

Optical reflectivity of graphite under pressure

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We have measured basal-plane reflectivity spectra of hexagonal graphite over the spectral range 0.5–3 eV at pressures up to 12 GPa ($T=300$ K). From the increase of the A_1 and A_2 near-infrared interband-transition thresholds we determine the pressure coefficient of the interlayer overlap parameter γ_1 of the Slonczewski-Weiss-McClure band model as $d \ln \gamma_1 / dP = 0.128(10) \text{ GPa}^{-1}$, which corresponds to a c -axis scaling coefficient $d \ln \gamma_1 / d \ln c = -5.35(20)$. The reflectivity of the high-pressure carbon phase formed above 14 GPa exhibits bleaching of interband absorption below 3 eV, which is consistent with an almost complete transformation to an sp^3 -bonded phase achieved at room temperature. We find evidence for the onset of sp^3 bond formation at pressures below 10 GPa.

INTRODUCTION

Graphite is a prototype layered crystal with strong covalent bonds within the two-dimensional hexagonal layers and much weaker bands between layers. The basic features of the electronic structure^{1–3} of graphite can be understood in a single-layer approximation.⁴ The weak interaction between successive lattice planes introduces small splittings and shift for the π and π^* bands. As a result of interlayer coupling, the near-infrared (ir) optical response shows two structures^{5,6} which arise from the A_1 and A_2 interband-transition thresholds about the K point near the Brillouin-zone edge (see Fig. 1). Within the Slonczewski-Weiss-McClure (SWM) band model^{1,2} the energies of these optical transitions are mainly deter-

mined by the overlap interaction parameter $\gamma_1 \approx 0.4$ eV for nearest-neighbor atoms on successive layers.^{7,8}

This paper reports on the pressure dependence of the optical reflectivity of hexagonal graphite in the spectral range from 0.5 to 3 eV. The primary motivation for this investigation was to determine the pressure dependence of the γ_1 parameter from the shift of the A_1 and A_2 interband-transition energies measured over an extended range of pressure ($P \leq 12$ GPa). Previous reflectivity⁸ and magnetoreflexion⁹ studies at low pressures ($P < 0.3$ GPa) yielded pressure coefficients for γ_1 which are in reasonable agreement with a theoretical calculation¹⁰ but are difficult to reconcile with the value obtained from an analysis¹¹ of Fermi surface and galvanomagnetic measurements under pressure (see Table I).

A second aspect of this work is related to the high-pressure phase transition of graphite. At roughly 15 GPa (increasing pressure) hexagonal graphite transforms to a new phase of carbon^{12–14} which is likely to be the sp^3 -bonded hexagonal form of diamond (wurtzite analog or "lonsdalite"). At least, this phase has been identified in samples which were recovered from pressure experiments at elevated temperatures ($T \geq 1000^\circ\text{C}$).¹³ From optical-reflectivity measurements under pressure we obtain information on the course of the phase transition and also an

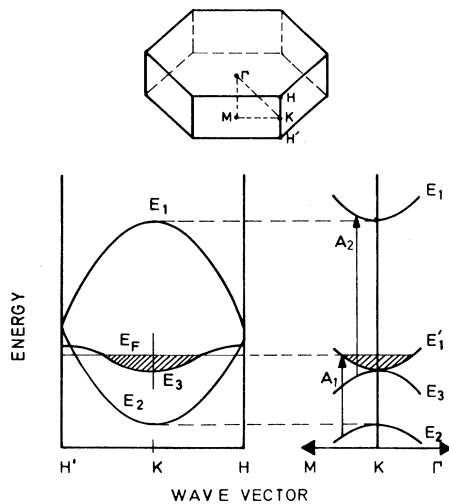


FIG. 1. Schematic band structure of hexagonal graphite near the edge of the Brillouin zone. The effect of trigonal warping is neglected. Arrows indicate A_1 and A_2 interband transitions.

TABLE I. Logarithmic pressure dependence of the SWM band parameter γ_1 .

Method	$d \ln \gamma_1 / dP$ (GPa^{-1})	Reference
Reflectivity	0.28(3)	8
Magnetoreflexion	0.24(4)	9
Theory	0.20	10
Analysis of data from Refs. 12–14	0.12 ^a	11
Reflectivity	0.128(10)	This work

^aAssumptions involved; see Ref. 11 for details.

indication as to what extent sp^3 bonds are formed already at room temperature.

EXPERIMENTAL DETAILS

Samples of 20- μm thickness and 100- μm edge length were prepared from natural graphite flakes.¹⁵ Reflectivity measurements under pressure were performed at 300 K by using a gasketed diamond-window pressure cell¹⁶ in combination with a micro-optical system similar to that described in Ref. 17. The ruby-luminescence method was used to measure pressure.¹⁸ The procedure for optical-reflectivity measurements in a diamond-window cell is described in detail elsewhere.^{17,19} Briefly, a flake of graphite was placed on one of the diamond windows, and the remaining volume of the gasket hole was filled with KCl being a solid pressure medium of low shear strength, thus providing quasihydrostatic conditions. The absolute reflectivity at near-normal incidence (6° off axis) was measured at the diamond-sample interface from focal spots of about 30 μm diameter. We denote this reflectivity by R_d . The R_d spectra reported below are corrected for absorption in the diamond window and for reflection losses at its external surface.

RESULTS AND DISCUSSION

Figure 2(a) shows reflectivity spectra for graphite at two different pressures (2.2 and 11.2 GPa). Because of the large refractive index of diamond, the reflectivity R_d is considerably lower than the reflectivity of graphite at a sample-vacuum interface. Superimposed on a falling background due to intraband and a continuum of interband transitions, the reflectivity spectra show two weak structures in the near-infrared spectral range, which shift

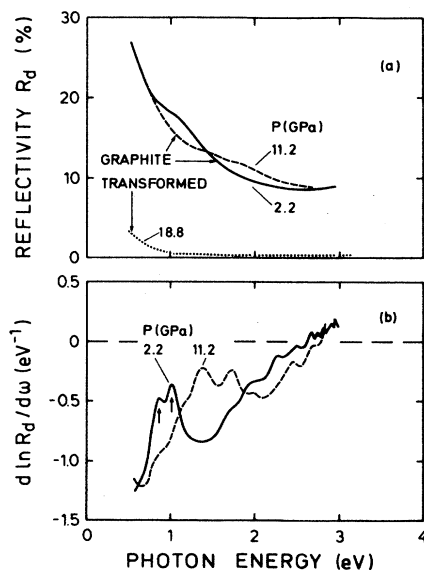


FIG. 2. (a) Basal-plane reflectivity spectra of graphite at 2.2 and 11.2 GPa and of transformed graphite at 18.8 GPa. Note that the absolute reflectivity R_d is measured at the interface between sample and diamond window. (b) Derivative spectra $d \ln R_d / d \omega$ of the reflectivity shown in (a).

to higher energy with increasing pressure. These structures are clearly resolved in the derivative spectra ($d \ln R_d / d \omega$) shown in Fig. 2(b).

The two pronounced local maxima in the derivative spectra are identified with the A_1 and A_2 interband transitions about the K point in the Brillouin zone. The A_1 threshold is from the occupied E_2 band to empty states in the E_3^1 band above the Fermi level E_F and the A_2 transition is from the E_3 band to the E_1 band (see Fig. 1). This picture is modified slightly, if trigonal warping is included. For a detailed discussion of the spectral dependence of the joint density of states and transition probabilities we refer to Ref. 20.

The pressure dependence of the A_1 and A_2 transition energies and their splitting ΔA is shown in Fig. 3(a). For a least-squares fit to the experimental data we use the relation

$$E(P)/E_0 = [(\eta_0/\eta')P + 1]^{\eta'} \quad (1)$$

The parameters zero-pressure energy E_0 , logarithmic pressure derivative $\eta_0 = (d \ln E / dP)_{P=0}$, and the pressure derivative η' are given in Table II. Within experimental uncertainty, the energies E_0 of the A_1 and A_2 structures at zero pressure thus obtained agree closely with those given in Ref. 8 (see Table II). This agreement partly justifies our simple procedure of defining the transition energies in terms of extrema of $d \ln R_d / d \omega$.

The logarithmic pressure coefficients of the A_1 and A_2 transition and of their splitting ΔA are considerably smaller than results from the earlier reflectivity study of graphite under pressure up to 0.3 GPa (Ref. 8, see Table I). In fact, in the case of the A_1 and A_2 transitions the discrepancy is so large in absolute energy shifts that it cannot be attributed to our simplified analysis of the reflectivity spectra.

If the pressure dependence of the in-plane overlap interaction (γ_0) and trigonal warping (γ_3) are neglected, the sum of the transition energies in terms of SWM band parameters may be written as⁷

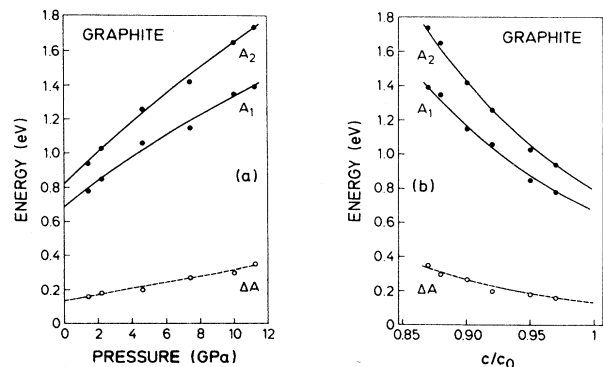


FIG. 3. (a) Energies of the local maxima of $d \ln R_d / d \omega$ (solid circles) as a function of pressure. The local maxima in the derivative spectra are attributed to the A_1 and A_2 interband transitions of graphite. Also shown is the splitting ΔA of these transitions (open circles). Solid and dashed lines refer to the result of fitting parameters in Eq. (1) to the experimental data. (b) Energies of the A_1 and A_2 transitions and their splitting ΔA as a function of c -axis lattice parameter. See text for solid lines.

TABLE II. First- and second-order pressure coefficients of the A_1 and A_2 transitions and their splitting ΔA in graphite. E_0 is the energy and $\eta_0 = (d \ln E / dP)_{P=0}$ is the logarithmic pressure derivative at $P=0$ GPa; η' is the pressure derivative of $d \ln E / dP$ [see Eq. (1)].

Transition	E_0 (eV)	η_0 (GPa $^{-1}$)	η'	Method
A_1	0.68(1)	0.127(7)	0.58(5)	Present work
	0.669	0.263(8)		Reflectivity ^a
	0.74			Thermomodulation ^b
A_2	0.81(1)	0.129(7)	0.65(5)	Present work
	0.847	0.307(20)		Reflectivity ^a
	0.88			Thermomodulation ^b
ΔA	0.13(1)	0.141(20)	1 ^c	Present work
	0.178	0.55		Reflectivity ^a

^aReference 8.

^bReference 6.

^cFixed parameter.

$$E(A_2) + E(A_1) = 4\gamma_1 - 4\gamma_2 + 2E_F \approx 4\gamma_1. \quad (2)$$

It is well established that $\gamma_2, E_F \ll \gamma_1$, which justifies the approximation on the right-hand side of Eq. (2). From the average of experimental values of η_0 we then have for the logarithmic pressure derivative of the first-order parameter γ_1

$$(d \ln \gamma_1 / dP)_0 = 0.128(10) \text{ GPa}^{-1}.$$

This result is consistent (see Table I) with, e.g., the value given by Dillon *et al.*,¹¹ which is based on high-pressure Fermi surface and magnetotransport measurements. We note a significant discrepancy not only with the value derived from an analysis of reflection spectra,⁸ but also with the value obtained from magnetoreflexion⁹ measurements at pressures up to 0.3 GPa. On the other hand, near-infrared optical reflection spectra of several stage-2 graphite-acceptor intercalation compounds (GIC's) measured at pressures up to 5 GPa and their analysis in terms of the model by Blinowsky *et al.*²¹ yields $d \ln \gamma_1 / d \ln P = 0.073$.²² This is about half the value for pristine graphite. The relative magnitude of the logarithmic pressure derivatives of γ_1 in graphite and stage-2 GIC's is physically reasonable, because the change in graphite-layer separation under pressure is expected to be smaller in stage-2 compounds as compared to pristine graphite.

The value of $d \ln(\Delta A) / dP$ has been associated with the logarithmic pressure derivative of the second-order parameter γ_5 of the SWM model (see, e.g., Ref. 8). On the other hand, the energy difference ΔA is not only determined by the γ_5 parameter, but effects arising from changes of e.g., trigonal warping, in-plane nearest-neighbor interaction, and transition matrix elements under pressure also have to be considered in a detailed analysis of the relatively small energy difference ΔA and its dependence on pressure. We think that the pressure coefficient of the γ_5 parameter cannot be determined from the present data to within reasonable error limits.

Figure 3(b) shows the dependence of the energies $E(A_1)$ and $E(A_2)$ on the c -axis lattice parameter. For the pressure to lattice-parameter conversion we have used the compression data of Ref. 23. The solid lines in Fig. 3(b) correspond to the relation

$$E(c) / E_0 = (c / c_0)^\delta \quad (3)$$

with parameter δ determined from a least-squares fit. We find $d \ln A_1 / d \ln c = -5.2(2)$ and $d \ln A_2 / d \ln c = -5.5(2)$. The average of these values gives

$$d \ln \gamma_1 / d \ln c = -5.35(20).$$

This is a direct determination of the scaling of γ_1 with interlayer separation.

The reflectivity of graphite changes drastically at the pressure-induced phase transition. Figure 2 shows a reflectivity spectrum of transformed graphite at 18.2 GPa. Except for the falling tail in the near-infrared spectral range, the absolute reflectivity R_d at the sample diamond interface is less than 0.005 and essentially structureless in the spectral range from 1 to 3 eV. The reflection spectrum of transformed graphite does not change significantly between 18 and 26 GPa. The extremely low reflectivity between 1 and 3 eV shows that the refractive index of transformed graphite is almost identical to that of the diamond window. In other words, the high-pressure optical response is consistent with the immediate formation of an sp^3 -bonded material at this phase transition.²⁴ We attribute the small increase of the reflectivity of the transformed material in the near-infrared range to optical transitions induced by impurities.

Due to the drastic change of the optical reflectivity, the phase transition can be easily detected by visual observation of the sample in the diamond window cell. We find that some samples start to develop black spots (of essentially zero reflectivity R_d in the visible range) indicating sp^3 bond formation at pressures as low as 9 GPa. According to visual observation full transformation of the samples is always achieved at about 17 GPa. The width of the transition range for increasing pressure appears to be determined by sample quality and by local stress concentrations. We note that the broadening of the high-frequency E_{2g} Raman line of graphite at pressures above ~ 9 GPa is also taken as evidence for the onset of sp^3 bond formation.²³

Figure 4 shows a pressure scan of the optical reflectivity at constant photon energy of 0.8 eV, starting

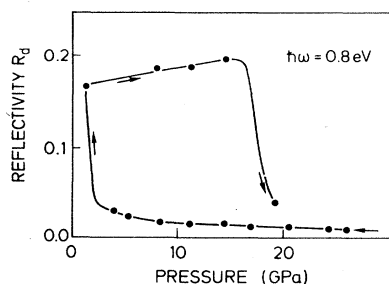


FIG. 4. Pressure scan of the near-infrared reflectivity of graphite and transformed graphite at constant photon energy of 0.8 eV.

at 26 GPa. Down to about 2 to 3 GPa we observe a slow increase of the reflectivity and then a sudden jump to a reflectivity level typical for the graphite phase. On increasing the pressure, the reflectivity drops again to a low level at about 16 GPa. This behavior closely resembles the large hysteresis shown by the pressure dependence of the electrical resistivity.¹³

The evidence from visible observation reported here for the onset of sp^3 bond formation near 9 GPa, the broadening of the high-frequency E_{2g} Raman mode at about the same pressure,²³ and the large hysteresis for the phase transition pressure leads us to suggest that the equilibrium pressure at $T=300$ K for the transition from hexagonal graphite to presumably hexagonal diamond is less than 10 GPa.

Recently, Fahy *et al.* have performed total-energy cal-

culations for the transition from rhombohedral graphite with $\cdots ABC \cdots$ layer staking to cubic diamond²⁵ and from a graphitic structure with $\cdots AA \cdots$ layer stacking to hexagonal diamond.²⁶ It would be interesting to see what the theoretical prediction would be (based on a similar *ab initio* theoretical approach) for the equilibrium transition pressure from hexagonal graphite to hexagonal diamond.

In conclusion, from a reflectivity study of hexagonal graphite up to 12 GPa, we have determined the pressure dependence of the A_1 and A_2 interband excitation energies and that of the SWM parameter γ_1 which determines the overlap interaction between nearest-neighbor atoms on successive layers. Our value for the logarithmic pressure dependence of γ_1 (see Table I) is in good agreement with the result derived from Fermi surface and magnetotransport measurements under pressure,¹¹ but at variance with pressure coefficients from previous optical studies^{8,9} at pressures below 0.3 GPa. The optical response of transformed graphite above 17 GPa is consistent with an almost complete transformation to an sp^3 -bonded phase achieved at room temperature. From visual observation as well as from previous Raman studies²³ at $T=300$ K we find evidence for the onset of sp^3 bond formation at pressures as low as 9 GPa.

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