

## Polaron Absorption Peak of Semiconducting SrTiO<sub>3</sub>

Yoon, Byung Gook

Department of Physics

(Received December 30, 1981)

### <Abstract>

Infrared(IR) absorption data of semiconducting SrTiO<sub>3</sub> published elsewhere<sup>1)</sup> are fitted with the small polaron theory. The agreement of the theory with experiment is excellent considering the fact that there is much error in IR experiment itself. So it is concluded that the 4.5 μm absorption peak of SrTiO<sub>3</sub> is mainly due to the small polaron absorption. Also the recent data at lower temperature are discussed, which were obtained by private communication.<sup>2)</sup>

### SrTiO<sub>3</sub> 반도체의 polaron 흡수 곡선

윤 병 국

물 리 학 과

(1981. 12. 30 접수)

### <요 약>

small polaron 이론을 SrTiO<sub>3</sub> 반도체의 적외선 영역 광흡수 계수의 알려진 실험 결과에 적용했다. 이론치와 실험치가 잘 일치했으므로 4.5μm 가 극대치인 흡수계수의 곡선은 주로 small polaron 에 의한 것이라고 결론지었다. 또한 최근에 입수한 저온 실험 결과에 대해서도 논의하였다.

### 1. Introduction

The infrared(IR) absorption peak at 4.5μm of semiconducting SrTiO<sub>3</sub> was first observed by Baer<sup>3)</sup>. He observed the edge of the peak for one sample and tried to explain the data with large polaron theory. Although the large polaron theory could give some qualitative explanation, the theoretical values of the absorption coefficient  $K$  were an order of magnitude lower than the experimental ones. After a year, Reik fitted Baer's data with his small polaron theory with some adjustable parameters<sup>4)</sup>.

In 1975, more extensive work on IR absorp-

tion of SrTiO<sub>3</sub> was carried out by C. Lee et. al.<sup>1)</sup> They observed the broad 4.5μm peak for almost all samples at room temperature. They also suggested the difficulty in applying large polaron theory, although dc conductivity and mobility data cannot be explained by the small polaron theory as well.

On the other hand, Engles proposed that carriers in SrTiO<sub>3</sub> might be a mixture of the small polarons and large polarons at room temperature, in order to explain the transport and IR data. If he were right, some wavelength region of the IR absorption data might be explained by the small polaron theory.<sup>5)</sup>

In this work the data of C. Lee et. al. for the wavelength near the 4.5μm peak are fitted

with the small polaron theory, which suggests that IR absorption near  $4.5\mu\text{m}$  might be due to the small polaron. Also more recent low temperature data of Brebner et. al. are discussed in this prospect.<sup>2)</sup> At first the result of Reik's small polaron theory is briefly described, and then the IR data are compared with the theory by simple numerical calculation.

## II. Result of Small Polaron Theory<sup>4), 6)</sup>

The small polaron theory begins with the Holstein Hamiltonian,

$$H = H_c + H_{ph} + H_{c-ph}$$

where  $H_c$  is the electronic energy,

$$H_c = \sum_s (\epsilon_s - \mu) C_s^\dagger C_s + \sum_{s,t} t_{s,t} (C_s^\dagger C_{s+t} - C_{s+t}^\dagger C_s)$$

$H_{ph}$  is the phonon energy,

$$H_{ph} = \sum_{q,\lambda} \hbar\omega_\lambda(q) b_{q,\lambda}^\dagger b_{q,\lambda}$$

and  $H_{c-ph}$  is the electron-phonon interaction,

$$H_{c-ph} = \sum_{q,\lambda,s} \hbar\omega_\lambda(q) \alpha_\lambda^{\frac{1}{2}}(q) i (b_{q,\lambda} e^{i\mathbf{r}_s} - b_{q,\lambda}^\dagger e^{-i\mathbf{r}_s}) \cdot C_s^\dagger C_s$$

In this Hamiltonian,  $s$  and  $t$  are indices of sites,  $t$  is the electronic resonance integral,  $\alpha$  is the coupling constant,

$$\alpha = \frac{A^2}{2\bar{\rho}V\hbar\omega_\lambda^2\sigma_\rho(q)} \text{ for } LO \text{ mode,}$$

( $A$ : deformation potential constant)

and all others are due to the convention.

We change this Hamiltonian by standard canonical transformation so that the polaron and the displaced phonon become the quasi-electron and excitation. Then we obtain the current correlation function and we get the frequency dependent conductivity  $\sigma(\omega, T)$  by the Kubo integration method.

Reik's result is that the absorption coefficient due to the hopping small polaron for the simple cubic lattice at not too low temperature becomes,

$$K(\omega, T) = \frac{Re\sigma_h(\omega, T)}{n_0 c \epsilon_0}$$

where  $Re\sigma_h(\omega, T)$  is real part of the hopping conductivity,

$$\begin{aligned} \sigma_h(\omega, T) &= \sigma(0, T) \frac{\sinh(\hbar\omega/2kT)}{\hbar\omega/2kT} \\ &\quad \frac{e^{-w^2-2r(w)}}{[1+(2ww_0\tau^2)^2]^{1/4}} \\ \sigma(0, T) &= \frac{2n_c e^2 \tau^2 z a^2 \pi^{\frac{1}{2}} \tau}{\hbar^2 kT} e^{-\eta t \tanh(\hbar\omega_c/4kT)} \\ r(w) &= \frac{1}{ww_0\tau^2} \ln\{2ww_0\tau^2 + [1+(2ww_0\tau^2)^2]^{\frac{1}{2}}\} \\ &\quad - \frac{1}{2(ww_0\tau^2)^2} \{[1+(2ww_0\tau^2)^2]^{\frac{1}{2}} - 1\} \\ \frac{1}{\tau^2} &= \frac{2\eta_0 w_0^2}{\sinh(\hbar\omega_0/2kT)} \end{aligned}$$

$w_0$ ; average phonon frequency

$\eta$ ; average phonon number

$$= \frac{W_H}{\frac{1}{4}\hbar\omega_0} \quad W_H; \text{ hopping energy}^{7)}$$

$J$ ; constant resonance integral for simple cubic lattice

$z$ ; coordination number

$a$ ; distance between nearest neighbors

$n_c$ ; number of carriers

## III. Calculation and Discussion

We calculated by simple numerical work the absorption coefficients of  $\text{SrTiO}_3$  using the parameters of Reik<sup>4)</sup>,

$$w_0 = 1.34 \times 10^{14} \text{ sec}^{-1}$$

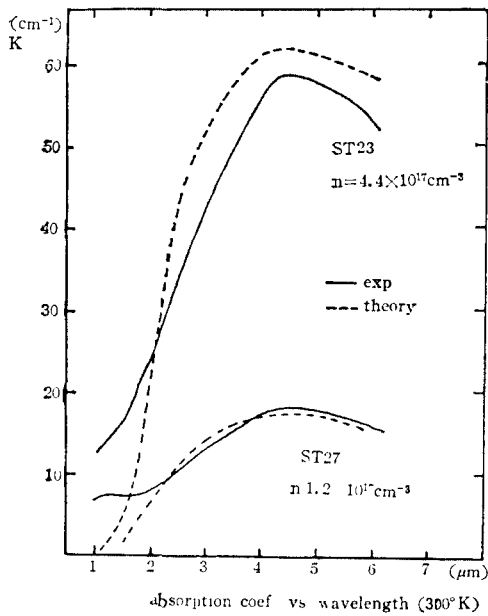
$$\tau = 2.8 \times 10^{-16} \text{ sec}$$

$$\eta = 5.1$$

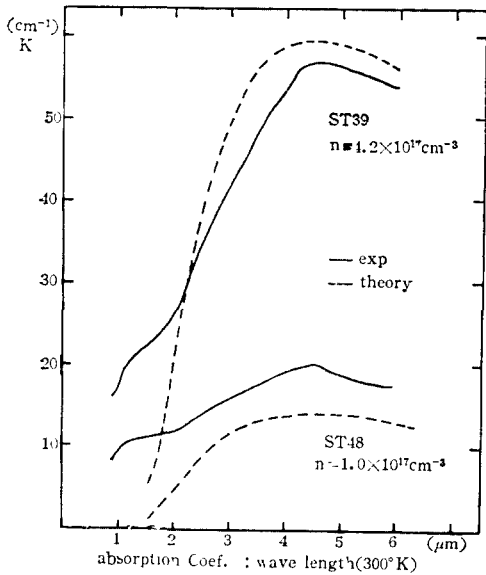
$$\mu_h = 3.3 \text{ cm}^2/V \text{ sec}$$

where  $\mu_h$  is the hopping mobility of the polaron. It was found that  $\eta=5.1$  yields the peak position at  $4.5\mu\text{m}$  compared with the original parameter  $\eta=5.3$  of Reik that gives the maximum at  $4.2\mu\text{m}$ . Most of the samples have peak at  $4.5\mu\text{m}$  and  $\eta=5.1$  was accepted.

With carrier concentrations of the samples in the literature<sup>1)</sup>, we could see in Fig.1&2 that the theory agrees with experiment fairly well for the wavelength  $\lambda > 2\mu\text{m}$ . The disagreement at shorter wavelength region may be due to the absorption by the carriers in band



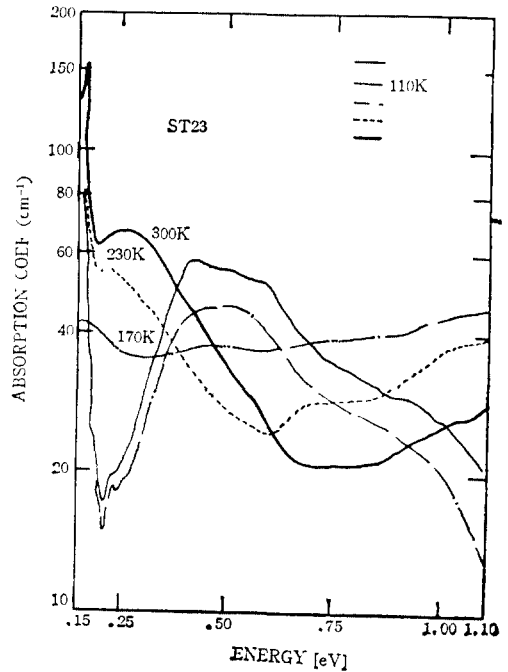
**Fig. 1 Comparison of the Small Polaron Theory with the Data of C. Lee et. al.**



**Fig. 2 Comparison of the Small Polaron Theory with the Data of C. Lee et. al.**

motion. Thus we concluded that the IR absorption peak at  $4.5\mu\text{m}$  is mainly due to the small polaron absorption.

Next we considered the lower temperature



**Fig. 3 Low Temperature Data of Brebner et. al.**

data of Brebner et. al. obtained by private communication which is shown in Fig.3. We could see that the maximum point moves to a longer wavelength region (*i.e.* to a higher photon energy region) as the measuring temperature becomes lower.

Small polaron formation is possible when the hopping energy  $W_H$  is large *i.e.* the average phonon number  $\left(\frac{W_H}{\frac{1}{4}\hbar\omega_0}\right)$  is large so that the strong phonon coupling is possible. In this case the polaron can be thought as an electron coupled with some number of average phonons. The hopping energy is given as<sup>7)</sup>,

$$W_H = 1/2 \frac{e^2}{k_p r_p}$$

where  $k_p$  is the effective polaronic dielectric constant

$$\frac{1}{k_p} = \frac{1}{k_c} - \frac{1}{k_{static}}$$

and  $r_p$  is the radius of polaron. It is well known that the static dielectric constant of  $\text{SrTiO}_3$  becomes larger at lower temperature.

So  $k_p$  may also become larger at lower temperature and we have smaller hopping energy, hence smaller average phonon number. At some lower temperature the small polaron formation

may be forbidden and the average phonon concept cannot be used. Indeed below 110K there appeared no corresponding peak except the phonon structures. The motion of the peak position with temperature is supposed to be mainly due to the change in  $\eta$ .

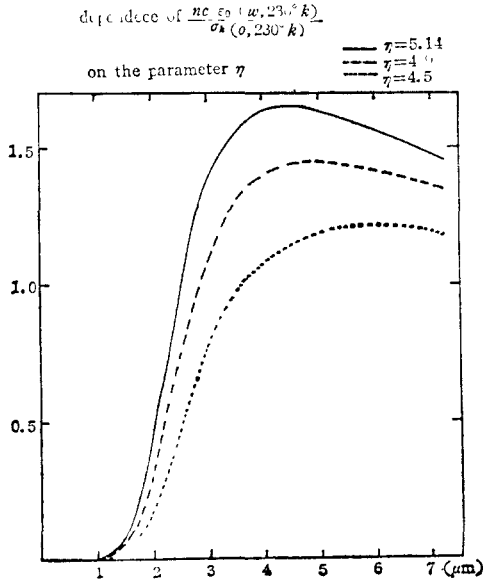
We calculated the absorption coefficient at several smaller  $\eta$  values and this is shown in Fig.4. We fitted the data at 230K with  $\eta=4.5$  and in Fig.5, we could see a good agreement with the data. During the calculation average phonon frequency was kept constant and the temperature dependence of other parameters was considered.

**IV. Conclusion and Acknowledgement**

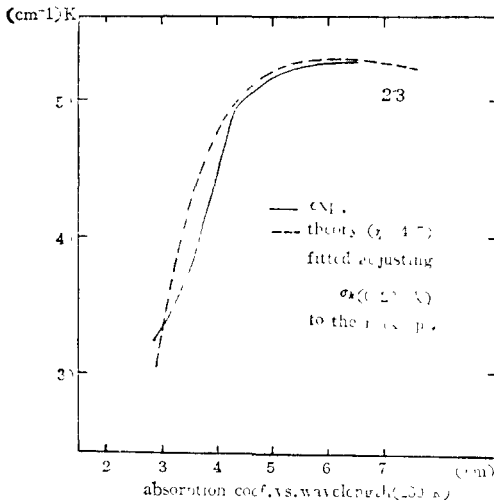
It has been concluded that the 4.5 $\mu$ m IR absorption peak at room temperature of the semiconducting SrTiO<sub>3</sub> is mainly due to the small polaron. It may be said that at higher temperature the peak moves to a longer wavelength and such an experiment is suggested. The author expresses deep gratitude to Prof. Brebner who sent the data before publication.

**References**

1. C. Lee, J. Destry and J.L. Brebner, Phys. Rev. **B11**, 2299(1975)
2. Brebner (1979), private communication.
3. W.S. Baer, Phys. Rev. **144**, 734 (1966).
4. H.G. Reik, Z. Physik, **203**, 346(1967).
5. D.M. Eagles, Phys. Rev. **145**, 645(1966).
6. H.G. Reik, in "Polarons in Ionic Crystals and Polar Semiconductors" ed. by Devereese, p.679, North Holland, Amsterdam, (1971).
7. N.F. Mott and E.A. Davis, "Electronic Processes in Non-Crystalline Materials" 2nd ed., p81, Clarendon Press, Oxford(1979).



**Fig.4 Dependence of the Absorption Coefficient on the Parameter  $\eta$**



**Fig.5 Comparison of the Theory with an Absorption Line of Fig.3**