

Far-Infrared Reflectance and Transmittance of Potassium Magnesium Fluoride and Magnesium Fluoride

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The room-temperature transmittance of KMgF_3 and MgF_2 have been measured from 800 to 70 cm^{-1} . Reflectance measurements were made over a wider range in the far infrared and the data have been analyzed using the Kramers-Kronig relationship to obtain the dielectric dispersion of these materials. Three resonances were observed for KMgF_3 and four were observed for MgF_2 as required by standard group theory and these have been related to presumed normal modes of vibration of the crystals.

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 obtain such information several studies¹⁻⁵ of the far-infrared and Raman spectra of the perovskite titanates and the related rutile have been recently reported. 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 current electronic absorption spectral studies of the compounds by one of us (JF), we present here the transmittance and reflectance spectra and the dielectric dispersion of potassium magnesium fluoride and magnesium fluoride as a prelude to a more comprehensive study of the vibrational nature of fluoride perovskites and their "rutile" counterparts.

EXPERIMENTAL

The room-temperature reflectances of potassium magnesium fluoride and magnesium fluoride have been measured using unpolarized radiation from 4000 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} using a "Carcinotron" source of 2-mm radiation at Lincoln Laboratory, MIT; the

samples were mounted at a 20° included-angle bend 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 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 about 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 MIT Spectroscopy Laboratory was used for measurements below 500 cm^{-1} .⁶ This instrument was improved by complete enclosure in a vacuum case,⁷ allowing 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. The KMgF_3 sample was a single crystal with a polished face about one-half 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 on finely divided powders dispersed in KBr matrices for measurements above 300 cm^{-1} and dispersed in polyethylene for measurements below 600 cm^{-1} .

DATA ANALYSIS

The real and imaginary parts of the complex dielectric constant ($\epsilon' = n^2 - k^2$ and $\epsilon'' = 2nk$), respectively, where n is the refractive index and k is the absorption

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¹ J. T. Last, *Phys. Rev.* **105**, 1740 (1957).

² A. S. Barker, Jr., and M. Tinkham, *Phys. Rev.* **125**, 1527 (1962).

³ W. G. Spitzer, R. C. Miller, D. A. Kleinman, and L. E. Howarth, *Phys. Rev.* **126**, 1710 (1962).

⁴ P. S. Narayanan and K. Vedam, *Z. Physik* **163**, 158 (1961).

⁵ C. H. Perry and B. N. Khanna, MIT Research Laboratory of Electronics, Quarterly Progress Report No. 71, 1963 (unpublished).

⁶ R. C. Lord and T. K. McCubbin, Jr., *J. Opt. Soc. Am.* **47**, 689 (1957).

⁷ C. H. Perry, Spectroscopy Laboratory and Research Laboratory of Electronics, Quarterly Progress Report No. 70, 1963 (unpublished).

coefficient, were obtained by transforming the reflectance data using the Kramers-Kronig relation.^{8,9} 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

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

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 MIT Computation Center.

DISCUSSION

Potassium magnesium fluoride possesses the cubic perovskite crystal structure, which belongs to the space group¹⁰ $0_h^1(P_{m3m})$ 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 0_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 six half-oxygen atoms. The latter are treated under the point group 0_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 Vadam,⁴ in reporting the Raman spectrum of strontium titanate, disagree with Last's conclusion and assert that there are in fact four nontranslatory triply-degenerate sets of infrared-active modes, all of which belong to species F_{1u} , and they quote Rajagopal's¹¹ treatment of the lattice dynamics of cubic perovskites as substantiating this contention. We feel that they have misinterpreted this latter 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 five triply-degenerate oscillations, of which one is the acoustical or translatory mode), and further 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

⁸ T. S. Robinson, Proc. Phys. Soc. (London) **B65**, 910 (1952).

⁹ F. Abeles and J. Mathieu, Ann. Phys. (Paris) **3**, 5 (1958).

¹⁰ R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., 1948), VII, A5.

¹¹ A. K. Rajagopal, Phys. Chem. Solids **23**, 633 (1962).

arrive at a conclusion in agreement with Last's. Procedures for determining the selection rules for optical transitions in crystals have been devised by Bhagavantam and Venkatarayudu¹² and have been extended by Winston and Halford.¹³ 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

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

where N is the order of the group; h_{ρ} the number of group operations falling under the class ρ ; $X_{\rho}'(\rho)$ and $X_i(\rho)$ are, respectively, the characters of the group operation ρ in the representation Γ and Γ_i ; and where

$$X_{\rho}'(\rho) = U_{\rho}(\pm 1 + 2 \cos \phi_{\rho}).$$

Proper rotations by ϕ take the positive sign and improper rotations take the negative sign. For point group operations, U_{ρ} is given by the number of atoms which remain invariant under the operation ρ . For space group operations, however, which are appropriate when considering crystals, U_{ρ} is the number of atoms in the repeating unit (for crystals, the unit cell) which, for a particular operation ρ , contain either the appropriate rotation axis, reflection plane or inversion center. When applied to KMgF_3 (which has an ideal cubic perovskite structure¹⁴), the above 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 1 and 2 show the transmittance and reflectance spectra of KMgF_3 , and Fig. 3 shows the real and imaginary part of the dielectric constant calculated

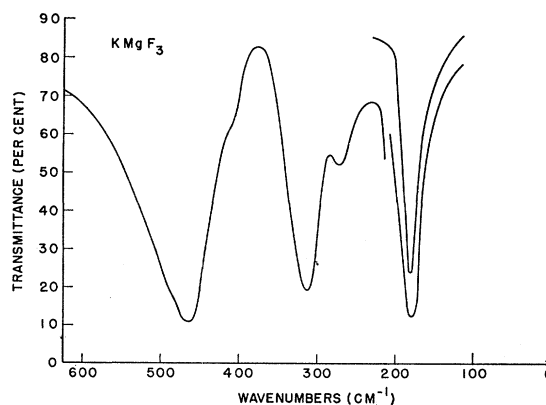
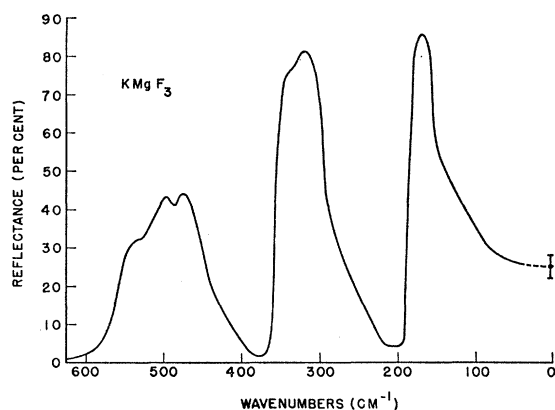


FIG. 1. Transmittance of KMgF_3 in polyethylene films.

¹² S. Bhagavantam and T. Venkatarayudu, Proc. Indian Acad. Sci. **9A**, 224 (1939).

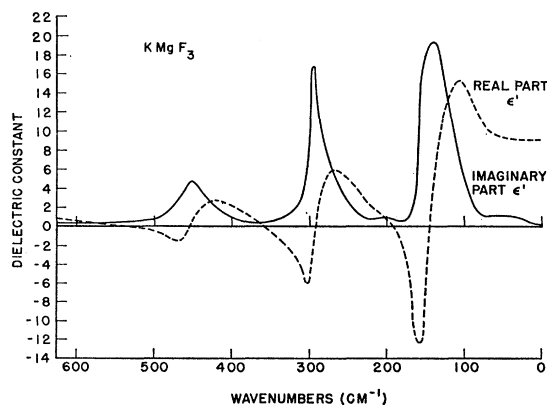
¹³ H. Winston and R. S. Halford, J. Chem. Phys. **17**, 607 (1949).

¹⁴ K. Knox (private communication).

FIG. 2. Reflectance of KMgF_3 .

from the reflectance data. The maxima of the imaginary part yields the true resonant frequencies, and these are listed together with assignments in Table I. 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.

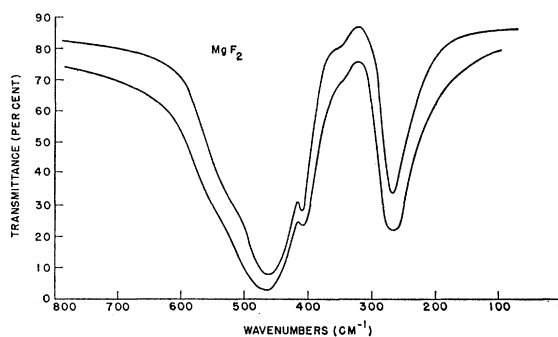
For magnesium fluoride, the tetragonal crystal structure is isomorphous with cassiterite (SnO_2) and belongs to the space group¹⁵ $D_{4h}^{14} [P_{42}/mmm]$ and contains two molecules of MgF_2 per unit cell. The magnesium atoms have D_{2h} site symmetry while that for the fluorine atoms is C_{2v} . Using the considerations outlined above, we find the vibrations belong to the following symmetry species of the D_{4h} space group (D_{4h}): $A_{1g} + A_{2g} + A_{2u} + B_{1g} + B_{2g} + 2B_{1u} + E_g + 3E_u$, 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 Narayanan¹⁶ and Matossi.¹⁷

FIG. 3. K-K analysis of reflectance data for KMgF_3 .

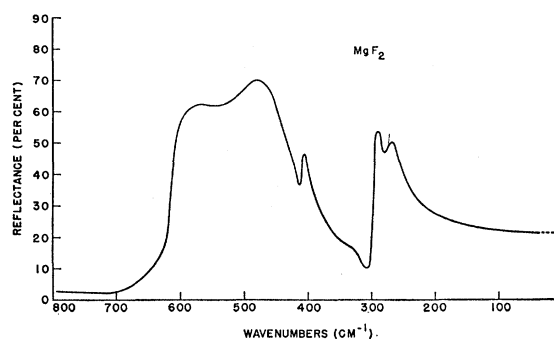
¹⁵ R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1951), IV, B1.

¹⁶ P. S. Narayanan, *J. Indian Acad. Sci.* 32, 279 (1950).

¹⁷ F. Matossi, *J. Chem. Phys.* 19, 1543 (1951).

FIG. 4. Transmittance of MgF_2 in polyethylene films.

The transmission and reflection spectra and the dielectric dispersion data for MgF_2 are shown in Figs. 4-6, and the resonant frequencies are listed in Table II. The A_{2u} and one of the E_u modes correspond to motions in which all the fluorine atoms are moving together in a direction opposite to that of all the Mg atoms. There is

FIG. 5. Reflectance of MgF_2 .

of course no "lattice" mode corresponding to that for KMgF_3 . The remaining two 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

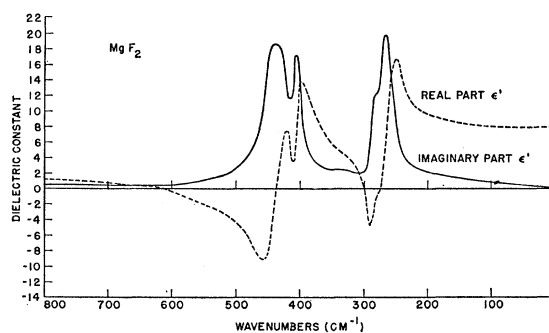
FIG. 6. K-K analysis of reflectance data for MgF_2 .

TABLE I. KMgF_3 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 .

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)

TABLE II. MgF_2 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 .

ν_1	435	E_u	MgF stretch
ν_2	405	E_u	MgF stretch—FMgF bend
ν_3	280	E_u	Pseudolattice modes where Mg moving one way and F in opposite
ν_4	265	A_{2u}	

around the magnesium atoms and the lattice is consequently made up of interpenetrating unit cells. Hence, a mode in one cell which could be described as predominantly a stretching mode automatically gives rise to a predominantly bending mode in all 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-inactive modes must be obtained from the Raman spectrum.

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Phase Transformation in Samarium Induced by High Pressure and Its Effect on the Antiferromagnetic Ordering

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Samarium undergoes a pressure induced phase transformation to double-hexagonal close-packed (La-type) structure at pressures around 40 kbar and temperatures near 300°C . It is retained metastably at atmospheric pressure. The new phase has a Néel temperature of 27°K as compared to 14.8°K noted for normal form of Sm. Pressure induced phase transformations observed in Gd, Sm, Ce, and La suggest that the sequence of polymorphic transformations under pressure in trivalent rare earths is in the order hcp \rightarrow Sm-type \rightarrow dhcp \rightarrow fcc.

WE wish to report a pressure induced phase transformation in samarium metal to the double-hexagonal close-packed (La-type) structure. The phase change is accompanied by a shift of the Néel temperature from 14.8°K to 27°K . This structural transformation in Sm, together with the recently reported pressure-induced phase change in hcp Gd^{2+} suggests that there might be a sequence of pressure-induced polymorphic transformations in the trivalent rare earths.

Bridgman³ was the first to measure resistivity and volume of Sm as a function of pressure; he found no unusual features. Recently, Stager and Drickamer⁴ have observed some minor deviations from normal behavior in the resistivity of Sm in the region 50 to 500 kbar.

In the present study, Sm was subjected to a pressure

of about 40 kbar in a piston cylinder apparatus at about 350°C , as well as at room temperature. The pressure medium was silicone oil (40 centistokes). A Teflon cell⁵ was used as the container for the oil and the cell was made to fit into a furnace assembly to facilitate heating. Because a large sample volume of about 1 cc was needed for magnetic studies, the furnace assembly was suitably dimensioned to fit into a 1-in.-diam and 2-in.-long pressure chamber. After the sample was subjected to the required pressure and temperature for about 15 min, temperature was reduced to ambient and pressure then released.

X-ray powder photographs of pressurized Sm were taken with $\text{CrK}\alpha$ radiation. The x-ray data (Table I) are consistent with the dhcp structure (La-type); the lattice constants are $a=3.618\pm 0.005 \text{ \AA}$, $c=11.66\pm 0.01 \text{ \AA}$. The density calculated from x-ray data is 7.555 g/cc for the dhcp phase as compared with 7.536

¹ J. M. Lock, Proc. Phys. Soc. (London) **B70**, 566 (1957).² A. Jayaraman and R. C. Sherwood, Phys. Rev. Letters **12**, 22 (1964).³ P. W. Bridgman, Proc. Am. Acad. Arts Sci. **83**, 1 (1954).⁴ R. A. Stager and H. G. Drickamer, Phys. Rev. **133**, A830 (1964).⁵ S. Geller, D. B. McWhan, and G. W. Hull, Jr., Science **140**, 62 (1963).