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Vibrational Spectroscopy of Solids under High Pressures. Part I. Raman Spectra of Inorganic Hexafluorometallate Compounds

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Raman spectra of a series of isomorphous hexafluorometallates ($TlSbF_6$; $BaMF_6$, M = Si, Ge, Sn, and Ti, space group $R\bar{3}m\text{–}D^5_{3d}$, $Z = 1$) have been measured under high pressures up to 25 kbar with a new opposed sapphire anvil cell. Pressure calibration has been achieved by means of the R_1 fluorescence band of ruby. The frequency of the only Raman active lattice mode (libration of the octahedral anion) of each compound shows a higher pressure dependence than do the internal vibrations of the anions. The E_g components of the ν_5 modes of the MF_6 octahedra which are coupled to the E_g lattice modes because of their same symmetries and small frequency differences exhibit higher pressure sensitivities than do the uncoupled internal modes. These findings may be used as a further means for symmetry assignment. $BaGeF_6$ undergoes a reversible phase transition at 9.6 kbar; the split librational modes of the high-pressure phase show the highest pressure dependences of up to about 3 $cm^{-1} \cdot kbar^{-1}$ found in this investigation.

1. Introduction

Due to qualitatively and/or quantitatively different molecular and lattice potentials in inorganic ionic solids the internal and lattice vibrations should behave differently under variations in the parameters of state. Low-temperature vibrational spectroscopy has already been extensively used to study such behavior in this context. In this investigation the newer and from the point of view of apparatus, simpler method of high-pressure spectroscopy has been used. Different pressure dependences of vibrational frequencies, half-bandwidths, and intensities have to be expected for internal and lattice vibrations.

The isomorphous hexafluorometallates of the $TlSbF_6$ type have been chosen for the first investigation in the program, behavior of internal and lattice vibrations under variations of parameters of state, because of the lucidity of their structures. The compounds $TlSbF_6$ and $BaMF_6$ (M = Si, Ge, Sn, and Ti) adopt monomolecular rhombohedral cells (space group $R\bar{3}\,m\text{–}D^5_{3d}$) with a slightly distorted CsCl arrangement of Tl^+ (Ba^{2+}) and SbF_6^- (MF_6^{2-}) (*1*). Both cations and hexafluoroanions occupy sites with symmetry $\bar{3}\,m\text{–}D_{3d}$, i.e., inversion centers.

2. Results and Discussion

For the above structural reasons the Raman spectra of the hexafluorometallates of the $TlSbF_6$ type are very simple. Thus all the translational vibrations of the anions and cations are of ungerade parity and are Raman inactive. As a result, only the gerade internal

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TABLE I

SYMMETRY CORRELATIONS FOR GERADE ANION MODES IN $TlSbF_6$ TYPE (SPACE GROUP $R\bar{3}m$–D_{3d}^5)

	Point group	Site group	Unit cell group
SbF_6^-	O_h	D_{3d}	D_{3d}
	$\nu_1 : a_{1g}$	a_{1g}	A_{1g}: ν_1, ν_5
	$\nu_2 : e_g$	e_g	E_g: ν_2, ν_5, Lib
	Lib: t_{1g}	a_{2g}	$A_{2g}{}^a$: Lib
	$\nu_5 : t_{2g}$		

[a] Raman inactive.

vibrations of the MF_6 anions $\Gamma_{\text{int}} = 2A_{1g} + 2E_g$, together with the MF_6 librations $\Gamma_{\text{lib}} = E_g$ are expected in the Raman spectra (cf. Table I).

For $BaMF_6$ (M = Si, Ge, and Ti) a splitting of the ν_5[1] vibrations into A_{1g} and E_g components, as predicted by unit cell group analysis, has not been observed at ambient temperatures and pressures; however, $BaTiF_6$ shows this splitting at lower temperatures (*3*). Since in all these compounds the half-bandwidths of these Raman bands are smaller than 5 cm^{-1}, possibly existent fine structure cannot be hidden by band broadening caused by long-range vibrational coupling. In these cases, the perturbations by the static fields of the environments seem to be too weak to lift the degeneracy of ν_5 by a measureable amount (*3*). An estimation of packing densities shows that for $BaSnF_6$ the packing should be denser and therefore the perturbating static field markedly stronger than in the other compounds $BaMF_6$. The special character of $BaSnF_6$ among the Ba compounds is also shown in the spectra since only in this case has the expected splitting of the ν_5 vibration into the A_{1g} and E_g components been found at room temperature. $TlSbF_6$ behaves similarly to $BaSnF_6$. By using isomorphous substitution with SiF_6^{2-}, GeF_6^{2-}, and TiF_6^{2-} in various host lattices, it has been shown that the expected splitting pattern appears for all the guest anions (*3*, *4*).

The recorded Raman spectra allow the pressure dependences $d\nu/dp$ to be determined. Anharmocity causes the crystal mode ν_i to be volume dependent according to

$$\gamma_i = \frac{-d \ln \nu_i}{d \ln V},$$

where V is the volume of the crystal and γ_i is the Grüneisen parameter, which may also be related to the pressure dependence of frequencies (*5*)

$$\gamma_i = \frac{1}{\chi_T \cdot \nu_i} \left(\frac{\partial \nu_i}{\partial p} \right)_T .$$

When the isothermal compressibility χ_T is unknown, as is the case here, one can calculate a modified Grüneisen parameter (*6*)

$$\gamma_i^* = \frac{1}{\nu_i} \left(\frac{\partial \nu_i}{\partial p} \right)_T ,$$

i.e.,

$$\gamma_i = \gamma_i^* / \chi_T .$$

As expected, for all the studied compounds the librations show the greatest pressure dependences.

Since the librations and ν_5 are only about 200 cm^{-1} apart in $BaSnF_6$ and $TlSbF_6$, these two vibrations are markedly mixed. Thus it is expected that the E_g components of the ν_5 vibrations which are coupled with the E_g librations should show considerably greater pressure dependences than the A_{1g} components. On this basis, the vibration of $TlSbF_6$ at 288.1 cm^{-1} must be of E_g symmetry with that at 275.3 cm^{-1} being of A_{1g} symmetry. This conclusion agrees with the findings from single-crystal Raman spectra (*3*, *4*). Since the pressure dependences of the internal vibrations of $TlSbF_6$ and $BaSnF_6$ are very similar, the bands of this latter at 258.9 and 277.9 cm^{-1} can be assigned as A_{1g} and E_g, respectively, with considerable confidence (cf. Table II). Discontinuities in pressure dependences of all vibrations of $BaGeF_6$ indicate a phase transition to a high-pressure modification (β-$BaGeF_6$) at 9.6 kbar. The vibrations of this β-phase show greater pres-

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[1] The conventional notation for normal modes of octahedral species is used (cf. for instance (*2*)).

TABLE II

FREQUENCIES IN SOME HEXAFLUOROMETALLATE COMPOUNDS AT AMBIENT PRESSURE AND TEMPERATURE, PRESSURE DEPENDENCES, AND ASSIGNMENTS OF RAMAN BANDS ($\lambda = 488.0$ nm, SLIT = 5 AND 10 cm^{-1})

Compound	ν_{Lib} (E_g)	ν_5 (A_{1g})	ν_5 (E_g)	ν_2 (E_g)	ν_1 (A_{1g})	
$BaSiF_6$	127.7	408.9		481.5	675.4	ν[a]
	0.95	0.25		0.53	0.45	$d\nu/dp$[b]
$BaGeF_6$[c]	128.3	338.5		488.3	640.0	ν
	0.50 (1.4, 3.1)	0.18 (0.48)		0.17 (0.55)	[d]	$d\nu/dp$
$BaTiF_6$	126.8	299.7		484.0	626.2	ν
	1.04	0.39		[d]	0.28	$d\nu/dp$
$BaSnF_6$	134.1	258.9	277.9	484.7	595.2	ν
	1.07	0.15	0.46	0.41	0.30	$d\nu/dp$
$TlSbF_6$	69.3	275.3	288.1	566.0	647.4	ν
	1.91	0.20	0.51	0.42	0.28	$d\nu/dp$

[a] Frequency at ambient pressure and temperature (cm^{-1}).

[b] Pressure dependence ($cm^{-1} \cdot kbar^{-1}$).

[c] In parentheses pressure dependences for the high-pressure modification, stable at pressures higher than 9.6 kbar.

[d] Overlapped by Raman bands of sapphire.

sure dependences than those of the α-phase stable under ambient pressure (cf. Table II). The phase transition is reversible. Although the degeneracy of the libration is obviously lifted in the β-phase (cf. Figs. 1 and 2), only a single band for the originally 3-fold degenerate ν_5 vibration is observable, as is the case at ambient pressure.

Concerning the pressure dependences of the ν_5 vibrations, $BaGeF_6$ in the α-phase shows

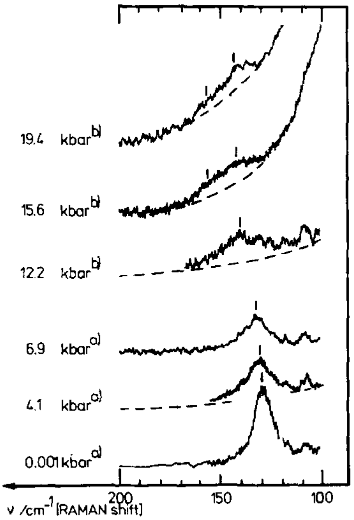

FIG. 1. Raman spectra of $BaGeF_6$, libration of GeF_6^{2-} (E_g). ($\lambda = 488.0$ nm, (a) slit 5 cm^{-1}, (b) slit 10 cm^{-1}.

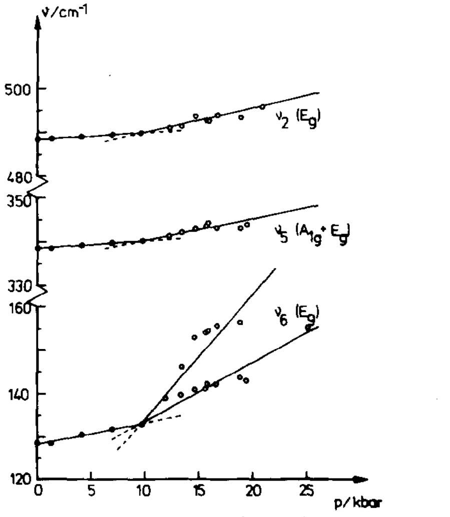

FIG. 2. Pressure dependences of vibrations of $BaGeF_6$. Straight lines have been obtained by conventional least-squares fit.

similarity to $BaSiF_6$, and in the β-phase to $BaTiF_6$. It seems that in the first case (α-$BaGeF_6$, $BaSiF_6$) the A_{1g} component, and in the second case (β-$BaGeF_6$, $BaTiF_6$) the E_g component, are very intense with narrow half-bandwidths, so that in these two different cases two different components determine the measured pressure dependences.

As a rule half-bandwidths grow and maximum intensities diminish under increasing pressures.

3. Conclusion

As expected, for the compounds studied the librations of the MF_6 anions show the greatest pressure dependences and the largest γ_i^* values (cf. Table III). The pressure dependences of the librations are found between 0.50 and 1.91 $cm^{-1} \cdot kbar^{-1}$ (up to about 3 $cm^{-1} \cdot kbar^{-1}$ for β-$BaGeF_6$) and for the internal vibrations of the MF_6 anions the values are between 0.15 and 0.53 $cm^{-1} \cdot kbar^{-1}$ (cf. Table II).

Internal vibrations coupling to lattice vibrations show stronger pressure dependences than do uncoupled internal vibrations. On this basis, internal vibrations with similar frequencies but of different symmetry species and therefore different possibilities of coupling to lattice vibrations may be assigned. To a limited extent high-pressure spectrometry can give similar information concerning the symmetry species assignment as do single-crystal spectra.

4. Experimental Methods

A new design for an opposed sapphire anvil cell has been used (applied maximum pressure 25 kbar). The adjustment of the opposed anvils is simplified by the separation of translatory and rotatory movements. In order to obtain a pressure distribution as homogeneous as possible a mild steel gasket has been inserted. Since in such a setup the pressure cannot be calculated from the area and applied force (which is a function of the deformation of the plate springs used) the sharp and intense R_1 fluorescence band of ruby at 694.3 nm $\triangleq 14.40 \times 10^3$ cm^{-1} has been used as an internal standard for pressure calibration (*7–11*) with a slope of the line pressure vs wavenumber shift of $dp/d\nu = 1.328 \pm 0.003$ $kbar \cdot cm^{-1}$ (*7*). Using argon ion laser excitation (488.0 and 514.5 nm) the R_1 band lies far from the vibrational spectra of the samples under investigation so that overlap and interference do not occur.

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TABLE III

MODIFIED GRÜNEISEN PARAMETERS $\gamma_i^* = (1/\nu_i)(\partial\nu_i/\partial p)_{p=0}$, IN KBAR, FOR SOME HEXAFLUOROMETALLATES

Compound	ν_{Lib} (E_g)	ν_5 (A_{1g})	ν_5 (E_g)	ν_2 (E_g)	ν_1 (A_{1g})
$BaSiF_6$	7.4	0.61		1.1	0.67
$BaGeF_6$ (α)	3.9	0.53		0.35	—
$BaGeF_6$ (β)[a]	11 23	1.4		1.1	—
$BaTiF_6$	8.20	1.3		—	0.45
$BaSnF_6$	7.98	0.58	1.7	0.85	0.50
$TlSbF_6$	27.6	0.73	1.8	0.74	0.43

[a] $p = 9.8$ kbar.

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