \tfrac{1}{2}\gamma_2\Gamma^2. \tag{14}$$

Near the K point only the E_3 band is close to the Fermi level, so that we will consider small perturbations about the E_3 band,

$$E(N) \equiv E_3 + \Delta E, \tag{15}$$

with

$$|\Delta E| \ll |E_3 - E_1|, \ |E_3 - E_2|. \tag{16}$$

As shown in the Appendix, keeping terms in Eq. (11) up to second order in ΔE, the magnetic energy levels about the Fermi level at the K point can be approximately described by

$$E_v(N_v) = E_3^0 - (N_v + \tfrac{1}{2})\hbar\omega_v^*, \tag{17}$$

$$E_c(N_c) = E_3^0 + (N_c + \tfrac{1}{2})\hbar\omega_c^*, \tag{18}$$

where E_3^0 is the K-point band edge energy and

$$\omega_v^* \equiv \frac{eH}{m_v^* c}, \tag{19}$$

$$\omega_c^* \equiv \frac{eH}{m_c^* c}, \tag{20}$$

and $N_{v,c} = 0, 1, 2, \ldots$ label the corresponding Landau levels. The valence and conduction cyclotron effective masses, m_v^* and m_c^*, are directly related to the various band parameters through

$$\frac{1}{m_v^*} = \frac{1}{m^*}(1 - 4\eta), \tag{21}$$

$$\frac{1}{m_c^*} = \frac{1}{m^*}(1 + 4\eta), \tag{22}$$

with

$$\frac{1}{m^*} = \frac{3}{4}\frac{a_0^2}{\hbar^2}\frac{\gamma_0^2}{\gamma_1} \tag{23}$$

and

$$\eta \equiv \frac{\gamma_4}{\gamma_0} - \frac{2\gamma_2 - 2\gamma_5 - \Delta}{8\gamma_1}. \tag{24}$$

The optical interband transitions are such that

$$\hbar\omega = E_c(N_c) - E_v(N_v) = (N_c + \tfrac{1}{2})\hbar\omega_c^* + (N_v + \tfrac{1}{2})\hbar\omega_v^*, \tag{25}$$

with the selection rule

$$N_c - N_v = \pm 1 \tag{26}$$

valid in the limit $\gamma_3 \to 0$. The plus sign in the selection rule corresponds to (−) circularly polarized radiation (electron cyclotron resonance) and the minus sign to (+) circular polarization (hole cyclotron resonance) using Schroeder's notation.[19] If we introduce $N \equiv N_c + N_v$ and use Eqs. (19)–(22), together with the condition given by Eq. (26), then Eq. (25) becomes

$$\hbar\omega = (N + 1 \mp 4\eta)\frac{e\hbar}{m^* c}H_N^{\pm}, \tag{27}$$

where the minus sign in the parenthesis is associated with the resonant fields H_N^+ for (+) polarization and the plus sign with resonant fields H_N^- for (−) polarization.

Equation (27) can be written in the form

$$\frac{1}{H_N^{\pm}} = \frac{1}{\hbar\omega}\frac{e\hbar}{m^* c}(N + 1 \mp 4\eta), \tag{28}$$

which shows that a plot of the inverse of the resonant fields $H_N^{\pm}$ vs (N+1) should give a straight line whose slope is proportional to the parameter combination γ_0^2/γ_1. On the other hand, the intersection of that straight line with the horizontal axis yields the band parameter combination given by Eq. (24). Figure 1 represents such a plot for resonant magnetic fields corresponding to (+) polarization at different photon energies. This figure shows that for a fixed photon energy, the experimental values for $1/H_N^+$ are very well represented by a straight line, whose slope is proportional to the incident photon energy as shown in the insert

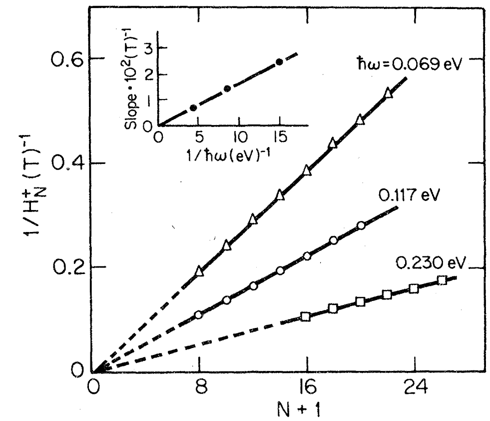

FIG. 1. Reciprocal of the resonant magnetic field H_N for (+) polarization vs (N+1), for different photon energies $\hbar\omega$. In the figure, N represents the sum of the quantum numbers corresponding to the two Landau levels involved in the interband transition. The resonant magnetic fields at $\hbar\omega = 0.117$ eV correspond to the present work. The data at $\hbar\omega = 0.069$, 0.230 eV are taken from Ref. 20, and the magnetic fields are given in Tesla.

to Fig. 1 where these slopes are plotted versus $(\hbar\omega)^{-1}$ for the three values of $\hbar\omega$ shown in the main body of the figure. The insert shows that Eq. (28) is very well satisfied, yielding a value of $m^* = 0.067 \pm 0.001$ m as defined in Eq. (23). Similar results are obtained for (−) polarization, yielding $m^* = 0.068 \pm 0.001$ m. The corresponding value for the ratio γ_1/γ_0^2 is $(4.0 \pm 0.1) \times 10^{-2}$ eV^{-1}, which agrees very well with the value $(3.8 \pm 0.5) \times 10^{-2}$ eV^{-1} obtained from a calculation[19,20] that takes γ_3 into account explicitly.[21] Because of the weak dependence of m^* on γ_3, the effect of γ_3 on $\partial \ln(\gamma_1/\gamma_0^2)/\partial p$ is expected to be a second-order effect. The intersection of the various straight lines with the horizontal axis of Fig. 1 yields a value for η in the range $0.04 < \eta < 0.10$. A more accurate determination for η can be made using data for both senses of circular polarization and the expression

$$\frac{H_N^+ - H_N^-}{H_N^+ + H_N^-} = 4\eta\,\frac{1}{N+1} \tag{29}$$

obtained from Eq. (27). From Eq. (29), η is obtained from the slope of a plot of $(H_N^+ - H_N^-)/(H_N^+ + H_N^-)$ vs $(N+1)^{-1}$. A least-squares fit of the experimental points corresponding to seven different photon energies,[20] yields the value $\eta = 0.048 \pm 0.007$, or $\gamma_4 = 0.044 \pm 0.024$ eV using the band parameters of Table II.

To indicate the range of validity of this two-band model, we summarize the approximations involved in the derivation: (a) $\gamma_3 = 0$. As shown by several authors,[17-19] this is a good approximation for the analysis of Landau-level *separations* in the high quantum-number limit. (b) The paramagnetic terms $(N+\frac{1}{2})\mu H$ in Eq. (5) are neglected. Even at the highest magnetic fields (15 T), used in the magnetoreflection experiments, those terms are very small compared with other pertinent energies.[22] (c) The Landau levels $E(N)$ are not very far away from the Fermi energy. More specifically, $|E(N)| \ll 2\gamma_1$ must be fulfilled. This condition puts some limits on the incident photon energy for which our model is valid. (d) Only first-order terms in $2\gamma_4/\gamma_0$ and $(2\gamma_2 - 2\gamma_5 - \Delta)/8\gamma_1$ are kept in the corresponding power series expansions. Because of the actual values of those two-band parameter combinations, $[2\gamma_4/\gamma_0 \simeq 0.028$ and $(2\gamma_2 - 2\gamma_5 - \Delta)/8\gamma_1 \simeq -0.034]$, this assumption represents a good approximation. Previous analysis of the magnetoreflection experiments[16] used the approximation $\gamma_5 = \gamma_2$ because of the lack of a direct determination of γ_5. A direct determination[4,23] of γ_5 shows that γ_5 is more nearly equal to $-\gamma_2$ than to $+\gamma_2$ so that the "correction term" $(2\gamma_2 - 2\gamma_5 - \Delta)/8\gamma_1$ in Eq. (24) becomes important.

The success of the two-band approximation in the determination of the band parameter combination γ_1/γ_0^2 justifies its use for studying the effect of pressure on the band parameters of graphite. Moreover, it suggests the use of this approximation in situations where only small departures occur in the corresponding atmospheric-pressure, zero-temperature graphite band parameters. Examples of such applications are dilute graphite intercalation compounds and irradiated graphite. It is important to note that the main limitation of the applicability of the two-band model is set by the condition $|\Delta E| \ll 2\gamma_1$. This condition restricts the use of the two-band model to relatively dilute graphite intercalation compounds such that the cutoff energy for the observation of magnetoreflection spectra is well within the limit of validity of the two-band model.

III. EXPERIMENTAL DETAILS

Magnetoreflection measurements from cleaved surfaces of highly oriented pyrolytic graphite (HOPG) at $T = 77$ K, were made at near normal incidence at atmospheric pressure and hydrostatic pressures up to 2 kbar, using helium as a pressure-transmitting fluid. The reflecting area of the samples was about 10×7 mm and their thickness about 2 mm.

The measurements were carried out in an experimental system specially designed and built to provide high pressure in addition to the usual high magnetic field and low temperature requirements of the magnetoreflection experiment. That system, described elsewhere,[24,25] includes an amplitude stabilized CO_2 laser operating at 10.6 μ (117 meV) to provide the necessary intensity and collimation, and a colinear He-Ne laser for alignment purposes. Because the selection rules for the observed transitions depend on the sense of circular polarization, the measurements were made using circularly polarized radiation obtained by placing a CsI Fresnel rhomb in the path of the linearly polarized beam coming out of the CO_2 laser.

The sample is enclosed in a Be-Cu pressure bomb provided with a Ge window, antireflection coated to 10.6 μ, and designed for operation up to 3 kbar pressure at liquid N_2 temperature. The hydrostatic pressure is applied to the sample by

TABLE II. Values of Slonczewski-Weiss-McClure band parameters and their pressure coefficients.

Parameters	Values (eV)	Values of $\partial \ln\gamma/\partial p$ (kbar)$^{-1}$
γ_0	3.16 [a]	−0.0016 [e,f]
γ_1	0.39 [b]	0.024 ± 0.004 [g]
γ_2	−0.019 [c]	0.011 ± 0.008 [h]
γ_4	0.044 [c,d]	0.022 [e]
γ_5	0.038 [b]	0.055 ± 0.016 [i]
Δ	−0.008 [a]	0.031 [e]
ϵ_F	−0.024 [c]	0.011 ± 0.008 [h]

[a] From Ref. 22.
[b] From Ref. 4.
[c] From a fit to the majority electron and hole DHVA periods using values of γ_0, γ_1, γ_5, and Δ from this table, by S. Y. Leung (unpublished).
[d] From present work.
[e] From Ref. 13.
[f] From pressure-dependent magnetoreflection H-point spectra $|\partial \ln\gamma_0/\partial p| < 0.005$ (kbar)$^{-1}$.
[g] From pressure-dependent magnetoreflection K-point spectra.
[h] From present analysis of Fermi-surface data of Ref. 1.
[i] From pressure-dependent optical K-point spectra of Ref. 4.

means of He gas. The liquid-N_2 Dewar containing the pressure bomb assembly is placed inside a 10.16 cm bore 10 T Bitter solenoid.

The pyrolytic graphite samples were mounted in the high-pressure vessel with their c axes parallel to the applied magnetic field. The sample surfaces were prepared by carefully peeling off a thin layer of graphite using sticky tape. This procedure produced mirror-like surfaces which were well suited to the reflectivity experiment.

IV. EXPERIMENTAL RESULTS AND ANALYSIS

A typical magnetoreflection spectrum of graphite at atmospheric pressure and $T=77$ K for (+) and (−) circularly polarized light at $\hbar\omega=117$ meV, is shown in Fig. 2. For each K-point transition, the Landau-level indices for the pertinent valence and conduction levels are indicated sequentially in parentheses. The H-point transitions are labeled by the integer m, and refer to the superposition of two transitions: $m\rightarrow m-1$ and $m+1\rightarrow m$, where m is identified with N in Eq. (5).[22]

Resonant fields for the K-point transitions are read at a point close to the reflectivity minimum where the steep high-field side of the resonance curve departs from a straight line in accordance with K-point magnetoreflection line shape calculations for graphite.[20] The resonance points for the H-point transitions are taken at the reflectivity maximum, in accordance with H-point line shape calculations.[22,26]

Under application of pressure, no change is observed in the line shape or qualitative appearance

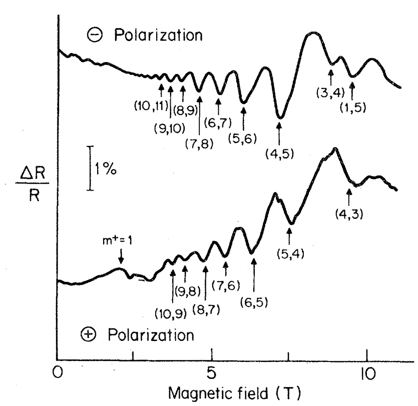

FIG. 2. Magnetoreflection traces for (+) and (−) circularly polarized light showing the K-series transitions (arrows pointing upward) and one H-series transition for (+) polarization (arrow pointing downward), for $\hbar\omega=0.117$ eV and $T=77$ K, at $p=1$ atm. Upon application of pressure, the magnetoreflection traces remain similar in appearance though the positions of the resonant magnetic fields associated with K-point transitions are shifted to higher values for both polarizations.

of the magnetoreflection spectra up to 2 kbar. Therefore, the same criteria as for the atmospheric pressure experiments are also applied in the analysis of the H-point and K-point line shapes of the magnetoreflection experiment under pressure. No measurable pressure-induced shift is observed in the resonant magnetic field for the H-point transition, but the resonant magnetic fields corresponding to K-point transitions are shifted to higher values for both polarizations upon application of hydrostatic pressure.

The insensitivity of the H-point resonances to the effect of pressure is an indication of the smallness of the pressure dependence of the band parameter γ_0. The resonant field H_m is related to the photon energy $\hbar\omega$ and the band parameters γ_0 and Δ through the expression[22]

$$\hbar\omega=\tfrac{1}{2}[\Delta^2+4mbH_m]^{1/2}+\tfrac{1}{2}[\Delta^2+4(m+1)bH_m]^{1/2}, \tag{30}$$

where

$$b\equiv\frac{3}{2}\,\frac{a_0^2e\gamma_0^2}{\hbar c}\simeq1.6\times10^{-3}\ \mathrm{eV^2/T}. \tag{31}$$

Since the $m=1$ H-point transition is sensitive to γ_0 but insensitive to Δ,[22] and the terms in $(\partial\ln a_0/\partial p)$ and $(\partial\ln\Delta/\partial p)$ make a negligible contribution to Eq. (30),[24] we obtain the approximate relation

$$\frac{\partial\ln H_m}{\partial p}\simeq-2\,\frac{\partial\ln\gamma_0}{\partial p}. \tag{32}$$

The experimental finding that $\partial\ln H_m/\partial p\simeq0$ within experimental error ($\lesssim|1\%|$ in the determination of H_m), leads to the result $|\partial\ln\gamma_0/\partial p|<0.005$ $(\mathrm{kbar})^{-1}$.

The pressure dependence of the resonant magnetic fields corresponding to interband K-point transitions has been analyzed in terms of the two-band model presented in Sec. II and is associated with the pressure dependence of m^* and η in Eqs. (23) and (24), giving rise to a change in the slope of a $1/H_N^{\pm}$ vs (N+1) plot, and in the intersection with the horizontal axis. The relative change of m^* with pressure, $(m^*(p)-m^*(0))/m^*(0)$ is shown in Fig. 3 for $p\leq2$ kbar, which is well within the linear pressure regime.[12] The straight line is the result of a least-squares fit to the experimental determinations (represented by circles) yielding a value of $(\partial\ln m^*/\partial p)=0.027\pm0.004$ $(\mathrm{kbar})^{-1}$. It has not been possible to determine quantitatively the change with pressure of the parameter combination η, because of the inaccuracy in the determination of η itself, and because data for only one photon energy are available from this pressure dependent study. Using Eq. (29) in differential form and data for the change in $H_N^+-H_N^-$ with pres-

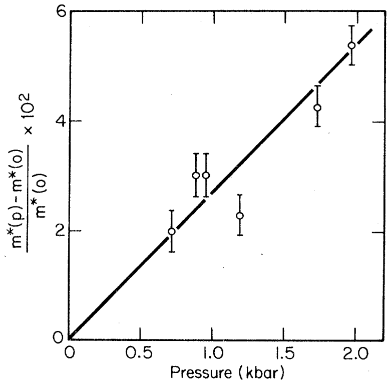

FIG. 3. Relative change of the effective mass (as defined in the two-band approximation) as a function of pressure. The circles correspond to experimental determinations from plots of $1/H_N$ vs (N+1) (see Fig. 1). The continuous line represents a linear least-squares fit of the experimental points.

sure, $\partial \ln\eta/\partial p$ has been evaluated and the results clearly show that η increases with pressure or $(\partial \ln\eta/\partial p)>0$. When the pressure dependence of the various band parameters which enter η are taken into account, the positive sign of $\partial \ln\eta/\partial p$ implies a positive sign for $\partial \ln\gamma_4/\partial p$.

From the definition of m^* [Eq. (23)], it follows that

$$\frac{\partial \ln\gamma_1}{\partial p} \simeq \frac{\partial \ln m^*}{\partial p} + 2\,\frac{\partial \ln\gamma_0}{\partial p}\,, \qquad (33)$$

where the term $2(\partial \ln a_0/\partial p)$ has been neglected because it is two orders of magnitude smaller than the leading term, $\partial \ln m^*/\partial p$. The only value reported for $\partial \ln\gamma_0/\partial p$ is Nagayoshi's theoretical estimate,[13] $\partial \ln\gamma_0/\partial p = -0.0016$ (kbar)$^{-1}$, which is consistent with our limit $|\partial \ln\gamma_0/\partial p| < 0.005$ (kbar)$^{-1}$. By using Nagayoshi's value for $\partial \ln\gamma_0/\partial p$ in Eq. (31) we obtain

$$\frac{\partial \ln\gamma_1}{\partial p} = 0.024 \pm 0.004\ (\text{kbar})^{-1}. \qquad (34)$$

V. DISCUSSION

Expressions for the pressure dependence of the band parameters γ_1 and γ_4 have been obtained using a two-band approximation to the SWMcC band model. An expression for the pressure dependence of γ_0 has been obtained directly from the SWMcC model.

Our experimental result for the pressure dependence of the band parameter γ_1 shows that γ_1 increases with pressure and the rate of change is about an order of magnitude larger than that for γ_0. These two results are physically reasonable, because γ_1 is related to the interaction between nearest-interlayer atoms and γ_0 is related to the interaction between neighboring atoms in a single layer plane. Under the effect of pressure, the interlayer distance decreases, and consequently that interaction should increase. On the other hand, compared with the interlayer interaction, the interlayer interaction should be almost unaffected by pressure, in agreement with our experimental results.

Our value for $\partial \ln\gamma_1/\partial p$ is compared with other determinations in Table I. The present result agrees well with the value obtained from near-infrared reflectivity measurements at zero magnetic field[4] and with Nagayoshi's[13] value based on first-principles calculations. The good agreement among all these relatively direct determinations of the pressure-dependence of γ_1 is significant. Poorer agreement is found when the relatively direct determinations are compared with more indirect determinations such as those obtained from Fermi-surface measurements.[1,2] This discrepancy is not surprising because of the simplifying assumptions employed in the more indirect determinations.

The sign of the pressure dependence of the band parameter γ_4 has been found to be positive, in agreement with the positive sign predicted theoretically.[13] This result is physically reasonable because an increase in pressure is expected to increase the overlap of wave functions on adjacent layers, thereby increasing the magnitude of the matrix elements which give rise to γ_4.

At this point it is worth raising the question about the validity of comparing values obtained from measurements made at different temperatures. The de Haas–van Alphen type experiments are usually done at liquid helium temperature, while our magnetoreflection results and the near-infrared data reported previously[4] were carried out at 77 K and room temperature, respectively. If the compressibility is the same in this range of temperatures, it is valid to compare values of parameters that depend exclusively on the lattice constants. To our knowledge, there are no reported values for the temperature dependence of the compressibility of graphite, between 4 and 300 K. It is possible, however, to estimate that dependence from the following argument. The interlayer spacing of graphite is known to decrease to 0.9952 and 0.9947 of its room temperature value at 77 K and 4.2 K, respectively.[27] This decrease is equivalent to the one produced by a pressure of ~3 kbar and ~3.3 kbar, respectively, according to Lynch and Drickamer[12] and to ~1.7 kbar and ~1.9 kbar, respectively, according to Kabalkina and Vereschagin.[28] Even though the compressibility of graphite is very pressure dependent in the 0–100 kbar interval,[12] the change of the compressibility between 0 and 3.3 kbar is only about 3%. As a consequence, the change of the compressibility of graphite between 300 and 4 K can be estimated to be of the order of 3%. This number is smaller than the uncertainty associated with the values to be compared for the pressure dependence of the band parameters, and consequently, the comparison of values corresponding to different temperatures (in the range $0<T<300$ K) is valid.

It is of interest to examine the implications of the pressure-dependent magnetoreflection results on previous measurements of the pressure dependence of the extremal Fermi-surface cross sectional areas. The expressions for the extremal cross sectional areas for majority (K-point) electrons S_e, majority holes S_h, and minority (H-point) holes S_m are (neglecting γ_3)

$$S_e = \frac{\pi}{\eta_0^2(1+\nu_0)^2}(2\gamma_2 - E_F)(\Delta - 2\gamma_1 + 2\gamma_5 - E_F), \quad (35)$$

$$S_h = \frac{\pi}{\eta_0^2(1-\nu_m)^2}(2\gamma_2\cos^2\psi - E_F) \times(\Delta + 2\gamma_1\cos\psi + 2\gamma_5\cos^2\psi - E_F), \quad (36)$$

$$S_m = \frac{\pi}{\eta_0^2}E_F(E_F - \Delta), \quad (37)$$

in which $\eta_0^2 = \frac{3}{4}\gamma_0^2 a_0^2$, $\nu_0 = 2\gamma_4/\gamma_0$, $\nu_m = 2\gamma_4\cos\psi/\gamma_0$, and $\cos\psi \simeq (E_F/6\gamma_2)^{1/2}$. The corresponding pressure derivatives are

$$\frac{\partial \ln S_e}{\partial p} = -\frac{2}{1+\nu_0}\frac{\partial \ln\gamma_0}{\partial p} - \frac{2\gamma_1}{A}\frac{\partial\ln\gamma_1}{\partial p} + \frac{2\gamma_2}{2\gamma_2 - E_F}\frac{\partial\ln\gamma_2}{\partial p} - \frac{2\nu_0}{1+\nu_0}\frac{\partial\ln\gamma_4}{\partial p} + \frac{2\gamma_5}{A}\frac{\partial\ln\gamma_5}{\partial p} + \frac{\Delta}{A}\frac{\partial\ln\Delta}{\partial p} - \left(\frac{E_F}{A} + \frac{E_F}{2\gamma_2 - E_F}\right)\frac{\partial\ln E_F}{\partial p}, \quad (38)$$

$$\frac{\partial \ln S_h}{\partial p} = -\frac{2}{1-\nu_m}\frac{\partial\ln\gamma_0}{\partial p} + \frac{2\gamma_1\cos\psi}{C}\frac{\partial\ln\gamma_1}{\partial p} - \left(\frac{\nu_m}{1-\nu_m} + \frac{\gamma_1\cos\psi + 2\gamma_5\cos^2\psi}{C}\right)\frac{\partial\ln\gamma_2}{\partial p} + \frac{2\nu_m}{1-\nu_m}\frac{\partial\ln\gamma_4}{\partial p} + \frac{2\gamma_5\cos^2\psi}{C}\frac{\partial\ln\gamma_5}{\partial p} + \frac{\Delta}{C}\frac{\partial\ln\Delta}{\partial p} + \left(\frac{1}{1-\nu_m} + \frac{\gamma_1\cos\psi + 2\gamma_5\cos^2\psi - E_F}{C}\right)\frac{\partial\ln E_F}{\partial p}, \quad (39)$$

$$\frac{\partial\ln S_m}{\partial p} = -\frac{2\ln\gamma_0}{\partial p} + \frac{2E_F - \Delta}{E_F - \Delta}\frac{\partial\ln E_F}{\partial p} - \frac{\Delta}{E_F - \Delta}\frac{\partial\ln\Delta}{\partial p}, \quad (40)$$

where $A = \Delta - 2\gamma_1 + 2\gamma_5 - E_F$, $B = 2\gamma_2\cos^2\psi - E_F$, and $C = \Delta + 2\gamma_1\cos\psi + 2\gamma_5\cos^2\psi - E_F$.

We note that the most important terms in Eqs. (38) and (39) involve the two unknowns $\partial\ln\gamma_2/\partial p$, $\partial\ln E_F/\partial p$, and the quantity $\partial\ln\gamma_1/\partial p$ which we have determined accurately from magnetoreflection experiments. Using measured values[1] for $(\partial\ln S_e/\partial p) = 0.034 \pm 0.006$ (kbar)$^{-1}$, $(\partial\ln S_h/\partial p) = 0.040 \pm 0.004$ (kbar)$^{-1}$, values for the band parameters from Table II, and Nagayoshi's theoretical values for those terms which make very small corrections to Eqs. (38) and (39) [i.e., $\partial\ln\gamma_0/\partial p = -0.0016$ (kbar)$^{-1}$, $\partial\ln\gamma_4/\partial p = 0.022$ (kbar)$^{-1}$, and $\partial\ln\Delta/\partial p = 0.031$ (kbar)$^{-1}$], we obtain $\partial\ln\gamma_2/\partial p = 0.011 \pm 0.008$ (kbar)$^{-1}$ and $\partial\ln E_F/\partial p = 0.011 \pm 0.008$ (kbar)$^{-1}$. Although the errors in $\partial\ln\gamma_2/\partial p$ and $\partial\ln E_F/\partial p$ are large, the present analysis casts doubt on the validity of the assumptions $\partial\ln|\gamma_2|/\partial p = 2\partial\ln|\gamma_1|/\partial p$ and $\partial\ln|\gamma_2|/\partial p = \partial\ln|\gamma_5|/\partial p$ used previously to interpret Fermi-surface data.[11] It is also of interest to mention that the values for $\partial\ln\gamma_2/\partial p$ and $\partial\ln E_F/\partial p$ determined in this way from experimental data are significantly smaller than the theoretical values obtained by Nagayoshi[13] for these quantities. To verify this conclusion concerning the validity of the assumptions $\partial\ln|\gamma_2|/\partial p = 2\partial\ln|\gamma_1|/\partial p = \partial\ln|\gamma_5|/\partial p$, we have calculated $\partial\ln S_e/\partial p$ and $\partial\ln S_h/\partial p$ assuming $\partial\ln|\gamma_2|/\partial p = 2\partial\ln|\gamma_1|/\partial p$, $\partial\ln|\gamma_2|/\partial p = \partial\ln|\gamma_5|/\partial p$, and $\partial\ln|E_F|/\partial p = \partial\ln|\gamma_2|/\partial p$ (since no direct measurement of $\partial\ln|E_F|/\partial p$ has been reported), and find the results for $\partial\ln S_e/\partial p$ and $\partial\ln S_h/\partial p$ to lie outside the reported experimental errors: $(\partial\ln S_e/\partial p)_{\text{model}} = 0.064 \pm 0.011$ to be compared with $(\partial\ln S_e/\partial p)_{\text{expt}} = 0.034 \pm 0.006$ and $(\partial\ln S_h/\partial p)_{\text{model}} = 0.053 \pm 0.009$ to be compared with $(\partial\ln S_h/\partial p)_{\text{expt}} = 0.040 \pm 0.004$.

Finally, a similar analysis for Eq. (40) yields $(\partial\ln S_m/\partial p) = 0.029 - 0.50(\partial\ln\Delta/\partial p)$ so that measurements of $(\partial\ln S_m/\partial p)$ would determine $(\partial\ln\Delta/\partial p)$. However, two minority de Haas-van Alphen periods have been reported for graphite, these periods being denoted by P_1 and P_2.[22,29] Unfortunately, the pressure dependence of the minority period given in the literature[1] corresponds to the period $P_1 = 1.35\times10^{-4}$ G^{-1} while the minority period associated with the H-point minority hole pocket[22] is $P_2 = 3.03\times10^{-4}$ G^{-1}. The formula given by Eq. (40) is for the extremal cross sectional area around the H-point, corresponding to period P_2. In view of the recent identification of the P_2-period with the H-point hole pocket, it would be of interest to measure the pressure coefficient $(\partial \ln S_m/\partial p)$ associated with the period P_2.

In conclusion, from magnetoreflection measurements, we have determined the pressure dependence of the parameter γ_1, set a limit for the pressure dependence of γ_0, and determined the sign of the pressure dependence of γ_4. These parameters appear in the SWMcC model describing the electronic band structure of graphite and are directly related to the interaction between nearest-neighbor atoms in the same layer (γ_0), between nearest-neighbor atoms in adjacent layers (γ_1), and to a transfer integral involving wave functions on adjacent layers (γ_4). The value of $(\partial \ln\gamma_1/\partial p) = 0.024 \pm 0.004\ (\text{kbar})^{-1}$ obtained from the magnetoreflection experiment (a) agrees well with other direct experimental determinations and theoretical calculations and (b) gives additional support for the use of the two-band model in cases where small changes of the band parameters are involved. This result is very important because it implies that a simple two-band model might be useful in the analysis of magnetoreflection measurements in dilute graphite intercalation compounds for which small changes in the resonant magnetic fields are found relative to their values in pristine graphite. The implications of the present determination of $\partial \ln\gamma_1/\partial p$ on previous pressure dependent Fermi-surface studies have been explored. Though the errors in the evaluation of $\partial \ln\gamma_2/\partial p$ and $\partial \ln E_F/\partial p$ are large, the present work casts doubts on previous assumptions that were used to interpret Fermi-surface and transport data,[1-3] namely, that $\partial \ln|\gamma_2|/\partial p \simeq 2\partial \ln|\gamma_1|/\partial p$ and $\partial \ln|\gamma_2|/\partial p \simeq \partial \ln|\gamma_5|/\partial p$. On the other hand, the assumption $\partial \ln\gamma_2/\partial p \simeq \partial \ln E_F/\partial p$ used by previous workers is consistent with the findings of the present work. The positive sign of $\partial \ln\gamma_2/\partial p$ and $\partial \ln E_F/\partial p$ implies that the application of pressure increases the band overlap and the volume of the electron and hole carrier pockets, in agreement with previous work.

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APPENDIX

We derive below approximate expressions for the magnetic energy levels near the K-point of the Brillouin zone, using the approximations $\gamma_3 = 0$ and $(E - E_3) = \Delta E \ll 2\gamma_1$. If we consider terms up to second order in ΔE as defined by Eq. (15), and use the approximation given by Eq. (16), Eq. (11) becomes

$$(1-\Lambda)(\Delta E)^2 + (N+\tfrac{1}{2})B(\omega_1+\omega_2)\Delta E + B^2 N(N+1)\,\omega_1\omega_2 = 0\,, \quad \text{(A1)}$$

where

$$\Lambda \equiv \frac{2(1+\nu^2)}{(E_3-E_1)(E_3-E_2)}(N+\tfrac{1}{2})B\,, \quad \text{(A2)}$$

$$\omega_1 \equiv \frac{(1-\nu)^2}{E_1 - E_3}\,, \quad \text{(A3)}$$

$$\omega_2 \equiv \frac{(1+\nu)^2}{E_2 - E_3}\,, \quad \text{(A4)}$$

and B is defined by Eq. (10). The solutions of Eq. (A1) are given by

$$\Delta E = \left(\frac{-(N+\tfrac{1}{2})(\omega_1+\omega_2) \pm \{(N+\tfrac{1}{2})^2(\omega_1-\omega_2)^2 + \omega_1\omega_2[1+4\Lambda N(N+1)]\}^{1/2}}{2(1-\Lambda)}\right)B\,. \quad \text{(A5)}$$

At the K point,

$$E_1 = \Delta + 2\gamma_1 + 2\gamma_5\,, \quad \text{(A6)}$$

$$E_2 = \Delta - 2\gamma_1 + 2\gamma_5\,, \quad \text{(A7)}$$

$$E_3 = 2\gamma_2 \equiv E_3^0\,, \quad \text{(A8)}$$

and

$$\nu_0 = \frac{2\gamma_4}{\gamma_0}\,. \quad \text{(A9)}$$

Keeping only first-order terms in the band-parameter combinations, $\nu_0 \equiv 2\gamma_4/\gamma_0 \simeq 0.028$ and $\beta \equiv (2\gamma_2 - 2\gamma_5 - \Delta)/8\gamma_1 \simeq -0.034$ in Eq. (A5), the Landau-energy levels at the K point about the Fermi level can be written as

$$E(N) = E_3^0 + \{(N+\tfrac{1}{2})4\eta \pm [N(N+1)]^{1/2}(1-\Lambda)^{1/2}\}\frac{\hbar\omega^*}{1-\Lambda}\,, \quad \text{(A10)}$$

where

$$\omega^* \equiv \frac{eH}{m^*c}, \tag{A11}$$

$$\Lambda \cong -(N+\tfrac{1}{2})\frac{\hbar\omega^*}{\gamma_1}, \tag{A12}$$

and $(1/m^*)$ and η are given by Eqs. (23) and (24), respectively. Let us assume that $|\Lambda| \ll 1$, a condition that is well satisfied in the magnetoreflection experiment. Also for $N \geq 4$, we have the approximate relation $[N(N+1)]^{1/2} \simeq N+\frac{1}{2}$ [e.g., for $N=4$, $N^{1/2}(N+1)^{1/2}=4.47$], so that

$$E(N) \simeq E_3^0 \pm (N+\tfrac{1}{2})(1\pm 4\eta)\hbar\omega^*. \tag{A13}$$

We define valence and conduction effective masses by Eqs. (21) and (22) and obtain the Landau levels for the valence band (−) and conduction band (+) given by Eqs. (17)–(20). Throughout the text we refer to Eqs. (17)–(20) as the two-band approximation for the K-point Landau levels near E_F.

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