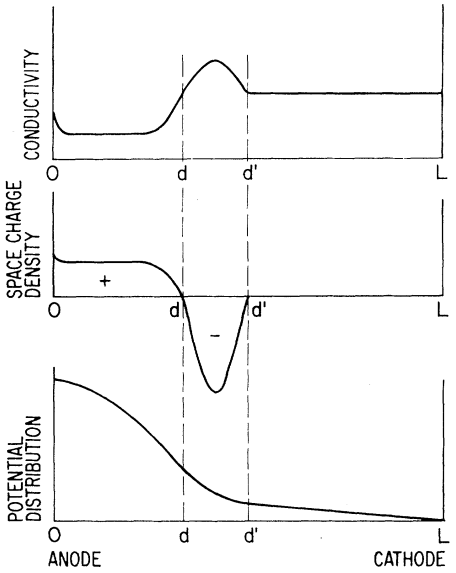

FIG. 1. Conductivity, space charge, and potential distribution in a long relaxation-case n-type semiconductor under forward bias. The distance origin is taken at the hole-injecting contact, from where the electron-depletion region expands into the bulk of the material. This configuration is unstable as shown in the text.

the carrier density increases. Therefore, we have to conclude that this configuration is not stable, and a region depleted of majority carriers cannot form under conditions of recombinative space-charge injection. The argument presented is independent of whether the negative space charge is accommodated in a small transition region, or whether it would spread over the entire region L-d'. Also, the presence of traps adds further detail to the argument but does not alter it. Finally, the inclusion of diffusion reinforces, but is not essential to, the argument.

The physics underlying the violation of the continuity equation is clear: If injected holes tend to decrease the electron concentration by recombination within a region d, the density of electrons outside d will be higher, and consequently a prerequisite for a *field-dominated* injection of electrons into d is fulfilled, namely, that a reservoir of electrons exists. Therefore, the relaxation of the positive space charge in d is no longer governed by the dielectric relaxation time $\tau_D = \epsilon\epsilon_0/\sigma$ (where ϵ is the dielectric constant, ϵ_0 is the permittivity, and σ is the conductivity), but by the much shorter transit time of the electrons through d. The injection of electrons, of course, will counteract the decrease in electron concentration and tend to restore their original density.

We would like to acknowledge stimulating discussions with M. A. Lampert and F. Stöckmann without, of course, committing them to the support of this particular argument.

[1]W. van Roosbroeck and H. C. Casey, Jr., in *Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge, Massachusetts, 1970,* edited by S. P. Keller, J. C. Hensel, and F. Stern, CONF-700801 (U.S. AEC Division of Technical Information, Springfield, Va., 1970).

[2]W. van Roosbroeck and H. C. Casey, Jr., Phys. Rev. B 5, 2154 (1972).

[3]H. Kiess and A. Rose, in Meeting of the Swiss Physical Society, Neuchâtel, Switzerland, May 1973 (unpublished).

Optical Investigation of π Bands in Graphite

G. Guizzetti,* L. Nosenzo,† E. Reguzzoni,† and G. Samoggia†
Istituto di Fisica dell'Università, 27100 Pavia, Italy
(Received 15 May 1973)

We report detailed measurements of thermoreflectance spectra of graphite in the 0.5–9-eV region. The observed structures are correlated with π interband transitions on the basis of existing energy-band calculations.

A large amount of experimental data on graphite[1] has been collected in recent years. However, their interpretation in terms of the energy-band structure has not been fully successful. In fact, although some success has been achieved in relating the observed physical properties to the characteristics of the overlapping π bands near the Fermi surface, discrepancies exist in attrib-

uting the structures observed in reflectivity spectra to specific interband transitions.

Recently, two papers reporting thermoreflectance (TR) spectra of graphite in the 5-eV region have been published[4,5]; however, they differ both in the experimental data and in the physical interpretation. Besides, the experimental methods and the line-shape fit in terms of interband transitions are not free of criticism. The direct-modulation technique may be a source of surface contamination, and it is unjustified to interpret oblique incidence data as if obtained under normal incidence.[5] It is arbitrary to fit data taken at *one* fixed temperature only in terms of broadening of a two-dimensional M_1 singularity[4] or only in terms of a shift of an M_1-type singularity.[5]

In order to obtain a full set of data we have measured the TR spectra of graphite from 0.5 to 9 eV in the temperature range 25–300°K. The measurements have been performed using Union Carbide flats of stress-annealed pyrolytic graphite cleaved to a thickness of about 0.3 mm. In order to avoid surface contamination due to soldering and carrier effects, we have preferred to modulate the temperature of the sample indirectly.[6] Two springs pressed the sample on a Ge heater. Monochromatic light from a McPherson model 218 monochromator was reflected at near normal incidence by the cleavage plane of the sample. The amplitude of the temperature modulation was about 1°K at 2 Hz. Vacuums of the order of 3×10^{-7} Torr were obtained by zeolite-cooled traps. The resulting $\Delta R/R$ in the 4–5-eV region was about 10^{-4}, to be compared with signals less than 10^{-5} previously reported.[4,5] Since it has been observed that TR spectra of badly cleaved samples showed spurious signals, here we report only reproducible results obtained from a comparative analysis of the spectra of ten different samples.

In the near-infrared region (Fig. 1) two well-defined structures have been observed, with zero crossing points (from positive to negative)[7] respectively placed at $E_1 = 0.74$ eV and $E_2 = 0.88$ eV at 80°K.

Recently, photoemission[8] and magnetoreflection[9] measurements have shown that, at the K point of the Brillouin zone of graphite, the energy separations between the twofold-degenerate K_3 level and the K_1 and K_2 levels are both about 0.8 eV (Fig. 2).

Because of symmetry considerations it is known that[10,11] only $K_1 \rightarrow K_3$ and $K_3 \rightarrow K_2$ transitions are allowed, and therefore one may assign the E_1 structure to transitions starting from K_1 to levels above the Fermi energy E_F around K_3 and E_2 from filled levels near K_3 to the upper band K_2. As a consequence of the semimetal nature of graphite, a change of the temperature of the crystal may affect the reflectivity spectra not only through the shift and broadening of interband transitions, but also through the broadening of the step in the Fermi distribution.[12,13] Such an effect is important for all transitions starting from or ending at the Fermi level. Let us observe that these two processes behave differently with respect to temperature. However, since no differences in the relative amplitude and line shape of the observed structures are detectable in our spectra between 30 and 300°K, we deduce that only one mechanism must predominate in this temperature range, but we are not able to tell which one of the two mechanisms is operative. Measurements at temperatures lower than 30°K would be useful for verifying our attribution. Alternative interband-transition assignments must wait for different experiments and for more accurate calculations of the joint density of states in the Brillouin zone.

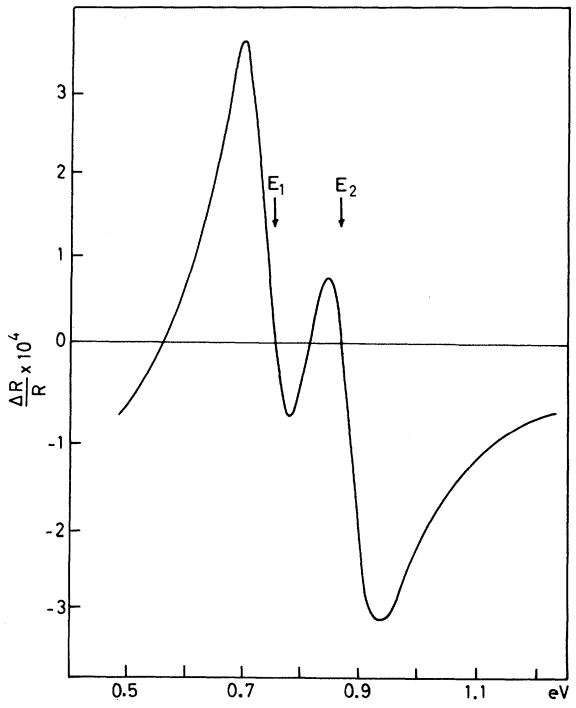

FIG. 1. TR spectra of graphite in the near-infrared region at 80°K temperature.

If the assignment of E_1, E_2 structures to K transitions is correct, the value of γ_1, one of the

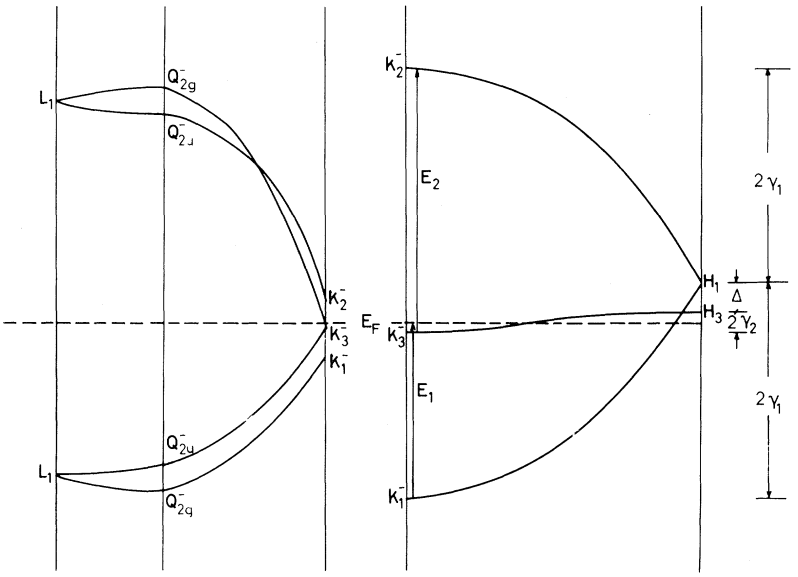

FIG. 2. Sketch of the π-band structure of three-dimensional graphite in the KH and KQL directions (after Refs. 1 and 11).

band parameters of the Slonczewski-Weiss model,[14] can be determined independently. In fact, from inspection of Fig. 2, one finds the following relations: $E_1+E_2\sim 4\gamma_1+\gamma_2\sim 4\gamma_1\sim 1.6$ eV and $E_1-E_2\sim 2\Delta+3\gamma_2\sim 0.14$ eV. From these it is possible to obtain $\gamma_1\sim 0.40$ eV, in good agreement with values from different experiments. The inaccuracy in the determination of the energies of E_1, E_2 transitions, due to the fact that peaks of $R(\omega)$ are usually shifted with respect to $\epsilon_2(\omega)$ and the structures are partially overlapping, does not allow an exact estimate of the value of Δ. In fact if we take (with respect to H_3) $E_F\sim 0.02$ eV[1] and $\gamma_2\sim|E_F|$, we find $\Delta\sim 0.04$ eV, which is too large with respect to the values reported in literature.[1]

No structures have been observed in the 1–4-eV region. In Fig. 3 the TR spectra beyond 4 eV are shown. A weak structure at 4.6 eV, a zero crossing point at 4.85 eV, and strong negative peaks at 6.8 and 7.6 eV are observed at 300°K. The structure at 4.6 eV might be assigned to some critical-point transition near L or Q points.[5,15]

The 4.85-eV structure, corresponding to a maximum of the reflectivity curve,[3] is generally assigned to Q-point transitions. No reproducible data have been obtained at low temperatures that could confirm the fine structure previously reported[5] and attributed to a splitting of the Q transition. No evidence of the reflectivity shoulder observed at 6.2 eV in reflectivity measurements[10] has been obtained.

The sharp negative structure centered at 6.8 eV corresponds to a plasma resonance of π electrons screened by the frequency-dependent dielectric constant associated with δ electrons.[2,3] Let us observe that, as remarked by Cardona,[16] the negative peak occurs very close to the plasma frequency. This structure shifts rigidly with temperature at the rate of about 10^{-3} eV/°K. The shift of ω_p cannot be explained as a change of the density of electrons, but it is probably associated with the shift of the position of interband σ transitions lying at energies greater than 10 eV.[2]

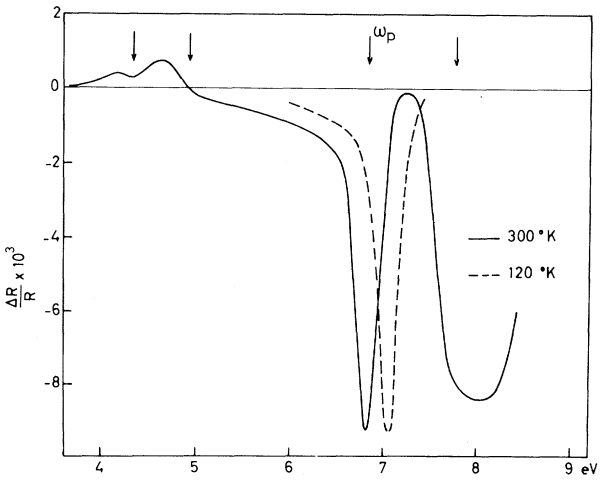

FIG. 3. TR spectra of graphite in the ultraviolet region.

A broad structure near 7.8 eV is observed in the TR spectra; however, because of the low light level, its line shape must be taken as tentative. Transitions associated with the K point, as suggested by pseudopotential calculation,[15] could account for this structure.

In order to obtain a more detailed description of the band structure of graphite, experiments at liquid-helium temperature and in a broader interval of energies are in progress.

*Istituto Nazionale di Fisica Nucleare, Sezione di Pavia.

†Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche.

[1]For a selective review of the experimental data concerning the energy-band structure of graphite, see J. W. McClure, in *The Physics of Semimetals and Narrow Gap Semiconductors*, edited by D. L. Carter and R. T. Bate (Pergamon, New York, 1971), p. 127.

[2]E. A. Taft and H. R. Philipp, Phys. Rev. 138, A197 (1965).

[3]D. L. Greenway, G. Harbeke, F. Bassani, and E. Tosatti, Phys. Rev. 178, 1340 (1969).

[4]A. Balzarotti and M. Grandolfo, Phys. Rev. Lett. 20, 9 (1968).

[5]M. Anderegg, B. Feuerbacher, and B. Fitton, Phys. Rev. Lett. 26, 760 (1971).

[6]L. Nosenzo, E. Reguzzoni, and G. Samoggia, Phys. Rev. Lett. 28, 1388 (1972).

[7]As a result of the difficulties of separating the different contributions to the thermoreflectance spectrum, in the following we shall discuss the signals as if only shift effects would be important. Under this assumption, the thermal-reflectivity spectrum is analyzed in the same way as the wavelength-modulation spectrum; see M. Welkowsky and R. Braunstein, Phys. Rev. 5, 497 (1972); G. Guizzetti, L. Nosenzo, E. Reguzzoni, and G. Samoggia, to be published.

[8]R. F. Willis, B. Feuerbacher, and B. Fitton, Phys. Rev. B 4, 2441 (1971).

[9]P. R. Schroeder, M. S. Dresselhaus, and A. Javan, in *The Physics of Semimetals and Narrow Gap Semiconductors*, edited by D. L. Carter and R. T. Bate (Pergamon, New York, 1971), p. 139.

[10]F. Bassani and G. Pastori Parravicini, Nuovo Cimento B50, 95 (1967).

[11]E. Doni and G. Pastori Parravicini, Nuovo Cimento A63, 117 (1969).

[12]R. Rosei and D. W. Lynch, Phys. Rev. B 5, 3883 (1972).

[13]R. Rosei, F. Antonangeli, and U. M. Grassano, to be published.

[14]J. C. Slonczewski and P. R. Weiss, Phys. Rev. 109, 272 (1958).

[15]W. Van Haeringen and H. G. Junginger, Solid State Commun. 7, 1723 (1969).

[16]M. Cardona, in *Modulation Spectroscopy*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1970), p. 117.

Observation of Excitonic Polarons at Cyclotron Resonance in Germanium

E. Otsuka, T. Ohyama, and T. Sanada
Department of Physics, College of General Education, Osaka University, Toyonaka, Osaka 560, Japan
(Received 25 April 1973)

A systematic double peaking of the cyclotron resonance signal has been observed in time resolution for germanium and is interpreted in terms of an idea which we tentatively call "excitonic polaron."

A time-resolved cyclotron-resonance approach to the physical behavior of excitons has proved to be useful for isolated and collective systems in germanium[1-3] and silicon.[4] In the course of experimental study in this field, the authors have come across a striking phenomenon, which shows up on rather limited occasions, but nevertheless is very distinct once it appears. We believe the phenomenon worth reporting and try to interpret it in terms of an idea which we would like to call "excitonic polaron."

The stage preparation is a conventional apparatus for measuring time-resolved cyclotron resonance at 35 GHz, and the player is a high-purity Toshiba germanium crystal. The microwave electric field is set parallel to ⟨100⟩. The plane surface onto which the photopulses from a xenon flash lamp shine at the repetition rate of 25 Hz is (100). The magnetic field is rotatable in this plane. Figure 1 shows traces of the time resolution for $H \| \langle 001 \rangle$ in which all the four electron valleys contribute a common resonance peak. The most remarkable thing is that the electron resonance is accompanied by a new strange peak on its higher magnetic field side, and both the magnetic field at which this strange peak appears and the intensity of the peak relative to the proper electron resonance signal depend on the delay