

IV. FAR INFRARED SPECTROSCOPY

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RESEARCH OBJECTIVES

The aim of this group is to continue the study of the properties of solids in the far infrared. Transmission and reflection measurements at room temperatures of three perovskite titanates have been completed. Temperature-dependent reflection measurements in the range 77-700°K are to be undertaken on these materials above their Curie temperatures to gain further understanding of their ferroelectric behavior. With this end in view, the study is being extended to zirconates, hafnates, and other perovskites that exhibit similar properties. Current solid-state research problems also include the infrared spectra of some antiferromagnetic materials and some inorganic compounds that have low internal molecular and lattice vibrations.

The study of low-temperature detectors for the 50-1000 μ region continues in cooperation with Professor R. C. Lord of the Spectroscopy Laboratory, M. I. T.* Detector noise measurements as a function of frequency are being undertaken to study the detectivity of these bolometers and ascertain the optimum chopping frequency. The evaluation of the performance of a commercial far infrared Michelson interferometer is expected to be carried out in the near future, but this will have to await delivery of the instrument. Interferometers should inherently make better use of the available energy than conventional spectrometers; this should decrease the time for taking spectra, as well as provide better resolution. Some modifications in the instrument will be necessary in order to make reflection studies and for low-temperature measurement, but these appear to be minor.

C. H. Perry

A. FAR INFRARED REFLECTANCE AND TRANSMITTANCE OF POTASSIUM MAGNESIUM FLUORIDE AND MAGNESIUM FLUORIDE

1. Introduction

Many compounds possessing the cubic perovskite crystal structure exhibit unusual properties, such as ferroelectricity and antiferromagnetism. Knowledge of the nature of the interatomic forces in the crystal should prove extremely useful in explaining these phenomena. To make such information available, several studies¹⁻⁵ of the far infrared and Raman spectra of the perovskite titanates and the related rutile have been reported recently. Some disagreement exists concerning the interpretation of these spectra. To furnish additional data to help resolve the disagreement, and to facilitate the interpretation of the electronic absorption spectral studies of the compounds made by one of us (J. F.), research on the transmittance and reflectance spectra and the dielectric dispersion of potassium magnesium fluoride and magnesium fluoride was undertaken as a prelude to a more comprehensive study of the vibrational nature of fluoride perovskites and their "rutile" counterparts.

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2. Experiment

The room-temperature reflectances of potassium magnesium fluoride and magnesium fluoride were measured by using unpolarized radiation from 4000 cm^{-1} to 30 cm^{-1} relative to the reflectance of a reference mirror coated with aluminum. Measurements were also made on each material at 5 cm^{-1} , with the use of a "Carcinotron" source of 2-mm radiation at Lincoln Laboratory, M. I. T.; the samples were mounted at a 20° included-angle bond in a light pipe, and the reflectances were compared with a reference mirror in the same position. The results were in reasonably close accord with our low-frequency far infrared measurements.

The infrared reflection spectra were recorded on a Perkin-Elmer Model 521 grating double-beam spectrophotometer, equipped to scan continuously from 4000 cm^{-1} to 250 cm^{-1} . A Perkin-Elmer reflectance attachment was used in this instrument, and the reflectance data were recorded at an angle of incidence of approximately 15° . Below 400 cm^{-1} , it was necessary to flush the instrument with evaporated liquid nitrogen to remove most of the water vapor. A single-beam grating spectrometer, constructed in the M. I. T. Spectroscopy Laboratory, was used for measurements below 500 cm^{-1} .⁶ This instrument was improved by complete enclosure in a vacuum case⁷; this procedure allowed water vapor to be entirely removed from the optical path and so provided smooth background spectra. Again, the angle of incidence for the reflection measurements was 15° . The samples used were grown at the Bell Telephone Laboratories, Inc. The KMgF_3 sample was a single crystal with a polished face approximately 0.5 inch square. The MgF_2 was not a single crystal and was more irregularly shaped, which necessitated a slight vignetting of the beam. Transmission measurements over the same range as for reflection were made on the two infrared instruments described above. The samples consisted of finely divided powders dispersed in KBr matrices for measurements above 300 cm^{-1} , and dispersed in polyethylene for measurements below 600 cm^{-1} .

3. Data Analysis

The real and imaginary parts of the complex dielectric constant, $\epsilon' = n^2 - k^2$ and $\epsilon'' = 2nk$ (where n is the refractive index, and k is the absorption coefficient) were obtained by transforming the reflectance data by using the Kramers-Kronig relation.⁸ In this, the reflectivity amplitude is given by $re^{-i\theta}$, where $r = R^{1/2}$, and R and $\theta(\nu)$ are respectively the reflectance and the associated phase angle, the latter being given by

$$\theta(\nu) = \frac{2\nu}{\pi} \int_0^\infty \frac{\ln [r(\nu')] d\nu'}{\nu^2 - \nu'^2}.$$

The infinite integral was evaluated by representing $\ln r(\nu')$ by straight-line segments between data points and programming the relationships for use on an IBM 7090 computer at the Computation Center, M. I. T.

4. Discussion

Potassium magnesium fluoride possesses the cubic perovskite crystal structure, which belongs to the space group $O_h^1 (P_{m3m})^9$ and contains one molecule per unit cell. Each atom of the same element in the crystal forms an equivalent set, but the site symmetry of the fluorine atoms is D_{4h} , while that of the magnesium and potassium atoms is O_h .

In discussing the number and symmetry species of the active vibrational modes in the perovskite $BaTiO_3$, Last¹ breaks down the twelve nontranslatory modes into one triply degenerate set of three lattice modes (F_{1u}) in which the TiO_3 group oscillates as an entity against the lattice of barium atoms and nine modes of vibration of a titanium atom surrounded by a regular octahedron of 6 half-oxygen atoms. The last are treated under the point group O_h and yield the result that there are two triply degenerate sets of F_{1u} infrared allowed modes and one triply degenerate F_{2u} infrared forbidden set of modes. Narayanan and Vedam,⁴ in reporting the Raman spectrum of strontium titanate, disagree with Last's conclusion and assert that there are, in fact, 4 nontranslatory triply degenerate sets of infrared-active modes, all of which belong to species F_{1u} , and they quote Rajagopal's¹⁰ treatment of the lattice dynamics of cubic perovskites as substantiating this contention. We feel that they have misinterpreted this work, for although Rajagopal states there are four triply degenerate fundamentals for a cubic ABO_3 structure, he does not specify to which symmetry species they belong. He does indicate, however, that his determinant of order fifteen factors into three of order five (indicating 5 triply degenerate oscillations, of which one is the acoustical or translatory mode), and furthermore that the ν_4 mode separates out. The cubic equation resulting from the removal of the translatory mode and the ν_4 vibration yields the three infrared-active vibrational modes described by Last.

We have used the following standard considerations to arrive at a conclusion that is in agreement with Last's. The number of normal modes of a particular symmetry species is given by n_i , the number of times the irreducible representation Γ_i corresponding to that species is contained in the reducible representation Γ . The group theoretical expression for n_i is

$$n_i = \frac{1}{N} \sum_{\rho} h_{\rho} X'_{\rho}(R) X_i(R),$$

where N is the order of the group, h_{ρ} the number of group operations falling under the

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class ρ , $X_\rho^i(R)$ and $X_i(R)$ are the characters of the group operation R in the representation Γ and Γ_i , respectively, and

$$X_\rho^i(R) = U_R(\pm 1 + 2 \cos \phi_R).$$

Proper rotations by ϕ take the positive sign, and improper rotations take the negative sign. For point group operations, U_R is given by the number of atoms that remain invariant under operation R . For space group operations, however, which are appropriate when considering crystals, U_R is the number of atoms in the repeating unit (for crystals, the unit cell) which, for a particular operation R , contains either the appropriate rotation axis, reflection plane or inversion center. When applied to KMgF_3 (which has an ideal cubic perovskite structure¹¹), these considerations yield $4F_{1u} + 1F_{2u}$ as the symmetry species of the normal modes, of which one F_{1u} is a translation and the F_{2u} mode is forbidden in the infrared. We find that such a conclusion is also in agreement with our experimental data. Figures IV-1 and IV-2 show the transmittance and reflectance spectra of KMgF_3 , and Fig. IV-3 shows the real and imaginary part of the dielectric constant calculated from the reflectance data. The maxima of the imaginary part yields the true resonant frequencies, and these are listed together with assignments in Table IV-1a. While we describe the various modes as bending and stretching, we realize that they are not pure modes, and knowledge of the actual form of the vibrations must await a complete normal coordinate analysis.

For magnesium fluoride, the tetragonal crystal structure is isomorphous with

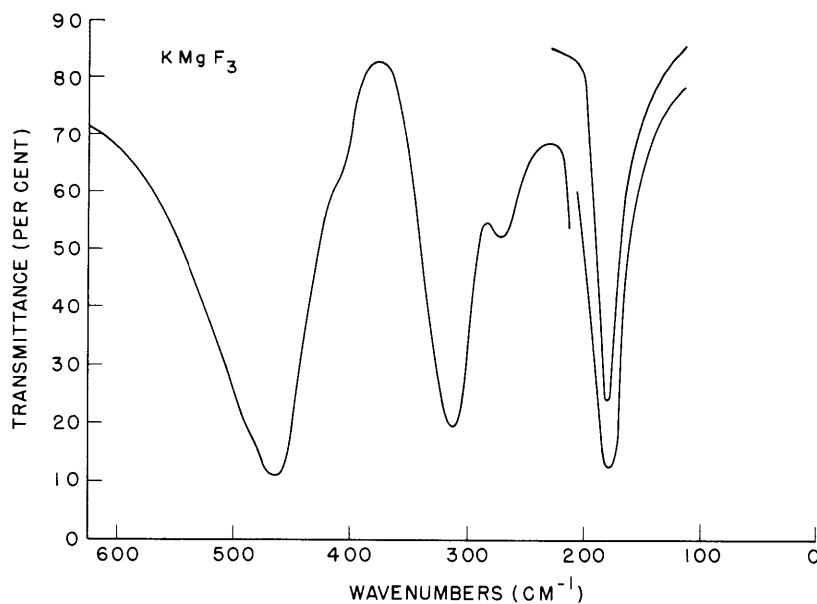


Fig. IV-1. Transmittance of KMgF_3 in polyethylene films.

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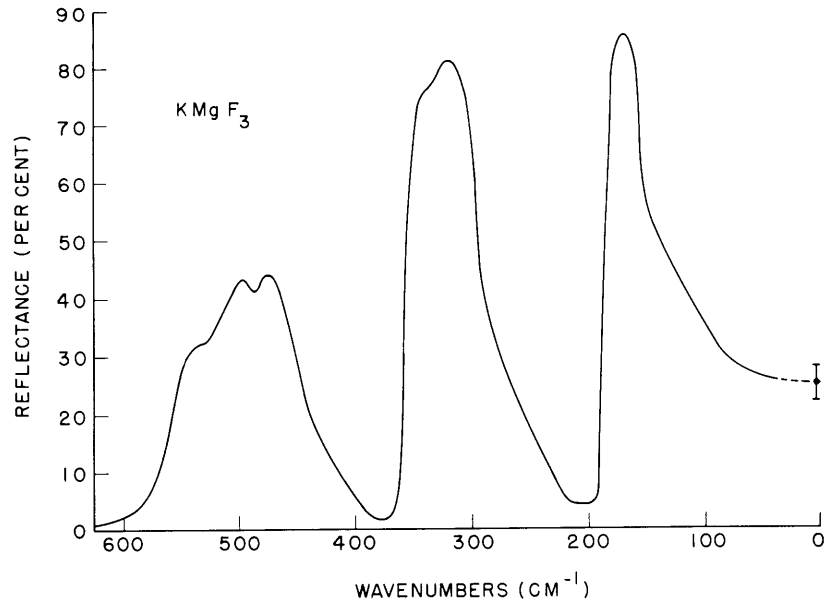


Fig. IV-2. Reflectance of KMgF_3 .

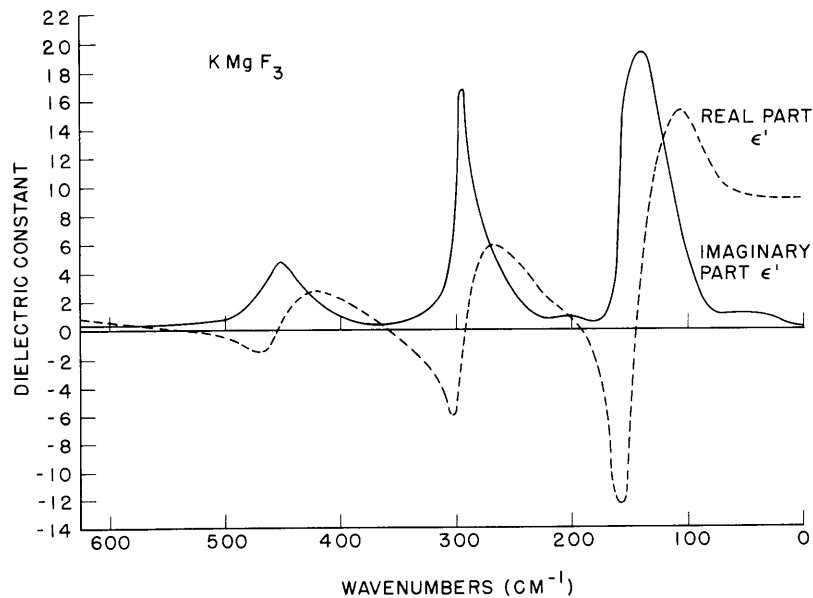


Fig. IV-3. K-K analysis of reflectance data for KMgF_3 .

cassiterite (SnO_2), belongs to the space group $D_{4h}^{14} [P_{4_2}/mnm]$,¹² and contains two molecules of MgF_2 per unit cell. The magnesium atoms have D_{2h} site symmetry, and the fluorine atoms have C_{2v} . Using the considerations outlined above, we find that the vibrations belong to the following symmetry species of the D_{4h} space group (D_{4h}):

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Table IV-1. Frequencies (in cm^{-1}) and symmetry of infrared modes obtained from K-K analysis of the reflection data for KMgF_3 and for MgF_2 .

(a) KMgF_3			
ν_1	450	F_{1u}	MgF stretch
ν_2	295	F_{1u}	FMgF bend
ν_3	140	F_{1u}	K-(MgF_3) stretch (lattice mode)
(b) MgF_2			
ν_1	435	E_u	MgF stretch
ν_2	405	E_u	MgF stretch - FMgF bend
ν_3	280	E_u	pseudo lattice modes with Mg moving one way and F in the opposite direction
ν_4	265	A_{2u}	

$A_{1g} + A_{2g} + A_{2u} + B_{1g} + B_{2g} + 2B_{1u} + E_g + 3E_u$, of which only the A_{2u} and $3E_u$ modes are infrared-active. This agrees with the results of the treatment of the rutile vibrations by Narayanan¹³ and Matossi.¹⁴

The transmission and reflection spectra and the dielectric dispersion data for MgF_2

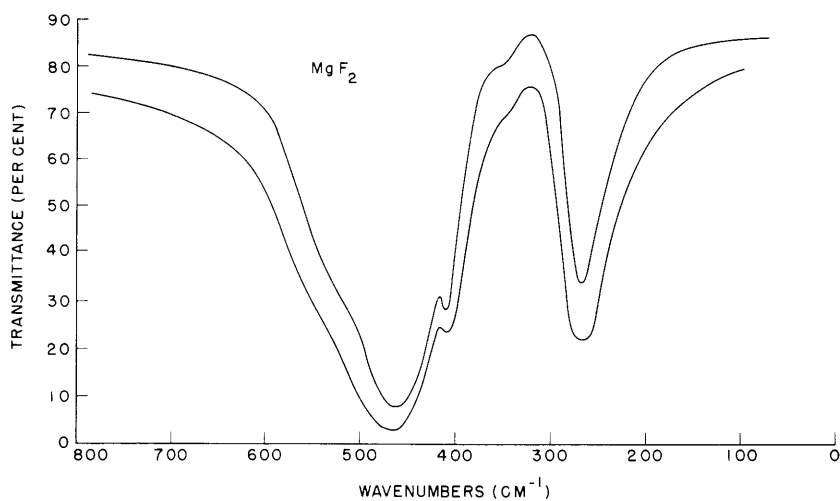


Fig. IV-4. Transmittance of MgF_2 in polyethylene films.

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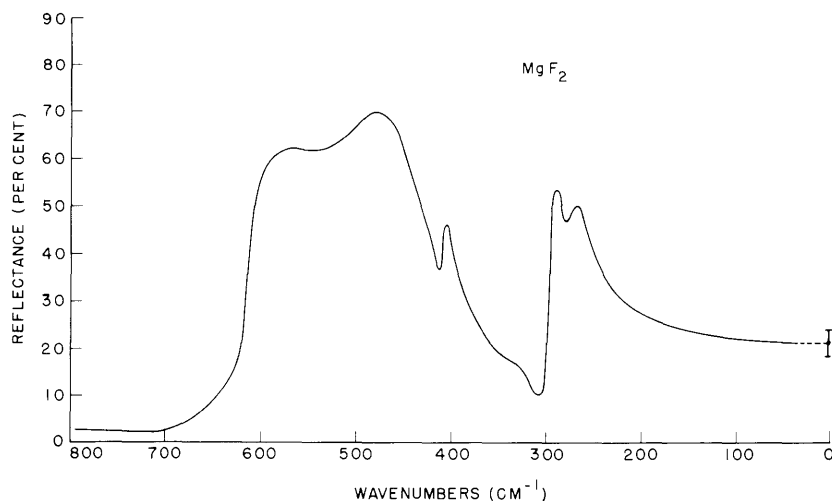


Fig. IV-5. Reflectance of MgF₂.

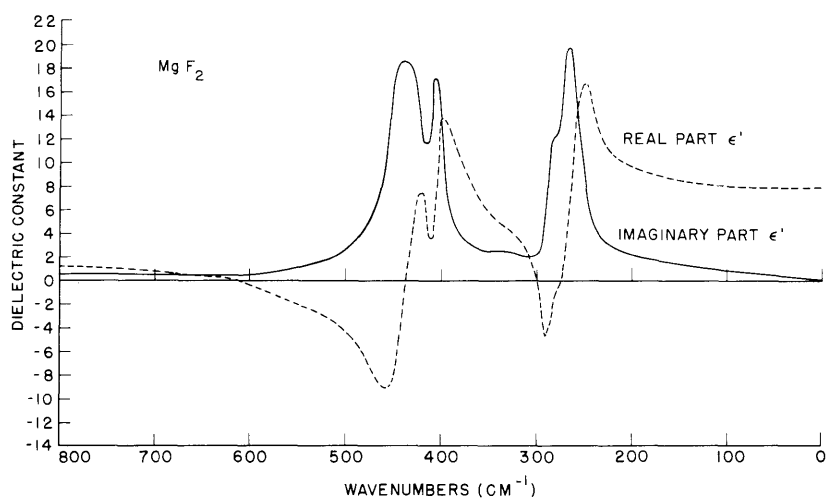


Fig. IV-6. K-K analysis of reflectance data for MgF₂.

are shown in Figs. IV-4, IV-5, and IV-6, and the resonant frequencies are listed in Table IV-1b. The A_{2u} and one of the E_u modes correspond to motions in which all of the fluorine atoms are moving together in a direction opposite to that of all the Mg atoms. There is, of course, no "lattice" mode corresponding to that for $KMgF_3$. The two remaining E_u modes can be considered as motions in which only the fluorine atoms are moving appreciably. The stretching and bending modes are more difficult to describe and less pure than for $KMgF_3$, since the fluorines in MgF_2 form an irregular octahedron around the magnesium atoms and consequently the lattice is made up of interpenetrating unit cells. Hence a mode in one cell which could be described as predominantly a

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stretching mode automatically gives rise to a predominantly bending mode in all of the interpenetrating cells. Again, a full description of the form of the vibrations must await a normal coordinate analysis for which the additional information regarding the frequencies of the infrared-active modes must be obtained from the Raman spectrum.

We wish to express our thanks to Professor R. C. Lord of M. I. T. for his encouragement in this work and for many helpful suggestions; to Dr. D. L. Wood of Bell Telephone Laboratories, Inc. for useful discussions; to Mr. J. Ballentyne of the Insulation Laboratory, M. I. T., for reflection measurements at 5 cm^{-1} taken at Lincoln Laboratory, M. I. T., and for the use of his K-K analysis program, and to Dr. H. J. Guggenheim and Dr. K. Knox of Bell Telephone Laboratories, Inc. for the crystal samples.

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(Dr. G. R. Hunt is now at the Air Force Cambridge Research Laboratories (CRFL), Bedford, Massachusetts. Dr. J. Ferguson is at Bell Telephone Laboratories, Inc., Murray Hill, New Jersey.)

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B. INFRARED ABSORPTION SPECTRA OF CRYSTALLINE K_2PtCl_4

1. Introduction

Many fundamental frequencies of inorganic molecules occur below 400 cm^{-1} . In particular, the stretching and bending frequencies of metal-halogen bonds and lattice

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vibrations occur in this region. We have made a preliminary investigation of K_2PtCl_4 with a view toward extending this study to other complex halides. A similar solid-state study of this molecule has been carried out recently by D. M. Adams and H. A. Gebbie,¹ using a far infrared interferometer. There is some disagreement, however, in the assignment of the infrared normal modes because we have found two additional infrared-active vibrations that were not observed by the previous authors. Owing to the presence of a center of symmetry in the unit cell of these crystals, there is a mutual exclusion rule between the infrared- and the Raman-active modes. The Raman spectra of the complex ion $(PtCl_4)^{2-}$ has been observed by H. Stammreich and R. Forneris,² and the assignment of the observed frequencies to the Raman-active modes can be made directly.

2. Experiment

Transmission measurements of crystalline K_2PtCl_4 suspended in polyethylene matrices³ have been studied from 400 to 60 cm^{-1} . The measurements above 250 cm^{-1} were made on a P-E double-beam spectrophotometer, and below 250 cm^{-1} they were recorded on the single-beam vacuum far infrared instrument.^{4,5} Preliminary investigation at room temperature showed a strong band at $\sim 320\text{ cm}^{-1}$, and two broad bands in the far infrared. Further experiments with samples of various thicknesses showed that the two broad bands were probably each split, and this was confirmed by transmission measurements at liquid-nitrogen temperature, with the use of the Limit Research

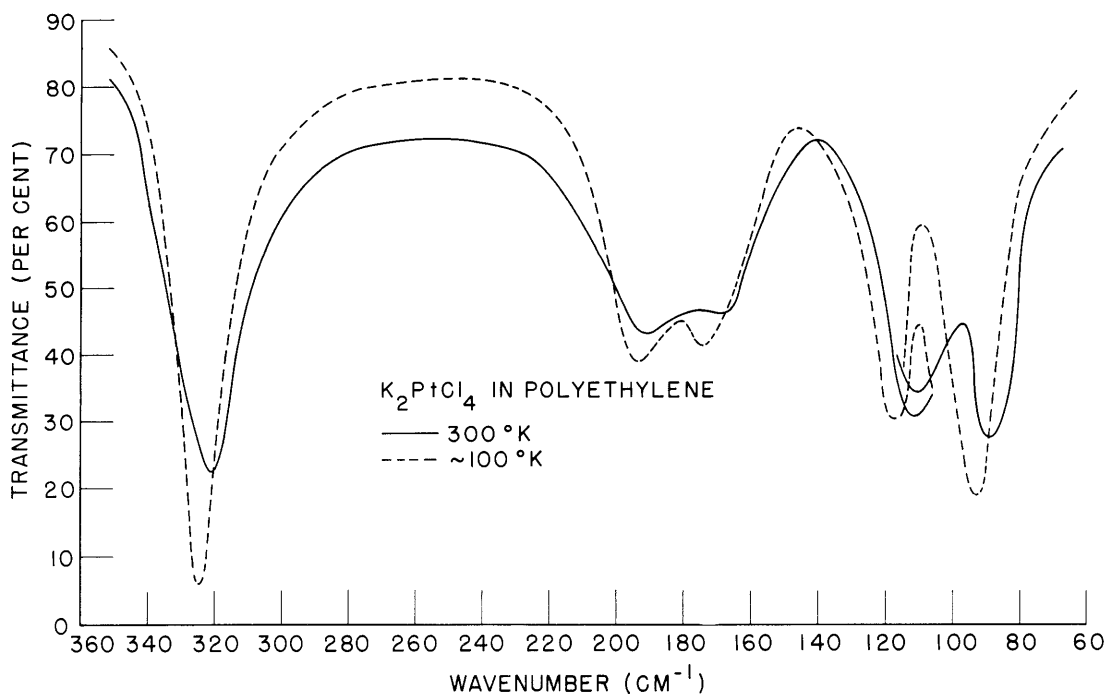


Fig. IV-7. Transmittance of K_2PtCl_4 in polyethylene from 60 cm^{-1} to 360 cm^{-1} .

Table IV-2. Internal and lattice vibrations in K_2PtCl_4 . Crystal Structure D'_{4h} , one molecule per unit cell.

Frequency (cm^{-1})		Approximate intensity	Species	Selection rules	Qualitative description
300°K	100°K				
89 ± 2	91 ± 1	strong	E_u	Infrared	Lattice mode (Doubly degenerate)
110 ± 2	117 ± 2	medium	A_{2u}	Infrared	Lattice mode
164	—	weak	B_{1g}	Raman	$PtCl_4$ I. P. bending
170 ± 5	174 ± 2	weak	A_{2u}	Infrared	$PtCl_4$ O. P. bending
190 ± 5	193 ± 2	weak	E_u	Infrared	$PtCl_4$ I. P. bending
304	—	strong	B_{2g}	Raman	$PtCl_4$ I. P. anti-symmetric stretching
321 ± 1	324 ± 1	strong	E_u	Infrared	$PtCl_4$ I. P. stretching
335	—	strong	A_{1g}	Raman	$PtCl_4$ I. P. symmetric stretching
—	—	—	B_{1u}	Inactive in infrared and Raman	$PtCl_4$ O. P. bending

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Corporation low-temperature cell both in the P-E 521 and in the far infrared instrument. The final results are shown in Fig. IV-7 for the sample of ~ 3 mg K_2PtCl_4 per square centimeter run at $\sim 300^\circ K$ and $\sim 100^\circ K$.

3. Discussion

The vibrational spectrum of $R_n(XY_4)$ molecules belonging to the D_{4h}^1 space group would be expected to consist of 5 nondegenerate and two doubly degenerate fundamental modes for the $(XY_4)^{n-}$ ion. The tetragonal crystal structure⁶ would cause the triply degenerate lattice modes to split into a nondegenerate and a doubly degenerate lattice mode.

Three Raman-active frequencies have been observed,² in full agreement with the selection rules, and the normal mode assignment can be made directly. Two doubly degenerate and one nondegenerate mode are active in the infrared, together with one degenerate and one nondegenerate lattice mode as described above. Five infrared-active vibrations have been observed in our results (see Fig. IV-7) and this is in full agreement with the selection rules. The frequencies, vibrational assignment and a short description of the motion are given in Table IV-2.

Macoll⁷ gives the approximate form of these normal vibrations and the symmetry species, with which all previous workers^{1,2} and the present authors agree. Adams and Gebbie,¹ however, in the assignment of their frequencies ignore the fact that they may not have been able to resolve all of the bands and also the possibility that one of the bands with which they associate an internal vibration may be a lattice mode. This

Table IV-3.

Frequency (cm^{-1})		Species	Qualitative description
Adams and Gebbie	This work		
320	321 ± 1	E_u	$PtCl_4$ I. P. stretching
183*	190 ± 5	E_u	$PtCl_4$ I. P. bending
93*	170 ± 5	A_{2u}	$PtCl_4$ O. P. bending
—	110 ± 2	A_{2u}	Lattice mode
—	89 ± 2	E_u	Lattice mode
*broad			

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can be seen more clearly in Table IV-3, in which our results are compared with those of Adams and Gebbie.

The complete removal of these ambiguities can only be accomplished by further measurements on materials of similar structure. Consequently, work is already in progress here on Rb_2PtCl_4 and Cs_2PtCl_4 . We would expect that the cation- (PtCl_4) lattice vibrations would be most changed, and we would expect to see the two lowest vibrations shift to even lower frequency, and little change in frequency for those associated with the PtCl_4 internal vibrations if our interpretation is correct.

Further study is proposed for the bromides of these materials, and also for PdII and AuIII (in place of the PtII), in order to determine the low internal molecular and lattice vibrations for all of these materials.

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