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## ELECTROABSORPTION IN RUTILE (TiO<sub>2</sub>)†

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The bands accounting for electrical conductivity in rutile have been of continuing interest to many investigators. The low carrier mobility has rendered as useless cyclotron resonance, de Haas-van Alphen measurements, and associated experimental techniques which have proven so valuable in the analysis of other materials. Conductivity and Hall-effect measurements<sup>1-3</sup> and, recently, piezoresistance measurements<sup>4</sup> have suggested multivalley conduction and high electron effective mass in this material, but because of the rather involved relationship such data have to possible band structures and various scattering mechanisms, the evidence supporting these conclusions cannot be regarded as having a unique interpretation. Optical measurements show the absorption edge of rutile is dichroic and has a strong temperature dependence.<sup>5,6</sup> It is, in general, difficult to resolve the different processes accounting for absorption from the measurement of the absorption spectrum in the vicinity of the edge. This is especially true of rutile because of the strong temperature dependence of its absorption tail.

Electroabsorption measurements have provided a more detailed understanding of the processes involved in the absorption of light at the edge in a number of materials, e.g., germanium<sup>7</sup> and silicon.<sup>7,8</sup> The results of such measurements on rutile, their interpretation, and their implications concerning the band structure and dichroic nature of this material at the absorption edge are reported herein.

Electroabsorption measurements were performed on rutile plates of approximately 100  $\mu$  thickness, each having the  $c$  axis and one of the  $a$  axes within the plane of the sample. Thin conducting platinum films vacuum-deposited on both sides of the Formvar-coated sample served as contacts for application of the perturbing electric field but did not interfere

substantially with the transmission of the light. A description of the measuring technique appears in a previous publication.<sup>8</sup>

Two crystals were studied in considerable detail. The first, which shall be referred to as crystal *A*, was fired in oxygen at 20 atm at 700°C for six hours; the second, crystal *B*, was obtained from another source and was fired in atmospheric air at 800°C for 12 h.<sup>9</sup> Two samples were obtained from crystal *A* and one from crystal *B*.

The electroabsorption spectrum of rutile was measured with light polarized with  $E$  parallel to  $c$  ( $E_{\parallel}$ ) and  $E$  perpendicular to  $c$  ( $E_{\perp}$ ), with perturbing electric fields ranging from  $1.5 \times 10^4$  V/cm to  $6 \times 10^4$  V/cm at temperatures ranging from 77 to 200°K. Difficulties encountered in calibration procedures limited the accuracy of the magnitude scaling of the various electroabsorption spectra to  $\pm 30\%$ , but relative accuracy within a given spectrum was limited only by noise. All results are similar to those presented in Fig. 1, which were obtained with an electric field of  $2 \times 10^4$  V/cm at 77°K. Stronger fields enhance and broaden all peaks, both positive and negative, but their magnitudes do not have the same dependence on field. As the temperature is raised, the effect fades in intensity and the peaks broaden. For instance, at 168°K the effect has faded to approximately one third in intensity and the peaks have broadened considerably. At room temperature the effect has diminished to the point that reasonable integration times are not adequate for detection. This dependence of intensity and peak width on temperature and the relationship of these results to the Urbach rule<sup>10</sup> will be dealt with in a future publication.

Several aspects of the data presented in Fig. 1 should be pointed out. Comparison of the results from the two crystals shows that the large low-energy positive (LEP) peak exhibited by

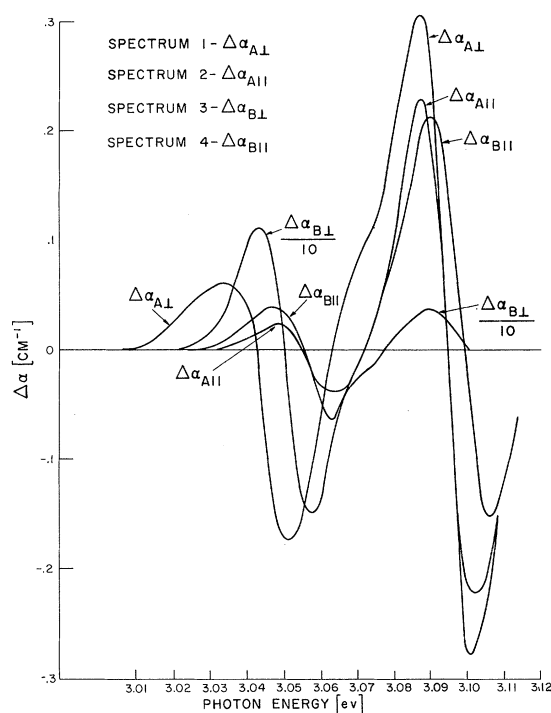


FIG. 1. Electroabsorption spectra exhibited by rutile crystals with electric fields of  $2 \times 10^4$  V/cm at 77°K.

crystal *B* with light polarized  $E_{\perp}$  is more than an order of magnitude larger than the other low-energy peaks exhibited by the two crystals. Except for the low-energy structures exhibited with  $E_{\perp}$ , the peaks in the two crystals are consistent in magnitude to within  $\pm 30\%$ . The positions of the LEP peaks with  $E_{\parallel}$  and similarly the high-energy positive (HEP) peaks exhibited by both crystals in both polarizations of the light are coincident in energy to within the error, which is considered to be  $\pm 3$  meV. However, the LEP peak exhibited by crystal *A* with  $E_{\perp}$  is 13 meV below the LEP peak observed with  $E_{\parallel}$ .

The above features are characteristic of the data obtained at all temperatures and all electric fields. An exception to this is the lack of coincidence of the HEP peak exhibited by crystal *B* with light polarized  $E_{\perp}$  at higher temperatures. Evidently it is displaced to slightly lower energies by the broadening of the strong low-energy structure.

High-resolution, long-integration-time measurements were performed on crystal *A* in the vicinity of the two low-energy peaks at temperatures of 77 and 168°K. These data are present-

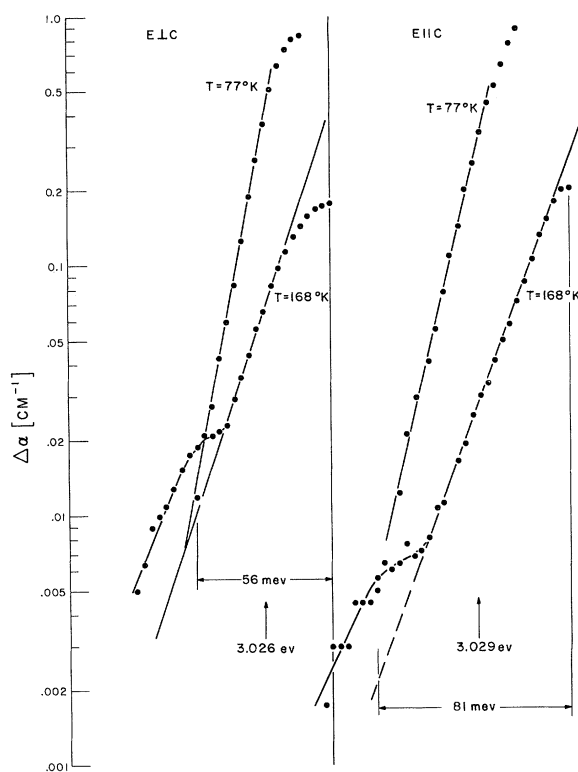


FIG. 2. Semilogarithmic presentation of electroabsorption spectra for photon energies up to the energies of the appropriate LEP peaks (see Fig. 1). These were exhibited by crystal *A* at 77 and 168°K with perturbing electric fields of  $6 \times 10^4$  V/cm.

ed in logarithmic form in Fig. 2. At 77°K the electroabsorption on the low-energy side of the LEP peaks exhibits an exponential dependence on energy, whereas at 168°K one observes the appearance of an additional small peak on the low-energy side of each of the two original peaks. The energy spacing between the temperature-dependent and original peaks is 81 meV for the parallel polarization of the light and 56 meV for the perpendicular polarization. The energy of the midpoint between the two peaks is, with the experimental error, the same for both polarizations. It is interesting that the broadening of the peaks due to the increase of temperature is revealed only in change of slope of the straight segments in this logarithmic presentation.

Similar analysis of the strong low-energy peak exhibited by crystal *B* shows single straight-line edges with temperature broadening. No suggestion of a peak on the low-energy edge is observed at temperatures as high as 200°K.

Comparison of the electroabsorption results for rutile as presented in Fig. 1 with theoretical calculations,<sup>11-15</sup> and previous experimental results<sup>7,8,16</sup> for other materials leads to the conclusion that the structure in each spectrum presented in Fig. 1 could not have been caused by a single absorption process. The fact that the HEP peak is larger in spectra 1, 2, and 4 than the LEP peak and the fact that the energy separation between the LEP and HEP peaks is practically independent of the electric field exclude the possibility of a single band-to-band transition with the HEP peak being a subsidiary peak related to the LEP peak. The fact that a strong negative peak follows the HEP peak excludes the possibility of a single direct band-to-bound state, or bound state-to-band absorption process.<sup>17</sup> Thus in each spectrum the LEP peak followed by the negative peak is interpreted as being due to one process, whereas the HEP peak followed by the negative peak is interpreted as being due to another process.

Comparison of the spectra of crystals *A* and *B* as previously discussed, together with the fact that the energy of the LEP peak in spectrum 3 varies with temperature in a slightly different way than the rest, leads to the conclusion that the strong low-energy structure in spectrum 3 is caused by a transition to or from an impurity state. On the other hand, the processes responsible for the remaining structures are considered intrinsic. An additional argument in favor of this interpretation is presented later.

Previous measurements of electroabsorption show that peaks caused by direct allowed transitions are characteristically larger (two orders of magnitude) than those caused by phonon-assisted transitions. The intrinsic structures observed in Fig. 1 are consistent in size only with direct unallowed or phonon-assisted transitions. On the other hand, the impurity structure must be associated with a direct allowed transition to account for the fact that it is substantially larger than the intrinsic structures.

The data presented in Fig. 2 demonstrate that the low-energy intrinsic peaks are due to phonon-assisted transitions involving the same initial and final states. The temperature-dependent structure on the low-energy side of these two peaks ( $E_{\parallel}$ ,  $E_{\perp}$ ) is due to electronic transitions assisted by the absorption of pho-

nons of energy 40.5 meV with  $E_{\parallel}$  and energy 28 meV with  $E_{\perp}$ , whereas the original peaks are due to emission of the same phonons. The ratios of magnitude of the emission to absorption peaks are larger than would be anticipated on the basis of a straightforward application of the Boltzmann factors by 3.1 for  $E_{\parallel}$  and 2.1 for  $E_{\perp}$ . This, however, would be expected if the primary intermediate state or states do not reside far above the electronic level accounting for this low-energy structure, since in such a case the energy denominators for these transition probabilities would have considerable influence. Intermediate states at approximately 130 meV above the final electronic state would provide good agreement with these experimental observations. The fact that no additional structure is observed in the vicinity of the midpoint due to direct allowed or unallowed transitions suggests the above phonon-assisted transitions are nonvertical.

The lack of a temperature-dependent peak on the low-energy side of the strong impurity peak in crystal *B* substantiates the conclusion that this structure is produced by an entirely different process than the LEP peak observed in crystal *A* with  $E_{\perp}$ .

The coincident high-energy structures have intensities consistent with phonon-emission-assisted processes or with unallowed direct transitions. The latter explanation is preferred because the former would require a very-low-symmetry phonon (a conduction-band minimum symmetry of  $C_s$  or less would be necessary if the valence-band maximum were at  $k=0$ ), or degenerate phonons to account for coincidence of these peaks in the two polarizations.

These results and interpretations are quite consistent with the indirect gap models proposed by Acket,<sup>3</sup> Bir et al.,<sup>4</sup> and Becker and Hosler.<sup>2</sup> If the higher conduction-band minimum proposed by Becker and Hosler is identified with the final state of the transition accounting for the HEP peak, it would reside approximately 78 meV above the true minimum. In addition, if this final state is at  $k=0$ , other bands would be anticipated in the vicinity of several tens of meV higher energy.<sup>18</sup> These could provide the necessary intermediate states required to account for the observed ratios of phonon-absorption- and phonon-emission-assisted peaks.

In addition to the conclusions pertinent to conductivity in this material, these results clearly indicate the intrinsic dichroism of the

absorption edge in rutile is due to the participation of different energy phonons in the fundamental absorptions of the two polarizations of the light. Clearly, the impurity observed here is capable of affecting the degree of dichroism.

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## EXPERIMENTAL OBSERVATION OF THE EXCITONIC MOLECULE

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The purpose of this Letter is to present experimental observations of the excitonic molecule, a stable complex in Si consisting of two electrons and two positive holes. It is hoped that this information will provide the impetus for the discovery of its effects in a wide variety of other materials.

The history of excitonic molecules goes back to 1946 when Wheeler<sup>1</sup> gave theoretical evidence for the existence of entities composed entirely of electrons and positrons. He considered an electron bound to a positron, an electron bound to two positrons, and two electrons bound to two positrons. He concluded that the first two entities should be stable against dissociation but not the last. The next year Hylleraas and Ore<sup>2</sup> showed that this entity should also be stable and gave it the name "positronium molecule." While evidence for the existence of the first of Wheeler's entities, positronium,<sup>3</sup> was found by Deutsch<sup>4</sup> and later by many others, no evidence for the existence of the positronium molecule has been reported.

In 1958 Lampert<sup>5</sup> pointed out that Wheeler's entities should exist in nonmetallic solids with positive holes in the role of positrons. He named

the entity produced by binding two positive holes to two electrons an "excitonic molecule."

The binding energy of the excitonic molecule can be estimated in two ways. (1) From the binding energy of the exciton in silicon,  $E_X = 8 \times 10^{-3}$  eV,<sup>6</sup> and the calculated value of the ratio of the dissociation energy of positronium,<sup>1</sup>  $E_{Ps} = 6.8$  eV, to that of the positronium molecule,<sup>7</sup>  $E_{Ps_2} = 0.135$  eV,  $E_{Ps}/E_{Ps_2} = E_X/E_{X_2}$ ,  $E_{X_2} = 0.16$  meV. (2) It has been shown<sup>8</sup> that binding energy of an exciton trapped at a neutral donor (or acceptor) is  $\sim 0.1$  the ionization energy of the donor (or acceptor), so that  $E_{X_2} = 0.1E_X \sim 0.8$  meV.

Evidence for the existence of the excitonic molecule was obtained from the recombination radiation from Si at low temperatures. The Si specimen was immersed in liquid He which was pumped below  $\lambda$  transition. High concentrations of excess electrons and holes were produced by focusing the light from a mercury arc<sup>9</sup> on one side of the specimen. Recombination radiation from the opposite side was analyzed with a spectrometer, detected by a lead sulfide cell, and recorded on a chart.

All of the detectable intrinsic recombination