

- <sup>1</sup>J. A. Woollam, Phys. Rev. B 3, 1148 (1971).  
<sup>2</sup>J. A. Woollam, NASA Report No. TN D-7037, 1971 (unpublished).  
<sup>3</sup>S. J. Williamson, S. Foner, and M. S. Dresselhaus, Phys. Rev. 140, A1429 (1965).  
<sup>4</sup>D. E. Soule, Phys. Rev. 112, 698 (1958).  
<sup>5</sup>J. W. McClure, Phys. Rev. 112, 715 (1958).  
<sup>6</sup>D. E. Soule, IBM J. Res. Develop. 8, 268 (1964).  
<sup>7</sup>J. R. Anderson, W. J. O'Sullivan, J. E. Schirber, and D. E. Soule, Phys. Rev. 164, 1038 (1967).  
<sup>8</sup>D. J. Flood, Phys. Letters 30A, 168 (1969).  
<sup>9</sup>D. J. Flood, NASA Report No. TN D-5488, 1969 (unpublished).  
<sup>10</sup>J. A. Woollam, Phys. Rev. Letters 25, 810 (1970).  
<sup>11</sup>I. L. Spain, D. A. Young, and A. R. Ubbelohde, Phil. Trans. Roy. Soc. London 262, 345 (1967).  
<sup>12</sup>D. Shoenberg, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland, Amsterdam, 1957), Vol. II, p. 226.  
<sup>13</sup>P. N. Argyres, Phys. Rev. 117, 315 (1960).  
<sup>14</sup>J. C. Slonczewski and P. R. Weiss, Phys. Rev. 109, 272 (1958).  
<sup>15</sup>J. W. McClure, Phys. Rev. 108, 612 (1957).  
<sup>16</sup>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American Physical Society Conference on the Physics of Semimetals and Narrow Gap Semiconductors, Dallas, Tex., 1970 (unpublished).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 magnetoreflexion 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was presented by Heflinger and Dresselhaus at the Tenth Biennial Conference on Carbon, Bethlehem, Pa., 1971 (unpublished), and these values are listed in Eq.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.)  
<sup>17</sup>J. W. McClure, Tenth Biennial Conference on Carbon, Bethlehem, Pa., 1971 (unpublished).  
<sup>18</sup>P. Nozières, Phys. Rev. 109, 1510 (1958).  
<sup>19</sup>S. J. Williamson (unpublished).  
<sup>20</sup>D. E. Soule, J. W. McClure, and L. B. Smith, Phys. Rev. 134, A453 (1964).  
<sup>21</sup>J. W. McClure and Y. Yafet, in *Proceedings of the Fifth Conference on Carbon* (Pergamon, New York, 1962), p. 22.  
<sup>22</sup>J. A. Woollam, Bull. Am. Phys. Soc. 16, 63 (1971).  
<sup>23</sup>J. W. McClure has made a detailed analysis (including  $\gamma_3$  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 [Results reported at the Tenth Biennial Conference on Carbon, Bethlehem, Pa., 1971 (unpublished).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.]  
<sup>24</sup>M. Tsukada and Y. Uemura, in Proceedings of the Ninth International Semiconductors Conference, Moscow, 1968, Vol. II, p. 1278 (unpublished).

## 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.<sup>1,2</sup> In clean surfaces this extra absorption is fairly large and disappears as the surface is slowly oxidized.<sup>3</sup> In a previous paper<sup>3</sup> 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<sup>4</sup> studied the influence of surface states on the photoelectric yield of ultrahigh vacu-

um (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.*,<sup>5</sup> Handler *et al.*,<sup>6</sup> and others<sup>7</sup> who studied the influence of states on surface conductance of Ge and Si. More recently Mönch<sup>8</sup> studied the effect of Cs coverage on surface conductivity and proposed a two-band model for the surface states. On the other hand Henzler,<sup>9</sup> 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.<sup>10</sup> The principal difficulty is the irregular termination of the lattice near the surface.

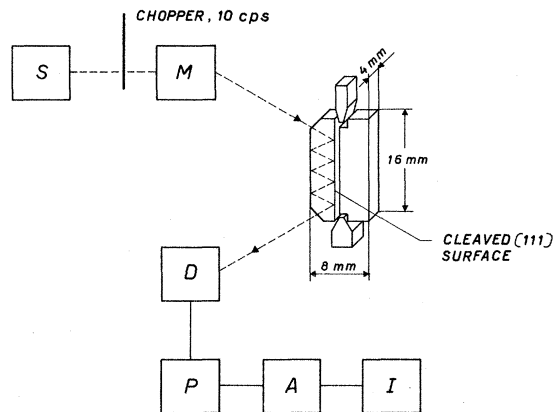


FIG. 1. Block diagram of the experimental apparatus and sketch of sample section; S is the electronically stabilized source, M the monochromator, D the PbSe detector, P the precision potentiometer, A the selective amplifier, and I the integrating digital voltmeter. The path of light is shown by the dashed line.

Recently, a new approach developed by Garcia-Moliner and Rubio<sup>11</sup> allows the calculation of the energy of the surface states, provided the Green's function of the crystal is known. By applying this method to a simplified model of a solid (usually called the Penn model), Bortolani *et al.*<sup>12</sup> calculated the dispersion curves of the surface states in Si and showed the existence of two bands in the gap.

#### EXPERIMENTAL APPARATUS

In order to study optical transitions involving surface states, a beam of monochromatic light was totally reflected, several times, at the surface of a semiconductor cleaved in UHV, as sketched in the sample section of Fig. 1, where the block di-

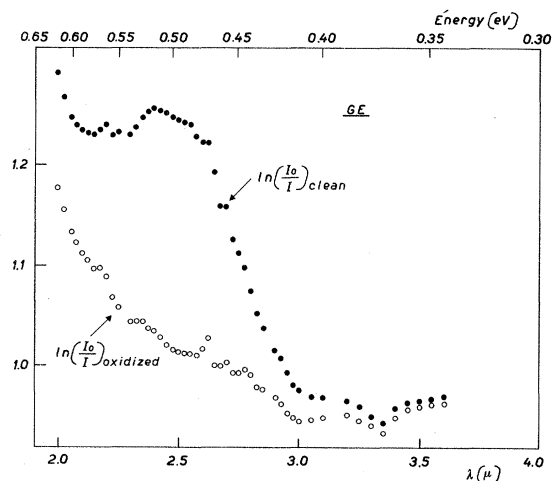


FIG. 2. Natural logarithm of the ratio  $I_0/I$  as a function of wavelength for a cleaved surface of Ge and for the same surface after oxidation.

agram of the apparatus is shown.

The intensity of the transmitted light was recorded as the surface was slowly oxidized. The initial vacuum of the order of  $10^{-10}$  Torr was obtained by means of a Vac-Ion pump and measured by a ionization gauge. The samples, positioned between two wedges as in Fig. 1, were cleaved along the (111) surface by means of a magnetically operated hammer. Oxidation was accomplished by letting oxygen into the system at pressures on the order of  $10^{-6}$  Torr. Two sapphire windows allowed the incident and emergent light to reach the sample and the detector, respectively. A third window allowed the inspection of the sample.

The source S of Fig. 1 was electronically stabilized and the PbSe (Kodak E type) detector was cooled to the temperature of boiling oxygen. Moreover, for each measurement, a portion of the monochromatic beam was made to bypass the sample and was monitored directly by the detector.

The detector signal was attenuated by the precision potentiometer P, in order to keep a fixed value at the amplifier A input. The output signal of the amplifier was averaged by an integrating digital voltmeter (block I). Since the effect to be detected was rather small and the time elapsed between the measurements on clean and oxidized surface was large, great care was taken to ensure the over-all stability of the apparatus. The accuracy of the measurements was on the order of 1%, with the

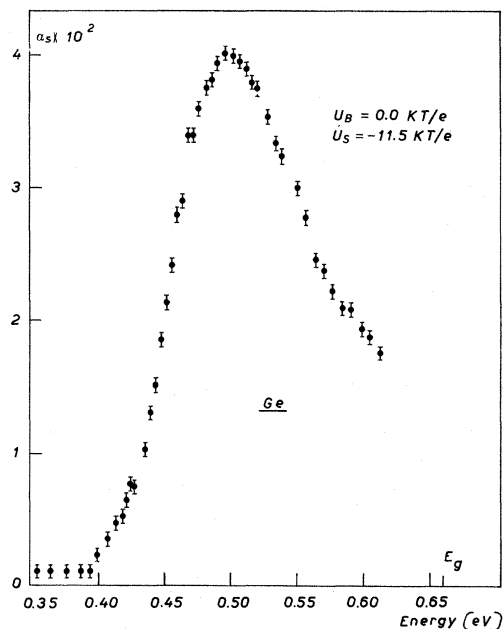


FIG. 3. Absorption constant  $\alpha_S$  vs photon energy for a surface of Ge cleaved in UHV. The almost constant absorption in the low-energy range is on the same order of the expected change of intraband hole absorption caused by the change of hole concentration during the oxidation.

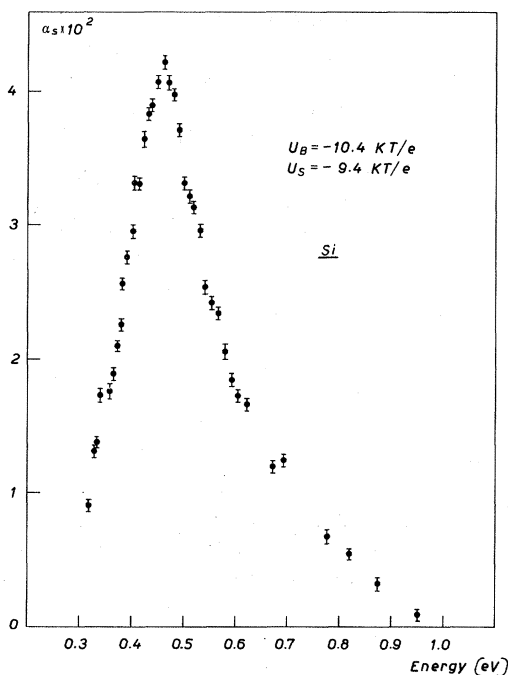


FIG. 4. Absorption constant  $\alpha_S$  vs photon energy for a UHV cleaved Si surface.

apparatus shown.

#### EXPERIMENTAL RESULTS AND DISCUSSION

The logarithm of the ratio between the intensities of light impinging on the sample  $I_0$  and that emerging from the sample  $I$  for a clean and oxidized surface of Ge as a function of wavelength is shown in Fig. 2.

The figure shows that the intensity of the transmitted light increases as the surface is oxidized.<sup>13</sup> Since the light is still totally reflected at the surface, the increase of  $I$  is due to the disappearance of absorbing "centers" in the surface layer.

The difference between the two curves of Fig. 2 gives the contribution to the absorption of the surface states on the clean surface directly.

In Fig. 3, the value

$$\alpha_S = \frac{1}{5} [\ln(I_0/I)_{\text{clean}} - \ln(I_0/I)_{\text{ox}}] \quad (1)$$

is plotted as a function of energy. The factor  $\frac{1}{5}$  is introduced to take into account the multiple reflection.  $\alpha_S$ , defined in (1), is identical with the absorption constant introduced by Bartoš<sup>14</sup> for a two-dimensional structure.

The almost constant value of  $\alpha_S$  at energies lower than 0.40 eV is of the same order as that expected from the change of optical absorption of holes, brought about by the variation of surface potential with the oxidation.<sup>15</sup> The same results for Si are shown in Fig. 4. As in the case of Ge the oxidation causes the disappearance of absorbing

centers at energies lower than the edge.

Various processes could explain the results of Figs. 3 and 4, namely, (i) optical transitions between two bands of surface states localized in the gap, one below and one above the Fermi level at the surface; (ii) optical transitions from the valence band to an empty band of surface states located in the gap; and (iii) optical transitions from a full band of surface states in the gap to the empty levels of the conduction band.

Though, in principle, it is not easy to distinguish among the processes mentioned above, especially with the lack of theoretical predictions, hypothesis (i) seems at present most likely. The reason is that it seems difficult to explain peaked curves like those of Figs. 3 and 4 under the hypotheses (ii) and (iii). In fact, for transitions between a localized state and a parabolic band, the joint density of states is expected to increase monotonically. The same behavior should hold also for Ge and Si near the threshold. On the other hand, a peaked joint density of states is expected for transitions between the levels of a two-dimensional structure.<sup>16</sup> However, it cannot be excluded *a priori* that part of the signal is due to processes (ii) and (iii).<sup>17</sup>

The case of Si is particularly interesting because it allows a comparison with other results obtained by electrical and photoelectrical methods.

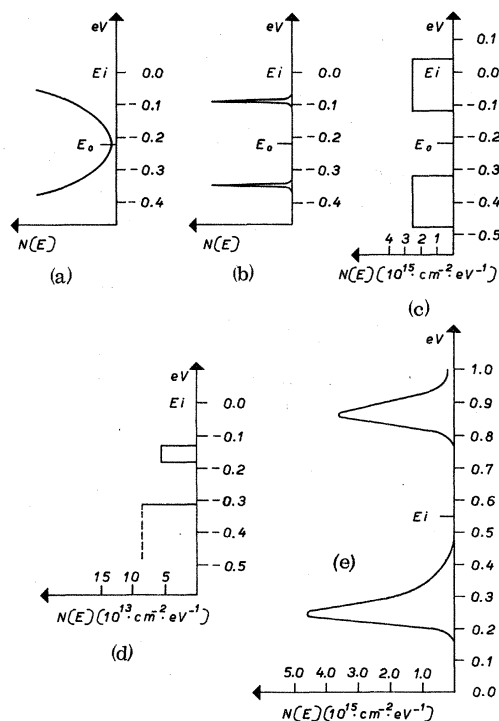


FIG. 5. Models of surface bands in silicon according to various authors: (a)–(c) from Allen and Gobeli (Ref. 4); (d) from Mönch (Ref. 8); (e) from theoretical calculations of Bortolani *et al.* (Ref. 12).

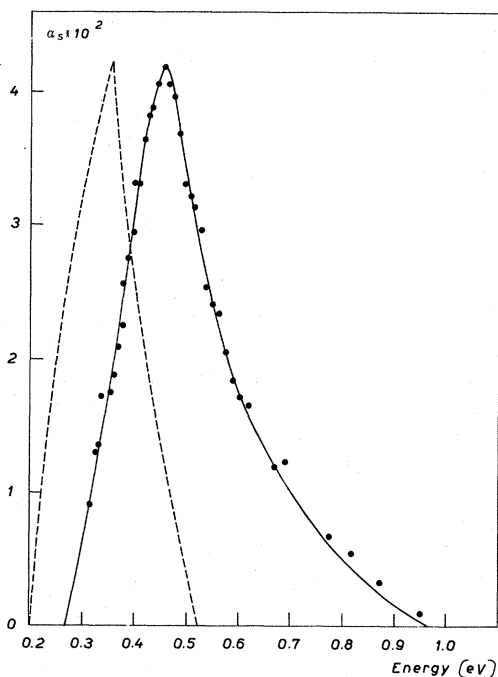


FIG. 6. Comparison of the experimental value (dots) of  $\alpha_S$  and that obtained from the density of states of Fig. 5(c) (dashed line) and from the histogram of Fig. 7 (solid line).

Allen and Gobeli, by measuring the difference between work function and photoelectric threshold in Si, proposed the three models shown in Figs. 5(a)–5(c), all consistent with their results. Handler and Aspnes found that their data on surface conductivity are in agreement with a model of two bands separated by a gap smaller than 0.32 eV. More recently, Mönch interpreted the change of conductivity, occurring when the surface is covered with Cs, with the model of surface states shown in Fig. 5(d). The theoretical calculations developed up to date do not allow a quantitative comparison with the experiments. However, Bortolani *et al.*, by applying the Green's-function method developed by Garcia-Moliner and Rubio, found a distribution of surface states with the density shown in Fig. 5(e). Preliminary results of Yndurain and Elices,<sup>18</sup> who use a more realistic model for the bulk structure of the semiconductor, also show two bands in the gap.

The optical results of Fig. 4, interpreted on the basis of hypothesis (i), allow the determination of the gap between the two bands of surface states and the sum of their widths. However, they do not allow a localization of the surface bands in the gap. Nevertheless, the results of Allen and Gobeli show that the surface levels are symmetrically located with respect to the neutrality level  $E_0$ . Under this hypothesis, the density of states of model (c) of

Allen and Gobeli give the absorption curve shown in Fig. 6, together with the experimental results for Si. The curve has been calculated under the hypothesis that the matrix element is constant and that only energy must be conserved in the optical transition. A better agreement can be obtained with the density of states shown in Fig. 7, which fits both our and Allen and Gobeli's results.

The results of Bortolani *et al.* are in qualitative agreement with the optical data, though the gap between the two bands of the surface states is too large. However, great care must be taken in deriving models for the density of states from optical results, since transitions from (or to) the valence (or conduction) band cannot be excluded and since conservation of  $\vec{k}$  at the surface is difficult to account for in absence of detailed calculations.

The number of states in the two bands of Fig. 7 cannot be obtained from optical measurements since the absolute value of the matrix element of the transition is not known. However, from a given distribution of states in the gap, the number of states can be evaluated by imposing the neutrality condition of the surface for the known position of the Fermi level. The total number of surface states turns out approximately  $1 \times 10^{14}$  for each band, which is not far from the value generally assumed for a clean surface.<sup>19</sup> With the above value and the experimental data of Figs. 3 and 4, the cross section of the optical-transition is  $4 \times 10^{-16}$  cm<sup>2</sup>, which is of the same order as that obtained from the optical measurements on real surfaces<sup>1</sup> and from the absorption coefficient of impurities in Si and Ge.<sup>20</sup>

The interpretation of our results in the case of Ge is more doubtful. Probably a model with two bands can also explain the optical results, provided the lower band is located, at least in part, into the valence band.

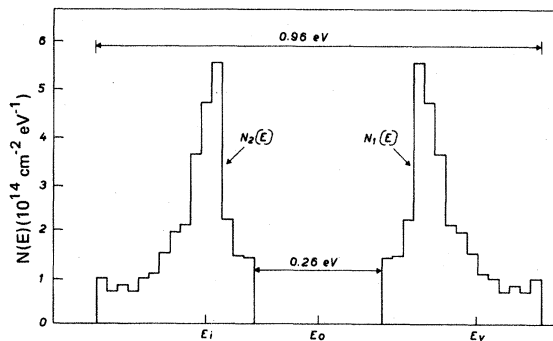


FIG. 7. Two-band model of the density of surface states in Si that fits the experimental values of  $\alpha_S$  (Fig. 6, solid line).  $E_v$ ,  $E_i$ , and  $E_0$  on the energy axis are, respectively, the top of the valence band, the intrinsic level, and the neutrality level at the surface.

- <sup>1</sup>N. J. Harrick, Phys. Rev. **125**, 1165 (1962).
- <sup>2</sup>G. Samoggia, A. Nucciotti, and G. Chiarotti, Phys. Rev. **144**, 749 (1966); G. Chiarotti, G. Del Signore, A. Frova, and G. Samoggia, Nuovo Cimento **26**, 403 (1962).
- <sup>3</sup>G. Chiarotti, G. Del Signore, and S. Nannarone, Phys. Rev. Letters **21**, 1170 (1968).
- <sup>4</sup>F. C. Allen and G. W. Gobeli, Surface Sci. **2**, 402 (1964); Phys. Rev. **127**, 150 (1962).
- <sup>5</sup>D. R. Palmer, S. R. Morrison, and C. E. Dauenbaugh, J. Phys. Chem. Solids **14**, 27 (1960); Phys. Rev. **129**, 608 (1963).
- <sup>6</sup>D. E. Aspnes and P. Handler, Surface Sci. **4**, 353 (1960).
- <sup>7</sup>For review of the subject see D. R. Frankl, *Electrical Properties of Semiconductor Surface* (Pergamon, New York, 1967); and A. Many, Y. Goldstein, and N. B. Grover, *Semiconductor Surfaces* (North-Holland, Amsterdam, 1965).
- <sup>8</sup>W. Mönch, Phys. Status Solidi **40**, 257 (1970).
- <sup>9</sup>M. Henzler, Surface Sci. **24**, 209 (1971).
- <sup>10</sup>V. Heine, Surface Sci. **2**, 1 (1964); and M. Henzler, *ibid.* **25**, 650 (1971).
- <sup>11</sup>F. Garcia-Moliner and J. Rubio, J. Phys. Chem. **2**, 1789 (1969).
- <sup>12</sup>V. Bortolani, C. Calandra, and A. Sghedoni, Phys. Letters **33A**, 193 (1971).
- <sup>13</sup>The change of transmitted light during oxidation goes on until an exposure of  $10^{-4}$  Torr min is reached. At the initial pressure of  $10^{-10}$  Torr, no change of transmission is detected in several hours.
- <sup>14</sup>I. Bartoš, Phys. Status Solidi **33**, 779 (1969).
- <sup>15</sup>In order to determine this contribution, the position of the Fermi level at the surface has been evaluated by following the change of surface conductance as the surface is exposed to dry and wet oxygen, until the minimum of conductivity is reached. From the measured value  $\Delta\sigma = 170 \mu\text{mho}$  per square, a value of  $u_s = -11.5kT/e$  is obtained, using  $u_B = 0$  and taking for the surface mobilities the experimental values of R. Missman and P. Handler [in *Proceedings of the International Conference on the Physics of Semiconductors, Rochester, 1958* (Pergamon, New York, 1959)]. The concentration of free holes in the space-charge region thus obtained is  $3 \times 10^{12} \text{ cm}^{-2}$  for the clean surface, and at least 2 orders of magnitude smaller for the oxidized one. By taking the optical data of W. Kaiser, R. J. Collins, and H. Y. Fan [Phys. Rev. **91**, 1380 (1953)] for hole intraband absorption the contribution of free holes to the  $\ln(I_0/I)_{\text{clean}}$  of Fig. 2 turns out to be on the order of  $4 \times 10^{-3}$ . [For more details see S. Nannarone and R. Pastore, Nota Interna No. 249 (Istituto di Fisica "G. Marconi," Università di Roma, 1969) (unpublished).]
- <sup>16</sup>F. Bassani, in *Proceedings of the International School of Physics Enrico Fermi, Course 34* (Academic, New York, 1966), p. 33.
- <sup>17</sup>In the case of Ge, however, hypothesis (iii) can be ruled out from the measured position of the Fermi level at the surface (see Ref. 15).
- <sup>18</sup>F. Yundurain (private communication).
- <sup>19</sup>See, for example, J. Koutecky and M. Tomasek, Phys. Rev. **120**, 1212 (1960); and J. J. Lander, G. W. Gobeli, and J. Morrison, J. Appl. Phys. **34**, 2298 (1963).
- <sup>20</sup>H. Y. Fan, W. Spitzer, and F. J. Collins, Phys. Rev. **101**, 566 (1956); and W. Spitzer and H. Y. Fan, *ibid.* **108**, 268 (1957).

## Microwave Magnetoabsorption at Low Temperatures in Semiconducting $\text{CdF}_2$ †\*

M. G. Adlerstein, ‡ P. S. Pershan, and Bernard J. Feldman

Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts 02138

(Received 14 May 1971)

Current models for the observed properties of semiconducting  $\text{CdF}_2$  differ in their predictions of polaron mass  $m_p$ . A peak with magnetic field in the low-temperature microwave absorption of semiconducting  $\text{CdF}_2$  has been interpreted in the literature as cyclotron resonance of polarons with  $m_p \sim 11m_e$ . If such a heavy mass were appropriate, semiconducting  $\text{CdF}_2$  would be unlike any of the conventional semiconductors. The presently reported measurements of microwave absorption as a function of applied magnetic field, impurity concentration, frequency, microwave polarization, and temperature enable us to rule out cyclotron resonance as a possible explanation for the absorption peak. Instead, the effect can be qualitatively interpreted by a model based on covalent bonding between donor impurities.

### I. INTRODUCTION

Pure  $\text{CdF}_2$  is a colorless insulator with a band gap of 6 eV. Doped with trivalent rare-earth impurities ( $\text{Re}^{+3}$ ), it can be made semiconducting (SC  $\text{CdF}_2$ ) by chemical treatment. At low temperatures, the conduction electrons are localized about the  $\text{Re}^{+3}$  ions substituted for divalent Cd ions. Above 77°K, a significant fraction of these donor traps are ionized.

SC  $\text{CdF}_2$  has been studied extensively as a physical system exhibiting strong electron-lattice coupling.<sup>1-7</sup> In this paper, we report the results of a study of microwave absorption as a function of applied magnetic field in SC  $\text{CdF}_2$  for temperatures between 1.1 and 2.1°K at  $\nu \sim 13$  GHz. The study was undertaken in an effort to resolve the discrepancy concerning the electron effective mass in this system. On the basis of measurements of thermoelectric power and Hall effect, Khosla and Matz<sup>7</sup>