# IV. FAR INFRARED SPECTROSCOPY

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## A. WORK COMPLETED

The theses listed below were submitted to the Department of Physics, M. I. T., May 1964, in partial fulfillment of the requirements for the degree of Bachelor of Science.

Jeanne H. Fertel, "Long-Wave Infrared Spectra of Alkali Salts of Some Noble-Metal Halide Complexes."

D. J. McCarthy, "Far Infrared Spectroscopic Study of the Perovskite Structure as Evidenced by Zirconate Compounds."

H. D. Wactlar, "Far Infrared Study of Collective Oscillations in Perovskites."

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## B. LONG-WAVE INFRARED SPECTRA OF ALKALI SALTS OF PLATINUM HALIDE COMPLEXES

The infrared absorption spectra of crystalline $K_2PtCl_4$ have recently been reported by Adams and Gebbie and by our group.[2] A more extensive study of alkali salts of platinum halide complexes has been completed and the results have indicated that our earlier predictions appear to be correct.

The molecules $R_2XY_4$ belong to the point group $D_{4h}$. They have a tetragonal crystal structure with one molecule per unit cell.[3]

Their spectra contain both bands arising from internal vibrations of the $XY_4^{-2}$ ions, and bands that are due to vibration of the lattice with respect to these ions. The $XY_4^{-2}$ ions have a square planar configuration and also belong to the point group $D_{4h}$. The symmetry species of their normal vibrations are listed in Table IV-1.

The figures in the column labeled $\Gamma_a$ give the number of normal vibrations in each symmetry species. All A and B species are nondegenerate, with the letters A and B referring to symmetry or antisymmetry with respect to $C_4$. The subscripts g and u refer to symmetry and asymmetry with respect to inversion, while 1 and 2 refer to symmetry or asymmetry with respect to $C_2'$. The letter E represents a doubly degenerate vibration. The spectrum of the $XY_4^{-2}$ ions would therefore be expected to consist of 5 nondegenerate and 2 doubly degenerate fundamental modes.

Table IV-1. Character Table.

| $D_{4h}$ | E | $2C_4$ | $C_2$ | $2C_2'$ | $2C_2''$ | i | $2S_4$ | $\sigma_h$ | $2\sigma_v$ | $2\sigma_d$ | $\Gamma_c$ | $\Gamma_a$ | Activity |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $A_{1g}$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | Raman |
| $A_{2g}$ | 1 | 1 | 1 | -1 | -1 | 1 | 1 | 1 | -1 | -1 | 1 | 0 | |
| $B_{1g}$ | 1 | -1 | 1 | 1 | -1 | 1 | -1 | 1 | 1 | -1 | 1 | 1 | Raman |
| $B_{2g}$ | 1 | -1 | 1 | -1 | 1 | 1 | -1 | 1 | -1 | 1 | 1 | 1 | Raman |
| $E_g$ | 2 | 0 | -2 | 0 | 0 | 2 | 0 | -2 | 0 | 0 | 1 | 0 | |
| $A_{1u}$ | 1 | 1 | 1 | 1 | 1 | -1 | -1 | -1 | -1 | -1 | 0 | 0 | |
| $A_{2u}$ | 1 | 1 | 1 | -1 | -1 | -1 | -1 | -1 | 1 | 1 | 2 | 1 | I. R. |
| $B_{1u}$ | 1 | -1 | 1 | 1 | -1 | -1 | 1 | -1 | -1 | 1 | 0 | 0 | |
| $B_{2u}$ | 1 | -1 | 1 | -1 | 1 | -1 | 1 | -1 | 1 | -1 | 1 | 1 | — |
| $E_u$ | 2 | 0 | -2 | 0 | 0 | -2 | 0 | 2 | 0 | 0 | 3 | 2 | I. R. |
| $X_c$ | 15 | 1 | -1 | -3 | -1 | -3 | -1 | 5 | 3 | 1 | | | |

The approximate form of these vibrations is shown in Fig. IV-1; they were first discussed by Macoll[4] for a square planar molecule.

The out-of-plane bending vibration $\nu_4$ is inactive in both the Raman and the infrared. There are three Raman-active fundamentals: the symmetric stretching $\nu_1$, the antisymmetric stretching $\nu_5$, and the in-plane bending vibration $\nu_3$. These have been observed, for the $PtCl_4^{-2}$ ion, by Stammreich and Forneris[5] who report the values listed in

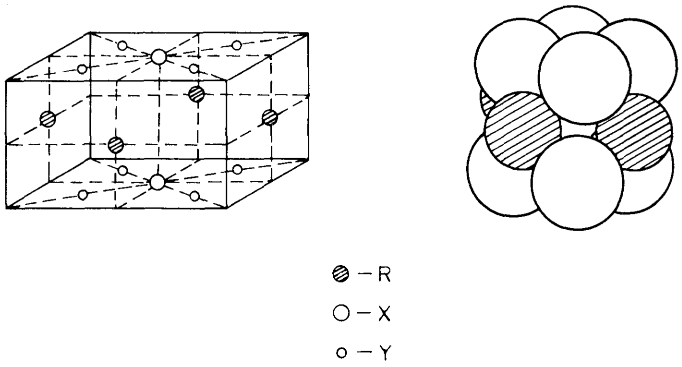


Fig. IV-1. Approximate form of the normal vibrations of an $R_2XY_4$ crystal.

Table IV-2. Because of the presence of a center of symmetry in these ions, the rule of mutual exclusion applies, and none of these vibrations appears in the infrared.

Table IV-2. Raman frequencies of $PtCl_4^{-2}$.

| Frequency ($cm^{-1}$) | Assignment | Species |
|---|---|---|
| 164 | $\nu_3$ | $B_{1g}$ |
| 304 | $\nu_5$ | $B_{2g}$ |
| 335 | $\nu_1$ | $A_{1g}$ |

The out-of-plane bending $\nu_2$, the in-plane stretching $\nu_6$, and the in-plane bending ($\nu_7$) vibrations are all active in the infrared. The tetragonal structure of the $R_2XY_4$ crystals gives rise to a nondegenerate and a doubly degenerate lattice mode. (See Figs. IV-1 and IV-2.) The complete infrared spectrum of these compounds would therefore be expected to consist of two nondegenerate and three doubly degenerate fundamental vibrations.

A solid-state study of $K_2PtCl_4$ and $K_2PtBr_4$ has been carried out by Adams and Gebbie,[1] who used a far infrared interferometer. They observed four bands in the $K_2PtBr_4$ spectrum, and only three, two of which were very broad, in the spectrum of $K_2PtCl_4$. In assigning the normal modes, they took these to be the three internal vibrations and ignored the possibility of lattice bands. Subsequent experiments, including transmission measurements at liquid-nitrogen temperature, have shown that several of the bands observed by Adams and Gebbie are in fact split, and we have been able to observe the expected 5 vibrations in most of the examined $R_2XY_4$ compounds, although not in all.

### 1. Experiment

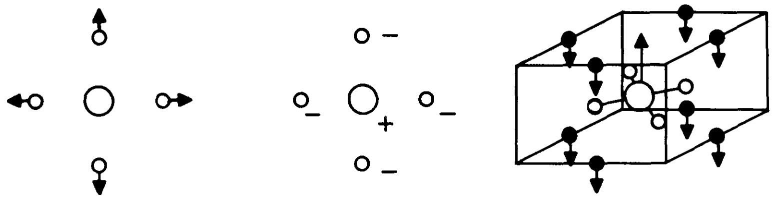
### a. Instrumentation

Transmission measurements above 250 $cm^{-1}$ were made on a Perkin-Elmer Model 521 double-beam spectrophotometer. Below 250 $cm^{-1}$, they were recorded on our single-beam vacuum far infrared spectrometer.[6, 7]

The room-temperature spectrum of $Cs_2PtBr_4$ below 80 $cm^{-1}$, and the complete spectra of $Rb_2PtBr_4$ and $Rb_2PtCl_4$ were taken by Dr. Howard Sloane, of Beckman Instruments, Inc., on the new IR-11 double-beam spectrophotometer.

### b. Preparation of Samples

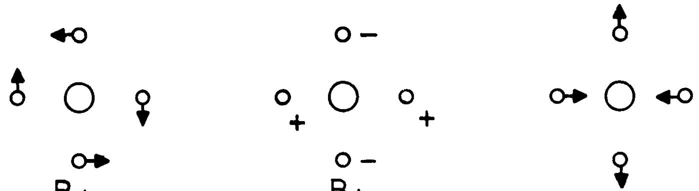
All samples were examined in the solid state, suspended in polyethylene matrices. They were prepared by pressing a mixture of powdered polyethylene and approximately



$A_{1g}$
I.P. SYMMETRIC STRETCHING

$A_{2u}$
O.P. BENDING

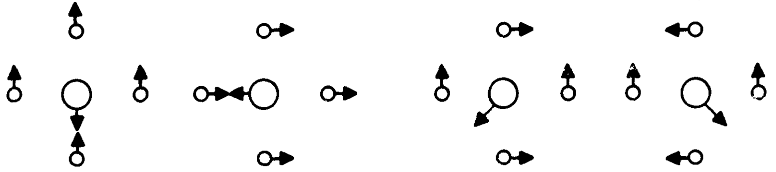
$A_{2u}$
LATTICE MODE



$B_{1g}$
I.P. BENDING

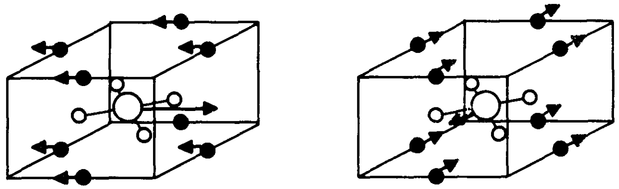
$B_{1u}$
O.P. BENDING

$B_{2g}$
I.P. ANTISYMMETRIC STRETCHING



$E_u$
I.P. STRETCHING

$E_u$
I.P. BENDING



$E_u$
LATTICE MODE

Fig. IV-2. Unit cell of $R_2XY_4$ and lattice vibrations of $R_2XY_4$.

10 per cent crystalline compound by weight at 18,000 lbs per square inch and at 120°C for two minutes. The resulting films were approximately 10 mils thick. A plain polyethylene film, prepared in the same manner, was used in front of the reference beam of the P-E 521.

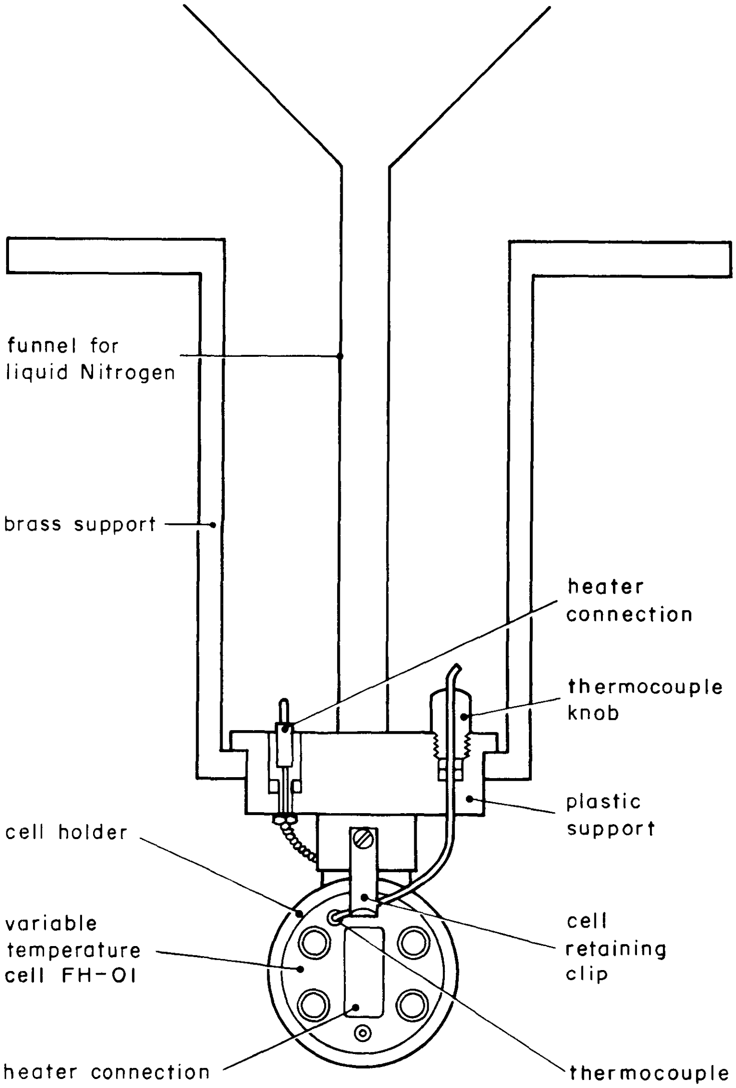


Fig. IV-3. Low-temperature cell.

For transmission measurements in both instruments at liquid-nitrogen temperature, the samples were mounted in our modified Limit Research Corporation low-temperature cell (see Fig. IV-3).

Dr. Sloane suspended the $Cs_2PtBr_4$ in a nujol mull to remove troublesome channel spectra in the polyethylene sample.

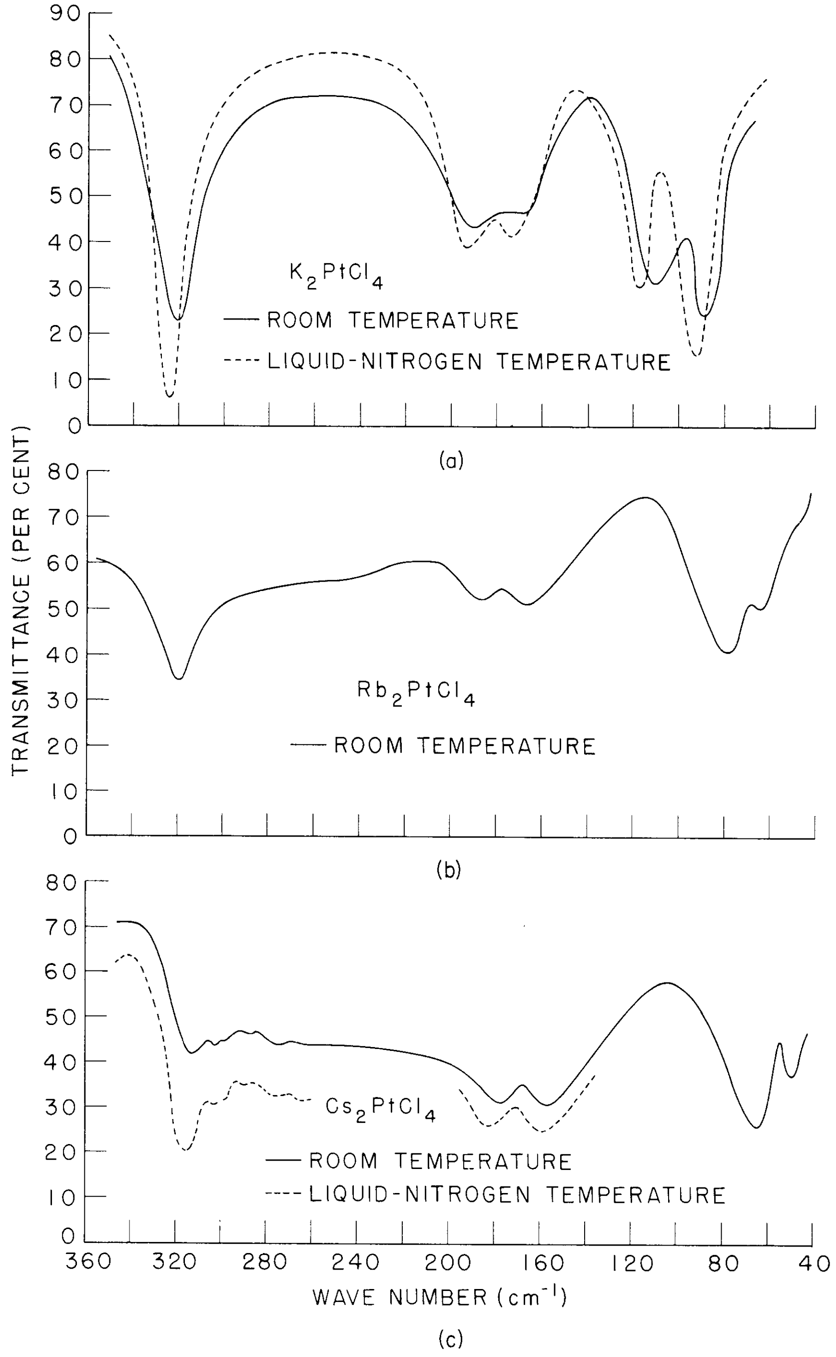


Fig. IV-4. Transmission spectra of $K_2PtCl_4$, $Rb_2PtCl_4$, $Cs_2PtCl_4$.

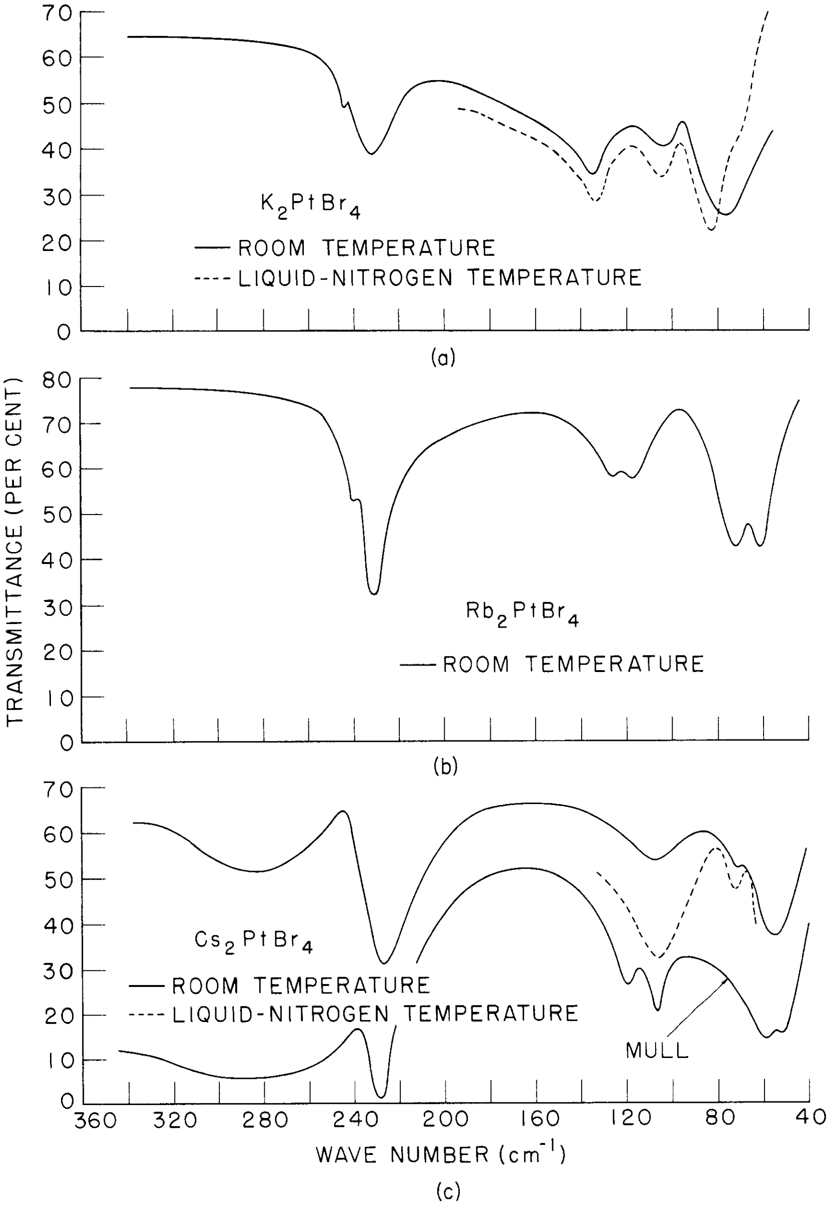


Fig. IV-5. Transmission spectra of $K_2PtBr_4$, $Rb_2PtBr_4$, $Cs_2PtBr_4$.

## 2. Results

The spectra of $K_2PtCl_4$, $Rb_2PtCl_4$, $Cs_2PtCl_4$, $K_2PtBr_4$, $Rb_2PtBr_4$, and $Cs_2PtBr_4$ are shown in Figs. IV-4 and IV-5. Most of the absorption bands were sufficiently intense to be observed at room temperature; however, in some cases, particularly those of $K_2PtCl_4$ and $Cs_2PtBr_4$, cooling the sample gave rise to a marked improvement in resolution. The frequencies, vibrational assignments, and relative intensities of the bands for the six compounds are listed in Table IV-3.

Table IV-3. Frequencies and intensities of absorption bands for square-planar halides.

| Compound | $\nu_6$ | $\nu_7$ | $\nu_2$ | Lattice Modes | |
|---|---|---|---|---|---|
| $K_2PtCl_4$ | 321 (s) | 191 (w) | 168 (w) | 111 (m) | 89 (s) |
| $Rb_2PtCl_4$ | 320 (s) | 186 (w) | 166 (w) | 79 (m) | 64 (w) |
| $Cs_2PtCl_4$ | 313 (w) | 177 (m) | 157 (m) | 65 (m) | 50 (m) |
| $K_2PtBr_4$ | 232 (s) | 135 (m) | | 104 (m) | 76 (s) |
| $Rb_2PtBr_4$ | 231 (s) | 126 (w) | 117 (w) | 72 (m) | 61 (m) |
| $Cs_2PtBr_4$ | 229 (s) | 120 (m) | 108 (m) | 60 (s) | 51 (s) |

(s) = strong, (m) = medium, (w) = weak, (vw) = very weak

## 3. Assignment of Normal Vibrations

The absorption spectra of the three $PtCl_4^{-2}$ compounds consists of five bands, in full agreement with the selection rules. Assignments of the observed frequencies to the infrared active normal modes can be made directly. The $PtCl_4^{-2}$ stretching vibration $\nu_6$ corresponds undoubtedly to the band of highest frequency: 313 $cm^{-1}$ for $Cs_2PtCl_4$, 320 $cm^{-1}$ for $Rb_2PtCl_4$, and 321 $cm^{-1}$ for $K_2PtCl_4$. The last value is approximately that given by Adams and Gebbie for the stretching vibration of $K_2PtCl_4$.[1]

The two bands of lowest frequency correspond to the lattice vibrations. This assignment is confirmed by the fact that these bands show the greatest variation in frequency among the three compounds. The two remaining bands are ascribed to the $PtCl_4^{-2}$ bending mode, the in-plane vibration $\nu_7$ being of slightly higher frequency than the out-of-plane vibration $\nu_2$.

The $Rb_2PtBr_4$ spectrum also contains the expected five bands and these are assigned as in the case of $Rb_2PtCl_4$. The spectrum of $K_2PtBr_4$ is less clear. Again, the highest frequency band can be assigned to the stretching vibration, and the lowest is undoubtedly a lattice mode. The other bands, however, can only be assigned tentatively. The $K_2PtBr_4$

band at 104 $cm^{-1}$ is too low in frequency to be a bending vibration and must therefore be the other lattice mode. Since even in the case of $Rb_2PtBr_4$ the bending vibrations were barely resolved, we have taken the 135 $cm^{-1}$ band of $K_2PtBr_4$ to be a combination of the unresolved bending vibrations.

The broad band at 280 $cm^{-1}$ in $Cs_2PtBr_4$ is probably a combination band, but as the Raman spectra has not been performed on the platinum bromide complex nothing definite can be proposed.

We would like to acknowledge the help and advice of Professor R. C. Lord and to thank Dr. H. J. Sloane, of Beckman Instruments, Fullerton, California, for running some of the spectra on the IR-11 and checking our results.

Jeanne H. Fertel, C. H. Perry

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## C. DIELECTRIC DISPERSION OF SOME PEROVSKITE ZIRCONATES

Recent investigations of the dielectric properties of the perovskite titanates of calcium, strontium, barium, and lead[1, 2] have been extended to measurements on the zirconates with the same cations. The reflectance measurements were treated with the Kramers-Kronig analysis to give the dielectric dispersion from which the frequencies of the presumed normal modes were obtained.

For a perovskite material of cubic symmetry we would expect to find three sets of triply degenerate infrared active modes of symmetry $F_{1u}$ and one 'silent' mode of $F_{2u}$ symmetry.[3] The approximate form of the infrared active vibrations are shown in Fig. IV-6 after Last.[4] Four frequencies have been found in some cases and these have been attributed to the fact that the $F_{2u}$ mode becomes active because of distortions of the cubic lattice to the monoclinic form.

### 1. Experiment

The reflectance measurements were made at room temperature on the instruments described in previous reports.[1-3] A measurement of the dielectric constant at 1 mc/sec (essentially $\epsilon_o$) of each material was made by Dr. G. Rupprecht and Dr. R. Bell of Tyco Laboratories Inc. These results were obtained from thin slices taken from the samples on which the infrared studies had been performed. The values of the dielectric constant compared favorably with our low-frequency measurements obtained from the reflectance data with the following equation used.

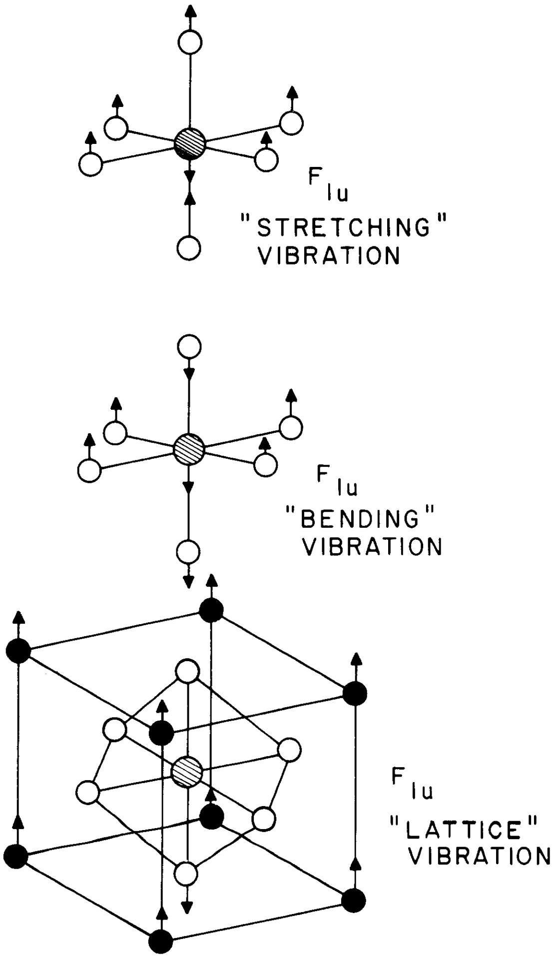

Fig. IV-6. Approximate form of the infrared active vibrations in a cubic perovskite crystal.

$$R_o = \left(\frac{\epsilon_o^{1/2} - 1}{\epsilon_o^{1/2} + 1}\right)^2$$

2. Discussion of the Results

The reflectance data were analyzed by means of the K-K treatment[1, 3] to obtain the real and imaginary parts of the dielectric constant. The reflectance curves and the corresponding dielectric dispersion are shown in Figs. IV-7 and IV-8.

A list of the normal modes is shown in Table IV-4 and direct comparison can be made with the results for the titanates. The tentative assignments of the titanates have been modified slightly in view of the data from the zirconates. A "fourth" frequency appears to be common in calcium, strontium, lead zirconate, and calcium and lead titanate. This mode has been assigned to the $F_{2u}$ mode, which becomes infrared active on account of distortions of the crystal lattice from the ideal perovskite structure. It has been described as a torsional mode of the oxygen octahedra by Narayanam and Vedam[5] in the case of strontium titanate on the basis of their Raman data. For this mode to become active not only will the oxygen octahedra be no longer regular but the zirconium atoms can no longer be sitting on a center of symmetry. This can easily be realized if the

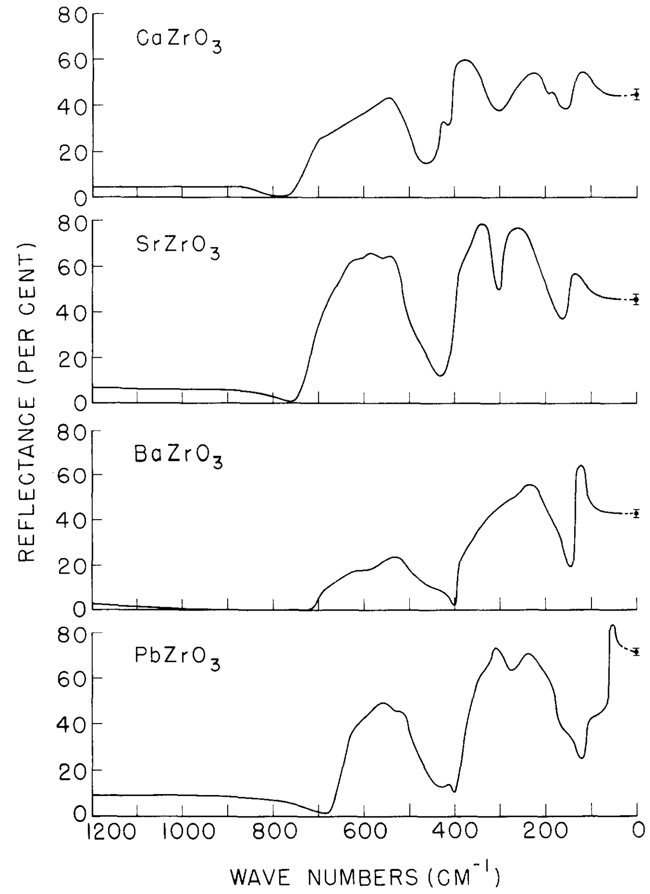

Fig. IV-7. Reflectance measurements.

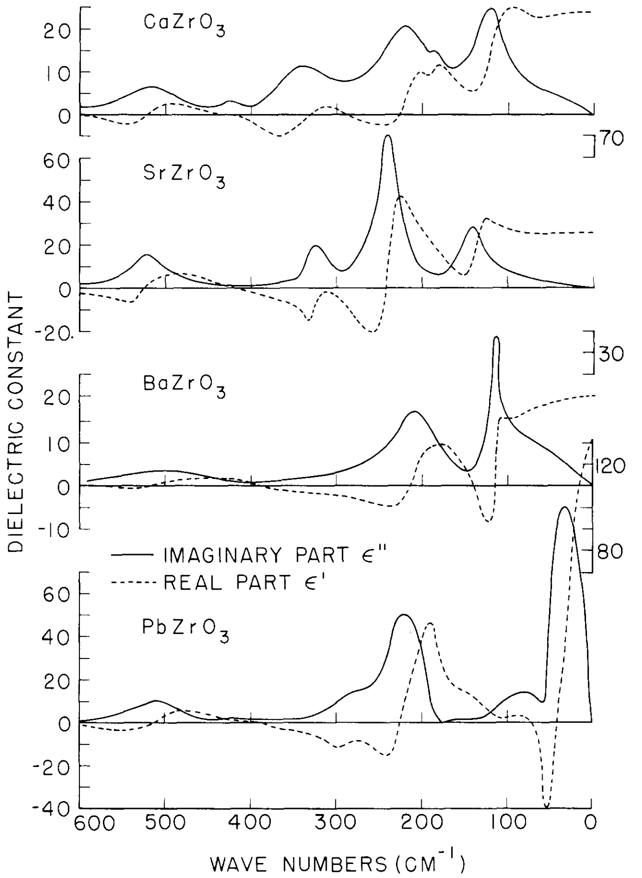

Fig. IV-8. Dielectric-constant measurements.

lattice is slightly sheared and from Megaw's x-ray data[6] this appears to be a common phenomenon among these structures. Some of our samples, however, are listed as ideal cubic perovskites but our results have indicated this "fourth" band. The distortions need only be slight to make this mode active and the x-ray work is probably not sensitive enough to accurately discern the positions of the zirconium atoms.

The fact that the lattice is distorted would of course split the degeneracies in all of the modes but the splitting may be small and consequently be unobservable in the reflectivity measurements.

From Table IV-4 it can be seen that there is a general trend for the $\nu_1$ and $\nu_2$ vibrations to be lower in the case of the zirconates, but the vibration $\nu_3$ (described as predominantly a bend) is in fact lower in the case of the titanates. Also the "lattice" mode $\nu_4$ is higher in the alkali earth zirconates, which is surprising. Since none of these materials exhibit any ferroelectric phenomena, it is possibly this effect in the titanates which causes the mode to be softer and consequently to move to lower frequencies.

Table IV-4. Frequencies (in $cm^{-1}$) and symmetry of infrared modes obtained from K-K analysis of the reflection data.

Titanates

| Sample | Crystal symmetry | $\nu_1$ (Ti-O stretch) | $\nu_2$ (Ti-$O_3$ torsion) | $\nu_3$ (Ti-O-Ti Bend) | $\nu_4$ (cation-$TiO_3$ lattice mode) |
|---|---|---|---|---|---|
| $CaTiO_3$ | Orthorhombic (Distorted multiple cell) | 549 $(B_1,B_2,A_1)$ | 443 $(B_1,B_2,A_2)$ | 179 $(B_1,B_2,A_1)$ | 148 $(B_1,B_2,A_1)$ |
| $SrTiC_3$ | Cubic $O_h^1$ $(P_m3_m)$ | 555 $(F_{1u})$ | --- $(F_{2u})$ | 185 $(F_{1u})$ | 100 $(F_{1u})$ |
| $BaTiO_3$ | Tetragonal | 491 $(E_u,A_1)$ | --- $(B_1,E_u)$ | 175<br>184 $(E_u,A_1)$ | 12 $(E_u,A_1)$ |
| $PbTiO_3$ | Tetragonal (?) (possibly distorted) | 530 $(E_u,A_1)$ | 400 $(B_1,B_2,A_2)$ | 220<br>172 $(E_u,A_1)$ | 83 $(E_u,A_1)$ |

Zirconates

| Sample | Crystal symmetry | $\nu_1$ (Zr-O stretch) | $\nu_2$ (Zr-$O_3$ torsion) | $\nu_3$ (Zr-O-Zr Bend) | $\nu_4$ (cation-$ZrO_3$ lattice mode) |
|---|---|---|---|---|---|
| $CaZrO_3$ | Orthorhombic (?) (possibly distorted) | 515 $(B_1,B_2,A_1)$ | 310 $(B_1,B_2,A_2)$ | 222 $(B_1,B_2,A_1)$ | 118(?) $(B_1,B_2,A_1)$ |
| $SrZrO_3$ | Cubic (?) (possibly distorted) | 522 $(B_1,B_2,A_1)$ | 325 $(B_1,B_2,A_2)$ | 240 $(B_1,B_2,A_1)$ | 143 $(B_1,B_2,A_1)$ |
| $BaZrO_3$ | Cubic | 505 $(F_{1u})$ | --- $(F_{2u})$ | 210 $(F_{1u})$ | 115 $(F_{1u})$ |
| $PbZrO_3$ | Distorted multiple cell | 508 $(B_1,B_2,A_1)$ | 290 $(B_1,B_2,A_2)$ | 221 $(B_1,B_2,A_1)$ | (80)<br>34 $(B_1,B_2,A_1)$ |

A list of the static dielectric-constant measurements at room temperature is given in Table IV-5. Although none of the alkali-earth zirconates exhibit ferroelectricity (compared with the titanates) lead zirconate has the property of being an antiferroelectric,[8] and we propose to study the temperature dependence of the reflectance curve above and below the Curie point where the structure undergoes a change from the cubic to the tetragonal form.[9]

Table IV-5. Dielectric constants (at 1 mc/sec).

| | |
|---|---|
| $CaZrO_3$ | 23.04 |
| $SrZrO_3$ | 25.10 |
| $BaZrO_3$ | 21.45 |
| $PbZrO_3$ | 130.1 |

We wish to thank Dr. G. Rupprecht and Dr. R. Bell, of Tyco Laboratories, Inc., Waltham, Massachusetts, for the samples and for making the dielectric-constant measurements at 1 mc/sec.

C. H. Perry, D. J. McCarthy

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## D. ANTIFERROMAGNETIC RESONANCE IN POTASSIUM SALTS

### 1. Theoretical Basis of This Research

### a. Exchange and Anisotropy Energies

A substance possessing a spontaneous magnetic moment (in the absence of an applied magnetic field) is classed as ferromagnetic. The Curie point, $T_c$, for a ferromagnet is the temperature above which the spontaneous moment vanishes. If a paramagnetic substance were subject to some interaction tending to line up the ionic and atomic magnetic moments, the substance would be ferromagnetic. Such an interaction field was proposed by George Weiss and was named for him. The orienting effect of the Weiss field, opposed by the motion of thermal agitation of the elementary moments, can be considered the equivalent of an effective magnetic field, $H_E$, acting on the electron spins. The interaction energy of a spin with the Weiss field must be of the order of magnitude of the thermal energy of a spin at the Curie point.

The physical origin of the Weiss field lies in the quantum-mechanical exchange integral, as pointed out by Heisenberg. On certain assumptions it can be shown that the energy of interaction of atoms i, j bearing spins $S_i, S_j$ contains a term

$$B_{ex} = -2JS_i \cdot S_j, \tag{1}$$

where J is the exchange integral and is related to the overlap of the charge distributions i, j.[1] This exchange energy is of electrostatic origin, expressing the difference in Coulomb interaction energy of the systems when the spins are parallel or antiparallel. This is a result of the hypothesis that the relative directions of two spins cannot be altered without making changes in the spatial charge distribution in the overlap region.

The anisotropy energy of a ferromagnetic crystal acts in such a way that the magnetization tends to be directed along certain definite crystallographic axes that are called easy or hard directions, determined by the relative difficulty in magnetizing the crystal along them. It has been observed experimentally that the energy required to magnetize a crystal to saturation in the hard direction is considerably greater than that required to saturate along a direction of easy magnetization. The excess energy required in the hard direction is the anisotropy energy.

One important mechanism is believed to be the combined effect of spin-orbit interaction and the partial quenching of the orbital angular momentum in the solid. The magnetization of the crystal "sees" the crystal lattice through orbital overlap of the electrons: the spin interacts with the orbital motion by means of the spin-orbit coupling, and the orbital motion in turn interacts with the crystal structure by means of the electrostatic fields and overlapping wave functions associated with neighboring atoms in the lattice.[1]

### b. Antiferromagnetic Model

In the derivation of the exchange energy it was assumed that the exchange integral J of Eq. 1 was positive. This assumption is required if the energy of the pair interaction with spins parallel is to be lower than the pair interaction describing the spins as antiparallel.[2] There are certain materials, however, which normally exhibit a paramagnetic behavior above a critical temperature $T_c$. As the temperature is lowered below $T_c$

the magnetization drops very sharply to zero. Such behavior may be explained by a negative exchange integral, for in this case the spontaneous effect at the transition temperature would be (at equilibrium) to align the adjacent spins antiparallel to their neighbors, thereby eliminating the net magnetization of the crystal. Such materials are called "antiferromagnets."

The temperature at which a crystal becomes antiferromagnetic is called the Néel temperature. This is not to be confused with the Curie temperature, the latter being defined in terms of magnetic susceptibility according to the Curie-Weiss law for antiferromagnetic materials:

$$\chi = \frac{c}{T + T_c}. \tag{2}$$

The change in sign between Eq. 2 and the Curie-Weiss law for ferromagnets follows from the change in the sign of J.

The behavior of antiferromagnets can be explained if we present a crystal model whose constituent atoms are distributed into two sublattices A and B such that the mean direction of spin in A is directed oppositely to that in B under the influence of the resultant internal field.[3] At low temperatures this field becomes more effective and the resultant spin less; at high temperatures the field disappears.

c. Resonance Conditions

Spin resonance in antiferromagnetic crystals at temperatures above the Curie point is similar to that observed in paramagnetic crystals. Below the Curie point, however, there is a strong effective field leading to a zero-field splitting of the resonance line. In the simplest situation at absolute zero the effective field, apart from the applied magnetic field, is given by[2,4,5,6]

$$H_{\text{eff}} = [H_A(2H_E+H_A)]^{1/2},$$

where $H_A$ is the effective anisotropy field of one sublattice, and $H_E$ is the exchange field. For $MnF_2$ the effective field amounts to $1.0 \times 10^5$ oe, corresponding to a zero-field splitting of 10 $cm^{-1}$.

The resonance frequency for uniaxial symmetry about the sublattice polarization axis should correspondingly be

$$\begin{aligned} \omega_o &= \gamma[H_A(2H_E+H_A)]^{1/2} \\ &= \gamma(2K/\chi_\perp)^{1/2}, \end{aligned}$$

where K is the anisotropy constant, and $\chi_\perp$ is the static susceptibility perpendicular to the easy axis.[7] These frequencies lie in the far infrared for many antiferromagnets.

Because the degree of antiferromagnetism changes with the temperature up to its Néel temperature, the resonant frequency is strongly temperature-dependent. This dependence for iron group fluorides has been observed by Ohlman and Tinkham[8] in $FeF_2$, and by Bloor and Martin[9] in $MnF_2$. The origin of this temperature dependence is discussed by Richards.[10]

## 2. Experimental Study and Results

### a. Experiment

An attempt was made to observe antiferromagnetic resonance in a collection of pressed powdered samples of potassium fluoride salts, $KMnF_3$, $KFeF_3$, $KCoF_3$, $KNiF_3$,

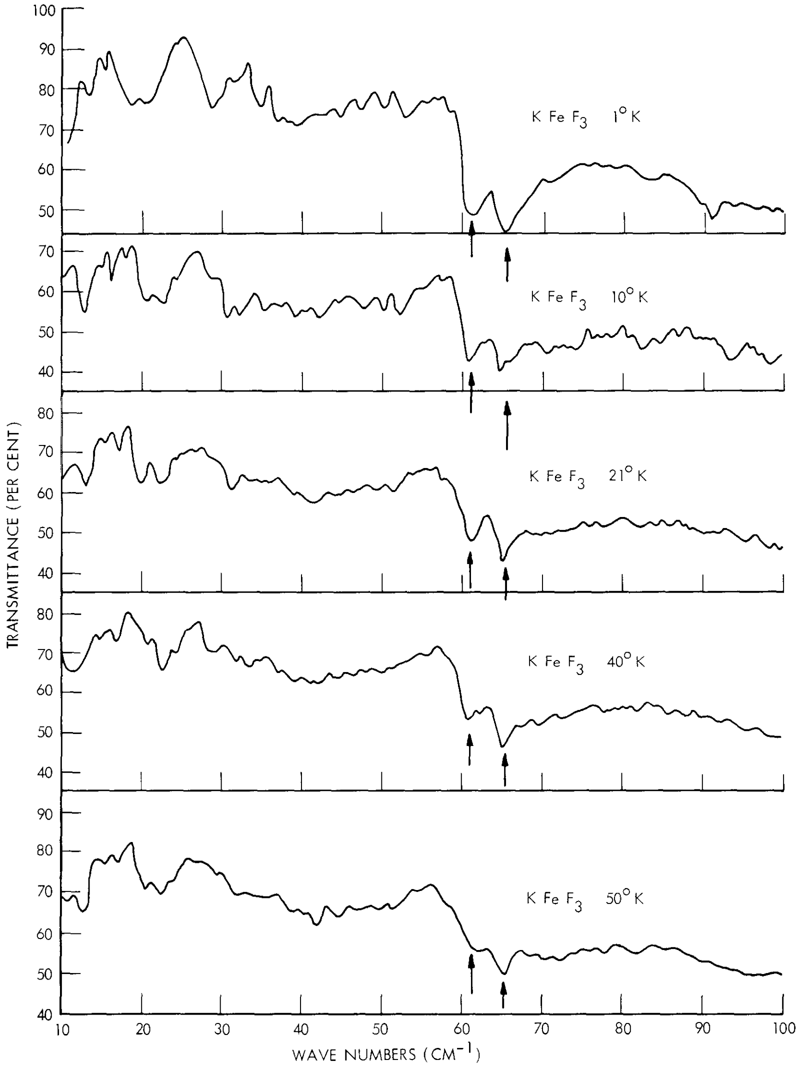

Fig. IV-9. Transmittance of $KFeF_3$ from 10-100 $cm^{-1}$ at various temperatures.

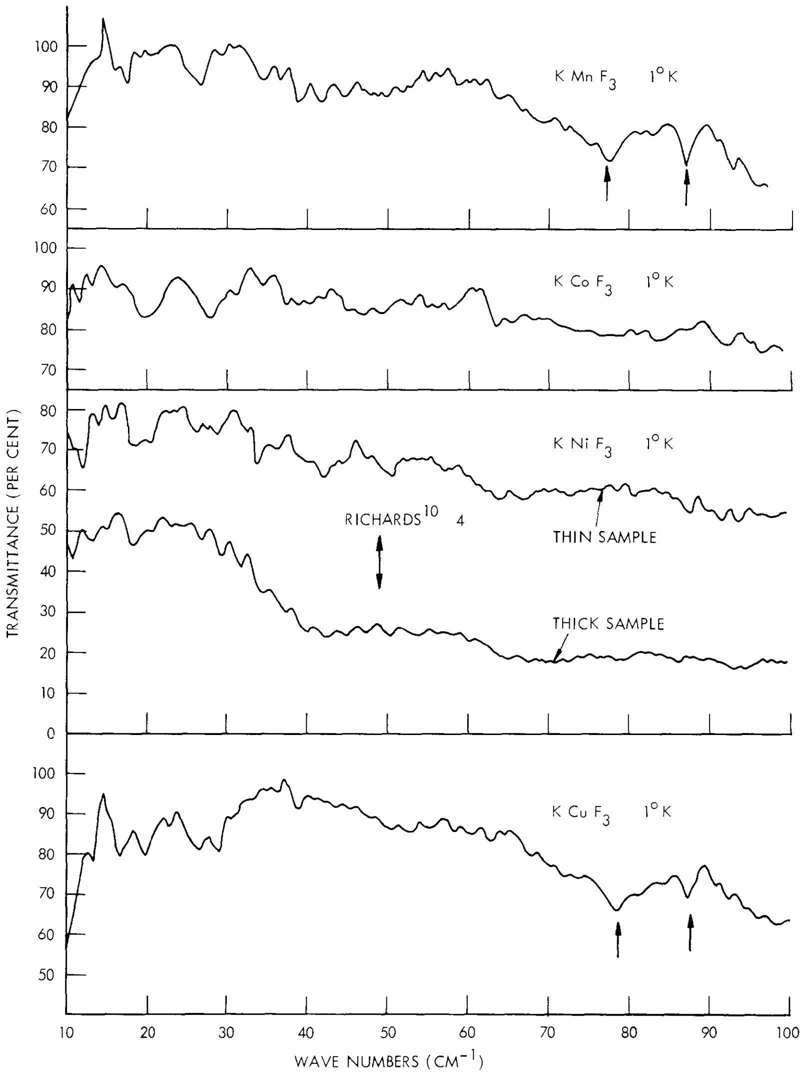

Fig. IV-10. Transmittance of $KMnF_3$, $KCoF_3$, $KNiF_3$, and $KCuF_3$ from 10-100 $cm^{-1}$ at 1°K.

and $KCuF_3$, the central atoms being successive transition elements.

Potassium-nickel fluoride has the cubic perovskite structure with nearest-neighbor spins oppositely directed along a cube axis, and has a Néel temperature of 273°K. Richards[10] reported observing a broad AFMR line in $KNiF_3$ at 1°K, but found it showed no measurable shift as the temperature was raised.

The powdered samples were supported in polyethylene matrices in a ratio of approximately 1:2 by weight. Pressed discs were made of the samples of 0.5-inch diameter and 0.016-inch thickness.

Transmission measurements were run at 1°K on the submillimeter interferometer in the Laboratory for Insulation Research, M. I. T.[11] The transformed interferograms are shown in Figs. IV-9 and IV-10. Because the intensities of the observed "resonances" are of the order of the noise level, two independent runs were made on each sample under the same conditions. If they both demonstrate dips at precisely the same frequency, they are assumed to be real and not just noise.

Because the strongest dips were seen in the transformed spectra of $KFeF_3$, a temperature study was performed on this sample at 1°K, 10°K, 21°K, 40°K, and 50°K. The results of these runs are illustrated in Fig. IV-9.

### b. Discussion of Results

Among those samples studied, several showed distinct absorptions, possibly antiferromagnetic resonances. $KMnF_3$ showed two resonances at $77.5 \pm 0.3$ cm$^{-1}$ and $91.5 \pm 0.3$ cm$^{-1}$. $KFeF_3$ showed two more distinct bands at $61.0 \pm 0.3$ cm$^{-1}$ and $65.0 \pm 0.3$ cm$^{-1}$. $KCuF_3$ showed less convincing bands at $75.5 \pm 0.3$ cm$^{-1}$ and $87.5 \pm 0.3$ cm$^{-1}$. No similar absorptions were discernible for the $KCoF_3$ or the $KNiF_3$.

Only one antiferromagnetic resonance band should be observed, and the temperature-dependent study of $KFeF_3$ showed no apparent shift of the bands at different temperatures. The resonances should lower and broaden as the temperature is raised to the Néel point. Richards[10] reported that $KNiF_3$ had a resonant frequency that increased sharply with temperature, disappearing at $0.22\ T_N$ (Néel temperature). This is in the opposite direction from that reported for the iron group fluorides.[8,9] Richards suggested that this was due either to the domain structure of his $KNiF_3$ or to an increase of the anisotropy energy with temperature, because of dynamic distortions of the lattice. A similar temperature dependence would be expected for $KFeF_3$.

From these results we have concluded that the observed bands are not antiferromagnetic in nature. The occurrence of the absorptions in the copper salt ($KCuF_3$) makes their antiferromagnetic nature increasingly suspect.

## 3. Suggestions for Further Study

We proposed to re-run the samples at helium temperatures, using the R11C FS-52 Fourier Spectrophotometer of this laboratory. This will provide a verification of the resonances in $KMnF_3$, $KFeF_3$ and $KCuF_3$.

The liquid-helium transmission of a thin slice of single crystal $KNiF_3$ will be investigated to either verify Richards' observations or support our present experimental evidence for the nonexistence of a band.[11]

It would be desirable to test the antiferromagnetic nature of the observed resonances by applying a strong external magnetic field to the sample. This should result in a shift of frequency of the resonance according to

$$\omega = \gamma\{[H_A(2H_E+H_A)]^{1/2} \pm H\}.$$

Here, H is a static externally applied field in the preferred direction whose application leads to two resonant conditions rather than one.[9]

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## E. FAR INFRARED SPECTRUM OF $Fe(CO)_5$

There has been some uncertainty about the far infrared spectrum of iron pentacarbonyl. Originally, Cotton and his co-workers[1] studied the spectrum of the liquid in the region 60-120 $cm^{-1}$, and reported two bands at 93 ± 3 $cm^{-1}$ and 75 ± 5 $cm^{-1}$. McDowell and Jones[2] investigated the vapor in the same region and found a prominent band at 104.4 ± 0.3 $cm^{-1}$. Recently, Edgell and others[3] reported a study of $Fe(CO)_5$ in the liquid phase and in cyclohexane solution over the range 65-135 $cm^{-1}$. They found only one broad band at 112 ± 1 $cm^{-1}$.

Because of these somewhat conflicting data, we have investigated the far infrared spectrum of $Fe(CO)_5$ from 35 $cm^{-1}$ to 120 $cm^{-1}$, using the spectrometer of Lord and McCubbin,[4] also used by Cotton,[1] which had recently been converted to vacuum operation.[5] Studies were made on the liquid at room temperature and on the solid phase at liquid-nitrogen temperature; the low-temperature cell described in Section IV-D, with

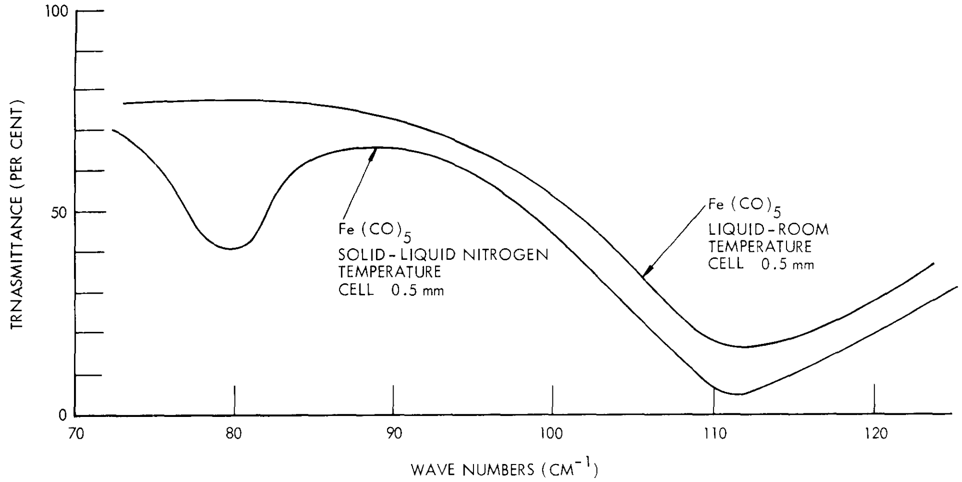

Fig. IV-11. Far infrared transmittance of Fe(CO)$_5$ in the solid and liquid phases from 70-120 cm$^{-1}$.

sample thicknesses of 0.2 mm, 0.5 mm, and 1.0 mm, was used. Vacuum-tight polyethylene cells manufactured by the Limit Research Corporation, Darien, Connecticut were employed. The spectrum is shown in Fig. IV-11. A broad band was found in the liquid phase at 111 ± 1 cm$^{-1}$. In the solid an additional band was observed at 80 ± 1 cm$^{-1}$. No other bands were found, although there was considerable generalized absorption in both the liquid and solid samples below 60 cm$^{-1}$.

Thus the results are in essential agreement with those of Edgell,[3] except for the new band appearing in the solid. This may be the low-frequency fundamental, $\nu_{15}$, which was estimated by Jones and McDowell[6] to be 74 cm$^{-1}$ in the vapor phase from combination bands, or it may be a characteristic frequency of the Fe(CO)$_5$ lattice.

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(Mr. Karl R. Loos, Research Assistant to Professor R. C. Lord in the Department of Physical Chemistry, is working in collaboration with our group in the Spectroscopy Laboratory, M. I. T.)

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