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STUDY OF OPTICAL PROPERTIES AND COLLECTIVE OSCILLATIONS
IN NEW SOLID-STATE MATERIALS AS A FUNCTION OF TEMPERATURE
USING INFRARED AND RAMAN TECHNIQUES

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Study of the Optical Properties and Collective Oscillations in New Solid Materials Over a Wide Temperature Range Using Infrared and Raman Techniques

1. Introduction

Application has been made to NASA for a renewal of the research program NGR 22-009-(237) on the study of optical properties and collective oscillations in solids over a wide range in temperature by the principal investigator and co-workers.

The facilities of the Solid State Spectroscopy Laboratory in the Department of Physics, Northeastern University, are unique for investigation of crystals in the far infrared region and for their Raman scattering properties. They now include a Perkin-Elmer 301 far infrared double-beam grating spectrophotometer (range 2.5-300 microns, $4000-30\text{ cm}^{-1}$) (on loan from NASA (ERC)); a continuously scanning far infrared Michelson interferometer (range 25-500 microns, $400-20\text{ cm}^{-1}$), and an additional Michelson interferometer (on loan from NASA (ERC)) to be used with an InSb 'electron' bolometer detector (under construction) operating at $\sim 1.5^\circ\text{K}$ (range 125-2000 microns, $80-5\text{ cm}^{-1}$). Specially constructed sample chambers and variable temperature cells provide facilities in both the grating instrument and the interferometer for polarization measurements and for low/high temperature transmission or reflection studies to be made on relatively small ($< 0.5\text{ cm}^2$) crystals.

A highly polarized laser is used for the Raman studies. The small cross section of the beam means that only small samples are required. Light-scattering cells are in operation from $2-900^\circ\text{K}$, and may be extended to 2000°K in the future. The Raman spectra for various scattering angle geometries are measured by using a Spex double spectrometer and, at present a Spectra-Physics 125 He-Ne $6328\text{ \AA}$ gas laser; the laser is on temporary loan from M.I.T. Different configurations of incident and scattered beam directions and polarizations relative to the different crystal axes are used to identify the various fundamental vibrations and the polarizability tensor components.

The two complementary techniques are carried out by graduate

assistants from the Department of Physics, M.I.T., and Northeastern University under the supervision of the principal investigator and Professor Robert P. Lowndes who has joined the group as a permanent faculty member. The initial cost of this program during the first year was mainly for the Raman spectrometer and detection equipment. We hope that the support will be maintained at this level for the renewal program so that the research can be successfully continued.

Recently, the investigators attended and presented papers at the International Conference on the Light Scattering Spectra of Solids, at New York University, and the Molecular Spectra and Structure Symposium, at Ohio State University, Columbus, Ohio. From the nature of the papers presented and the experimental techniques discussed it has become increasingly clear that in order to compete in this rapidly developing field an Argon or Krypton ion laser is essential as a monochromatic source. The Argon source is especially important, as the power output can be ten or twenty times that of the He-Ne laser; photomultiplier efficiency is at least five times better, and the scattering efficiency is improved approximately threefold. This means a considerable increase in signal-to-noise and resolution. New and exciting experiments on metals, semiconductors, magnon scattering, superconductors, mixed crystals, electronic Raman effect, electric field induced scattering and a host of other effects are now within the bounds of reality and hold bright prospects for the future. Consequently, an extremely high priority was given to the purchase of a 2-watt Argon laser for the benefit of developing new technical results in the field of light scattering. Because of lack of funds, this vital piece of equipment could not be obtained; however, the loan from NASA (ERC) of the Space Rays 1-2 watt Argon laser now makes all of these new experiments possible. Installation of a rigid table, safety water switches, and an adjustable Brewster prism to select the various laser lines is now being accomplished, and we expect to make a direct comparison in March, 1969.

2. Objectives and Significance of the Work

The investigation of the optical properties and collective oscillations in some recently developed new materials will provide information about such useful applications as low-temperature filter materials for long-wave

infrared radiation, new laser host crystals, crystals as electro-optic devices, and the limitations of these materials under extreme environmental conditions. (Of current interest are various antiferroelectrics, ferroelectrics, antiferromagnets, piezoelectrics, certain semiconductors and insulators.) A basic understanding of the lattice dynamics and phonon structure of these systems when they undergo various phase transitions as a function of temperature is also an important feature of the problem, in order to relate their optical properties to the detailed crystallographic characteristics. Second-order spectra provide data on such properties as combined density of states and also give some indication of nonlinear optical effects. These measurements provide useful data for predicting general engineering and research applications.

3. Instrumentation

The infrared instrumentation is completely self-contained, together with the necessary cryostats, etc., for studying the optical properties of materials from 2.5-2000 microns over a wide temperature range. The addition of the FS-720 Fourier spectrometer (NASA) will now make it possible to investigate a wider variety of materials, especially at low frequencies. The Spex 1400 double spectrometer is designed principally to reduce scattered light and is especially advantageous in Raman spectroscopy in which weak lines must be measured in the proximity of an intense laser line.

As we have mentioned, the addition of a commercial Argon ion laser source is essential in order to obtain the most significant and topical results on important experiments. Considerable work has been done to make the laser operational (installation of a new cathode, heat shield, water lines, electrical connections, stability monitoring device, and feedback operation) and the laser is producing in excess of 1 watt power in all lines.

4. Materials to Be Investigated

The materials studied as a function of temperature have included mixed alkali halides, several ferroelectrics such as SrTiO_3 , CaTiO_3 , mixed crystals of Na/KTaO_3 , K(TaNb)O_3 , and KNbO_3 . Other materials

possessing phase transitions include the ammonium halides. Several rare-earth fluorides, including LaF_3 , CeF_3 , PrF_3 , and NdF_3 , have been investigated for phonon spectrum and electronic structure. The program for the coming year includes mixed alkali halides, some semiconductors, new ferroelectrics like SbSI and crystals isomorphic with KDP , Ba/SrTiO_3 , and other mixed ferroelectrics, antiferromagnetic materials having perovskite structure, for example, KNiF_3 , KMnF_3 , RbNiF_3 , and rare-earth doped materials of the alkali-earth fluorides. Further work on doped rare-earth fluorides, for example, $\text{LaF}_3:\text{H}_2\text{O}^{3+}$, $\text{LaF}_3:\text{Sm}^{3+}$, etc., will continue, together with other host lattices that show bi-refrangent properties. Trigonal tellurium and proustite and other nonlinear materials are also currently being investigated.

Further investigations should be made on heavier rare-earth fluorides crystallizing in the slightly less dense YF_3 structure and the chlorides and bromides of both the lanthanide and actinide elements with the UF_3 structure. It is also proposed to start investigations of metals, alloys, and superconductors with Raman scattering techniques now that an Ar^+ laser can be used in conjunction with the Spex double monochromator.

5. Future Work

The infrared and Raman investigations are now again in progress after the Solid State Spectroscopy group transferred to the Physics Department, Northeastern University, in September 1968. The majority of the facilities are now completed, except that some of the variable low-temperature equipment remains to be set up, and the computer programs are in the process of being translated for the Northeastern University computer. The studies of the optical properties and collective oscillations in various new solid-state materials continue to provide basic information on their lattice dynamics and indicate their applications as optical devices under varying environmental conditions. Some of the materials to be investigated have been listed in section 4.

Since October 1968, this project has virtually been unsupported, as the funds were almost completely exhausted while the investigators were at M. I. T. The remaining funds have been used primarily for manuscript

and figure preparation but the cost share of publication of the four or five projects will presumably have to be taken from the renewal grant.

Summary of Work Accomplished

1. Optical Phonons in Tysonite Rare-Earth Fluorides

Results have been obtained in the far infrared interferometric research program to assess the potential use of the rare-earth fluorides as host materials for solid-state lasers. Kramers-Kronig analyses of the polarized lattice-vibration reflection spectra of LaF_3 , CeF_3 , NdF_3 , and PrF_3 , taken at temperatures down to 8°K have led to an assignment of the crystal symmetry for these materials and provided the real and imaginary parts of the dielectric constant.

The far infrared reflectance spectra of the four tysonite rare-earth fluorides show at least six infrared active modes polarized parallel to the c-axis, and at least ten more perpendicular to the c-axis. These measurements alone are sufficient to eliminate both the D_{6h}^4 bimolecular cell (2 modes with $E//c$, 2 modes with $E \perp c$) and the D_{6h}^3 hexamolecular cell (4 modes $E//c$, 7 modes $E \perp c$) proposed by previous researchers. Based upon Raman scattering, Bauman and Porto, in September 1967, proposed a D_{3d}^4 hexamolecular cell (6 modes $E//c$, 11 modes $E \perp c$). Our measurements of the infrared active lattice vibrations would tend to support the structure; however, we have observed polarized infrared electronic transitions for Pr^{3+} at ~ 66 and 90 cm^{-1} . Bauman and Porto also report seeing the same two transitions in Raman scattering, which is impossible for the rare-earth ion transition with $E//c$ in the D_{3d}^4 structure. Consequently, the infrared and Raman activities, permissible in over twenty mathematically different uniaxial crystal structures, were investigated. Two of the hexamolecular structures look equally probable at this time, and are being investigated further. An assessment of the nonlinear interactions in these materials has been obtained.

2. Far Infrared Electronic Transitions in Tysonite Rare-Earth Fluorides

Electronics transitions between the crystalline Stark levels of the ground state manifold of Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , and Er^{3+} held in LaF_3 , CeF_3 , PrF_3 , and NdF_3 host lattices have been investigated by using far infrared spectroscopy in the frequency range $30\text{-}120 \text{ cm}^{-1}$. No transitions were observed for either Ce^{3+} or Sm^{3+} ions held in the various host

lattices, a factor in contradiction to energy-level schemes predicted from previous fluorescence and optical absorption measurements. Low-energy ($40\text{--}100\text{ cm}^{-1}$) electronic transitions between the ground state and first excited states of the ${}^3\text{H}_4\text{Pr}^{3+}$; ${}^4\text{I}_9\text{Nd}^{3+}$ and $4\text{I}_{15/2}\text{Er}^{3+}$ Stark multiplets have been observed at 66 and 90 cm^{-1} ; _____ cm^{-1} ; and _____ cm^{-1} , respectively. These transitions were confirmed to be electronics from polarization studies, and the Zeeman splitting of these levels in magnetic fields up to 150 KG .

3. Phonon Spectra and Phase Transitions in the Ammonium Halides

The infrared and Raman lattice spectra of several ammonium halides have been investigated as a function of temperature from $4\text{--}300^\circ\text{K}$. One infrared active (reststrahlen) mode is observed in the disordered cubic phase. In the ordered cubic phase for NH_4Cl , ND_4Cl (phase III) and NH_4Br , ND_4Br (phase IV), the main lattice mode is simultaneously infrared and Raman active. The temperature dependence of the frequency and damping constant has been studied extensively by using both techniques. In the tetragonal phase (D_{4h}^7 ($\text{P4}/\text{mmm}$)) for NH_4Br , ND_4Br and NH_4I (phase III), five bands are observed in the Raman spectrum corresponding to the four translational modes and one vibrational mode. The infrared spectrum shows only one translational lattice mode. The frequencies and symmetries of the $\underline{k} \approx 0$ allowed modes in the various phase transitions have been obtained. The nature of the interatomic interactions governing the extent of the ionic distortions and the compressibilities of these solids is now being studied.

4. Optical Phonons in Mixed Sodium Potassium Tantalates

The dielectric data as a function of temperature on this mixed-crystal system have been outlined by Davis. In the mixed system the Curie point rises to a maximum of 65°K for a sample containing 48% NaTaO_3 and falls for higher concentrations. At approximately 72% NaTaO_3 the ferroelectric transition disappears. The departure from Curie-Weiss law behavior as T_c is approached is more significant, as the concentration of NaTaO_3 is increased. For materials in the range $35\text{--}50\%$ NaTaO_3 , an anomalous "plateau" in the dielectric behavior

is observed. This could arise from a second-order ferroelectric transition at 50°K and a transition to a structurally different ferroelectric phase (e.g., tetragonal) at 37°K, as observed in the 40% sample. As primarily second-order Raman spectra were observed, the infrared results helped to positively identify the presence of any first-order bands. The interpretation of the second-order Raman spectrum of KTaO_3 has been discussed by Perry, Fertel, and McNelly and by Nielson and Skinner. A similar analysis has been applied to the mixed crystals. The temperature dependence of the intensities of the bands has been used to differentiate between possible combination and difference processes which contribute to the multiphonon spectrum. Although a classical Brillouin zone is not well-defined for these mixed crystals, the multiphonon spectrum behaves as if it were due only to critical points at the edge of a pseudo-Brillouin zone.

At 49°K the ($\text{Na}_{0.4}:\text{K}_{0.6}$) spectrum displays a very small first-order contribution, whereas at 36.5°K additional bands appear at 42, 128, 200, 225, 572, and 850 cm^{-1} . These are indicative of a structural change, but at a temperature below that established for the ferroelectric transition. Similar bands are present in the 85% NaTaO_3 sample's spectra, the distorted perovskite structure allowing all zone modes to be Raman active.

The band around 225 cm^{-1} in the two crystals with highest Na content could be the normally inactive " F_{2u} " mode in the cubic phase now being Raman active. Comparison between the infrared and Raman vibrations having their origin as first-order modes are generally in good agreement, thereby confirming the supposition that for all sodium concentrations in the paraelectric phase, the Raman spectrum is essentially a profile of the combined density of states.

5. Temperature-Dependent Phonon Spectrum of PbTiO_3

The frequencies and symmetries of the allowed $\underline{k} \approx 0$ transverse and longitudinal modes were obtained from a Kramers-Kronig analysis of far infrared reflectance data taken between 80-800°K. Above the Curie temperature (760°K), PbTiO_3 exhibits a broad second-order Raman spectrum. Below this temperature - in the ferroelectric tetragonal phase - a first-order spectrum is superimposed which increases in

strength as the temperature is lowered. The bands in PbTiO_3 observed just below T_c at about 65, 120, 185, 280, and 495 cm^{-1} show a shift of approximately 4, 5, 8, 2, and 3.5 cm^{-1} per 100°K , respectively, to higher frequency as the temperature is lowered. The relative contributions of the various modes to the dielectric dispersion indicate that the lowest frequency mode is the "softest." Other modes of the same symmetry also contribute significantly to the temperature dependence of ϵ_0 , and they may also approach some type of instability in the paraelectric phase.

6. Phonon Spectra and Phase Transitions in Potassium Tantalate-Niobate Mixed Crystals

Except for the highest Ta concentrations, the mixed crystals $\text{K}(\text{Ta:Nb})\text{O}_3$ exist in cubic, tetragonal, orthorhombic, and rhombohedral phases at successively lower temperatures. In the cubic phase, the Raman spectra for all compositions are entirely second-order and resemble those of $(\text{Na:K})\text{TaO}_3$ in its cubic phase. In the other phases, a first-order spectrum is superimposed. At each phase transition this first-order spectrum changes markedly, but in no cases are all Raman-allowed transitions visible as discrete peaks. This could arise either from an insufficient distortion from cubic symmetry or from the ambiguity of phonon wave vector orientation with respect to the major axes of the crystal. The temperature dependence of the frequencies associated with lines identifiable exclusively as first-order is very small, generally being no greater than 1% per 100°K . This is usually less than the error in determining the frequency, and indicates that the associated phonons play a negligible part in the variation in dielectric constant and in the phase transition. The behavior of the scattering near the exciting line, however, would suggest that in the majority of cases an overdamped phonon of low-frequency exists and plays the major role in the phase transition. Infrared studies tend to substantiate this.

The change in the spectra at the phase transitions have allowed a careful study of the corresponding transition temperatures. These are found to agree well with Triebwasser through the range of composition to within the error with which it is known, and considerable hysteresis is

noted for those samples with 100% Nb and 75% Nb.

Some of the frequencies may be unambiguously assigned phonons on the basis of the (Na:K)TaO₃ work and the infrared measurements of KNbO₃. These are LO₄ (838 cm⁻¹), TO₄ⁱ (604 cm⁻¹), and TO₄ (530 cm⁻¹), where TO₄ⁱ and TO₄ are the highest transverse optic mode split by anisotropy in the crystal. Also, work on other perovskites indicates that the frequency at 292 cm⁻¹ (rhombohedral phase) or 298 cm⁻¹ (orthorhombic phase) may be identified with the TO₃ mode, which in the cubic phase has "F_{2u}" symmetry and is therefore infrared and Raman inactive.

Papers Presented at Meetings and Publications from the First Year of Support

The results are of basic importance for comparison with theoretical considerations and will be submitted for publication in appropriate journals, such as Physical Review, Journal of Applied Physics, Journal of Chemical Physics, and Journal of the Optical Society of America.

At present, seven papers are being written for publication in leading journals. This work has stemmed directly from NASA support of this program during the preceding year.

1. "Optical Phonons in Tysonite Rare-Earth Fluorides," R. P. Lowndes,* J. F. Parrish, and C. H. Perry (submitted to Phys. Rev.).
2. "Far Infrared Electronic Transitions in Tysonite Rare-Earth Fluorides," J. F. Parrish,* R. P. Lowndes, and C. H. Perry ($\text{LaF}_3:\text{Nd}^{3+}$ - submitted to Physics Letters).
3. "The Phonon Spectra and Phase Transitions in the Ammonium Halides," C. H. Perry and R. P. Lowndes (submitted to J. Chem. Phys.).
4. "The Temperature Dependent Phonon Spectrum of PbTiO_3 ," C. H. Perry* and N. E. Tornberg (to be submitted to Phys. Rev.).
5. "The Phonon Spectra and Phase Transitions in Potassium Tantalate-Niobate Mixed Crystals," N. E. Tornberg* and C. H. Perry (in preparation).
6. "The Raman Spectra of PbTiO_3 and Solid Solutions of NaTaO_3 - KTaO_3 and KTaO_3 - KNbO_3 ," C. H. Perry† and N. E. Tornberg.
7. "Optical Phonons in Mixed Sodium-Potassium Tantalates," C. H. Perry and N. E. Tornberg (submitted to Phys. Rev.).

* Presented at the Molecular Spectroscopy and Structure Symposium, Ohio State University, Columbus, Ohio, September 3-7, 1968.

† Published in the Proceedings of the International Conference on Light Scattering Spectra of Solids, New York University, New York, September 3-6, 1968. (Ed. G. B. Wright, Springer-Verlag, New York, 1969, Paper F-3.)