V. OPTICAL AND INFRARED SPECTROSCOPY[*]

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A. IMPURITY-INDUCED ABSORPTION IN PEROVSKITE FLUORIDES

The fundamental lattice vibrations and multiphonon bands in various perovskite fluorides have been investigated by Perry and Young,[1,2] and the study of the far infrared absorption spectra (below 100 cm^{-1}) of these materials was initiated to find antiferromagnetic resonance (AFMR) in $KNiF_3$. A strong band at 49 cm^{-1} confirmed a similar line reported by Richards[3] which he assigned to AFMR. The same sample of $KNiF_3$ was subjected to magnetic fields of up to 150 kG at the Francis Bitter National Magnet Laboratory, M. I. T. A field of this magnitude would be expected to shift an AFMR frequency by ~15 cm^{-1}. No shifts were observed, however, in the strong band at 49 cm^{-1} or in several sharp weaker bands that were also observed (Fig. V-1). $KNiF_3$ has nearest-neighbor spins oppositely directed along a cube axis, and is particularly interesting because it undergoes no measurable distortion below T_N ($T_N=275°$). Further evidence that the observed bands in $KNiF_3$ were not in fact of magnetic origin was found when a second sample of $KNiF_3$, grown at a later time, displayed a considerably different spectrum. The strong band at 49 cm^{-1} was greatly reduced in strength, and the weaker bands were not evident (Figs. V-2 and V-3). The temperature dependence of the 49 cm^{-1} band was found to be opposite to that expected of AFMR. The dependence of the absorption spectrum on the particular sample, and the lack of sensitivity to a strong magnetic field indicate that the observed absorption bands are due only to impurities. Table V-1 compares some of the properties of various perovskite fluorides. Examination of these crystals at low temperatures has shown many absorption bands below 100 cm^{-1}, most of which are probably impurity-induced. $KMgF_3$, a diamagnetic crystal, shows a band at 52 cm^{-1} which seems to correspond to the $KNiF_3$ band at 49 cm^{-1} and there are also bands located at 64, 73, 88 and 135 cm^{-1}. The spectrum again depends on the sample, although not as strongly as is observed with $KNiF_3$ (Fig. V-4). The mixed crystal system $K(Mg/Ni)F_3$ was also investigated, and the frequency of the strongest band,
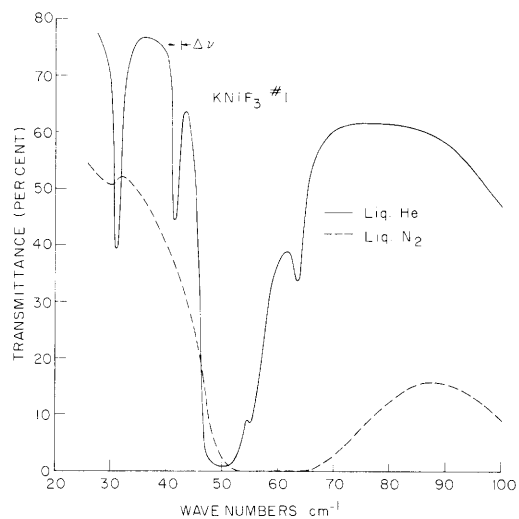
Fig. V-1.   Transmission of KNiF$_3$ (sample #1) at liquid-
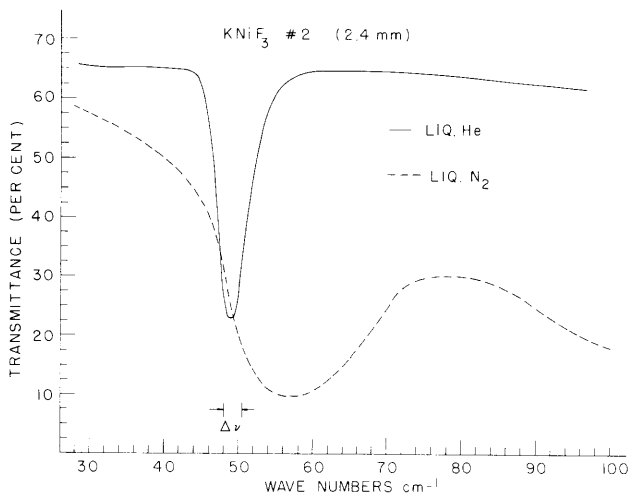helium and liquid-nitrogen temperature.

Fig. V-2.

Transmission of KNiF$_3$ (sample #2) at
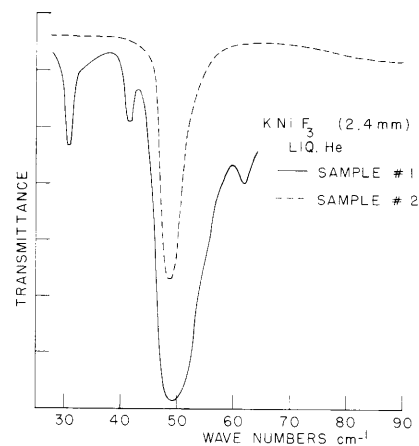liquid-helium and liquid-nitrogen temper-
ature.

Fig. V-3.

KNiF$_3$ transmission spectra at liquid-
helium temperature, showing comparison
between the two samples grown at differ-
ent times.

Table V-1. Properties of cubic perovskite fluorides.

Crystal	Neel Temperature (°K)	Cubic Lattice Constant at 300°K (A)	Temperature at which structure changes (°K)
$KMgF_3$	diamagnetic	4.000	—
$KNiF_3$	275	4.014	remains cubic
$KZnF_3$	diamagnetic	4.055	—
$KCoF_3$	114	4.068	114 (tetragonal)
$RbMnF_3$	82	4.240	cubic through 20

~50 cm^{-1}, varied smoothly with the relative concentrations of Mg and Ni. No other bands could be traced through the whole range of concentration with confidence (Fig. V-5).

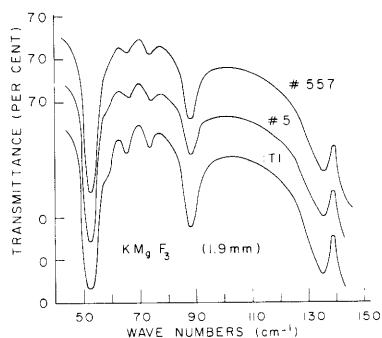Three other crystals which were investigated were $K(Zn:1\%Ni)F_3$, $RbMnF_3$ and

Fig. V-4. $KMgF_2$ transmission spectra at liquid-helium temperature. The three samples from different sources show almost identical spectra.

$KCoF_3$ (Figs. V-6 and V-7). In each of these crystals absorption bands were found which may be attributable to impurities. (The strongest band shown for $RbMnF_3$ is the lowest frequency lattice band). $KCoF_3$ exhibits a large number of absorption bands, of varying intensities and widths. It is possible that one of these may be an AFMR band, as no field measurements have been made.

It is interesting that the strongest impurity bands found ($KNiF_3$:49 cm^{-1}; $KMgF_3$:52 and 88 cm^{-1}; $KZnF_3$:25 cm^{-1}, and possibly $KCoF_3$:23 cm^{-1}) all show the same unusual temperature dependence, as shown in Figs. V-1, V-2, V-6, and V-7. In addition to broadening with increasing temperature these bands shift to higher frequencies, and this type of temperature dependence may be expected from a very
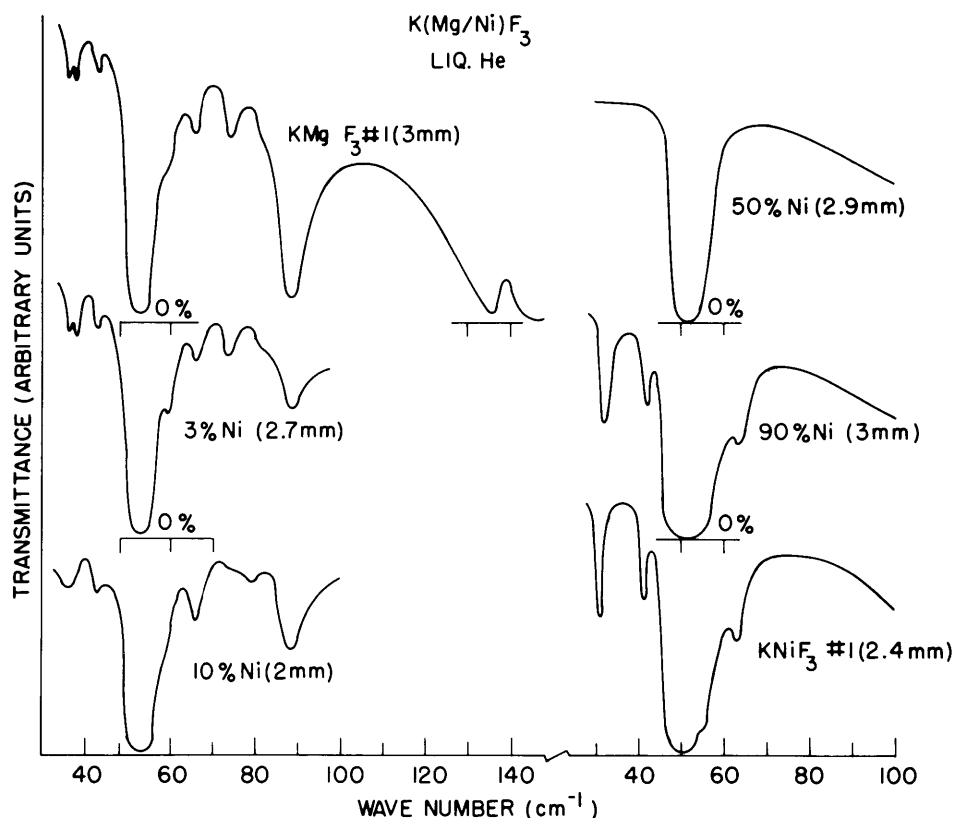
Fig. V-5. Transmission of $K(Mg_x:Ni_{1-x})F_3$ at liquid-helium temperature as a function of composition.

loosely bound impurity situated on a lattice site. Here, the energy level scheme has increasingly spaced levels that are populated when the temperature is raised and the centroid of absorption moves to higher frequency.

Spin wave dispersion in antiferromagnetic $KMnF_3$ at 4.2°K has been observed when using neutron inelastic scattering.[4] From these results, the magnon frequency at $q = 0.8|q|$ A^{-1} in the [100] direction was ~68 cm^{-1}. No band in the region of 136 cm^{-1} (i. e., two-magnon electric-dipole absorption) was observed and it is quite likely that none of the bands in any of the antiferromagnetic perovskites can be attributed to two-magnon absorption (compared, for example, with those found[5] in MnF_2).

N. E. Tornberg has also investigated the Raman spectrum of several of the crystals at 20°K, but no similar bands were found and there was only an indication of an extremely weak two-phonon spectrum. Again no bands were observed that could be attributed to two-magnon transitions as observed in FeF_2.[6]

Most of the crystals investigated were subjected to spectrographic analysis to obtain semiquantitative values for the impurity concentrations. These are summarized in
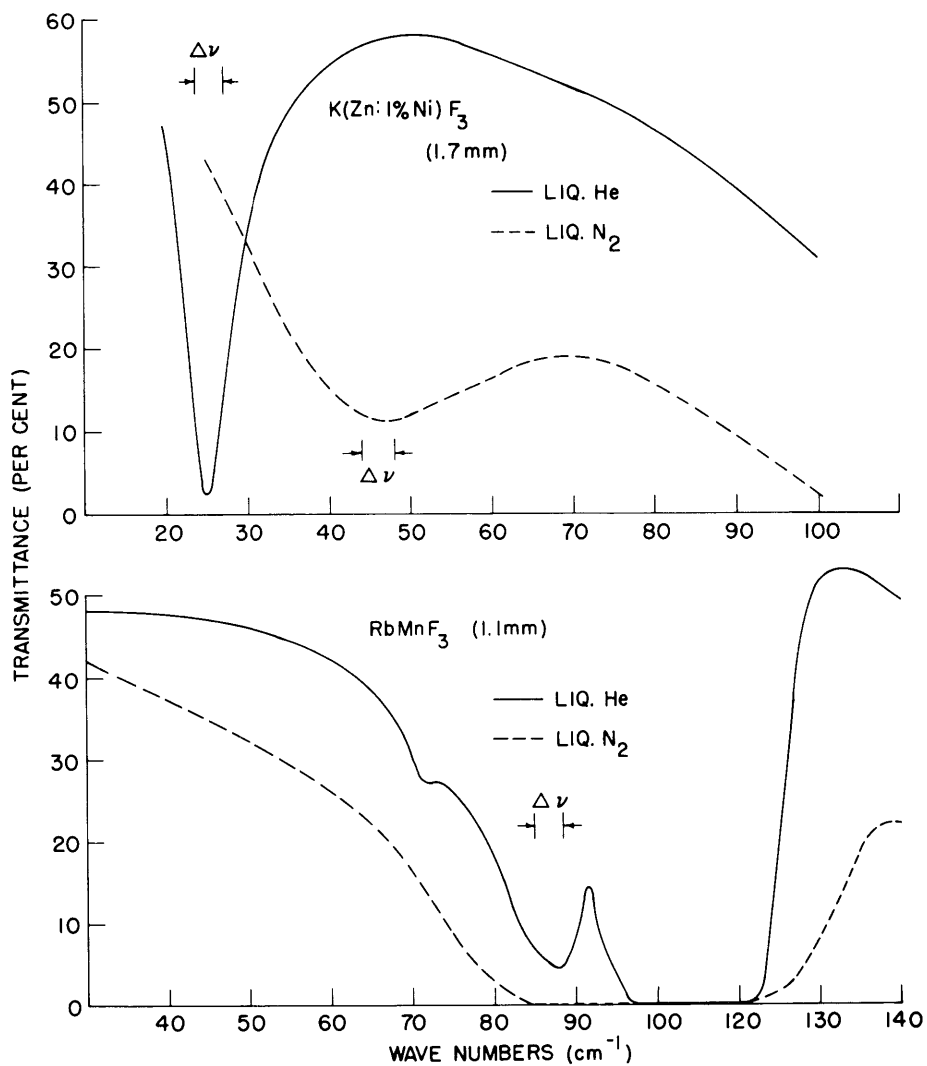
Fig. V-6. Transmission of K(Zn:1%Ni)F$_3$ and RbMnF$_3$ at liquid-helium and liquid-nitrogen temperature.

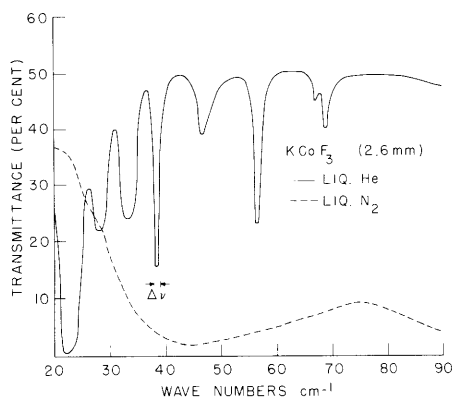Fig. V-7. Transmission of KCoF$_3$ at liquid-helium and liquid-nitrogen temperature.

Table V-2. Impurity concentrations (in parts per million) for the investigated fluoride crystals.

	$10^3 - 10^4$	$10^2 - 10^3$	$10 - 10^2$
$KNiF_3$ #1	Ba, Sr	Na	Ca, Co, Al
$KNiF_3$ #2	—	Na	Ca, Mg
$KMgF_3$ #1	—	Ca	NaNi
$KMgF_3$ #557	—	—	Ca, NaNi
$KMgF_3$ #T1	—	—	Ca, Na, Fe
$KMgF_3$ *	Na	O, Si, Fe	Cl, Ca
$KMgF_3$ #5	—	—	Ca, Na
$KZnF_3$ (1% Ni)	Ni	Fe	Ca, Mg, Na
$RbMnF_3$	—	—	Ca, K, Na, Zn
$KCoF_3$	—	—	Ca, Ni, Cu, Mg, Na, Zn

*Mass spectroscopic analysis.

Table V-2, and fall approximately within the ranges specified.

In all samples Na and Ca are present, and possibly these impurities are the ones responsible for the main absorptions in $KMgF_3$ and $KNiF_3$. The main difference, however, between $KNiF_3$ #1 and #2 samples (see Fig. V-3) is the large doping of Ba and Sr in #1; these may be responsible for the additional lines seen in the $KNiF_3$ (#1) spectrum.

There is some discrepancy between the mass spectroscopic analysis and the spectrographic analysis for the $KMgF_3$ sample. The mass spectrographic analysis also indicates, however, the presence of oxygen and chlorine (not detectable by emission analysis), and no doubt all of the samples contain these substitutional impurities.

Consequently, although the spectra yield a large amount of information, it is virtually impossible, at this point, to make assignments and attempt theoretical calculations. The materials obviously contain numerous impurities, and unless more pure starting materials are available that are then doped with a known impurity, it appears to be a hopeless task to identify any of the bands. Nevertheless, the results show that great

precaution must be excercised in the interpretation of any weak band observed at low temperatures in this frequency range (10-150 cm^{-1}) where absorptions attributable to small concentrations of impurities can be considerably significant.

We would like to thank Dr. H. Guggenheim of the Bell Telephone Laboratories, Inc., and Dr. A. Linz of the Materials Center, M.I.T., for many of the samples. This permitted comparisons between samples from different sources, but even this additional information has not aided in the interpretation.

D. J. Muehlner, C. H. Perry

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