

charge density  $\tau = \epsilon/4\pi\sigma_0$  (where  $\epsilon$  is the electronic susceptibility) is usually small as compared with the time  $(\Gamma\omega)^{-1}$ . It is the case that we have considered above. [Indeed, in particular we have omitted the terms containing the space-charge density in Eq. (2).] In such a case the difference between the acoustoelectric and usual semiconducting system is essential, and there is no connection between negative differential conductivity and acoustical stability.

<sup>1</sup>See, for instance, J. Okada and H. Matino, *J. Appl. Phys. (Japan)* **3**, 698 (1964); H. R. Carleton, H. Kroger, and E. W. Prohofsky, *Proc. IEEE* **53**, 1452 (1965); P. O. Sliva and R. Bray, *Phys. Rev. Letters* **14**, 372 (1965); G. S. Hobson and E. G. S. Paige, *J. Phys. Soc. Japan Suppl.* **21**, 464 (1966).

<sup>2</sup>The reflected sound may act as another source of feedback. We concern ourselves with the case where

the reflected waves may be neglected.

<sup>3</sup>V. L. Gurevich and B. D. Laikhtman, *Zh. Eksperim. i Teor. Fiz.* **49**, 960 (1965) [translation: *Soviet Phys. -JETP* **22**, 668 (1966)].

<sup>4</sup>R. Katilius, *Fiz. Tverd. Tela* **10**, 458 (1968) [translation: *Soviet Phys. -Solid State* **10**, 359 (1968)].

<sup>5</sup>There is also another stationary regime in the region *EDA0B* but it appears to be unstable.

<sup>6</sup>V. L. Gurevich, V. D. Kagan, and B. D. Laikhtman, *Zh. Eksperim. i Teor. Fiz.* **54**, 188 (1968) [translation: *Soviet Phys. -JETP* **27**, 102 (1968)].

<sup>7</sup>W. H. Haydl and C. F. Quate, *Appl. Phys. Letters* **7**, 45 (1965); P. O. Sliva and R. Bray, *Phys. Rev. Letters* **14**, 372 (1965); A. Many and J. Balberg, *Phys. Letters* **21**, 486 (1966).

<sup>8</sup>J. H. McFee, P. K. Tien, and H. L. Hodges, *J. Appl. Phys.* **38**, 1721 (1967).

<sup>9</sup>The "pinned" domains and associated damped current oscillation were investigated recently by P. K. Tien [*Phys. Rev.* **171**, 970 (1968)] by means of numerical calculation.

## STUDY OF GENERATION AND RECOMBINATION OF FREE CARRIERS IN SrTiO<sub>3</sub> BY TWO-PHOTON EXCITATION

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Free-carrier absorption was observed in intrinsic crystals of strontium titanate when excited by two-photon absorption of laser pulses. The temperature dependence of the recombination time was found to be exponential, with an activation energy of 0.105 eV. This energy may correspond to the depth of the valleys at the edges of the Brillouin zone in the lowest conduction band or to the activation energy of localized traps.

This paper describes some transient measurements of free-carrier absorption which were carried out with intrinsic crystals of strontium titanate (SrTiO<sub>3</sub>) using two-photon excitation. This method permitted a simple measurement of the free-carrier recombination time and its dependence on temperature. Using the results of Baer's work<sup>1</sup> it was also possible to deduce a figure for the two-photon absorption coefficient for the material.

In addition, if the recombination process is through direct transitions, the activation energy obtained from the temperature dependence of the recombination time would give a direct measure of the valley depths in the conduction band.

SrTiO<sub>3</sub> is a transparent insulator crystal with an optical energy gap of 3.2 eV.<sup>2</sup> The optical properties of the pure crystals have been studied by several workers in the field.<sup>3</sup> It is characterized by a sharp absorption band edge near 3900 Å and essentially zero absorption in the visible re-

gion of the spectrum. The optical properties of reduced and iron- and molybdenum-doped SrTiO<sub>3</sub> crystals were studied by Gandy.<sup>4</sup> Baer<sup>1</sup> studied the free-carrier absorption in reduced SrTiO<sub>3</sub> in the region from 0.4 to 5 μm.

Tight-binding calculations by Kahn and Leyendecker<sup>5</sup> showed that the crystal has an oxygen 2*p* valence band and a titanium 3*d* conduction band with minima along the <100> cubic axis at the edges of the Brillouin zone.

SrTiO<sub>3</sub> doped with various impurities was found to exhibit very strong photochromic behavior.<sup>6</sup> It was also shown that considerable coloration could be induced in the photochromic samples via two-photon excitation of electron-hole pairs by high-intensity laser pulses.<sup>7</sup>

The samples used for this work were cut from a boule purchased from the National Lead Company and polished on both faces to optical quality. The crystals were grown by the flame-fusion technique.

The experiments consisted of monitoring the transmitted intensity of a probe cw laser beam during and after the application of a very high-intensity Q-switched ruby-laser pulse. The ruby laser produced pulses of about 250 mJ with about 20-nsec duration. The risetime resolution of the system was about 15 nsec, limited mostly by the preamplifier in the oscilloscope.

A 0.3-cm thick sample was placed perpendicular to the weakly focused ruby-laser beam and the monitor laser was aligned to strike the center of the area covered by the pulse. The monitor beam was about 1 mm in diameter, and an aperture was used to block scattered light. The ruby-laser intensity was measured at each occurrence by diverting about 8% of its power to a high-speed photodiode which was calibrated to measure pulse intensity at the center of the focused beam at the position of the sample.

The photomultiplier measuring the transmitted intensity of the monitor laser was connected to the oscilloscope through a 170-nsec delay line. The two inputs of the preamplifier were added algebraically and were displayed on a single trace, the delay line separating the two events in time. This technique permits recording the ruby-laser pulse intensity at each instance without a dual-beam oscilloscope.

The photograph in Fig. 1 shows the ruby-laser pulse followed by a decrease in the transmitted intensity of the He-Ne laser ( $\lambda = 6328 \text{ \AA}$ ) used as probe. The induced absorption is seen to decay quite rapidly at room temperature dropping to 50% of its maximum in about 0.2  $\mu\text{sec}$ .

The intensity dependence of the induced absorption at 6328  $\text{\AA}$  was investigated by varying the power of the ruby-laser pulse. This was accomplished by adding a few drops of  $\text{CuSO}_4$  solution, which absorbs strongly at the ruby frequency, to

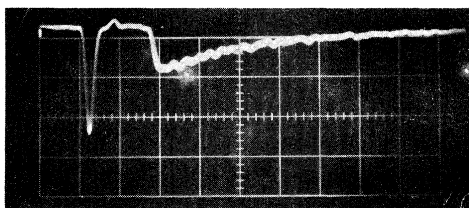


FIG. 1. Photograph showing ruby laser pulse followed by the change in transmitted intensity of the He-Ne monitor laser beam ( $\lambda = 6328 \text{ \AA}$ ). Time scale, 100-nsec/div. Laser pulse calibration, 1 div = 110 MW/cm<sup>2</sup>. Monitor beam calibration, 4.2 divisions of deflection correspond to transmitted intensity with no induced absorption.

an optical cell filled with distilled water. The cell was never moved so as not to disturb the alignment or the calibration and the pulse intensity was measured past the attenuator cell. The results of this test are plotted in Fig. 2, where the points are seen to follow quite closely a parabolic curve. At the higher intensities, however, the induced absorption is seen to be consistently lower than would be expected from a square dependence. This is attributed to the first-order absorption of the ruby-laser pulse by the free carriers as they are generated. Since the absorption coefficient should be linearly related to the concentration of generated carriers, the above results are consistent with what one would expect from two-photon generation of electron-hole pairs. (The density of states corresponding to transitions at the double photon energy is quite large, as is evidenced by the very strong absorption of the material at wavelengths around 3450  $\text{\AA}$ .)

From the data for free-carrier absorption versus concentration obtained by Baer, the absorption cross section for free carriers at 6328  $\text{\AA}$  is

$$\sigma(6328 \text{ \AA}) \approx 3.1 \times 10^{-18} \text{ cm}^2.$$

Ignoring the fact that, unlike the case of the reduced samples used by Baer, the absorption

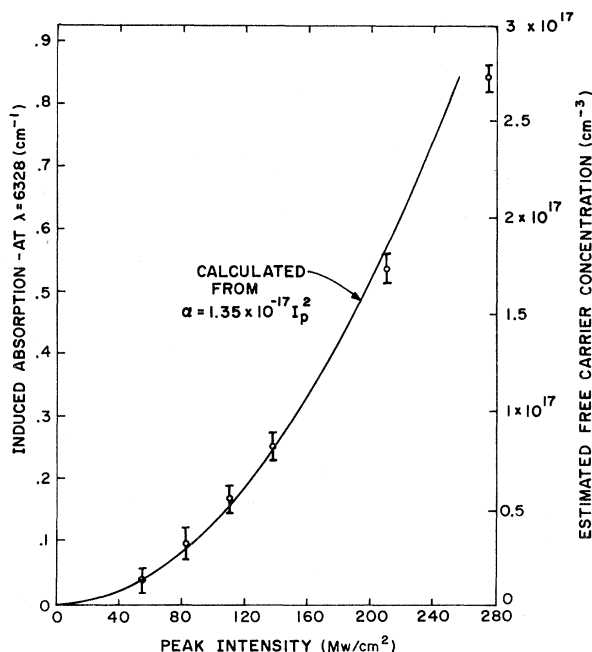


FIG. 2. Induced absorption at 6328  $\text{\AA}$  versus peak intensity of ruby-laser pulse.

measured here could be due to both electrons and holes, one can use the curve of Fig. 2 to give an estimate of the number of electron-hole pairs excited by a given pulse. This estimate was used to compute the scales for free-carrier concentration shown in Fig. 2.

From these figures of concentration versus intensity and the assumption of a Gaussian-shaped pulse with a measured half-width of 13 nsec, it is straightforward to calculate a value for the two-photon absorption coefficient for SrTiO<sub>3</sub> at the ruby-laser wavelength:

$$\alpha'(6943 \text{ \AA}) \approx 2.5 \times 10^{-10} I \text{ cm}^{-1},$$

where  $I$  is the intensity in W/cm<sup>2</sup> and  $\alpha'$  is defined in the conventional manner by

$$dI/dx = -\alpha' I(x).$$

The wavelength dependence of the induced absorption was investigated by measuring the induced absorption at 4579 and 5145 Å using an argon-ion laser as a probe. The resulting induced absorption coefficients ( $\alpha$ ) are given below. They were measured with a peak pulse intensity of about 260 MW/cm<sup>2</sup>. The relative accuracy of the measured values of  $\alpha$  is estimated to be better than  $\pm 10\%$  while the absolute accuracy should be better than  $\pm 30\%$ .

$\lambda$ (Å)	$\alpha$ (cm <sup>-1</sup> )
4579	0.34
5145	0.46
6328	0.77

The absorption is seen to increase with wavelength following quite closely the  $\lambda^{2.5}$  dependence encountered by Baer, except that no peak was observed at 5145 Å. This peak was attributed by Baer to absorption from an electron trapped at an oxygen vacancy and such a defect should not appear in significant concentrations in our sample.

The effect of temperature on the recombination time was investigated by placing a sample in a cold-finger Dewar and recording the decay of the induced absorption at temperatures between the ambient temperature and 77°K. The decay times to one-half the maximum absorption are plotted in Fig. 3 for the range between room temperature and 145°K. They show a definite exponential variation of the decay time with inverse temperature in this range. At 77°K the decay showed a different shape from that at the warmer

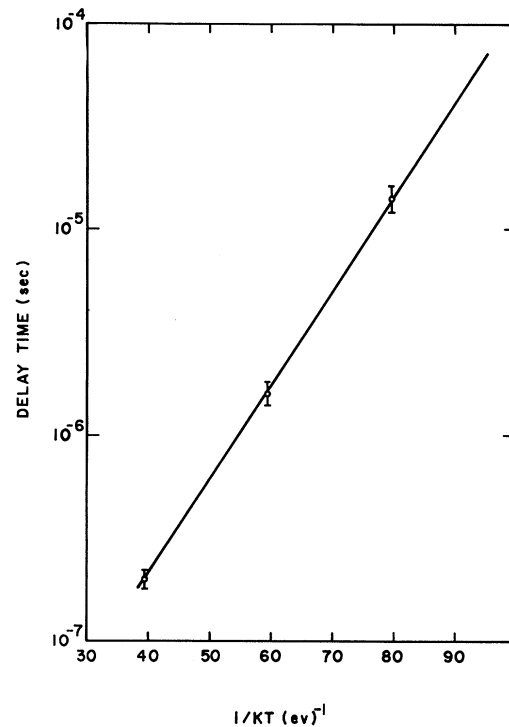


FIG. 3. Decay time of induced absorption versus temperature (peak pulse intensity  $\approx 240$  MW/cm<sup>2</sup>).

temperatures; it is characterized by a very fast initial decay for a few milliseconds, followed by a long tail lasting a few tenths of a second.

The magnitude of the induced absorption and its wavelength dependence seem quite consistent with the interpretation of the phenomenon as free-carrier absorption. Some preliminary photoconductivity measurements have been carried out at room temperature and have shown electrical conduction with the same decay time as the free-carrier absorption. The nonlinear absorption coefficient that was obtained from the data is also consistent with the results obtained in the nonlinear coloration experiments on the photochromic samples of SrTiO<sub>3</sub>.<sup>7</sup> The more difficult question relates to the interpretation of the mechanism responsible for the observed decay time and its variation with temperature. The decay times observed at room temperature could be explained in terms of direct recombination or in terms of impurity-aided recombinations. Even though SrTiO<sub>3</sub> is an indirect band-gap insulator, the valley minima of the lowest conduction band are presumed to occur less than 0.1 eV below the energy at the center of the Brillouin zone.<sup>5</sup> This would imply that a substantial percentage of the electrons would be at the center

of the Brillouin zone where they could undergo direct recombination with holes in the valence band. A direct-recombination model such as this could also explain the temperature variation of the recombination time if one assumes that the activation energy corresponds to the depth of the valley minima of the lowest conduction band. If this were the situation, at very high temperatures one should measure the direct recombination time while at very low temperatures one could (ideally) measure the indirect recombination time, because all the electrons would be at the edges of the Brillouin zone. The estimates of valley depth given by Kahn and Leyendecker<sup>5</sup> were between 0.02 and 0.05 eV, which is considerably lower than our activation energy of 0.105 eV. However, recent experimental determination of electronic effective mass by Parker and Yahia<sup>8</sup> indicate a greater curvature of the valley minima than was estimated by Kahn and Leyendecker, suggesting that the valley depth may be larger than what was estimated.

A somewhat more straightforward interpretation of the temperature dependence of the results would be to assume that there are impurity states at about 0.105 eV below the conduction band which trap a larger percentage of the electrons as the temperature is lowered. One problem with this interpretation is the fact that experimental results showed no significant change in the induced absorption at 6328 Å as the temperature was lowered from room temperature to 145°K. Since, at the lower temperature, a great

majority of the electrons would have to be in the traps, this interpretation would require that the absorption cross section of the electron in the trap and that of the free carrier be the same. This is possible although it would seem to be an unlikely coincidence.

Other explanations for the observed recombination behavior are also conceivable at this stage and more thorough photoconductivity and fluorescence measurements will be required to further clarify the choice of models.

It is a pleasure to acknowledge several fruitful discussions with Dr. Albert Rose. The authors are also grateful for consultations and suggestions of various other members of the staff at RCA Laboratories and for the experimental assistance of Mr. L. Levin.

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## EXCITON-PHONON BOUND STATE: A NEW QUASIPARTICLE\*

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We point out that an exciton and an optical phonon may form a bound state which moves through the crystal. Calculated binding energies and oscillator strengths for this new quasiparticle lend support to recent suggestions that strong exciton-phonon mixing is present in the optical spectra of some ionic crystals.

In the optical spectra of some ionic crystals such as ZnO,<sup>1</sup> MgO and BeO,<sup>2</sup> and TiCl and TiBr,<sup>3</sup> the separation of the first exciton peak and a higher energy companion is less than the energy  $\omega_0$  of the LO phonon by a fraction  $\Delta \sim 10\%$ . Also, spectral lines associated with the bound exciton in AgBr:I,<sup>4</sup> although observed at energy separations close to  $\omega_0$  in emission, occur at

separations nearly 30% smaller than  $\omega_0$  in absorption. These facts suggest that (1) the companion structure may be associated with phonon sidebands and (2) final-state interaction between the exciton and phonon leads to a negative energy shift of this structure. To help clarify the situation, we present model calculations which demonstrate the possibility of bound states of the ex-

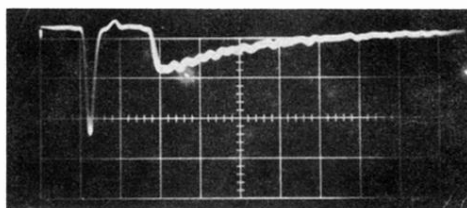


FIG. 1. Photograph showing ruby laser pulse followed by the change in transmitted intensity of the He-Ne monitor laser beam ( $\lambda = 6328 \text{ \AA}$ ). Time scale, 100-nsec/div. Laser pulse calibration, 1 div = 110 MW/cm<sup>2</sup>. Monitor beam calibration, 4.2 divisions of deflection correspond to transmitted intensity with no induced absorption.