

FIG. 2. Dependence of emission intensity on injection current. Straight line,  $h\nu = 1.2$  eV; dashed line,  $h\nu = 0.7$  eV.

imum. The probability for this event is proportional to  $n^2p$  or  $np^2$ , respectively. In this band extremum the carrier "thermalizes" and is able to recombine radiatively with a carrier of the opposite sign. Thus the probability of photon emission is proportional to  $n^2p^2$  in agreement with the result given in Fig. 2.

Since the observed activation energy is less than 0.4 eV, we assume that the Auger recombination is not a direct process as described by Beattie and Landsberg, but an indirect one. Momentum conservation is satisfied by participation of a phonon, so that no activation energy is necessary for the Auger recombination. The occurrence of the direct process as observed in impact ionization experiments at room tem-

perature is not in contradiction to our explanation. In these experiments electrical fields are used which cause an electron temperature as high as some thousands of degrees Kelvin.<sup>6</sup> As in the case of radiative recombination in Ge the indirect process is predominant at low temperatures, while at high temperatures the direct process is predominant. Since in the Auger recombination no activation energy is necessary, the observed activation energy should be equal to the energy difference between the observed photon energy and the low-energy limit of the emission band. For this limit we get  $0.95 \pm 0.03$  eV. This value is in good agreement with the energy difference between the absolute conduction-band minimum and the maximum of the split-off valence band. According to Lax and Halpern<sup>7</sup> this value is 0.94 eV. From this result it is concluded that the Auger particle is a hole.

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## ANALYSIS OF CRITICAL POINTS OF GRAPHITE FROM TEMPERATURE-MODULATED REFLECTANCE

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The optical properties of graphite are known from absorption and reflectivity experiments<sup>1</sup> over a wide range of wavelengths, though the absolute measurements are not sensitive enough to allow a definite assignment of the observed structure to transitions at critical points in

the calculated band structure.

In this Letter we report the differential reflectance of graphite crystals measured in the energy range 4-6.5 eV by modulating the optical constants of the crystals with temperature.<sup>2</sup> The results indicate that the strong peak around

5 eV, previously observed in absolute reflectivity measurements, is due to an  $M_1$  saddle-point singularity. In addition they show a structure at 5.96 eV, resolved by this technique for the first time, which is related to an  $M_0$  transition occurring at the center of the Brillouin zone.

The fractional change of reflectance  $\Delta R/R$  versus photon energy is given in Fig. 1. The temperature of the samples was periodically changed by passing a 10-Hz square-wave current through them; for the current densities used in our experiment the temperature modulation, although not measured accurately, did not exceed about a tenth of a degree. The average temperature was kept near 300°K by properly refrigerating the crystals. Phase-sensitive technique was employed to detect the ac component of the reflected light. All the measurements were taken at near-normal incidence using unpolarized light.

In Fig. 2 we show the corresponding changes of the real and imaginary parts of the dielectric constant  $\Delta\epsilon_1$  and  $\Delta\epsilon_2$  as derived from the data of Fig. 1 by application of the Kramers-Kronig dispersion relation. The values of  $\epsilon_1$  and  $\epsilon_2$  used in this calculation were taken from the experimental data of Taft and Philipp.<sup>1</sup>

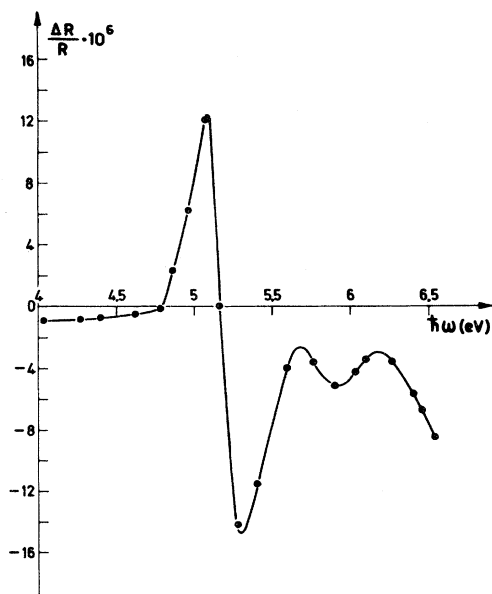


FIG. 1. Relative change of reflectance  $\Delta R/R$  with temperature versus photon energy. The sign of  $\Delta R/R$  has been chosen positive for reflectance increasing upon increase of temperature. Peak current through the samples is  $\sim 0.3$  A.

The results suggest that the effect of temperature is to shift one of the observed critical points ( $M_0$ ) and to broaden the other one ( $M_1$ ) because of the electron-phonon interaction.

Since graphite is a strongly anisotropic material with respect to one crystalline direction ( $c$  axis), its optical properties can be conveniently studied in the two-dimensional model. In this approximation, which neglects the bond between different carbon-layer planes, the critical points reduce to those of  $M_0$  and  $M_1$  type, which give rise, respectively, to step and logarithmic singularities in the joint density of states.<sup>3</sup>

Let us assume that the shape of  $\Delta\epsilon_2$  in Fig. 2 is due to the overlapping of the contributions of two critical points of  $M_1$  and  $M_0$  type, located, respectively, at 5.11 and 5.96 eV. The logarithmic singularity has been described by means of a Lorentzian function, and the lifetime broadening of the  $M_0$  point has been introduced through a convolution integral,<sup>4</sup> using a Lorentzian parameter  $\Gamma$ . Differentiation of  $\epsilon_2$  with respect to  $\Gamma$  gives the following for the  $M_1$  critical point:

$$\Delta\epsilon_2 = \frac{(\Delta\epsilon_2)_{E_c}}{1 + (E - E_c/\Gamma)^2} + \frac{2(\epsilon_2)_{E_c} (E - E_c)^2}{\Gamma^3 [1 + (E - E_c/\Gamma)^2]^2} \Delta\Gamma, \quad (1)$$

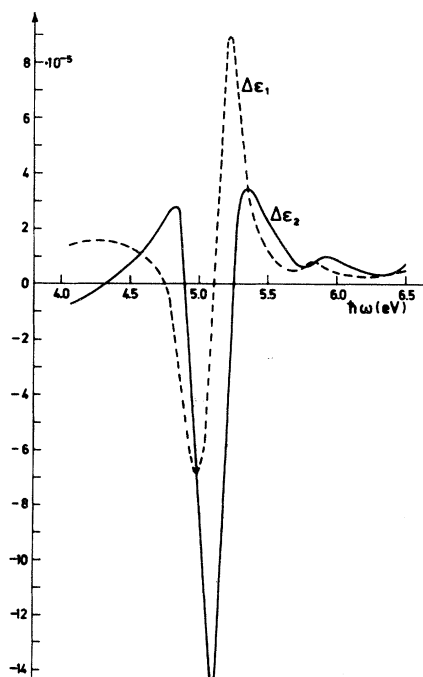


FIG. 2. Thermomodulation of the real and imaginary parts of the dielectric constant (from data of Fig. 1).

where  $E_c$  is the energy of the critical point, and  $\Delta\Gamma$  the temperature modulation of  $\Gamma$ . The agreement with the experiment near 5 eV is rather good taking  $\Gamma = 185$  meV; from the value of  $\Delta\Gamma$  we estimate a temperature modulation  $\Delta T$  of about  $0.1^\circ\text{K}$ .

The effect of the temperature on the  $M_0$  singularity seems to be a shift of the structure to lower energies rather than a simple lifetime broadening as for the  $M_1$ -type critical point. In this case we get

$$\Delta\epsilon_2 = -\frac{A\Delta E_c}{\Gamma[1 + (E - E_c)/\Gamma]^2 E_c^2}, \quad (2)$$

where  $A$  is an appropriate constant factor and  $\Delta E_c$  the energy shift of the critical point.

The expressions (1) and (2) are shown in Fig. 3 and compared with the experimental  $\Delta\epsilon_2$  curve. The best fit for the  $M_0$  transition is obtained for  $\Gamma = 172$  meV.

Recent calculations of the band structure of graphite<sup>5</sup> attribute the sharp peak<sup>1</sup> observed in  $\epsilon_2$  at 4.5 eV to an  $M_1$  saddle-point transition occurring at  $Q$  in the Brillouin zone, and find the threshold of the transitions between  $\sigma$  bands near 6 eV (at  $k=0$ ). This assignment agrees quite well with our results; the discrepancy of the energy position of the  $M_1$  point may depend to some extent on the narrow range of energies used in the evaluation of the Kramers-Kronig integral. The broadening of the  $M_1$  saddle point due to the electron-phonon interaction is in line with a recent theoretical result.<sup>6</sup> The shorter lifetime of this critical point is due to the existence of conduction states of lower energy<sup>5</sup> into which the electrons are scattered.

The sensitivity of the experimental method can be inferred by observing that the  $M_0$  threshold does not appear in the absolute reflectivity measurements while it is well resolved in our differential experiment. Further investigations in the vacuum uv region of the spectrum and at lower temperatures are in progress.

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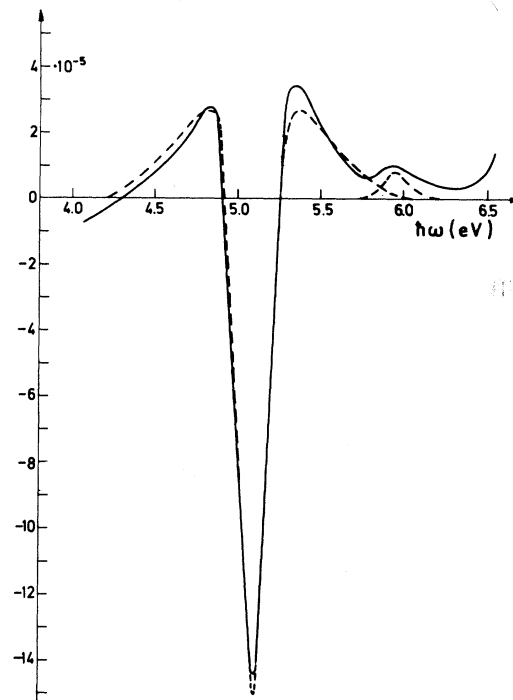


FIG. 3. Comparison between the experimental (solid lines) and theoretical (dashed lines) change of  $\epsilon_2$  due to an  $M_1$  saddle point located at 5.11 eV and an  $M_0$  threshold at 5.96 eV.

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