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Pressure Dependence of the Infrared-Active Optical Phonon Modes in Alkaline-Earth Fluorides*

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The pressure dependence of the infrared-active optical phonon mode (ν_{TO_1}) in alkaline-earth fluorides has been determined up to 45 kbar. The dependence is found to be less than the Raman-active optical phonon mode. The pressure dependence of the ν_{TO_1} mode is observed to decrease in the order $CaF_2 > SrF_2 > BaF_2$, while the Raman mode remains rather constant with pressure. Grüneisen parameters have been determined and are compared with those obtained for AB-type crystals.

I. INTRODUCTION

The importance of the alkaline-earth fluorides as host lattices for paramagnetic ions has recently been recognized.[1–5] Knowledge of the behavior of the optical phonons in the pure alkaline-earth fluorides, under varying degrees of temperature and pressure, is of utmost importance toward understanding the behavior of the doped crystals. Recently, room-temperature reflectivity and transmission measurements have been made on CaF_2, SrF_2, and BaF_2.[1,6,7] Low-temperature studies on these salts to 77°K have also been made.[1] Infrared spectra of these materials in a krypton matrix at 20°K were reported.[8] A pressure study on the Raman-active modes has been made.[9] No infrared studies of these materials at high pressure are available. Previously, in our laboratory, we have studied the pressure dependencies of the optical modes of a number of ionic and pseudoionic crystals of the type AB, where A and B may be singly or doubly charged.[10]

Table I. Pressure dependence of ν_{LO_1}, ν_{TO_1}, and ($\nu_{LO_2}=\nu_{TO_2}$, modes in alkaline-earth fluorides.

	Infrared		Raman
	$d\nu_{LO_1}/dp$ (cm^{-1}/kbar)[a]	$d\nu_{TO_1}/dp$ (cm^{-1}/kbar)[a]	$d\nu_{LO_2=TO_2}/dp$ (cm^{-1}/kbar)[b]
CaF_2 (crystal)	c	0.49	0.72
CaF_2 (powder)	0.25	0.55	c
SrF_2 (powder)	c	0.40	0.70
BaF_2 (crystal)	c	0.27	0.80
BaF_2 (powder)	c	0.27	c

[a] Up to 45 kbar.
[b] Up to 10 kbar.
[c] Not observed.

Comparison of pressure studies on the AB_2 crystals with those of ionic crystals of the type AB would be of interest. This paper reports on the study made of the pressure dependencies of the infrared-active phonon modes in CaF_2, SrF_2, and BaF_2.

II. EXPERIMENTAL

The high-pressure measurements were made with an opposed diamond-anvil cell, using a Perkin–Elmer 301 far-infrared spectrophotometer equipped with a 6× beam condenser. Details of the technique and the method of pressure calibration have been described elsewhere.[11,12]

The anhydrous powdered salts (CaF_2, SrF_2, BaF_2, PbF_2, and CdF_2) used were obtained from Alfa Organics. The crystal CaF_2 was obtained from Mitra of the Electrical Engineering Department of the University of Rhode Island, Kingston, Rhode Island. The crystal BaF_2 came from Harshaw Chemical Co. The powdered samples were all dried in an oven at 200°C prior to use. All grinding and sampling was done in a glove box with a dry-nitrogen atmosphere.

Table II. Grüneisen parameters for the alkaline-earth fluorides.[a]

	(cm^{-1})[b]		γ_{TO}	
	ν_{LO_1}	ν_{TO_1}	ir	Raman
CaF_2	466	262	1.8	1.9
SrF_2	···	225		
BaF_2	···	189	0.8	1.8

[a] Compressibility data taken from C. Wong and D. E. Schuele [J. Phys. Chem. Solids **28**, 1225 (1967)] and D. Gerlich [Phys. Rev. **135**, A1331 (1964)] for CaF_2 and BaF_2 (no such data available for SrF_2).
[b] Infrared frequencies.

III. RESULTS AND DISCUSSION

The alkaline-earth fluorides have a fluorite-type structure and belong to the $O_h^5(F_m3_m)$ space group,[13] with $Z=1$. The factor group selection rules for the long-wavelength phonons allow one infrared-active optical mode (ν_1), and one Raman-active optical mode (ν_2):

$$\Gamma = F_{1u}(\mathrm{ir}) + F_{2g}(\mathrm{R}).$$

There are nine branches to the phonon dispersion curves, six of which belong to the optical modes ($F_{1u}+F_{2g}$), and three are acoustic modes. The Raman-active vibration is degenerate ($\nu_{LO_2}=\nu_{TO_2}$) at $k\simeq 0$, whereas the infrared-active vibration is split ($\nu_{LO_1}+\nu_{TO_1}$) due to the ionic character of the crystals. (Here *LO* and *TO* designate the longitudinal and transverse optic branches.) Under normal conditions of perpendicular incident radiation to the sample the ν_{LO_1} mode is not observed. However, under conditions as outlined by Berreman[14] (thin film and oblique infrared radiation), the *LO* modes may be observed. In this study, the ν_{LO_1} mode has only been observed for CaF_2, since this is the most ionic of the crystals studied and the ν_{LO_1} and ν_{TO_1} modes are well separated. For less ionic crystals such as SrF_2 and BaF_2 the separation is smaller, and the ν_{LO_1} mode is lost under the envelope of the more intense ν_{TO_1} mode.

The pressure dependence for the fluorides studied in this paper are tabulated in Table I and plots of ν_{TO_1} vs pressure in kilobars are indicated in Fig. 1. Table I also shows comparisons to the pressure dependence of the Raman-active mode.[9] Table II shows the ambient-pressure frequencies for these solids. The pressure dependence of the ν_{TO_1} mode is observed to decrease from CaF_2 to SrF_2 to BaF_2. A similar trend has been observed for other crystals as the mass of the anion or cation increases.[10,15] It also may be noted that the pressure dependence of the ν_{LO_1} mode in CaF_2 is much less than that demonstrated by the ν_{TO_1} mode. This behavior has also been previously noted for other ionic crystals.[16,17]

Comparison of the pressure dependence of the ν_{TO_1} mode with the Raman-active mode indicates that certain differences exist. Whereas the $d\nu_{TO_1}/dp$ dependence varies with mass, the $d(\nu_{LO_2}=\nu_{TO_2})dp$ dependence remains rather constant. The infrared active mode is known to involve the vibration of the metal ions moving against the cage of surrounding anions and therefore should be dependent on mass, whereas the Raman-active mode is not so dependent since only fluorine atoms are moving during the vibration (the alkaline earth metal remaining stationary).

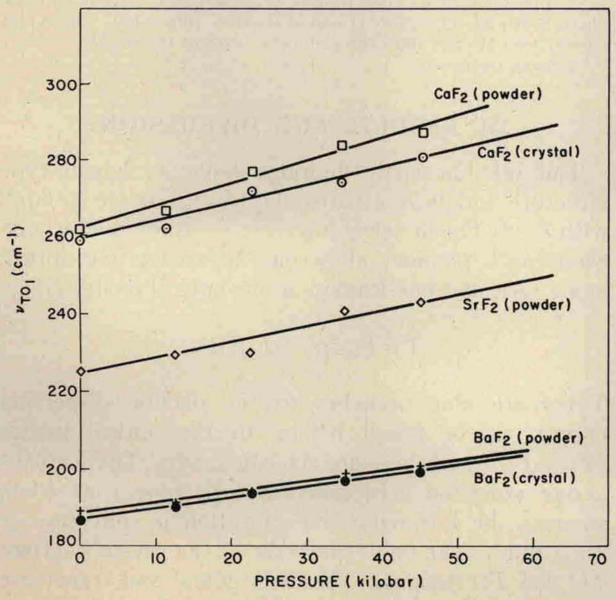

FIG. 1. Pressure dependences of the ν_{TO_1} mode in alkaline-earth fluorides.

TABLE III. Pressure effects on ν_{LO_1}, ν_{TO_1} modes of PbF_2 and CdF_2.[18]

	(cm^{-1}/kbar)			
	ν_{LO_1}	$d\nu_{LO_1}/dp$	ν_{TO_1}	$d\nu_{TO_1}/dp$
PbF_2	332	0.30	106	Not observed
CdF_2	374	Not observed	217	0.0

The Grüneisen parameter γ is defined by Eq. (1),

$$\gamma_{TO}=\frac{(d\nu_{TO}/dp)_T}{\nu_{TO}\chi}, \tag{1}$$

where χ is the isothermal compressibility. The mode Grüneisen parameters for the long-wavelength *TO* phonons for CaF_2, SrF_2, and BaF_2 have been obtained since isothermal compressibility data are available. The Grüneisen parameters are the first determined for AB_2-type molecules from experimental data. The γ values from the Raman and infrared data (Table II) are found to be considerably lower than γ values obtained for ionic AB-type molecules.[12] No ready explanation is presently available, although the models which are proposed for AB molecules may not necessarily fit AB_2-type molecules.

Other fluorite-type crystals were also examined under pressure. The results for PbF_2 and CdF_2 are summarized in Table III. The ν_{TO_1} mode was not observed in this work. A previous value of 106 cm^{-1} has been reported for the mode.[18]

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