

## RAMAN SCATTERING FROM CONDUCTION ELECTRONS IN $\text{KTaO}_3$

Hiromoto Uwe,\* Kunihiro Oka, Hiromi Unoki and Tunetaro Sakudo\*

Electrotechnical Laboratory  
Sakura, Ibaraki 305, Japan

\*Institute of Applied Physics  
University of Tsukuba  
Sakura, Ibaraki 305, Japan

Raman spectra of the semiconducting  $\text{KTaO}_3$  are found to show, in addition to the phonon spectra of the non-doped  $\text{KTaO}_3$ , the following new features; (a) a line with temperature-dependent frequency in the region below  $60 \text{ cm}^{-1}$ , and (b) a broad line centered around  $3200 \text{ cm}^{-1}$ . The line (a) is ascribed to the lowest-frequency plasmon-LO phonon coupled-mode. The line (b) may possibly be due to an interband Raman-transition of the electrons, which are excited from the bottom of the zone-center warped bands to the spin-orbit split-off band.

### I. Introduction

$\text{KTaO}_3$ , an ideal cubic perovskite-type crystal, has a Raman-inactive ferroelectric soft phonon whose frequency decreases with lowering temperature from  $70 \text{ cm}^{-1}$  at 200 K to c. a.  $20 \text{ cm}^{-1}$  at 4.2 K [1]. By introducing appropriate impurities,  $\text{KTaO}_3$  is known to become the n-type degenerate semiconductor. Shubnikov-de Haas experiments were recently done for the purpose of investigating the structure of the conduction band [2,3]. We will report here experiments of Raman scattering due to the soft plasmon-LO phonon coupled-mode as well as an electronic Raman scattering which was found in the high-frequency Raman-shift-region. We used an Ar-ion laser as the excitation source, since the blue-coloured semiconducting crystal is transparent at wave-lengths of 4880 or 5145 Å.

### II. Soft Plasmon-Phonon coupled-Mode

We have found a soft coupled-mode of the plasmon and the LO phonon in semiconducting  $\text{KTaO}_3$  in the low frequency region of Raman spectra. Figure (1) shows temperature variation of Raman profile of the sample A ( $n=1.0 \times 10^{19} \text{ cm}^{-3}$ ) and sample B ( $n=1.0 \times 10^{18} \text{ cm}^{-3}$ ). The Raman shift of the low-concentration sample is found to be smaller than that of the high concentration one. With lowering temperature the Raman shift decreases and the line-width sharpens. These characteristics strongly indicate that the observed Raman-line is due to the lowest frequency plasmon-LO phonon coupled-mode; the coupled mode is Raman-active due to the density fluctuation of the conduction electrons and the Raman frequency takes the position just below that of the TO phonon whence to exhibit similar temperature variation of the ferroelectric mode.

The Raman spectra in Fig.(1) could be decomposed by the least-square-fit method into the scattering of the damped harmonic oscillator and the background one. Figures (2) and (3) show respectively the undamped frequency thus obtained and damping rate corresponding to the full-half-width. Temperature dependence of the undamped frequency is found to be more gradual than that of the ferroelectric mode in the pure crystals. The damping rate at the temperature of 20 K corresponds well to the collision rate of the conduction electron obtained from the mobility value ( $10^4 \text{ cm}^2/\text{Vs}$ ), and the temperature dependence follows approximately  $T^3$  law for the sample A.

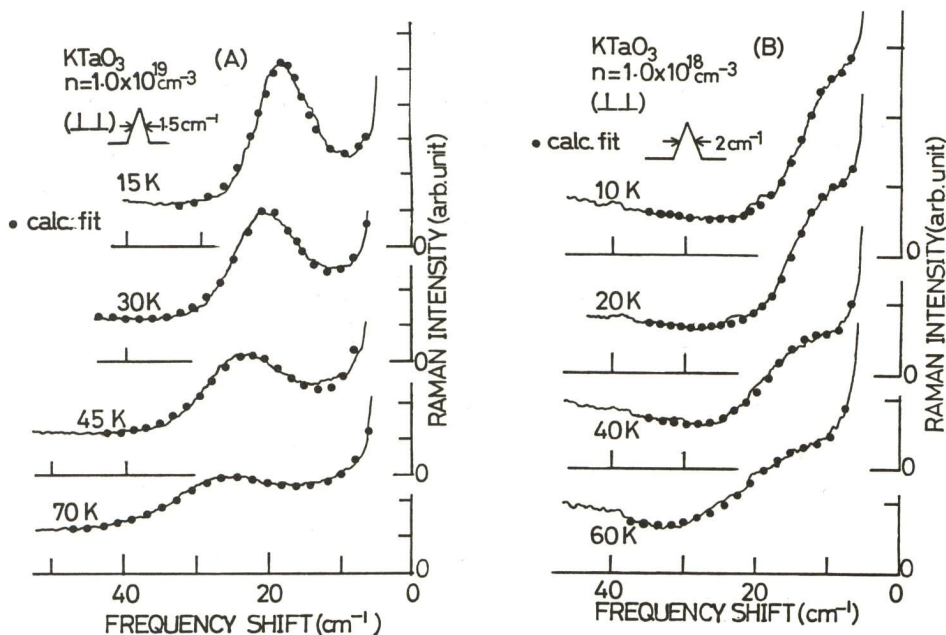


Fig. 1 Temperature variations of Raman spectra of the soft plasmon-LO phonon coupled mode for the samples of the conduction-electron concentration (A)  $n = 1.0 \times 10^{19} \text{ cm}^{-3}$  and (B)  $n = 1.0 \times 10^{18} \text{ cm}^{-3}$

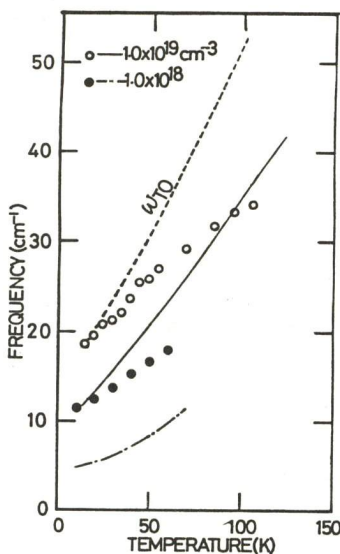


Fig. 2 Temperature variations of the undamped frequencies of the soft plasmon-LO phonon coupled-mode: Solid and chain curves are theoretical ones for the samples of  $n = 1.0 \times 10^{19} \text{ cm}^{-3}$  and  $1.0 \times 10^{18} \text{ cm}^{-3}$ , respectively. A dotted curve shows the frequencies of the soft TO phonon in the non-doped crystal [1].

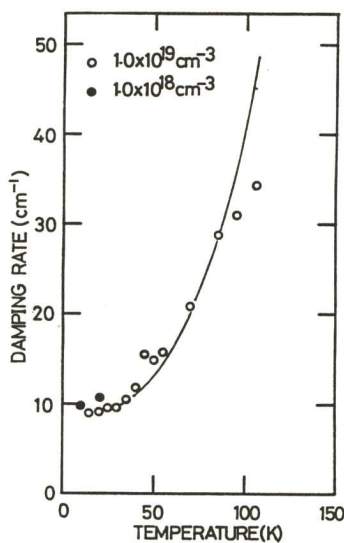


Fig. 3 Temperature variation of the damping rate of the soft plasmon-LO phonon coupled-mode: The solid line is due to  $T^3$  law for the sample of  $n = 1.0 \times 10^{19} \text{ cm}^{-3}$ .

### III. Broad Raman-Line in High-Frequency Region

In the high frequency region of Raman shift, we found a broad Raman-peak centered around  $3200 \text{ cm}^{-1}$ . The position was irrespective of the kind of impurities (Sr or Ca) and the intensity was proportional to the concentration of the conduction electrons; the line was absent in the non-doped crystal. Figure (4) shows change of the scattering profile of the sample A as a function of temperature. These spectra are normalized on assuming the intensity of the 2 LO scattering around  $1800 \text{ cm}^{-1}$  to be constant in the measured temperature range; furthermore, the spectra are corrected for the spectral sensitivity of the detecting system over the wide frequency range and also for the Drude-absorption of the red-shifted scattering. We find that, with lowering temperature, the peak intensity grows whereas the line width decreases, the integrated intensity being constant or larger in the low temperatures. This scattering is evidently due to the electronic Raman effect, not to the phonon one, because the frequency is so high when compared with that of the highest second-order Raman scattering around  $1800 \text{ cm}^{-1}$ . The origin of the scattering will be discussed in the following section.

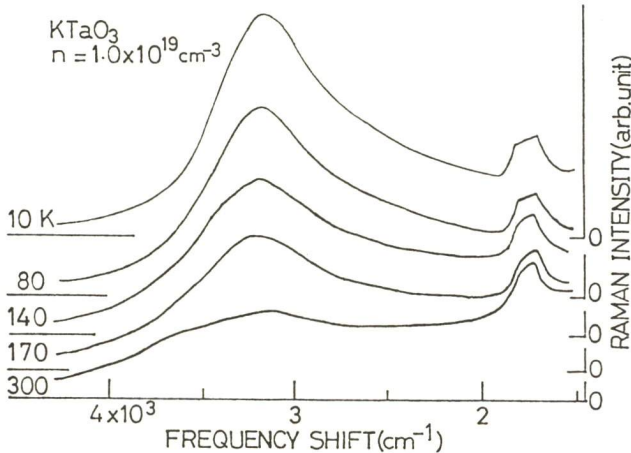


Fig. 4 Temperature variation of the electronic Raman scattering in a region of high-frequency shift for the sample of  $n=1.0 \times 10^{19} \text{ cm}^{-3}$

### IV. Discussion

The frequency of the plasmon-LO phonon coupled-mode is determined from the zeros of the following dielectric response function in the long wave-length limit;

$$\epsilon = \epsilon_{\infty} \prod_{i=1}^4 \frac{\omega^2 - \omega_{ti}^2}{\omega^2 - \omega_{li}^2} - \epsilon_{\infty} \frac{\omega_p^2}{\omega^2}, \quad (1)$$

where  $\epsilon_{\infty}$  ( $=4.62$ ) is the optical dielectric constant,  $\omega_{ti}$  and  $\omega_{li}$  are the frequencies of the  $i$ -th LO and TO phonon, respectively ( $\omega_{t1}=196$ ,  $\omega_{t2}=274$ ,  $\omega_{t3}=547$ ,  $\omega_{t4}=183$ ,  $\omega_{l1}=274$ ,  $\omega_{l2}=421$ ,  $\omega_{l3}=837$  in  $\text{cm}^{-1}$  and  $\omega_{t1}$  is the temperature dependent frequency of the soft ferroelectric mode shown in Fig. (2)). Since the effective-mass is known experimentally [2,3], plasmon frequency can respectively be estimated as  $\omega_p^A=537 \text{ cm}^{-1}$  and  $\omega_p^B=170 \text{ cm}^{-1}$  for the samples A and B and rather irrespective of the  $p$ -conduction-band model. The lowest frequencies thus obtained are shown in Fig.(2), which indicates that there exists considerable discrepancy between the theory and experiment for both of the samples A and B. This analysis is based on the assumption that the soft TO frequency in the semiconducting crystals takes the same value as in the non-doped crystal; however, the conduction electron may affect the soft TO phonon [4]. For further analysis of the data, we need the experimental value of the soft TO frequency in the semiconducting crystal.



Next, we discuss about the high-frequency Raman-line presented in Sec.III. The central frequency of the spectral line ( $3200\text{ cm}^{-1}$ ) corresponds well to the energy separation  $\Delta$  between the spin-orbit split-off band and the conduction one at  $\Gamma$  point in the Brillouin-zone ( $\Delta=3800\text{ cm}^{-1}$ ; Mattheiss's value by the method of interpolation [5]). Thus, on the basis of the zone-center warped-band model, the observed line may possibly be ascribed to the interband electronic Raman-transition between them. The line shape of the broad Raman-line is lorentzian-type rather than gaussian-one; the line-width corresponds to the lifetime of the electron in the final state in the scattering process: The estimated lifetime is, for example,  $5.3 \times 10^{-14}$  sec at 10 K and  $2.4 \times 10^{-14}$  sec at 300 K.

#### References

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