

VIII. OPTICAL AND INFRARED SPECTROSCOPY*

Academic and Research Staff

Professor C. H. Perry

Graduate Students

Jeanne H. Fertel
D. J. Muehlner

J. F. Parrish
N. Tornberg

RESEARCH OBJECTIVES AND SUMMARY OF RESEARCH

The activities of this group have been concentrated on the study of the optical properties of solids determined by both infrared and Raman spectroscopy. This work is being extended to the study of low-frequency electronic and magnetic transitions in solids at liquid-helium temperatures.

1. Interferometric Spectroscopy^{1, 2}

The far infrared Michelson interferometer has been operating successfully over the wavelength range 25-1000 μ on a reasonably routine basis. A step-drive sampling interval is being considered and the frequency range has now been extended almost to 650 cm^{-1} . A 2^{12} bit analog-to-digital converter and a new lock-in amplifier are expected to yield more accurate intensity measurements so that full use can be made of the low-temperature bolometer.

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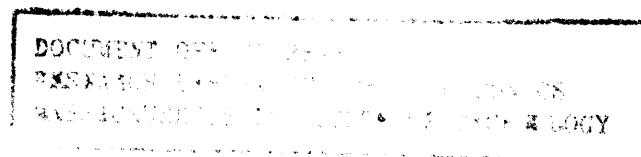
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2. Lattice Vibrations

a. Infrared Spectra of Solids

The far infrared instrumentation has been described in previous reports and publications.^{1, 2} Materials investigated have included BN;³ CdSe;⁴ Mg₂Sn;⁵ NH₄Cl and NH₄Br;⁶ KTaO₃;⁷ M₂PdX₄, PdL₄X₂, and trans and cis isomers PdL₂X₂ (with M = NH₄⁺, K⁺, Rb⁺ or Cs⁺; L = NH₃; X = Cl⁻, Br⁻ or I⁻);⁸ some ABF₃ fluoride perovskites⁹ (with A = K⁺ or Rb⁺; B = Mg²⁺, Ni²⁺, Co²⁺, Mn²⁺, Zn²⁺, and Mg_xNi_{1-x}²⁺) and some

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tektites.¹⁰ A temperature-dependent study of the dielectric dispersion of some alkali halides and related ionic crystals continues and will include some mixed crystals of simple alkali halides. Some mixed semiconductors, ferroelectrics, antiferromagnetic materials and other organic solids will be investigated. We also propose to study condensed-phase gases.

b. Raman Spectra of Solids

The temperature-dependent Raman spectrum of NH_4Cl , ND_4Cl , NH_4Br ,¹¹ $(\text{Na}_x\text{K}_{1-x})\text{TaO}_3$,¹² KTaO_3 ,¹³ and SrTiO_3 (see Sec. VIII-B) have been studied, and this work continues so that it can be complementary to the far infrared measurements. A Spectra-Physics 125 He/Ne laser is to be incorporated with the present spectrometer, and considerable improvement in signal-to-noise ratio and sample handling is to be expected. A new improved gas-flow Dewar system is being constructed for accurate low-temperature measurements in the region of various phase transitions.

C. H. Perry

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A. WORK COMPLETED

A thesis, entitled "Normal Vibrations of Cubic Fluoride Perovskites" was submitted by E. F. Young to the Department of Physics, M.I.T., August 1966, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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B. TEMPERATURE DEPENDENCE OF THE RAMAN SPECTRUM OF KTaO_3
AND SrTiO_3

1. Introduction

The Raman spectrum of single crystals KTaO_3 and SrTiO_3 have been observed from 30-1200 cm^{-1} frequency shift from the 22,938 cm^{-1} mercury "e" line over the temperature range 4-440°K. The room-temperature Raman spectrum of SrTiO_3 has been previously observed by Narayanan and Vedam,¹ and their results are in qualitative agreement with our measurements. Both SrTiO_3 and KTaO_3 are paraelectric cubic crystals at room temperature and apart from a slight structural change in SrTiO_3 at 110°K² no observation of the onset of ferroelectricity has been observed above a few degrees Kelvin. These crystals exhibit a Curie-Weiss law behavior,³ however, and recent theories of ferroelectricity in perovskite crystals⁵ have been confirmed experimentally for both of these crystals.⁶⁻⁸

The temperature-dependent Raman spectra observed in this work has been interpreted mainly as second-order spectra in both cases. The known cubic symmetry implies three first-order infrared active modes and one infrared and Raman inactive mode, together with the translational modes, none of which are first-order Raman active. Narayanam and Vedam¹ have erroneously interpreted their results as a first-order spectrum for SrTiO_3 .

2. Experiment

The Raman spectrum was obtained on several different samples by using a Cary 81 spectrophotometer. A gas-flow technique, which has been described previously,⁸ was used to obtain sample temperatures at 4-440°K. The spectra at various temperatures for KTaO_3 are shown in Fig. VIII-1, and for SrTiO_3 in Fig. VIII-2.

3. Discussion

The temperature-dependent spectra for KTaO_3 are surprisingly strong and complex. No correlation with the known infrared bands⁹ could be seen, however, and the spectra have been interpreted as primarily second order. Table VIII-1

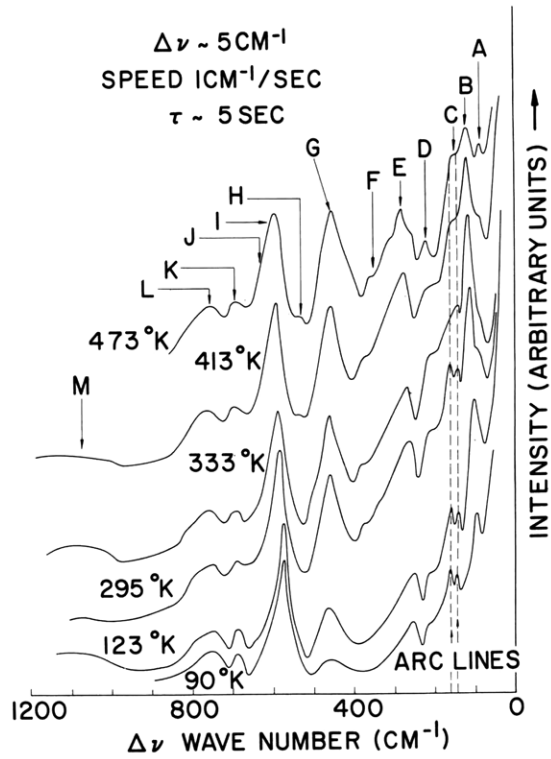


Fig. VIII-1. Spectra for KTaO_3 at various temperatures.

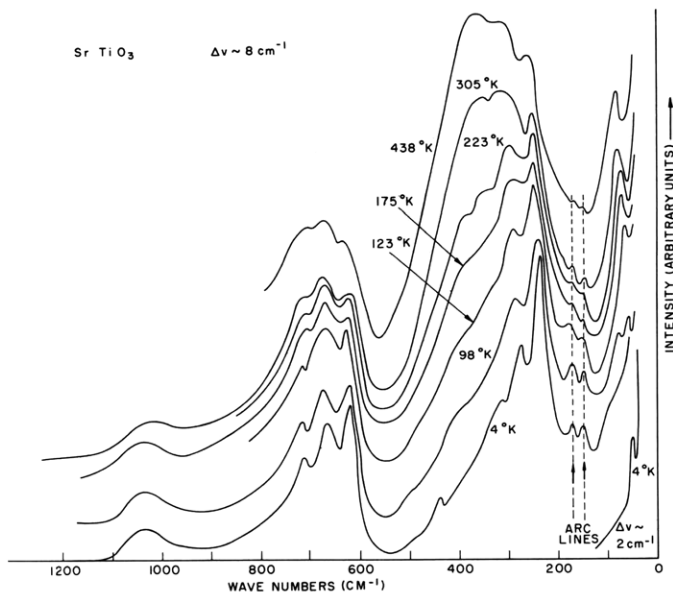


Fig. VIII-2. Spectra for SrTiO_3 at various temperatures.

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shows the frequency dependence of the various peaks as a function of temperature. Of particular interest are the bands at $\sim 125 \text{ cm}^{-1}$ and 460 cm^{-1} . The intensity of the latter band decreases as the temperature is lowered, which indicates the presence of a difference band, whereas the intensity of the former band increases with a decrease in temperature, thereby showing a combination process. This effect is true for a number of other bands, although not to such a marked extent.

From Table VIII-1 it can be seen that most of the frequencies slowly increase with increasing temperature. This behavior is somewhat unusual but may be the influence of the "soft" ferroelectric mode which markedly lowers its frequency as the temperature is lowered toward the "Curie" temperature at 3°K .⁸ All of the bands have been interpreted in terms of combinations of phonons at the edge of the Brillouin zone where both energy and momentum considerations can be satisfied and the density of states is high. The assignment of the multi-phonon peaks at 295°K are given in Table VIII-2, together with the averaged energies (in cm^{-1}) at the edge of the Brillouin zone.

Table VIII-1. Temperature dependence of the second-order Raman spectra of KTaO_3 (in cm^{-1}).

	90°K	123°K	295°K	333°K	348°K	413°K	473°K
A	—	—	—	100 ± 8sh	100 ± 8sh	100 ± 8	100 ± 8
B	105	110 ± 5	118 ± 5	120 ± 8	122 ± 8	127 ± 10	132 ± 10
C	—	—	—	160 ± 15sh	160 ± 15sh	160 ± 15sh	160 ± 15sh
D	230 ± 10sh	230 ± 10sh	230 ± 10sh	230 ± 10sh	230 ± 10sh	230 ± 10sh	233 ± 10
E	253 ± 5	256 ± 5	265 ± 5	268 ± 5	270 ± 5	277 ± 5	286 ± 5
F	—	—	370 ± 10sh	370 ± 10sh	370 ± 10sh	370 ± 10sh	370 ± 10sh
G	458 ±	458 ± 5	460 ± 5	460 ± 5	461 ± 5	463 ± 5	465 ± 5
H	—	—	—	—	—	530 ± 10sh	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		

sh = shoulder.

Table VIII-2. Assignment to the multi-phonon peaks at 295°K for KTaO_3 .

	Observed (cm^{-1})	Calculated (cm^{-1})	Assignment
A	100	100	TO_2 -LA
B	120	120	TA +LA
C	160	140	O_4 - TO_2
		170	LO_2 -LA
		170	LO_1 - TO_2
D	230	225	TO_1 -LA
		225	TO_2 +TA
E	270	290	LO_2 +TA
		275	TO_2 +LA
F	375	360	TO_3 - TO_2
G	460	465	TO_3 -LA
H	530	530	LO_1 + TO_2
I	590	585	TO_3 +TA
		585	O_4 + LO_2
		595	LO_1 + LO_2
J	650	640	O_4 + TO_1
		650	LO_1 + TO_1
K	690	690	LO_1 + O_4
		705	LO_3 +TA
L	760	740	TO_3 + TO_2
		755	LO_3 +LA
M	1100	1020	LO_3 + TO_3
		1210	LO_3 + LO_1

H at 473°K only.

J observed in IR only.

K and L observed in IR and Raman.

Average energies (in cm^{-1}) at the edge of the Brillouin zone.

TA 35 TO_1 310 TO_2 190 TO_3 540 O_4 330.

LA 90 LO_1 360 LO_2 255 LO_3 670.

Table VIII-3. Raman bands observed in SrTiO_3 .

	4°K	78°K	98°K	123°K	175°K	223°K	305°K	438°K
A	45 ± 5	60 ± 5		65 ± 5	65 ± 5	75 ± 5	80 ± 5	85 ± 5
B	63 ± 8	75 ± 8						
C	85 ± 8							
D	235 ± 5		235 ± 5	240 ± 5	240 ± 8	240 ± 8	250 ± 10	250 ± 15
E	280 ± 5		285 ± 8	290 ± 10	295 ± 10	300 ± 15	310 ± 15	320 ± 20
F	315 ± 10		—	325 ± 20	—	350 ± 15	360 ± 15	360 ± 15
G	—		400 ± 20	400 ± 20	375 ± 20	380 ± 20	—	—
H	445 ± 5							
I	615 ± 5		620 ± 5	620 ± 8	625 ± 10	620 ± 10	620 ± 10	630 ± 10
J	670 ± 10		675 ± 10	675 ± 10	680 ± 10	675 ± 10	675 ± 10	680 ± 10
K	720 ± 10		720 ± 10	720 ± 10	715 ± 10	715 ± 10	720 ± 10	715 ± 10
L	1035 ± 20				1035 ± 20		1030 ± 20	

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Cowley¹⁰ has discussed thoroughly the lattice dynamics and phase transitions in SrTiO₃, based on both experimental and theoretical studies. The frequency versus wave-vector dispersion curves for some of the normal modes were measured by neutron spectroscopy.¹⁰

The Raman spectra of SrTiO₃ as a function of temperature is shown in Fig. VIII-2 and is drastically different from that of KTaO₃.

The spectra consist of three main bands centered around 85, 320, and 640 cm⁻¹. The two broad bands show considerable structure and these smaller peaks are quite temperature-dependent. The highest frequency band appears to consist mainly of summation processes, whilst the central peak, from its marked temperature dependence, appears to consist of both sum and difference multi-phonon processes. The frequency-versus-temperature dependence is shown in Table VIII-3 and the assignments are given in Table VIII-4. In most cases, the interpretation has been made from the neutron dispersion curves given by Cowley.¹⁰ Low-frequency bands observed in the spectra below the phase transition are not fully understood, however. The strongly temperature-dependent line (A) which occurs at 85 cm⁻¹ at room temperature and which appears to lower to ~40 cm⁻¹ at 4°K could be the first-order ferroelectric "soft" mode (TO₁) at the zone center, although the frequency dependence with temperature is not quite the same as that observed in the infrared and neutron measurements.^{6,7} The other bands (B and C), shown at 78°K and 4°K close to the Rayleigh line, are probably due to additional first-order lattice modes appearing with the transition of the crystal to the tetragonal phase, or they may be caused by the crystal splitting up into small domains as proposed by Rimai and de Mars.² On the other hand, it is possible to attribute these bands to difference processes but it appears to be unlikely that they would still be present at liquid-helium temperatures.

The temperature dependence of the spectrum between 250 cm⁻¹ and 410 cm⁻¹ can be explained by assuming that difference multi-phonon processes occur in this region. Possible combinations are the following.

<u>Observed</u>	<u>Assignment</u>	<u>Calculated (cm⁻¹)</u>
Broad Band 250-400 cm ⁻¹	TO ₃ -TO ₂	330
	LO ₂ -TO ₂	360
	TO ₃ -LA	365
	LO ₂ -LA	395
	TO ₃ -TO ₁	405
	TO ₃ -TA	410

Table VIII-4. Assignment to the multi-phonon peaks at 305°K for SrTiO₃.

	Observed (cm ⁻¹)	Calculated (cm ⁻¹)	Assignment
D	250	240	TO ₁ +TA
E	310	285	LA +TA
		290	LA +TO ₁
		315	TO ₁ +TO ₂ (in zone)
		320	TA +TO ₂
		325	TO ₁ +TO ₂
F	360	365	TO ₂ +LA
G	380 ^a	385	LO ₁ +TA
		390	LO ₁ +TO ₁
H	445 ^b	430	LA +LO ₁
		450	TA + O ₄
		455	TO ₁ + O ₄
			LA + O ₄ ¹
I	620	620	O ₄ + O ₄ ¹
J	675	670	TO ₃ +TA
		675	TO ₃ +TO ₁
		680	LO ₂ +TA
		685	LO ₂ +TO ₁
		695	LO ₂ +TA
K	720	725	LA +LO ₂
L	1030	1025	LO ₃ +LO ₁
		1050	LO ₃ + O ₄ ¹

^a98°K-223°K.

^b4°K.

Table VIII-4a. Average energies (in cm⁻¹) at the edge of the Brillouin zone.

TA - 120	LA - 165
TO ₁ - 125	LO ₁ - 265
TO ₂ - 200	O ₄ ¹ - 290
O ₄ - 330	LO ₂ - 560
TO ₃ - 530	LO ₃ - 760

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In conclusion, it appears that these multi-phonon Raman spectra are extremely difficult to interpret with any certainty. Cowley's results for SrTiO_3 can be assigned, but there is a multiple choice in most cases. The results of the energies of the dispersion curves at the edge of the Brillouin zone for KTaO_3 are quite tentative. Consequently, one must await the complete neutron spectrum as a function of wave vector so that worth-while dynamical calculations can be made of the phonon dispersion curves. We would like to thank Professor A. Smakula and Dr. A. Linz of the Materials Center, M.I.T., for the samples.

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

[Mr. T. F. McNelly is now in the Physics Department, Cornell University, Ithaca, New York.]

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