

RESEARCH ARTICLE | SEPTEMBER 01 1967

## Temperature Dependence of the Raman Spectrum of $\text{SrTiO}_3$ and $\text{KTaO}_3$

C. H. Perry; Jeanne H. Fertel; T. F. McNelly



*J. Chem. Phys.* 47, 1619–1625 (1967)

<https://doi.org/10.1063/1.1712142>



### Articles You May Be Interested In

Molecular beam epitaxy of  $\text{KTaO}_3$

*J. Vac. Sci. Technol. A* (February 2023)

Superconductivity at epitaxial  $\text{LaTiO}_3$ – $\text{KTaO}_3$  interfaces

*APL Mater.* (June 2023)

Electronic band structure of superconducting  $\text{KTaO}_3$  (111) interfaces

*APL Mater.* (December 2023)



Nanotechnology &  
Materials Science



Optics &  
Photonics



Impedance  
Analysis



Scanning Probe  
Microscopy



Sensors



Failure Analysis &  
Semiconductors



Unlock the Full Spectrum.  
From DC to 8.5 GHz.

Your Application. Measured.

[Find out more](#)



due to its proximity to  $B_{1g}$  and  $A_g$  states. A unique feature of two-photon absorption, as demonstrated by these two molecules, is the polarization dependence of the absorption cross section. This is true even for a system of randomly oriented molecules.

## VI. SUMMARY

In this paper we have developed a theoretical framework which can be applied to two-photon absorption in aromatic molecules. We have applied this treatment to the absorption of two ruby laser photons by anthracene and 9,10-dichloroanthracene. The theory is developed subject to the following assumptions:

- (1) Only electric dipole transitions are considered.
- (2) Only in-plane transitions are included. The out of plane transitions are much weaker and are at much higher energies than the lower  $\pi\pi^*$  states.
- (3) For the application to anthracene and 9,10-dichloroanthracene it is assumed that there is only one electronic state, the  $B_{2u}$  state, at twice the energy of a ruby photon.

With these limitations in mind we have:

- (1) Extended the theory of two-photon absorption to include the vibronic mixing between different electronic states.

(2) Derived expressions which relate the possible transition pathways to the following experimental quantities. First, the relative absorption cross sections of linearly versus circularly polarized exciting light and second, the polarization on the fluorescence resulting from two-photon excitation by linearly polarized light.

(3) Determined for anthracene and 9,10-dichloroanthracene the relative contributions of the three possible pathways:

- (a) both photons absorbed along the long axis,
- (b) both photons absorbed along the short axis,
- (c) one photon absorbed along the short axis and the other photon absorbed along the long axis.

(4) Determined for anthracene and 9,10-dichloroanthracene the relative contributions of the possible final vibronic states (one containing a  $b_{2u}$  vibration and the other a  $b_{3u}$  vibration) to the absorption of two ruby photons.

## ACKNOWLEDGMENTS

The authors wish to thank Professor Joshua Jortner of the Tel-Aviv University and Professor Albert Gold and Professor John Hernandez of the University of Rochester for sending preprints of their respective papers prior to publication. The authors also wish to thank Mr. Fred Rodgers for technical assistance.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 47, NUMBER 5 1 SEPTEMBER 1967

## Temperature Dependence of the Raman Spectrum of $\text{SrTiO}_3$ and $\text{KTaO}_3$ \*

C. H. PERRY, JEANNE H. FERTEL AND T. F. MCNELLY†

*Spectroscopy Laboratory‡ and Research Laboratory of Electronics,§ Massachusetts Institute of Technology, Cambridge, Massachusetts*  
(Received 3 May 1967)

The temperature dependence of the second-order Raman spectrum of  $\text{SrTiO}_3$  and  $\text{KTaO}_3$  has been observed over the temperature range 4°–473°K using the mercury 4358-Å exciting line. From group-theoretical arguments for cubic perovskite lattices the spectra have been interpreted in terms of phonon pairs at critical points in the Brillouin zone using the experimental and theoretical dispersion curves determined by Cowley for  $\text{SrTiO}_3$ . Limited neutron data are available for  $\text{KTaO}_3$ , but the spectrum has been interpreted by analogy with the results for  $\text{SrTiO}_3$ . The energies of the phonon branches at the critical  $X$  point in the Brillouin zone have been deduced from the observed Raman spectra.

## INTRODUCTION

The Raman spectrum of single crystals of  $\text{SrTiO}_3$  and  $\text{KTaO}_3$  has been observed from 30–1200- $\text{cm}^{-1}$  frequency shift from the 22 938  $\text{cm}^{-1}$  mercury “e” line over the temperature range 4°–473°K. The temperature dependence of the Raman spectrum of ferroelectric  $\text{BaTiO}_3$  has been measured previously and for this

material the bands were primarily interpreted as a first-order spectrum.<sup>1</sup> The room-temperature Raman spectrum of  $\text{SrTiO}_3$  has been previously reported by Narayanan and Vadam<sup>2</sup> and their experimental results are in qualitative agreement with our measurements. Both  $\text{SrTiO}_3$  and  $\text{KTaO}_3$  are paraelectric cubic crystals at room temperature and apart from a slight structural change in  $\text{SrTiO}_3$  at 110°K<sup>3</sup> and a possible phase transition in  $\text{KTaO}_3$  at about 10°K,<sup>4</sup> no observation

\* This work is supported in part by the U.S. Air Force Cambridge Research Laboratories under Contract AF19(628)-6066.

† Present address: Department of Physics, Cornell University, Ithaca, N. Y.

‡ The work of this laboratory is supported in part by the National Science Foundation, Grant No. GP-4923.

§ This work is supported in part by the Joint Services Electronics Program under Contract No. DA36-039-AMC-03200(E).

<sup>1</sup> C. H. Perry and D. B. Hall, *Phys. Rev. Letters* **15**, 700 (1965).

<sup>2</sup> P. S. Narayanan and K. Vadam, *Z. Physik* **163**, 158 (1961).

<sup>3</sup> L. Rimai and G. A. deMars, *Phys. Rev.* **123**, 702 (1962).

<sup>4</sup> G. Shirane, R. Nathans, and V. J. Minkiewicz (private communication).

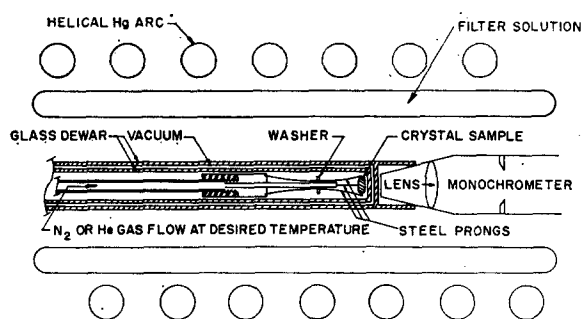


FIG. 1. The gas-flow cell used for both high- and low-temperature Raman measurements.

of the onset of ferroelectricity has been observed above a few degrees Kelvin. The crystals are seen to obey a Curie-Weiss-law behavior above 70°K and have extrapolated Curie temperatures of 35° and 3°K, respectively.<sup>5-7</sup> Recent theories of ferroelectricity in perovskite crystals<sup>8-10</sup> have been confirmed experimentally for both these materials.<sup>4,11-13</sup>

The known cubic symmetry implies that for long-wavelength vibrations there are three first-order infrared-active modes, one infrared- and Raman-inactive mode, and the zero-frequency translational modes. The temperature-dependent Raman spectra observed in this work have been interpreted primarily as second order and arise from combinations, overtones, and differences of phonon frequencies at critical points in the Brillouin zone. For SrTiO<sub>3</sub> the interpretation of the structure in the Raman spectrum was accomplished by using Cowley's results for the phonon dispersion curves determined both by means of neutron spectroscopy and theoretically.<sup>14</sup> For KTaO<sub>3</sub> the assignment of the phonon frequencies was obtained by analogy with the results for SrTiO<sub>3</sub> and the limited inelastic scattering data of Shirane *et al.*<sup>4</sup>

### EXPERIMENTAL

A Cary 81 spectrophotometer using the conventional 4358-Å mercury *e* line (22 938 cm<sup>-1</sup>) was used for excitation in all cases. The Raman spectra were observed in the Stokes region only. No polarization measurements were taken, and the crystals were randomly oriented. The wavelength dependence of the background radiation was due only to Rayleigh scattering and no intensity variations attributable to fluorescence were observed.

The KTaO<sub>3</sub> samples were top-seeded solution-grown materials and three separate crystals were investigated ranging in size from a 5 mm×5 mm×5 mm highly polished cube (used initially for Brillouin scattering investigations<sup>15</sup>), a 3 mm×3 mm×8 mm unpolished crystal to a 3 mm×10 mm×12 mm sample highly polished on the 12 mm×10 mm sides for the far-infrared measurements of the ferroelectric "soft" mode.<sup>13</sup> All three samples gave identical spectra and appeared to be independent of the surface polish.

Two of the SrTiO<sub>3</sub> samples investigated were flame-fusion grown and were almost colorless. One crystal was 15 mm long and frustum shaped with polished ends having diameters 5 and 9 mm. The other crystal was about 7 mm×5 mm×3 mm and highly polished on the flat sides. (Sample cut from the one used for far-infrared reflectance measurements.<sup>16</sup>) These two crystals gave identical spectra. The third sample was a solution-grown crystal and was considerably discolored due to impurities. No Raman spectrum could be observed with this crystal at any temperature. The flame-fusion crystals on the other hand were considerably strained and this factor could possibly contribute to the Raman spectrum. However, the solution-grown materials had a high absorption coefficient in the region of the exciting line due to the impurities and this was probably the factor that contributed to the nonappearance of a Raman spectrum. Investigation of this crystal with a different exciting line where the absorption coefficient is considerably reduced (for example, 6328-Å He/Ne) would be a useful comparison.

As mentioned previously, the spectra appeared to be identical as far as the relative intensities of the features of the spectra were concerned for the several different crystals and random orientations investigated. No drastic changes in the spectrum were observed below the phase transition in SrTiO<sub>3</sub> at 110°K. In this phase some difference in the spectrum might be expected if the change from cubic symmetry would be sufficient to possibly split degeneracies or allow new lines. However, no marked change in the spectrum was observed within the experimental error of measurement apart from the possibility of one additional band below 100 cm<sup>-1</sup>.

A double-walled glass vacuum jacket was used for both cooled and heated measurements. The Raman spectra above room temperature were obtained by using preheated nitrogen gas that was caused to flow through a transfer tube and around the sample (see Fig. 1). A calibrated copper-constantan thermocouple was attached to the sample. The temperature was maintained by monitoring the output of the thermocouple and fine adjustment of the gas-flow system controlled the temperature of the crystal environment to ±1°K for the duration of the spectrum. This ar-

<sup>5</sup> R. O. Bell and G. Rupprecht, Phys. Rev. **129**, 90 (1963).

<sup>6</sup> G. Rupprecht and R. O. Bell, Phys. Rev. **135**, A748 (1964).

<sup>7</sup> S. H. Wemple, Phys. Rev. **137**, A1575 (1965).

<sup>8</sup> W. Cochran, Advan. Phys. **9**, 387 (1960).

<sup>9</sup> P. W. Anderson, *Fizika Dielektrikov*, G. I. Skanavi, Ed. (Akad. Nank. S.S.S.R. Fizicheskii Inst. in P. N. Lebedeva, Moscow, 1960).

<sup>10</sup> T. Nakamura, J. Phys. Soc. Japan **20**, 491 (1966).

<sup>11</sup> A. S. Barker, Jr., and M. Tinkham, Phys. Rev. **125**, 1527 (1962).

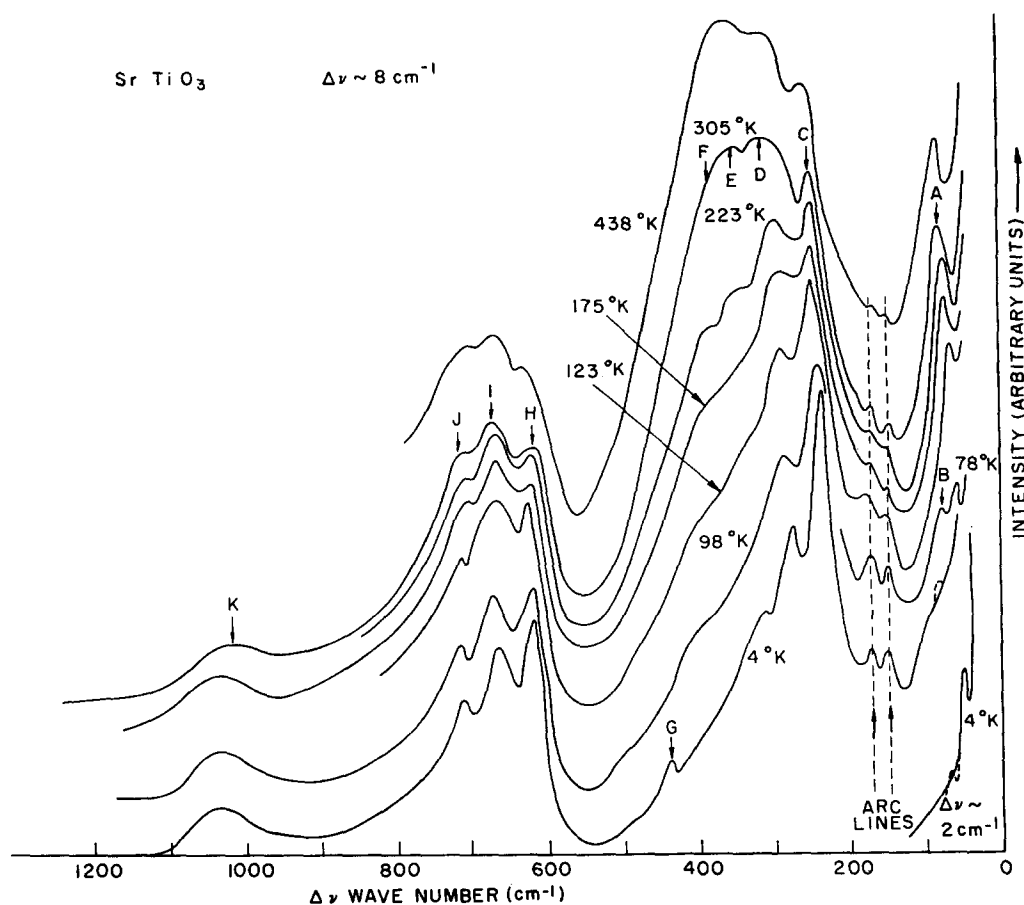
<sup>12</sup> R. A. Cowley, Phys. Rev. Letters **9**, 159 (1962).

<sup>13</sup> C. H. Perry and T. F. McNelly, Phys. Rev. **154**, 456 (1967).

<sup>14</sup> R. A. Cowley, Phys. Rev. **134**, A981 (1964).

<sup>15</sup> J. B. Lastovka (private communication).

<sup>16</sup> C. H. Perry, B. N. Khanna, and G. Rupprecht, Phys. Rev. **135**, A408 (1964).

FIG. 2. The temperature-dependent Raman spectrum of  $\text{SrTiO}_3$ .

rangement was repeated from room temperature down to liquid-nitrogen temperature with the same precision by controlling the flow of gas exchanging in a coil immersed in liquid nitrogen. Liquid-helium temperatures were obtained by using a vacuum-jacketed transfer tube and continuously transferring liquid helium from a storage vessel up to the back of the sample. Constant temperature was monitored by a carbon resistance thermometer placed beside the sample. No scattering effect attributable to the liquid-helium droplets was observed. The transfer line and sample arrangement in the glass Dewar system allowed rapid sample changing and liquid-helium temperatures could be achieved after only 2 min of transferring.

The spectra at the various temperatures are shown in Fig. 2 for  $\text{SrTiO}_3$  and in Fig. 3 for  $\text{KTaO}_3$ . The relative intensity of all the graphs is linear and the scale is essentially the same for all of them but slightly shifted for optimum display. Each spectrum is an average of as many as six runs made at a given temperature. The two "arc" lines at  $\sim 145$  and  $169 \text{ cm}^{-1}$  have been included. Apart from "calibration" points their presence was unfortunate and undesirable but their intensity appears to be a function of the age of the filter solution and current in the Toronto arc and

they cannot be removed completely. Consequently, bands appearing or disappearing as a function of temperature in the vicinity of these lines were somewhat doubtful unless the Raman bands were quite strong. Tables I and II show the temperature dependence of the main peaks for the two materials.

### DISCUSSION

Both  $\text{SrTiO}_3$  and  $\text{KTaO}_3$  are paraelectric cubic perovskites and have the space group  $Pm\bar{3}m$ . Simple group theory predicts three triply degenerate infrared-active (optic) modes, one triply degenerate infrared- and Raman-inactive (optic) mode, and one triply degenerate translational (acoustic) mode. The effect of the macroscopic electric field in the crystal splits the degeneracy of some of the modes at the zone center (symmetry point  $\Gamma$ ,  $k \approx 0$ ) resulting in three doubly degenerate transverse optic modes and three single longitudinal modes (all can be obtained from infrared measurements<sup>17</sup> from poles and zeros in the dielectric constants<sup>18</sup>); one doubly degenerate transverse optic mode and one longitudinal optic mode; (these modes

<sup>17</sup> R. C. Miller and W. G. Spitzer, Phys. Rev. **129**, 94 (1963).

<sup>18</sup> A. S. Baker, Jr., Phys. Rev. **132**, 1476 (1963).

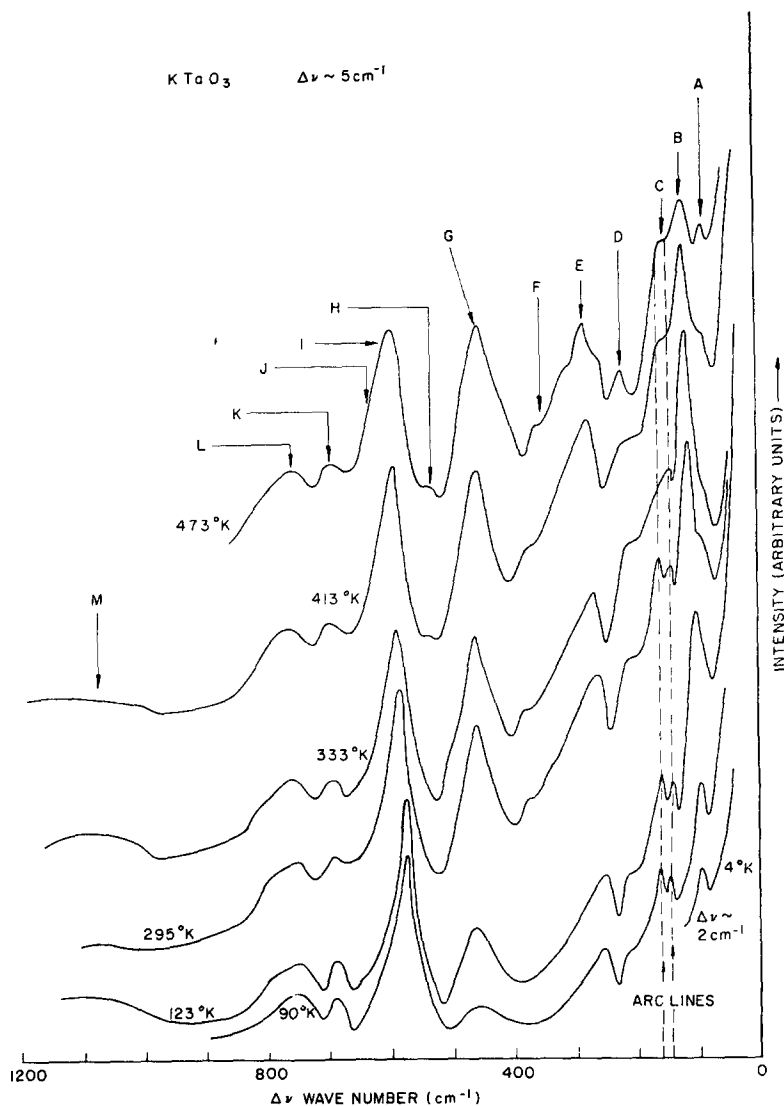


FIG. 3. The temperature-dependent Raman spectrum of  $\text{KTaO}_3$ .

are degenerate at the zone center and are not first-order infrared or Raman active; for  $\text{SrTiO}_3$ , Cowley<sup>14</sup> obtained a value of  $265 \text{ cm}^{-1}$  at the zone center using neutron diffraction) and three acoustic modes with  $\omega=0$ .

At the zone edge for symmetry point  $X$  (here the

designation of symmetry points according to Bouckaert *et al.*<sup>19</sup> is used) there are four doubly degenerate transverse optic modes, four longitudinal optic modes, a doubly degenerate transverse acoustic mode, and a single longitudinal acoustic mode. At the critical point

TABLE I. Raman bands observed in  $\text{SrTiO}_3$  as a function of temperature (frequencies are all in  $\text{cm}^{-1}$ ).

	4°K	78°K	98°K	123°K	175°K	223°K	305°K	438°K
A	49±5	60±5		65±5	65±5	75±5	80±5	85±5
B	(~70)	(75±8)						
C	235±5		235±5	240±5	240±8	240±8	250±10	250±10
D	280±5		285±8	290±10	295±10	300±15	310±15	320±20
E	315±10		...	325±20	...	350±15	360±15	360±15
F	...		400±20	400±20	375±20	380±20	...	...
G	445±5							
H	615±5		620±5	620±8	625±10	620±10	620±10	630±10
I	670±10		675±10	657±10	680±10	675±10	675±10	680±10
J	720±10		720±10	720±10	715±10	715±10	720±10	715±10
K	1035±20				1035±20		1030±20	

<sup>19</sup> L. P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. **50**, 58 (1936).

TABLE II. Raman bands observed in  $\text{KTaO}_3$  as a function of temperature (frequencies are all in  $\text{cm}^{-1}$ ).<sup>a</sup>

	4°K	90°K	123°K	295°K	333°K	348°K	413°K	473°K
A		...	...	...	100±8 sh	100±8 sh	100±8	100±8
B	95±5	105±5	110±5	118±5	120±8	122±8	127±10	132±10
C		...	...	...	160±15 sh	160±15 sh	160±15 sh	160±15 sh
D		230±10 sh	230±10 sh	230±10 sh	230±10 sh	230±10 sh	230±10 sh	233±10
E		253±5	256±5	265±5	268±5	270±5	277±5	286±5
F		...	...	370±10 sh	370±10 sh	370±10 sh	370±10 sh	370±10 sh
G		458±5	458±5	460±5	460±5	461±5	463±5	465±5
H		...	...	...	...	...	530±10 sh	530±10
I		580±5	582±5	587±5	592±5	592±8	596±10	598±10
K		685±15	686±15	688±15	693±15	695±15	695±20	695±20
L		750±15	750±15	760±15	760±15	765±20	765±20	770±20
M			1100±50	1100±50	1100±50	1100±50		

<sup>a</sup> sh denotes shoulder.

X this results in 10 discrete phonon branches to contribute to the multiphonon processes seen in the Raman spectrum of each crystal.

Loudon<sup>20,21</sup> has derived the general space-group selection rules for two-phonon Raman scattering for any crystal lattice possessing inversion symmetry. As these crystals possess this property, the selection rules can be summarized in the following manner. Two-phonon combination states (two phonons belonging to different branches) and two-phonon overtone states (two phonons belonging to the same branch) are active in second-order Raman scattering for wave vectors at general and symmetry points in the Brillouin zone.

Consequently, at the X point alone 45 summation bands, 45 difference bands, and 10 overtone bands are possible to contribute to the second-order Raman spectrum. Fortunately, the temperature-dependent study eliminates a large number of difference processes and with the experimental and theoretical results of Cowley<sup>14</sup> for  $\text{SrTiO}_3$  it is possible to interpret the Raman spectrum in terms of phonon pairs at specific symmetry points in the Brillouin zone corresponding to density-of-states maxima.

However in most cases the spectra have only been assigned at the X point in the  $[1, 0, 0]$  direction as these are the only values that have been measured by neutron spectroscopy. Cowley's theoretical dispersion branches in the  $[1, 1, 0]$  and  $[1, 1, 1]$  directions vary considerably for the various models investigated. Where the models did not agree with experimental data (e.g., infrared measurements at the  $\Gamma$  point) an estimated energy for the same branch at the X point of zone was used and these parameters were adjusted to give an optimum fit to the data. Obviously the L and W points will also contribute to the Raman spectra investigated and likewise will extrema of the branches at  $\Delta$ ,  $\Lambda$ , and  $\Sigma$ . Some possible transitions at the  $\Delta$  point were estimated.

<sup>20</sup> R. Loudon, *Advan. Phys.* **14**, 423 (1960).<sup>21</sup> R. Loudon, *Phys. Rev.* **137**, A1784 (1965).

## INTERPRETATION OF THE DATA

### $\text{SrTiO}_3$

The results of Narayanan and Vedam<sup>2</sup> are in qualitative agreement with our measurements at room temperature, but the positions of the lines observed are somewhat different. These workers stated that their spectra is first order, but our results indicate that their interpretation is probably incorrect. Firstly their group-theoretical arguments are not completely justified as there are only three infrared active modes and one "silent" mode for a cubic perovskite crystal. Secondly none of the frequencies agree with previous infrared measurements,<sup>11,17</sup> apart from the lowest frequency mode which may be the ferroelectric "soft" mode as discussed later.

The Raman spectrum for  $\text{SrTiO}_3$  (see Fig. 2) shows that the intensity of the scattered radiation is centered in four main regions,  $<150$ , 200–500, 600–800, and 1000–1100  $\text{cm}^{-1}$ . The two lowest regions show a reduction in the band contour as the temperature is lowered indicating that difference processes contribute considerably to the spectrum. Below 70°K most of the difference processes present in the spectrum have disappeared and it consists of summation and overtone bands only.

The most remarkable band in the spectrum is the lowest frequency peak. It has a marked temperature dependence going from 85  $\text{cm}^{-1}$  at 438°K to 49  $\text{cm}^{-1}$  at 4°K. It is impossible to assign this band to a combination at an X point in the zone. Its temperature dependence is not quite the same as the ferroelectric "soft" mode observed by Barker and Tinkham and by Cowley for  $\text{SrTiO}_3$  and so it does not appear to be a fundamental of the  $\text{TO}_1$  mode at the center of the zone, being Raman active due to distortion from cubic symmetry. Possibly it is some type of overtone from the ferroelectric "soft" mode at a different critical point in the zone as its existence at 4°K precludes any possible difference band.

TABLE III. Assignment of possible two-phonon difference processes for SrTiO<sub>3</sub>.

Observed (cm <sup>-1</sup> )	Calculated (cm <sup>-1</sup> )	Assignment	Remarks
<i>E, F</i>	250	TO <sub>4</sub> -LO <sub>1</sub>	Broad band in the region of <i>E, F</i> diminishes in intensity as the temperature is lowered.
Broad band 250-400	260	LO <sub>3</sub> -LO <sub>2</sub>	
	280	LO <sub>3</sub> -LO <sub>1</sub>	
	330	TO <sub>4</sub> -TO <sub>2</sub>	
	360	LO <sub>3</sub> -TO <sub>2</sub>	
	370	TO <sub>4</sub> -LA	
	400	LO <sub>3</sub> -LA	

TABLE IV. Assignment of the two-phonon peaks for SrTiO<sub>3</sub> at room temperature.

	Obs <sup>a</sup> (cm <sup>-1</sup> )	Calc (cm <sup>-1</sup> )	Assignment	Remarks
<i>A</i>	80±10	90	TO <sub>1</sub> (Γ) 2TO <sub>1</sub> (?)	b Strong; sharp especially at 4°K
<i>B</i>	75±8	? ?		c; very weak
<i>C</i>	250±20	220	2TA	d Very strong
		230	TA+TO <sub>1</sub>	
		240	2TO <sub>1</sub>	
		260	TA+LA	
<i>D</i>	310±20	270	TO <sub>1</sub> +LA	d; broad
		300	2LA	
		300	TA+TO <sub>2</sub>	
		310	TO <sub>1</sub> +TO <sub>2</sub>	
		315	TO <sub>1</sub> (Δ)+TO <sub>2</sub> (Δ)	
<i>E</i>	360±30	340	TO <sub>2</sub> +LA	e
<i>F</i>	380±20	380	LO <sub>1</sub> +TA	
		380	2TO <sub>2</sub>	
		390	TO <sub>1</sub> +LO <sub>1</sub>	
<i>G</i>	445	440	TO <sub>3</sub> +TA	Present only at 4°K
		440	LO <sub>2</sub> +LA	
		450	TO <sub>1</sub> +TO <sub>3</sub>	
		460	LO <sub>1</sub> +TO <sub>2</sub>	
<i>H</i>	620±20	600	TO <sub>3</sub> +LO <sub>1</sub>	Medium, broad
		620	LO <sub>2</sub> +TO <sub>3</sub>	
		630	TA+TO <sub>4</sub>	
		640	TO <sub>1</sub> +TO <sub>4</sub>	
<i>I</i>	675±20	660	TA+LO <sub>3</sub>	Medium; broad
		660	2TO <sub>3</sub>	
		670	TO <sub>1</sub> +LO <sub>3</sub>	
		670	TO <sub>4</sub> +LA	
<i>J</i>	720±20	700	LA+LO <sub>3</sub>	Medium; broad
		710	TO <sub>4</sub> +TO <sub>2</sub>	
		740±20 <sup>f</sup>	LO <sub>3</sub> +TO <sub>2</sub>	
<i>K</i>	1030±50	1040	2TO <sub>4</sub>	Broad
		1040	LO <sub>1</sub> +LO <sub>4</sub>	
		1060	LO <sub>2</sub> +LO <sub>4</sub>	

<sup>a</sup> The error on the observed frequencies is some estimate of the half-width or of the bands.

<sup>b</sup> Frequency lowers drastically as temperature is lowered but temperature dependence does not agree with Cowley's neutron data<sup>14</sup> for Γ point. Possibly a combination band at some other critical point in the zone. Presence of the band at 4°K precludes a difference process.

<sup>c</sup> This weak band appears below the 110°K phase transition but its existence at 4°K could not be repeated on every occasion.

<sup>d</sup> Frequency lowers as temperature is lowered.

<sup>e</sup> Intensity diminishes as temperature is lowered.

<sup>f</sup> Observed also in the infrared reflectance spectrum.<sup>16</sup>

The broad bands also show structure and these smaller peaks are quite temperature dependent in relation to both frequency and intensity and indicate that these may be some combination of the TO<sub>1</sub> and the TA, as both these lower their frequencies at the edge of the zone as the temperature is lowered.

There is also another band *B* which appears in the 78°K spectrum. Again this cannot be fully explained in terms of the *X* point and a similar explanation to the other low-frequency mode may account for this low-frequency peak as well. The transition to the tetragonal phase may have some bearing on its appearance. Conversely it may be caused by the crystal splitting up into small domains as proposed by Rimai and deMars<sup>3</sup> as the crystal does show birefringence at this temperature.

The temperature dependence of the spectrum between 250-410 cm<sup>-1</sup> can be explained by assuming that difference processes occur in this region. Possible combinations are given in Table III. The other fre-

TABLE V. Frequencies of phonon branches at the center and edge of the Brillouin zone for SrTiO<sub>3</sub>.

	Γ (cm <sup>-1</sup> )	X (cm <sup>-1</sup> )
TA	0	110
LA	0	150
TO <sub>1</sub>	90	120
LO <sub>1</sub>	173	270
TO <sub>2</sub>	178	190
LO <sub>2</sub>	265 <sup>a</sup>	290
TO <sub>3</sub>	265 <sup>a</sup>	330
LO <sub>3</sub>	473	550
TO <sub>4</sub>	544	540
LO <sub>4</sub>	815	770

<sup>a</sup> Obtained from neutron results only.<sup>14</sup> Other Γ point values obtained from neutron<sup>14</sup> and ir results.<sup>16</sup> X-point values obtained from neutron data<sup>14</sup> and from assignment of the multiphonon peaks in the Raman spectrum.

quencies at room temperature, the calculated values, and assignments for SrTiO<sub>3</sub> are listed in Table IV.

Even in the case of SrTiO<sub>3</sub> where most of the frequencies at the *X* point are reasonably well known there are many multiple choices. The frequencies at the Γ point (taken from infrared and neutron measurements) and those deduced at the *X* point from the Raman measurements are listed in Table V.

### KTaO<sub>3</sub>

Only four neutron results for the *X* point are known and the remaining six frequencies at the edge of the zone have been deduced to give the best calculated values to agree with peak positions observed in the experimental data listed in Table II. The spectra shown in Fig. 3 are considerably different from the results for SrTiO<sub>3</sub>. The spectra indicate bands throughout the entire region from 90-1200 cm<sup>-1</sup>. There is a marked temperature dependence of the spectra, especially the large reduction in intensity of the band around 460 cm<sup>-1</sup>. The band at 125 cm<sup>-1</sup> (*B*) shows a

considerable temperature dependence of the frequency which lowers as the temperature is lowered. However, it is not as marked as the lowest frequency band in  $\text{SrTiO}_3$ . The interpretation of this band in  $\text{KTaO}_3$  as  $2\text{TA}(X)$  is in reasonable agreement with the neutron results which indicate the same type of dependence. Band  $E$  has similar characteristics which again is in agreement if the combination  $\text{TO}_2 + \text{TA}$  is correct. The combination  $\text{TA} + \text{LO}_3$  and  $\text{TA} + \text{TO}_4$  about  $595 \text{ cm}^{-1}$  at room temperature also falls into this category.

TABLE VI. Assignment of the two-phonon peaks for  $\text{KTaO}_3$  at room temperature.

	Obs <sup>a</sup> ( $\text{cm}^{-1}$ )	Calc ( $\text{cm}^{-1}$ )	Assignment	Remarks
A	$100 \pm 8$	105 105	$\text{TO}_1 - \text{TA}$ $\text{LO}_2 - \text{LA}$	Weak; b
B	$120 \pm 10$	130	$2\text{TA}$	Strong; c
C	$160 \pm 20$	150 160	$\text{TO}_2 - \text{TA}$ $\text{LA} - \text{TA}$	a; hidden under arc lines.
D	$230 \pm 20$	235	$\text{TO}_1 + \text{TA}$	Weak; d
E	$270 \pm 20$	280 290	$\text{TO}_2 + \text{TA}$ $\text{LA} + \text{TA}$	Broad; c
F	$375 \pm 10$	375 385 395	$\text{TO}_1 - \text{TO}_1$ $\text{TO}_1 + \text{TO}_2$ $\text{TO}_1 + \text{LA}$	Weak; d
G	$460 \pm 40$	430 440 445 450 455 480	$2\text{TO}_2$ $\text{TO}_2 + \text{LA}$ $\text{TO}_1 + \text{LO}_1$ $2\text{LA}$ $\text{LO}_3 - \text{TA}$ $\text{TO}_4 - \text{TA}$	Broad; strong; d
H	$530 \pm 10$	530	$\text{TO}_1 + \text{TO}_3$	Weak; b
I	$590 \pm 40$	575 580 585 585 610 620	$\text{TO}_2 + \text{TO}_3$ $2\text{LO}_1$ $\text{TO}_3 + \text{LA}$ $\text{LO}_3 + \text{TA}$ $\text{TO}_4 + \text{TA}$ $\text{LO}_1 + \text{LO}_2$	Broad; strong;
J	$650 \pm 10$	650 660	$\text{LO}_1 + \text{TO}_3$ $2\text{LO}_2$	Weak; e; not observed in Raman
K	$700 \pm 20$	690 690 715 720	$\text{LO}_2 + \text{TO}_3$ $\text{TO}_1 + \text{LO}_3$ $\text{TO}_1 + \text{TO}_4$ $2\text{TO}_3$	Medium, broad; e
L	$760 \pm 30$	735 745 760 770	$\text{TO}_2 + \text{LO}_3$ $\text{LA} + \text{LO}_3$ $\text{TO}_2 + \text{TO}_4$ $\text{LA} + \text{TO}_4$	Broad; e
M	$1100 \pm 100$	1005 1015 1040 1065 1080 1090 1120 1150	$\text{LO}_4 + \text{TO}_2$ $\text{LA} + \text{LO}_4$ $2\text{LO}_3$ $\text{TO}_4 + \text{LO}_3$ $\text{LO}_1 + \text{LO}_4$ $2\text{TO}_4$ $\text{LO}_2 + \text{LO}_4$ $\text{TO}_3 + \text{LO}_4$	Very broad; weak

<sup>a</sup> The error on the observed frequencies is some estimate of the half-width of the peaks.

<sup>b</sup> Band disappears at low temperatures.

<sup>c</sup> Frequency lowers as the temperature is lowered.

<sup>d</sup> Band disappears slowly or diminishes intensity as the temperature is lowered.

<sup>e</sup> Present also in the infrared reflectance spectrum obtained in this laboratory.

TABLE VII. Frequencies of phonon branches at the center and edge of the Brillouin zone for  $\text{KTaO}_3$ .

	$\Gamma$ ( $\text{cm}^{-1}$ )	X ( $\text{cm}^{-1}$ )
TA	0	65
LA	0	225
$\text{TO}_1$	88 <sup>a</sup>	170
$\text{LO}_1$	188	290
$\text{TO}_2$	199	215
$\text{LO}_2$	(290)	330
$\text{TO}_3$	(290)	360
$\text{LO}_3$	423	520
$\text{TO}_4$	549	545
$\text{LO}_4$	833	790

<sup>a</sup> Obtained from neutron<sup>4</sup> and ir results.<sup>18</sup> Other  $\Gamma$  point values obtained from ir results.<sup>18,17</sup> X-point values obtained from neutron data<sup>4</sup> and from the multiphonon peaks in the Raman spectrum.

The experimental frequencies, calculated values and assignments are listed in Table VI and the zone center and zone edge frequencies deduced from the Raman data are shown in Table VII.

## CONCLUSIONS

The temperature-dependent Raman spectra of  $\text{SrTiO}_3$  and  $\text{KTaO}_3$  have been used to differentiate between possible combination and summation processes and difference processes which contribute to the multiphonon spectrum of these two cubic perovskite materials. With the aid of experimental and theoretical phonon dispersion curves obtained from the neutron-diffraction data, the energies of the phonon branches at the edge of the Brillouin zone at the X point have been deduced and the results indicate that the observed structure in the Raman spectrum even in these complicated crystals with a large number of atoms per unit can be interpreted with a reasonable degree of satisfaction. Only two-phonon processes have been considered, and the bands observed have been assumed to belong to the X point in the zone where the combined density of states is high. However, other critical points obviously contribute to the multiphonon spectrum and the frequencies listed in Tables V and VII should possibly be considered more as an average set at the edge of the Brillouin zone.

These measurements reflect the need, as has been stated before,<sup>22</sup> that laser sources, higher resolution, and depolarization measurements for the various orientations of the crystal over the same type of temperature range would probably provide additional information for more detailed theoretical analyses especially about the critical points in the Brillouin zone.

## ACKNOWLEDGMENTS

The authors wish to thank Professor A. Smakula, Dr. A. Linz, and Mr. V. Belruss of the Materials Center, M.I.T., for the samples.

<sup>22</sup> E. Burstein, F. A. Johnson, and R. Loudon, Phys. Rev. **139**, A1239 (1965).