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## Electronic Conduction in Slightly Reduced Strontium Titanate at Low Temperatures\*

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The electronic transport properties of slightly reduced pure strontium titanate have been studied at low temperatures between 2 and 300 °K. The temperature dependence of resistivity, Hall coefficient, and Hall mobility showed different features from previous results for doped and reduced crystals with higher carrier concentrations. Specifically, the mobility at liquid-helium temperatures is small (5–700 cm<sup>2</sup>/V sec) and increases with carrier concentration. Optical-absorption measurements showed the existence of several compensating acceptor levels and that the dominant mechanism of electron scattering was by longitudinal optical phonons at room temperature. Further, the data show that a specialized form of ionized-impurity scattering may play a role at low temperatures. A discussion of our experimental results is presented and it is concluded that an explanation of these in terms of a model of impurity-band conduction is appropriate.

### I. INTRODUCTION

Electronic transport in semiconducting SrTiO<sub>3</sub> has been studied by several authors.<sup>1–4</sup> In the low-temperature studies, large electronic mobilities were found ranging from 10<sup>3</sup> to 2×10<sup>4</sup> cm<sup>2</sup>/V sec for crystals with carrier concentrations between 10<sup>17</sup> and 5×10<sup>20</sup> cm<sup>-3</sup>. According to Tufte and Chapman<sup>2</sup> and Frederikse *et al.*<sup>3</sup> the Hall mobility at liquid-helium temperature decreases with increasing carrier concentration and from this these authors concluded that the mobility at low temperatures was limited by ionized impurity scattering even though the magnitude of the theoretical and experimental values of mobility did not agree too well.

Tufte and Chapman<sup>2</sup> used the Mansfield formula<sup>5</sup> in the limit of large degeneracy to calculate mobility by ionized-impurity scattering at low tem-

peratures and found that the calculated value was about 60 times larger than the experimental value for their Nb-doped sample. They attributed this large discrepancy to a compensation effect due to lattice defects. On the other hand, Frederikse *et al.*<sup>3</sup> followed Gulyaev's treatment<sup>6</sup> using the optical value for the dielectric constant in the expressions for the screening length and the effective Bohr radius. In this case theory underestimates the experimental mobility by a factor of 2–3 for the Nb- and La-doped samples, and overestimates by a factor of 2–4 for the hydrogen-reduced samples. Also, concentration dependence of mobility by theoretical calculation was much slower than that of experimental data. The validity of the use of the optical dielectric constant needs further discussion.

Another unexplained feature of the low-temperature results is that the mobility is much larger in the doped crystals than in the reduced samples.

Results on lightly reduced crystals<sup>1,2</sup> show a strong carrier freeze-out effect indicating the existence of a relatively deep nonhydrogenic-type donor level. On the other hand, doped crystals do not show any carrier freeze-out effect. Moreover, the temperature dependence of resistivity and Hall mobility in vacuum-reduced crystals<sup>1</sup> show some complications which are not understood. These facts indicate that the electronic transport in lightly vacuum-reduced crystals may be quite different from that in a doped or hydrogen-reduced crystal.

Thus the transport properties at low temperatures in reduced strontium titanate, especially in the vacuum-reduced crystals with low carrier concentration, are not clear cut. Furthermore, there are no low-temperature measurements on crystals with very low carrier concentration. Frederikse *et al.*<sup>1</sup> reported measurements on a sample (VR-5) with small carrier concentration, but could not obtain data at temperatures below 40°K due to the high resistance of this crystal at these temperatures. The measurements of Parker and Yahia<sup>4</sup> are on crystals of low carrier concentration but at relatively high temperatures. The purpose of this work, therefore, is to describe low-temperature measurements in reduced strontium titanate with a view to explaining scattering and conduction mechanism in this material for extremely low carrier concentrations.

## II. EXPERIMENTAL PROCEDURE

Single crystals of pure SrTiO<sub>3</sub> of dimensions

15×4×0.75 mm<sup>3</sup> were obtained from the National Lead Company. The crystals were reduced in fore-pump vacuum ranging from 30–0.5 μ of Hg at temperatures between 650 and 1000° C. Annealing and reducing conditions are listed in Table I. With a clean system (relatively free of fore-pump oil) of vacuum better than a few micron of Hg, reduction was essentially impossible, while annealing of the crystal in air before reduction slowed down the reduction rate. The crystals used for the electrical measurements were those which were reduced at a pressure higher than some 20 μ of Hg.

Electrical contacts were made with indium solder by wetting the crystal surface with indium using an ultrasonic soldering gun. A conventional dc four-probe method was employed for the measurements of the resistivity and Hall coefficient. The voltages across the potential probes were measured by a high impedance (>10<sup>10</sup> Ω) digital voltmeter (five digit, model LM1426, Solartron Electronics). The magnetic field used for the measurement of Hall coefficients was 7.5 kG.

Temperature control of the sample was effected by changing the pressure in the inner Dewar containing the liquid coolant in which the samples were immersed (freon 12, liquid nitrogen, liquid hydrogen, and liquid helium). The temperature of the specimens was monitored by a copper-constantan thermocouple and a L&N type K-2 potentiometer was used to measure the thermocouple voltages.

The crystals used for the optical-absorption measurements were polished on a rotating wax lap

TABLE I. History of reduction and heat treatment, strontium titanate.

Sample no.	Annealing	Reduction (in °C)	Time (in h)	Vacuum (in μ)	$\rho$ at 300°K (in Ω cm)	Coloration
ST1	No	700	1	20	11.2	Slightly blueish
ST2	No	800	1	20	2.43	Blue
	Etched with KOH at 500°C, 1 h	...	...	...	...	Complete decoloration
ST3	No	900	1	20	0.555	Dark blue
ST4	...	750	1	20	3.50	Light blue
	...	1000	4	1	>10 <sup>9</sup>	Complete decoloration
ST5	...	850	1	20	0.594	Dark blue
ST6	...	650	1 $\frac{1}{4}$	25	24.5	Slightly dark
ST7	1000°C, 4 air	700	1	5	>10 <sup>9</sup>	No color
		800	$\frac{1}{2}$	1	>10 <sup>9</sup>	No color
		1000	4	<1	>10 <sup>9</sup>	No color
ST8	1000°C, 4 air	700	1	5	>10 <sup>9</sup>	No color
		800	$\frac{1}{2}$	1	>10 <sup>9</sup>	No color
		1000	42	5	>10 <sup>9</sup>	No color
ST9	...	1000	2	3	>10 <sup>9</sup>	No color
ST10	...	850	1	1	>10 <sup>9</sup>	No color
TS1	...	800	1	20	1.19	Blue
TS2	...	700	1	20	11.3	Light blue

TABLE II. Resistivity and Hall data for reduced strontium titanate.

Sample no.	$\rho$ ( $\Omega\text{cm}$ )	300 °K			4.2 °K			Acti- vation energy (eV)	
		$R_H$ ( $\text{cm}^3\text{C}^{-1}$ )	$\mu_H$ ( $\text{cm}^2\text{V}^{-1}\text{sec}^{-1}$ )	$n$ ( $\text{cm}^{-3}$ )	$\rho$ ( $\Omega\text{cm}$ )	$R_H$ ( $\text{cm}^3\text{C}^{-1}$ )	$\mu_H$ ( $\text{cm}^2\text{V}^{-1}\text{sec}^{-1}$ )		$n$ ( $\text{cm}^{-3}$ )
ST3	0.555	2.33	3.81	$2.68 \times 10^{18}$	0.237	155.8	657	$4.01 \times 10^{16}$	0.035
ST5	0.594	1.93	3.25	$3.25 \times 10^{18}$	0.507	162.2	320	$3.85 \times 10^{16}$	0.045
ST2	2.43	10.6	4.38	$5.87 \times 10^{17}$	2.83	209.5	74.0	$2.99 \times 10^{16}$	0.07
ST4	3.50	12.7	3.62	$4.94 \times 10^{17}$	4.23	272.5	64.5	$2.29 \times 10^{16}$	0.075
ST1	11.2	53.0	4.72	$1.18 \times 10^{17}$	95.8	1457	15.4	$4.28 \times 10^{15}$	0.08
ST6	24.5	81.0	3.30	$7.72 \times 10^{16}$	$4.74 \times 10^4$	$\sim 2 \times 10^5$	$\sim 4.2$	$\sim 3 \times 10^{13}$	...

using a slurry of Linde Type A, B, and C polishing powder of diameter ranging from 0.05–1.0  $\mu$ . For the measurement of transmitted light intensity as a function of wavelength, a Czerny-Turner scanning spectrometer (model 78-466, Jarrel-Ash) was used together with an EMI 9558Q photomultiplier tube as a detector. A 150-W quartz iodine lamp was used as a light source. In order to determine the effect of reduction of the crystals on their absorption, a comparative method was used: The light was passed through two crystals of identical thickness and surface preparation, one of which was reduced and the other unreduced. The logarithm of the ratio of transmitted intensity through an unreduced crystal to that through a reduced crystal gave a direct measure of the relative absorption coefficient associated with the reduction process. A sample-in sample-out method was also employed to obtain absolute values of absorption coefficient.

Since the reduction time for our samples was relatively short compared to those reported by others,<sup>1-3</sup> we performed optical-absorption measurements on a thick crystal by sectioning in order to check the uniformity of the reduction. A crystal of thickness 2.1 mm was reduced at 800 °C for 1 h in 20- $\mu$  vacuum and the absorption coefficient obtained, then the thickness was reduced to 1.27 mm by grinding off both faces and the absorption coefficient was measured again. The crystal was thinned down further to 0.66 mm and another measurement on absorption coefficient was carried out. The values of absorption coefficient obtained in this way did not show any significant variation, an argument for a uniform reduction.

### III. EXPERIMENTAL RESULTS

Some typical results obtained at temperatures between 300 and 2 °K are shown in Table II. The carrier concentration in the measured samples at 4.2 °K are extremely small ranging from  $3 \times 10^{13}$  to  $4 \times 10^{16} \text{ cm}^{-3}$  compared to the samples used by others<sup>1-3</sup> ( $10^{17}$  to  $5 \times 10^{20} \text{ cm}^{-3}$ ). In contrast to previous results obtained for the Nb- (or La-) doped

and hydrogen-reduced crystals,<sup>2,3</sup> the present work shows entirely different features in the transport at low temperatures. Figure 1 shows the log-log plot of the resistivity-vs-reciprocal-temperature

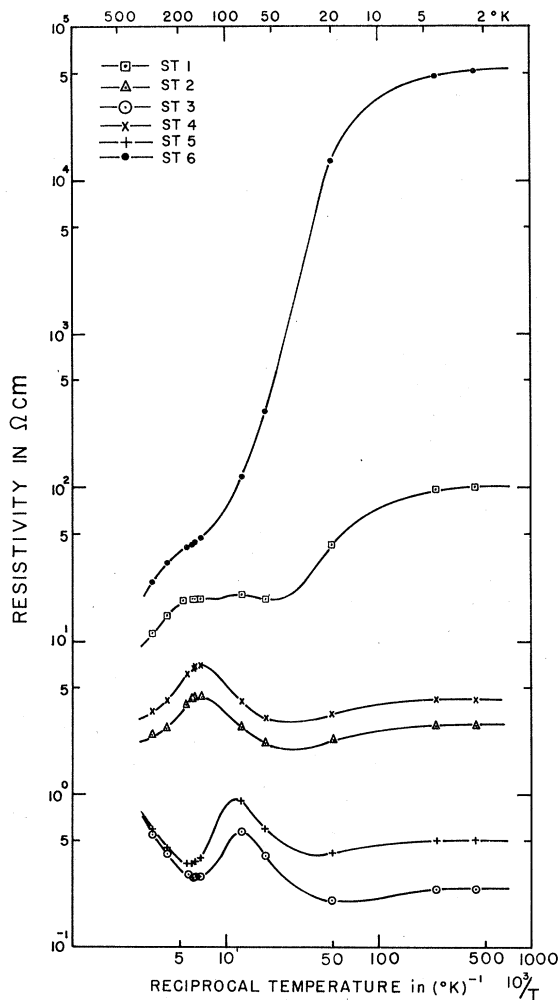


FIG. 1. Log-log plot of resistivity-vs-reciprocal-temperature curves. Note the shift of maxima of the curves toward lower temperatures as the degree of reduction increases (as resistivity decreases).

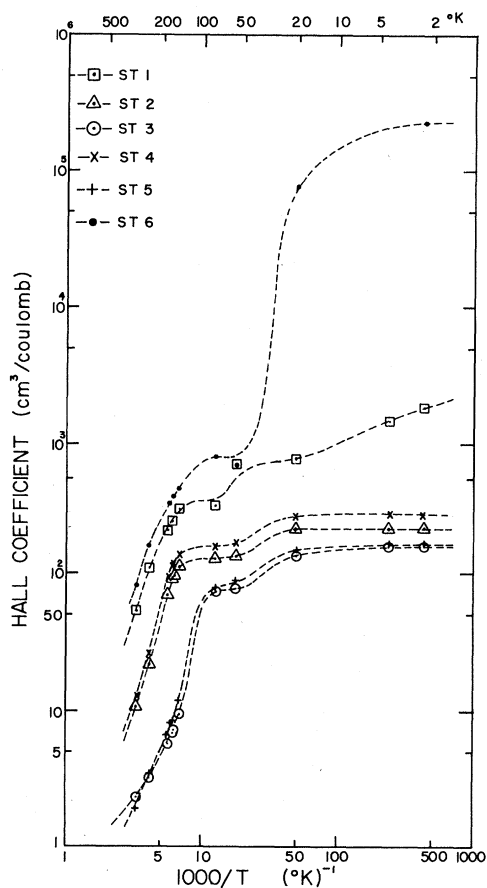


FIG. 2. Plot of Hall coefficient vs reciprocal-temperature curves on a log-log scale. Samples show a jump in Hall coefficient near 40°K.

curves. The curves show maxima and minima at different temperatures depending upon the degree of reduction of the samples. The lower the resistivity the lower is the temperature of the maximum. This is due to the lower ionization energy for the samples with lower resistivity as shown in the last column of Table II. The reason for this will be given later. As the temperature is lowered the resistivity in some crystals with relatively high carrier concentration decreases due to the increase in mobility and then increases sharply due to the rapid freezing out of the carrier (faster than the rate of mobility increase) as can be seen from the curves in Fig. 2 in which the Hall coefficient is plotted against  $1/T$ . The rapid freezing out of carriers near room temperature implies the existence of a deep-lying nonhydrogenic level. Starting from room temperature, the Hall coefficient rises rapidly and then levels off at about 20°K (Fig. 2). There is a sudden change in Hall coefficients by about a factor of 2 near 40°K. The reason for this is not clear at this point. It may be due to the freezing out of one of the doubly charged

donor levels (e.g., oxygen vacancy) or due to another effect such as a transition from a paraelectric to a ferroelectric state which occurs at about 45°K.<sup>7</sup> Anomalies in Hall mobility and Seebeck coefficient at around 45°K were also observed by Frederikse *et al.*<sup>1</sup> in vacuum-reduced crystals. Yasunaga<sup>8</sup> reported anomalies in photoconductivity and in Hall mobility at this temperature. Figure 3 is the semilog plot of the carrier concentration against  $1/T$  near room temperature. From the slope of this plot, the activation energy for ionization, i.e., the depth of the low-lying level, can be obtained<sup>9</sup> (Table II). Actual substitution of experimental data into the formulas given in the Ref. 9 shows that the degree of compensation in all our samples is very small and consequently that the activation energies given in Table II correspond to a half of the ionization energy. As one can see from the last column of Table II, this energy is higher for the samples with lower carrier concentration. This concentration dependence of the activation energy is due to the increase in the overlap of the electronic wave functions as the concentration increases. Due to the large dielectric constant, the width of the impurity band formed as a result of the overlap is appreciable, enough to cause a reduction in the energy gap between the top of the im-

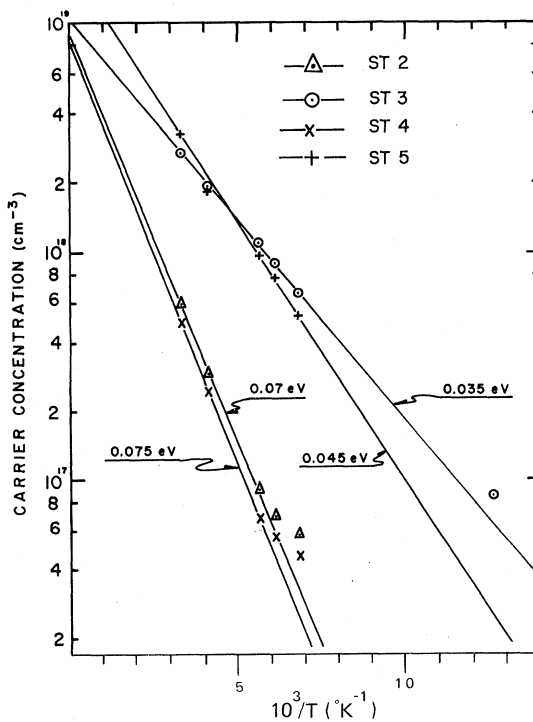


FIG. 3. Temperature dependence of carrier concentration near the freeze-out temperature. Energy values indicated are donor ionization energies and are obtained directly from the slope. In the case of very small compensation these values should be multiplied by 2 (Ref. 9).

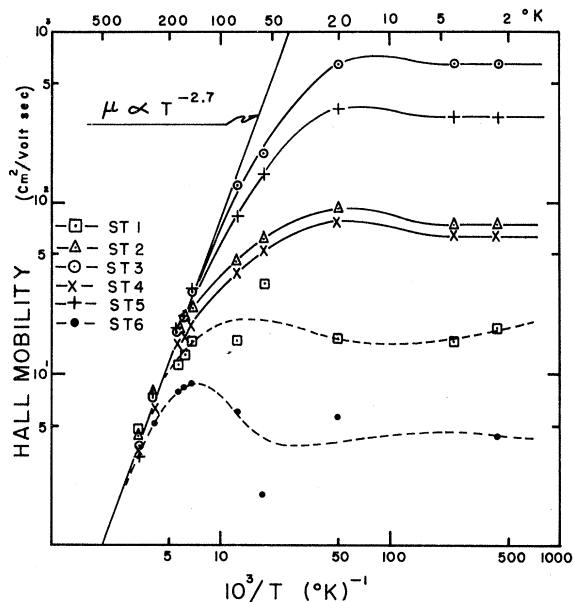


FIG. 4. Temperature dependence of Hall mobility.

purity band and the bottom of the conduction band.

Hall mobility vs  $1/T$  curves are shown in Fig. 4. Except for the very slightly reduced samples, the mobility above  $150^\circ\text{K}$  is proportional to  $T^{-2.7}$  agreeing with previous results.<sup>1,2</sup> The most striking feature is that at low temperatures, the mobility values are quite small ranging between 5 and  $700\text{ cm}^2/\text{V sec}$  and smaller for the samples with lower degrees of reduction. This result implies that ionized impurity scattering in the usual conduction band cannot be the dominant limiting process at low temperatures, and further substantiation for this conclusion is that the carrier concentration is very small in our samples, making ionized impurity scattering unlikely. Also scattering by neutral impurities (which can have a fairly large concentration at low temperatures,  $\sim 10^{18}\text{ cm}^{-3}$ , column 5 of Table II) cannot be the dominant mechanism in effect, as the mobility would then increase for samples of lower carrier concentration, contrary to our observations. As stated in Sec. I, our results on this point differ from those of previous workers,<sup>2,3</sup> in which carrier concentrations remain constant at all temperatures and Hall mobility decreases with increase in impurity concentration, consistent with the usual ionized impurity scattering at low temperatures. To explain our results, a different model from the one invoked previously<sup>2,3</sup> must be used, and there is no conflict here in the sense that, since the carrier concentration of our samples at liquid-helium temperatures is several orders of magnitude smaller than any reported previously, a completely different mechanism of electronic conduction and scattering is pos-

sible. In order to account for our concentration dependence, we will consider two possibilities: (a) an explanation in terms of impurity-band conduction; and (b) scattering by centers which, in contrast to ionized or neutral impurities, could exist in higher concentrations in samples with a lower degree of reduction, e.g., dislocation lines. We will consider both these possibilities in greater detail in Sec. IV.

In addition to the measurements mentioned above, we have made optical-absorption measurements in the visible region in order to clarify the mechanisms of conduction and scattering. The absorption coefficient vs wavelength curves of samples ST3 and TS1 at room temperature and at  $2.2^\circ\text{K}$  are shown in Fig. 5. The curves show several broad absorption bands in the visible region (4300, 4700, and possibly at  $5250\text{ \AA}$ ). It is to be noted that Gandy<sup>10</sup> and Baer<sup>11</sup> observed broad absorption peaks at 4300 and  $5200\text{ \AA}$ , respectively, for the reduced samples. The absorption coefficient of the thick sample (TS1) shows a power-law dependence on wavelength, while we could not confirm a power-law dependence for the thin sample (ST3), due probably to complications arising from the absorption bands located around  $5000\text{ \AA}$ . The exponent at low temperatures increases somewhat from that at room temperature: In sample TS1 it increased from 2.5 at room temperature to 2.9 at  $2.2^\circ\text{K}$ . The room-temperature value of 2.5 agrees with that observed by Baer<sup>11</sup> who also observed an absorption peak at  $5200\text{ \AA}$  for a heavily reduced crystal. According to calculations of Visvanathan<sup>12</sup> and Gurevich *et al.*<sup>13</sup> the absorption coefficient for free carriers varies as  $\lambda^{2.5}$  for electron scattering by longitudinal optical phonons, and  $\lambda^{3.0}$  for scattering by ionized impurities, whereas the free-carrier absorption for scattering from acoustical phonons<sup>14</sup> is proportional to  $\lambda^{1.5-2.0}$ . According to the theoretical results of, e.g., Gurevich *et al.*<sup>13</sup> and others,<sup>15</sup> the absorption coefficient  $K_{\text{LO}}$  for scattering by longitudinal optical phonons is given, under the conditions  $\hbar\omega_i \gg kT$  and  $\hbar(\omega - \omega_i) \gg kT$ , by

$$K_{\text{LO}} = \frac{8\pi e^2 \alpha N}{3ncm^* \omega_i} \left( \frac{\lambda}{\lambda_i} \right)^{2.5} \left( 1 - \frac{\lambda}{\lambda_i} \right)^{1/2}, \quad (1)$$

where  $N$  is the free-carrier concentration,  $\alpha$  is the electron-phonon coupling constant,  $m^*$  is the optical effective mass,  $\omega_i$  and  $\lambda_i$  are the frequency and wavelength of LO phonons, respectively,  $c$  is the velocity of light, and  $n$  is the refractive index. Note in Eq. (1) that  $K_{\text{LO}}$  is independent of temperature and that  $\lambda/\lambda_i \ll 1$ . Thus,  $K_{\text{LO}}$  is directly proportional to carrier concentration  $N$  and to  $\lambda^{2.5}$  with all the other parameters held essentially constant. The calculated values for  $K_{\text{LO}}$  using the above equation were found to be too small compared to the ob-

served values.<sup>11,15</sup> Wemple<sup>15</sup> found that the ratio of the observed to the calculated value was about 5 for  $\text{KTaO}_3$ , while Baer<sup>11</sup> found it to be 15 for  $\text{SrTiO}_3$  at room temperature. Using the values<sup>3</sup>  $m = 2m_0$ ,  $\alpha = 3$ ,  $\hbar\omega_i = 0.1$  eV,  $K_{\text{LO}}^{\text{calc}} \approx 2.0$   $\text{cm}^{-1}$ , while  $K_{\text{LO}}^{\text{obs}} = 32.7$  for ST3 at  $0.7$   $\mu$ . Thus we also obtain a discrepancy of a factor of about 16. As noted by Baer,<sup>11</sup> however, the calculation by Feynman *et al.*<sup>15</sup> requires the inclusion in Eq. (1) of a factor of  $(v/w)^3$ , where  $v$  and  $w$  are variational parameters. The  $(v/w)^3$  increases rapidly as  $\alpha$  increases: It is 2.4 for  $\alpha = 3$  and 48 for  $\alpha = 7$ . By inclusion of this factor,  $K_{\text{LO}}^{\text{calc}} \approx 6$ , thus, the discrepancy is now a factor of 5. If the effective mass is larger, then  $\alpha$ , and consequently  $(v/w)^3$ , becomes larger, resulting in a larger value of  $K_{\text{LO}}^{\text{calc}}$  and reducing the discrepancy between the observed and calculated value. Thus, our optical data indicate that at room temperature the dominant scattering is by longitudinal optical modes, agreeing with previous results.<sup>2-4,11</sup> At low temperatures, the picture is not so clear. There seems to be a slight increase in the slope of the absorption vs wavelength curves relative to the value at room temperature. This implies that ionized impurity scattering may play a role in the absorption. As will be discussed in Sec. IV, the contribution to the optical absorption by electrons scattered by ionized impurities increases as the temperature decreases. This may explain the slight increase in absorption coefficient at 2.2°K from its value at 300°K (see Fig. 5). We must stress, however, that the major contribution to the absorption even at low temperatures is still associated with the emission of optical phonons (see the discussion in Sec. IV).

The most striking result of our optical-absorption measurements is that the absorption coefficient does not decrease drastically at low temperatures as may be expected from the Hall data. From our Hall data (Table II) we know that the carrier concentration of ST3 at liquid-helium temperature is only 1.5% of that at room temperature. We therefore expect a small fraction of the room-temperature absorption at liquid-helium temperatures. In fact the absorption coefficient is somewhat larger at 2.2°K than at room temperature. This discrepancy also may be accounted for on the impurity-band model to be discussed in Sec. IV.

#### IV. MODELS

We first consider a model in which electronic transport at low temperature is due to impurity-band conduction.<sup>16</sup> Suppose there are  $N_D$  donor levels at an energy  $E_D$  ( $\sim 0.04$ – $0.08$  eV) below the bottom of the conduction band and low-lying acceptor levels of concentration  $N_A$ . From the optical-absorption measurements (Fig. 5 and Ref. 9) we see the

existence of deep-lying (acceptor) levels at 2.4–2.9 eV below the conduction band. As mentioned earlier, the result of substitution into equations given in Ref. 9 and the smallness of the absorption peaks suggest that  $N_D \gg N_A$ . Thus, at sufficiently low temperatures ( $kT \ll E_D$ ), all the electrons are frozen to the donor and acceptor levels and essentially no conduction electrons exist. The conduction is then due to the motion of electrons at the compensated donor levels through the electronic vacant sites. Positively charged, ionized donor sites (we will call these electron vacancies hereafter) act as apparent carriers and the concentration of this electron vacancy at the donor level is  $N_A$ . Thus, at low temperatures the carrier concentration is small and constant of value  $N_A$ , while at room temperature the carrier concentration is of order  $N_D$  due to thermal excitations into the conduction band from the donor levels.

Even though the apparent carrier is a positively charged electron vacancy, the sign of the Hall coefficient will still be negative since this vacancy always moves opposite to the electron motion, giving the same Hall field as that of an electron. In line with the argument by Mott and Twose<sup>16</sup> it is hard to see how the phases of electrons scattered by a completely disordered lattice match sufficiently well for

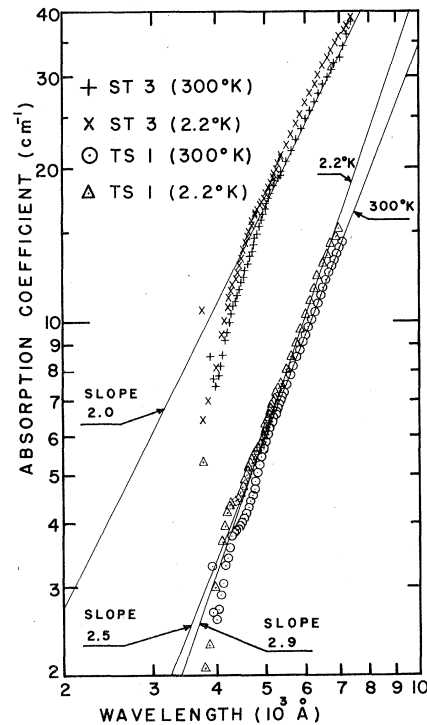


FIG. 5. Log-log plot of absorption coefficient vs wavelength at room temperature and at  $\lambda$  point (2.2°K). Fundamental absorption edge starts at 3875  $\text{\AA}$  (3.2 eV) at room temperature and at 3750  $\text{\AA}$  (3.3 eV) at 2.2°K.

electrons of any energy to show a negative effective mass, a necessary condition for behavior characteristic of a positive hole. Thus, having a negative Hall coefficient does not contradict this model.

Next we consider the resistivity vs  $1/T$  curve (Fig. 1). As the temperature is lowered from room temperature, the resistivity decreases due to the rapid increase in mobility. The deionization (carrier freezing out) effect then sets in causing a rapid increase in resistivity. At a certain temperature at which the contribution to the conductivity by the electrons (or electron vacancies) in the impurity band exceeds that due to the conduction electrons, the resistivity will start to decrease again because the carrier density in the impurity band stays constant, while the electron mobility in the impurity band keeps increasing as the temperature decreases. The mobility increases because the overlap in electronic wave functions at impurity centers increases due to the increase in static dielectric constant with decrease in temperature,<sup>7</sup> resulting in an increase in the width of the impurity band and in a decrease of the effective mass. At sufficiently low temperatures, the mobility and, consequently, the resistivity, becomes constant as the dielectric constant reaches a saturation value<sup>7</sup> (Figs. 1 and 4).

As the impurity concentration decreases (as the degree of reduction is lowered), the overlap of the wave functions becomes smaller. This decreasing overlap reduces the width of the band and increases the effective mass, with an attendant decrease in mobility. This is why the mobilities in the crystals with smaller degree of reduction have smaller values, contrary to previous results.<sup>2,3</sup> The most probable reason that other authors did not observe impurity-band-type conduction in the reduced samples is that with relatively high donor concentrations ( $>10^{17}$  cm<sup>-3</sup>) the overlap in the wave functions becomes so large that the conduction becomes metallic<sup>16</sup> and the impurity band becomes a part of the conduction band. In Nb-doped samples one will never see any impurity-band-type conduction because these donor impurities are of the hydrogenic type and, consequently, form very shallow levels ( $>10^{-4}$  eV).

Next, we consider the temperature dependence of Hall coefficient  $R_H$ . As  $T$  is decreased from room temperature, due to the finite separation of the impurity band from the conduction band (0.04–0.08 eV), the carrier concentration in the conduction band decreases rapidly, causing  $R_H$  to increase rapidly. Impurity-band conduction, then, takes over below a certain temperature and  $R_H$  becomes constant due to the constant carrier concentration in the impurity band (Fig. 2). Now we examine this point in more detail: If we have two kinds of carriers, i. e., one in the conduction band and the other in the impurity band, the Hall coefficient in the limit of low magnetic field will be given by

$$R_H = \frac{n_C \mu_C \mu_C^H + n_I \mu_I \mu_I^H}{e (n_C \mu_C + n_I \mu_I)^2}, \quad (2)$$

where  $n_C$ ,  $\mu_C$ , and  $\mu_C^H$  are the concentration, drift mobility, and Hall mobility of electron in the conduction band, respectively, while  $n_I$ ,  $\mu_I$ , and  $\mu_I^H$  are the corresponding quantities in the impurity band. If total number of carriers in the conduction band and impurity band is independent of temperature, i. e., if  $n_C + n_I = \text{const}$ , then  $R_H$  has a maximum when  $n_C e \mu_C = n_I e \mu_I$ .<sup>16</sup> In other words, a maximum in  $R_H$  will appear at a temperature such that the conduction by carriers in the conduction and impurity band becomes equal. According to our model, on the other hand, a charge carrier in the impurity band is an electron vacancy so that the total number of carriers is no longer constant. Since these electron vacancies are produced both by compensation and by excitation of an electron into the conduction band  $n_I = n_C + N_A$ , where  $N_A$  is the concentration of compensating acceptor levels. In this case,  $R_H$  can still have maximum but only if  $\mu_I^H / \mu_C^H \leq \sqrt{2} - 1$ . At low temperatures ( $<20$  °K) this condition is always met, since  $\mu_C^H \gg \mu_I^H$ . On the other hand, when impurity-band conduction takes over the dominant role at relatively high temperatures ( $\sim 100$  °K) as in our samples,  $\mu_C^H$  is not necessarily much larger than  $\mu_I^H$ . Consequently, the above condition for the existence of a maximum may no longer be met. This explains why our samples do not show any maximum in  $R_H$  vs  $1/T$  curves (Fig. 2). Our computer calculations, taking parameters in Eq. (2) consistent with our experimental data, show that there is no maximum in  $R_H$  for our samples except for those with the lowest impurity concentration (ST1 and ST6).

We next take up the optical-absorption measurements in terms of impurity-band model. As we stated before, the absorption coefficient at 2.2 °K is a factor of 100 too large compared to the value expected from Hall data, assuming that optical absorption is due to free electrons in the conduction band. According to our impurity-band picture, there are essentially no free carriers in the conduction band at low temperatures. Instead, the electron in the impurity band is mobile due to compensation and to large overlap in wave functions at low temperatures. Possible processes of free-carrier absorption are shown in Fig. 6(a): An electron in a low-energy state  $A$  in the conduction band is excited to a virtual state  $B$  by absorbing a photon and then goes to a final excited state  $D$  in the conduction band by the emission or absorption of a phonon. Or alternatively, an electron in state  $A$  interacts with a phonon first and goes to a virtual state  $C$  and then is excited to a final state  $D$  by absorbing a photon. Since the impurity band is very close to the conduction band, we may think of a similar process occurring for an electron in the impurity band that is

excited to a higher state in the conduction band as shown in Fig. 6(b). In drawing this diagram we have assumed that, for a disordered structure like an impurity band, any rigorous application of selection rules for an interband transition is rather arbitrary.

Now let us determine the number of electrons available for optical absorption using the impurity-band model. At room temperature, for per unit volume we have  $N$  free electrons in the conduction band and  $N_D - N - N_A$  electrons in the impurity band, giving the total number of electrons available for optical absorption  $N_D - N_A$ , where  $N_D$  is the impurity concentration at donor levels (impurity band) and  $N_A$  is concentration of compensating acceptor levels. At low temperatures, we have  $N=0$ , but the density of electrons in the impurity band is  $N_D - N_A$ , so that total number of electrons available for the optical absorption remains *unchanged*.

Since  $kT \ll \hbar\omega_i$ , at all temperatures below 300 °K, the contribution to optical absorption by a process of absorption of LO phonons is negligible compared to that by a process of emission of phonons, even at room temperature. Optical absorption with emission of phonons is equally likely at all temperatures, thus the optical-absorption coefficient associated with LO-phonon scattering is expected to be temperature independent in this material at all temperatures below 300 °K. On the other hand, at low temperatures, carrier absorption due to ionized-

impurity scattering may become important. According to Visvanathan,<sup>12</sup> the free-carrier absorption coefficient for the ionized-impurity scattering is given by

$$K_{\text{imp}} = - \frac{8N_i N Z^2 e^6 \lambda^3}{3\pi m^* \hbar c^4 n \epsilon^2 (2\pi m^* kT)^{1/2}}, \quad \hbar\omega \gg kT \quad (3)$$

where  $\hbar\omega$  is the absorbed photon energy,  $\lambda$  is the wavelength of the photon,  $N_i$  is the concentration of ionized impurities,  $N$  is the concentration of free carriers,  $Ze$  is the charge of an impurity ion, and  $\epsilon$  is the dielectric constant. In the process of optical absorption, the movement of the electrons in the electromagnetic field of visible light is so rapid that only the electronic contribution to the dielectric response is involved in interactions between the electrons and the ionized impurities. We should therefore use the optical value for the dielectric constant rather than the static value in this specific case. Then  $\epsilon$  is independent of temperature  $T$ , and  $K_{\text{imp}}$  becomes proportional to  $T^{-1/2}$ . Thus, at sufficiently low temperatures, the free-carrier absorption by ionized-impurity scattering can be significant. The contribution of impurity scattering to the absorption should be added to that of optical-phonon scattering. Thus the total absorption can be larger at low temperatures than that at room temperature. As a numerical example, for  $m = 2m_0$ ,  $\epsilon = 5$ , and  $T = 2.2$  °K, substitution of the experimental data for ST3 in Eq. (3) gives  $K_{\text{imp}}^{\text{calc}} = 1.4 \times 10^{-2} \text{ cm}^{-1}$  for a singly ionized impurity and  $5.6 \times 10^{-2} \text{ cm}^{-1}$  for a doubly ionized impurity. In any case  $K_{\text{imp}}^{\text{calc}}$  is much smaller ( $\sim 1\%$ ) than  $K_{\text{LO}}^{\text{calc}}$ , thus, we expect but small change in absorption coefficient at low temperatures. The Hall data at low temperatures gives small values for the carrier concentration because the Hall coefficient is a measure of the number of *vacant electron sites* in the impurity levels, such vacancies appearing as charge carriers (just like holes in a valence band). The absorption coefficient, on the other hand, gives a measure of available electron concentration rather than the concentration of electron vacancies. It is in these terms, that of an impurity-band model, that both the transport and optical data may be understood.

Now let us turn to the model b in which additional scattering centers such as dislocations are presumed to control the mobility at low temperatures. Paladino *et al.*<sup>17</sup> and Rhodes *et al.*<sup>18</sup> found a strong dependence of the ionic diffusion in SrTiO<sub>3</sub> on the dislocation density. According to these authors the dislocation density ranges from  $3.0 \times 10^5 \text{ cm}^{-2}$  for well annealed crystals to  $2.9 \times 10^7 \text{ cm}^{-2}$  for highly strained (12.4%) crystals. Unannealed crystals have a dislocation density of around  $10^6 \text{ cm}^{-2}$ . If we have a high enough dislocation density, we can account for the concentration dependence of the mobility: For crystals with smaller degree of reduction,

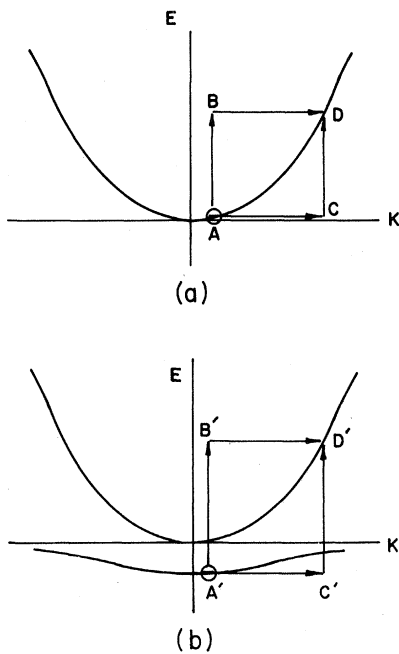


FIG. 6. (a) Processes of free-carrier absorption for electrons in the conduction band. (b) Similar processes for electrons in an impurity band.



we expect a higher dislocation density due to smaller annealing during the reduction process, giving a smaller value of mobility. But the dislocation density even in an unannealed crystal is too low ( $10^6 \text{ cm}^{-2}$ ) to give enough scattering: According to the calculations by Dexter and Seitz,<sup>19</sup> the contribution to scattering by the strain field of dislocations is negligible for a density up to  $10^8 \text{ cm}^{-2}$ . The theoretical treatment by Read,<sup>20</sup> in which dislocations act as acceptor centers forming a negative line charge surrounded by a positive space charge, gives a somewhat larger contribution to the scattering. In this case, dislocation densities up to  $10^6 \text{ cm}^{-2}$  would give no significant contribution to the scattering, even at low temperatures. Some measurements on Ge show no indication of scattering by dislocations at low temperatures with densities up to  $10^6 \text{ cm}^{-2}$ . Paladino *et al.*<sup>17</sup> found that annealing at  $1800^\circ\text{C}$  in air for 6 h reduced the dislocation density only by a factor of 2 from that of an unannealed crystal (from  $1.4 \times 10^6$  to  $6.6 \times 10^5 \text{ cm}^{-2}$ ). Since the crystals in the present work were reduced for an hour at temperatures below  $900^\circ\text{C}$ , we expect but small differences in the dislocation density among the

samples. Thus one cannot explain the present results which show that mobilities at liquid-helium temperature differ by a factor of more than 100 from the crystals with heaviest reduction (ST3) to the one with lightest reduction (ST6). The result of optical-absorption measurements is also against this model. The fact that the absorption coefficient is nearly proportional to  $\lambda^3$  at low temperatures leads to the conclusion that ionized-impurity scattering is likely to be more important than the scattering by dislocation at low temperatures. In view of these facts it is hard to believe that dislocations are the major scattering centers at low temperatures.

Our conclusion is that the impurity-band model used in the analysis of our results gives a satisfactory explanation for a diversity of transport and optical data in lightly reduced strontium titanate crystals.

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