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Raman-scattering study of crystallized MF_3 compounds (M = Al,Cr,Ga,V,Fe,In): An approach to the short-range-order force constants

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The cubic-rhombohedral structural phase transition that occurs in MF_3 compounds (M=Al,Cr,Ga,V,Fe,In) is studied by calorimetric measurements (differential scanning calorimetry, differential thermal analysis) and by Raman and by Raman scattering. The transition temperatures and the hysteresis are determined with precision. The Raman spectra of MF_3 fluorides have been collected at room temperature and high temperature. An assignment of the four Raman-active modes of the rhombohedral phase is proposed on the basis of group-theory analysis in the cubic phase. The temperature study of Raman spectra indicates the presence of two soft modes due to the condensation of the triply degenerate R_5 mode of the cubic phase [at the $R(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ point of the first cubic Brillouin zone]. The Raman data are used to adjust the parameters of a rigid-ion model and to deduce short-range interaction parameters assuming constant ratio A_t/B_t. The F-F short-range interactions are obtained for a wide range of interionic distances, and their behavior is physically reasonable. The calculated phonon spectra and the phonon density of states are presented. The latter exhibits an important discontinuity at the soft-mode frequencies.

INTRODUCTION

The structural phase transitions in compounds built with MX_6 octahedra have suggested a great number of investigations during recent years. In this framework, the study of compounds like the MF_3 fluorides is undertaken on account of the fact that they are the most simple systems of octahedra linked together by corners and that they exhibit a cubic-rhombohedral phase transition. This transition, encountered in almost all the MF_3 compounds isomorphous to the ReO_3 structure, is due to octahedra rotation, around their threefold axis.

The interest in these compounds comes from such common properties while the unit from which they are built (octahedron) and the temperature of transition vary over a fairly wide range. These characteristics make this family a very convenient system to learn about the origin of the instabilities in structures built with connected octahedra.

The knowledge of the phonon spectrum is important for studying the phase transition. As shown in a recent paper[1] the phonon spectrum of AlF_3 calculated with a rigid-ion model can be described by only three parameters which can be estimated from the Raman-scattering date alone (collected in the rhombohedral phase). Actually in the present case this approach is really necessary since up to now the crystals available have been too small to perform an inelastic neutron scattering investigation (up to now only crystals grown by hydrothermal synthesis,[2] in vapor phase,[3] or by the flux method[4,5] have been obtained, and they are often twinned, with a maximum size of 1 mm^3). From the calculated phonon spectrum of AlF_3 it has been predicted that the soft-mode frequency should be easily deduced from the one-phonon density of states.[1] Moreover, the study of the whole family makes it possible to calculate the fluorine-fluorine interaction versus interionic distances over a wide range, and to predict the interaction between trivalent cation and fluorine, which has been reported only in case of aluminum.[6] Such data are useful to predict the phonon spectrum of more complex structures such as tetrafluoroaluminates $A^{I}M^{III}F_4$, which undergo a great variety of structural phase transitions. Actually in such compounds the number of interactions is so important that the calculation of the force constants would require a great number of experimental data which can be done only in a limited number of cases.[6] Calculated phonon spectra also are necessary to analyze the structure of the luminescence spectra.[7]

Knowledge of force constants in crystallized MF_3 compounds will be essential for the study of MF_3 fluorides in the amorphous state, which is one of the simplest systems prepared in this state. Especially it was thus thought of interest to explain Raman spectra collected on amorphous MF_3 and to obtain some additional information to interpret interactions between octahedra in these amorphous compounds.[8]

RELATED STRUCTURES FOR MF_3 COMPOUNDS

In MF_3 compounds an important variation of the coordination is observed with increasing size of the M^{3+} cation. For MF_3 fluorides with $0.5 \leq r_{M^{3+}} \leq 0.8$ Å, the structural arrangement can be fairly well described in terms of octahedra MF_6 connected to each other by corners only. In most of the cases the room temperature symmetry is rhombohedral with space group $R\bar{3}c$ (D_{3d}^6 No. 167) and is derived from the ReO_3 cubic type by an alternate rotation of octahedra around their threefold axis. This structure was previously proposed for VF_3 by Jack and Gutmann[9] and recently refined on single crystals.[10] The same structure is observed for CrF_3,[11,12] GaF_3,[12,13] TiF_3,[14] and FeF_3.[15] Note that in the case of FeF_3 the structure was also confirmed on single crystals by Leblanc *et al.*[16] Though many authors have proposed an $R32$ or $R\bar{3}$ space group for AlF_3,[17,18] it was recently shown by Daniel *et al.*[1] by x-ray powder diffraction study and confirmed by Raman scattering that this compound is isostructural with the VF_3 type structure and exhibits an $R\bar{3}c$ space group. InF_3 is the limit case for MF_3 compounds with $R\bar{3}c$ symmetry.[18] Actually the In^{3+} cation is much larger than in other trifluorides and gives rise probably to an important distortion of InF_6 octahedra which may include a lower symmetry. MnF_3 has a lower monoclinic symmetry ($C2/c$) because of a Jahn-Teller effect[19] (the vibrational study of this compound is not reported here).

PHASE TRANSITIONS IN MF_3 COMPOUNDS

Several studies have been previously performed to investigate the structural phase transition which appears in MF_3 compounds (AlF_3: Refs. 20 and 21; FeF_3: Ref. 22; CrF_3: Ref. 11; other MF_3: Ref. 12). The purpose of this work is to determine with precision transition temperatures and examine the hysteresis which occurs at the transition. Experiments have been performed by differential scanning calorimetry (Perkin-Elmer model DSC4) in aluminium cups for a temperature range up to 550 °C or by differential thermal analysis (DTA Netzsch model 404S) in platinum crucible for higher temperatures. Products used are MF_3 powders recrystallized in sealed platinum tubes at high-temperature. All experiments are performed at various rates of cooling and heating in order to determine with precision the transition temperatures by extrapolation of the measured temperatures versus the rate of cooling and heating.[1]

In all cases a large endothermic peak is observed with an important hystersis which establishes the real first-order character of the transition. Table I summarized experimental results for T_c, ΔT (hysteresis), and the transition enthalpy ΔH. No obvious relations between T_c or ΔT and the ionic radius of the cations r_{M^3} appear. Note that we have detected a phase transition in MnF_3 but its nature is not known.

RAMAN SCATTERING STUDY

Experimental

A Raman-scattering study was performed on crystal samples. AlF_3 was grown either from vapor phase (sealed platinum tube heated at 850 °C for 4 d) or by the flux technique (AlF_3 powder in a 12% mol PbF_2–88 mol % $PbCl_2$ flux cooled at 2 °C/h from 950 °C down to 650 °C). A typical size for crystals is 1 mm^3. GaF_3 and InF_3 were also obtained by the sublimation method. On the other hand the compounds CrF_3, VF_3, and FeF_3 were grown by hydrothermal synthesis (powder in 49% HF solution at 450 °C for 60 h in platinum tube): however, crystal size is much smaller than in the first methods (10^{-3} mm^3). Raman spectra were collected on a DILOR Z-24 single channel triple monochromator spectrometer coupled with a COHERENT-INNOVA 90-3 argon ion laser. The 514.5 nm excitation line was used with an incident power not exceeding 1 W for transparent samples (AlF_3, GaF_3, InF_3) and limited to 250 mW in colored crystals (FeF_3, CrF_3; green; VF_3: yellow-green) because of their high absorption. In view of the small size of the samples, experiments have been performed only under microscope. High-temperature experiments were performed with a heating stage CHAIX-MECA between the room temperature and 600 °C. However, crystals are always damaged before this maximum temperature considering the high sensibility of MF_3 compounds to hydrolysis. Thus, for FeF_3, the higher experimental temperature was 250 °C.

Results and discussion

According to the space group in the rhombohedral phase ($R\bar{3}c$) four Raman-active modes are expected:

TABLE I. DSC and DTA results for MF_3 compounds. Standard deviations are given in parentheses.

MF_3	$r_{M^{3+}}$ (Å)	$T_{c\min}$ (°C)	$T_{c\max}$ (°C)	ΔT (°C)	ΔH (cal/g)	Expt.
AlF_3	0.535	448.0(5)	456.0(5)	8(1)	1.7(1)	DSC
CrF_3	0.615	974(2)	985(2)	11(4)		DTA
GaF_3	0.620	807(2)	833(2)	26(4)		DTA
VF_3	0.640	489.8(5)	497.8(5)	8(1)	0.60(5)	DSC
FeF_3	0.645	373.5(1)	388(1)	15(2)	1.75(1)	DSC
MnF_3	0.645	650(2)	667(2)	17(2)		DTA
TiF_3	0.670	65(1)	71(1)	6(2)	0.5(1)	DSC
InF_3	0.800	373.0(5)	393.5(5)	20(1)	2.4(1)	DSC

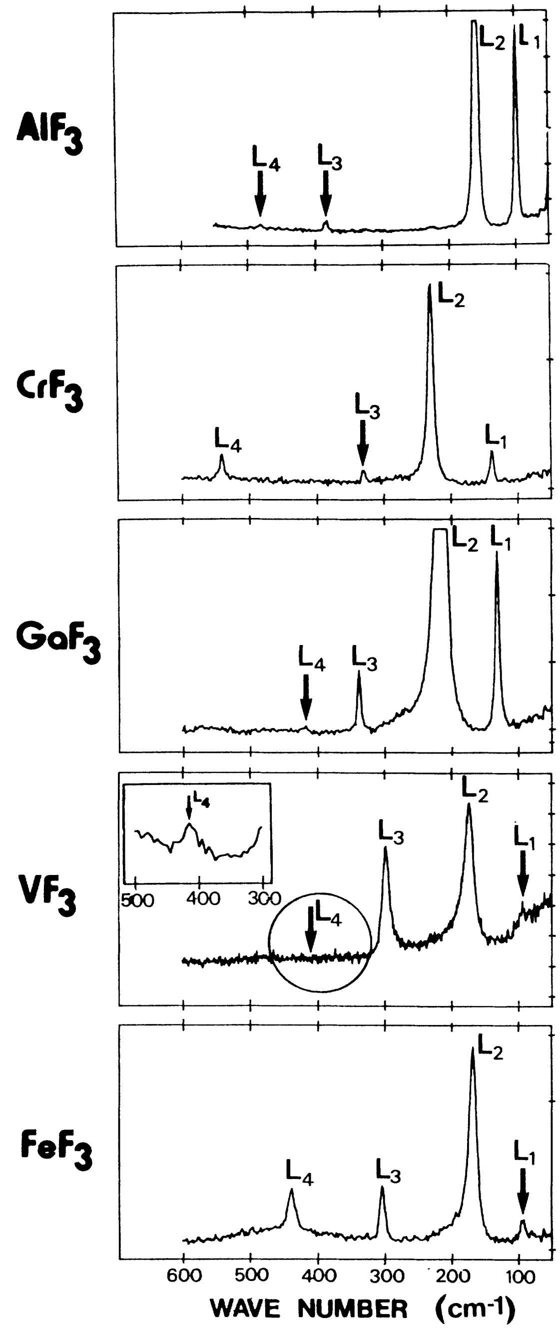

FIG. 1. Room temperature Raman spectra of AlF_3, CrF_3, GaF_3, VF_3, and FeF_3.

$1A_{1g}$ and $3E_g$. On the contrary in the cubic phase ($Pm\bar{3}m$ space group) no Raman mode is predicted. The experimental Raman spectra of AlF_3, CrF_3, GaF_3, FeF_3, and VF_3 are very similar and exhibit the four expected Raman lines (Fig. 1). When heating the samples the first two lines (L_1,L_2) of Raman spectra decrease in frequency, while the third line undergoes only a small frequency change and the last line (L_4) is wholly independent of the temperature. The occurrence of two soft modes establishes the displacive character of the first-order phase transition. As an example the temperature behavior of the two soft modes and the third Raman line of GaF_3 is given in Fig. 2. In all cases the temperature dependence of the L_1 and L_2 Raman lines in MF_3 compounds (M =Al,Cr,Ga,Fe,V) is fairly well described, as shown in Fig. 3, by a power law of Landau type:

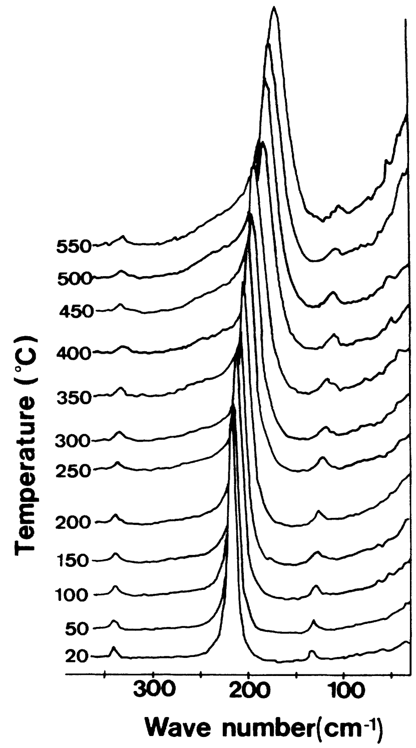

FIG. 2. Temperature dependence of the GaF_3 Raman lines (Raman spectra were collected from 20 °C up to 550 °C).

$$\omega \approx (T_0 - T)^{1/2} ,$$

where the T_0 temperature is obtained by crossing the curve $\omega^3 = f(T)$ with the temperature axis. It is observed that T_0 is much larger than T_c, which is the transition temperature measured by thermal analysis or when Raman lines disappear. This fact is consistent with the first-order character of the transition. We observe the following values for T_0:

* AlF_3 T_0=700 °C (973 K)
* CrF_3 T_0=1440 °C (1713 K)
* GaF_3 T_0=1300 °C (1573 K)
* VF_3 T_0=870 °C (1143 K)
* FeF_3 T_0=740 °C (1013 K)

* AlF_3 T_c=450 °C (723 K) T_c/T_0=0.74
* CrF_3 T_c=980 °C (1253 K) T_c/T_0=0.73
* GaF_3 T_c=830 °C (1103 K) T_c/T_0=0.70
* VF_3 T_c=500 °C (773 K) T_c/T_0=0.68
* FeF_3 T_c=380 °C (653 K) T_c/T_0=0.64

A similar slope is observed (≈ 14 cm^{-2}/K for the L_1 line, ≈ 35 cm^{-2}/K for the L_2 line) for all $\omega^2 = f(T)$ curves of Figs. 3(a) and 3(b). This result makes it possible to think that a common mechanism is at the origin of these transitions. It can be noted that T_c (K)/T_0 (K) decreases when $r_{M^{3+}}$ increases.

According to the symmetry of the high- and low-temperature phase, the structural phase transition can be attributed to the condensation of a zone boundary mode located at $R(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ point of the cubic Brillouin zone. Moreover, from compatability diagrams established between the two phases,[1] it is shown that the R_5 mode (Kovalev labeling[23]) of the cubic phase, which is an octahedra rotation mode, responsible for the transition, gives rise to two soft modes A_{1g} and E_g in agreement with our experimental Raman spectra. The E_g mode can be supposed to have a lower frequency than the A_{1g} mode taking into account the results obtained in fluoroperovskites by Rousseau *et al.*[24] This is also confirmed by the calculation of the phonon spectrum in the rhombohedral phase.[25] The two other E_g modes come from R_3 and R_4 modes of the cubic phase. Since the R_3 mode is a stretching mode, it exhibits a probably higher frequency than the R_4 octahedron distortion mode. Table II shows the assignment proposed for room temperature Raman lines of AlF_3, CrF_3, GaF_3, FeF_3, and VF_3.

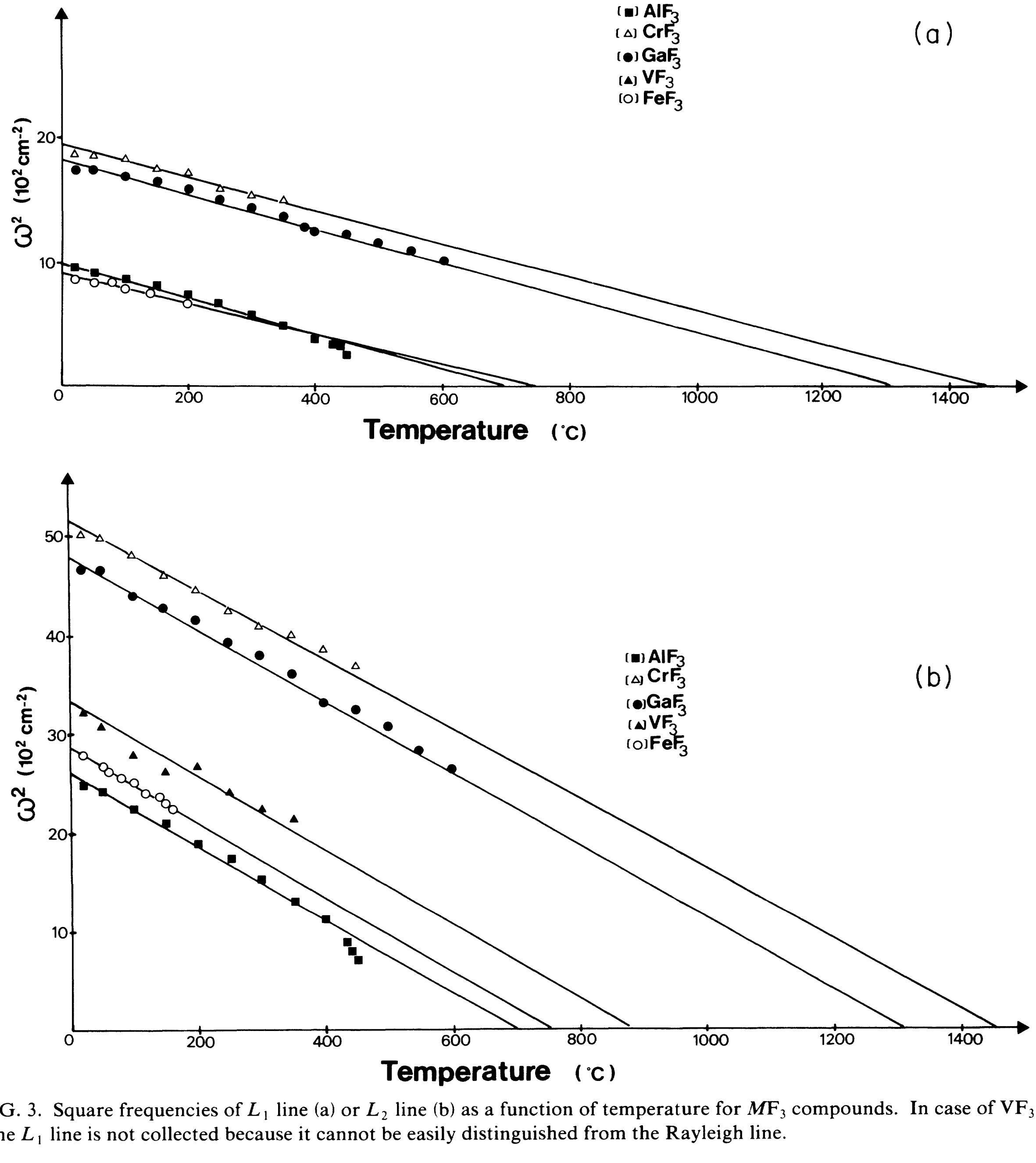

FIG. 3. Square frequencies of L_1 line (a) or L_2 line (b) as a function of temperature for MF_3 compounds. In case of VF_3, $\omega^2 = f(T)$ for the L_1 line is not collected because it cannot be easily distinguished from the Rayleigh line.

TABLE II. Assignment of room temperature Raman lines in case of AlF$_3$, CrF$_3$, GaF$_3$, VF$_3$, and FeF$_3$.

MF$_3$	$E_g(R_5)$ (cm^{-1})	$A_{1g}(R_5)$ (cm^{-1})	$E_g(R_4)$ (cm^{-1})	$E_g(R_3)$ (cm^{-1})
AlF$_3$	98	158	383	481
CrF$_3$	140	228	330	540
GaF$_3$	132	216	338	418
VF$_3$	95	180	300	415
FeF$_3$	94	168	304	440

In case of InF$_3$, we observed five lines on room temperature Raman spectrum, located at 102, 196, 210, 266, and 428 cm^{-1}. This fact is not consistent with the reported $R\bar{3}c$ symmetry. Therefore it can be supposed that the large cation size in InF$_3$ induces a lower symmetry and a future reinvestigation of the crystal structure is necessary in order to interpret this Raman spectrum.

Raman spectra of TiF$_3$ were not collected, because it was not possible to obtain pure crystal samples by the usual methods previously described.

TABLE III. Interaction constants and electric charges. Index $i=1$ (respectively, $i=2$) is used for M—F bond (respectively F—F bond). It has been supposed that $B_i=-A_i/10$ (as in alkali-metal halides) and $Z_M+3Z_F=0$.

MF$_3$	$r_{M^{3+}}$ (Å)	A_1 (N/m)	A_2 (N/m)	Z_F
AlF$_3$	0.535	236.25	20.20	−0.701
CrF$_3$	0.615	277.71	10.46	−0.749
GaF$_3$	0.620	180.84	15.62	−0.650
VF$_3$	0.640	172.89	10.80	−0.644
FeF$_3$	0.645	189.91	10.61	−0.666
InF$_3$	0.800	180.94	6.84	−0.696

LATTICE DYNAMICS

Knowledge of the order of magnitude of force constants in crystallized materials is very useful to throw light on the mechanism of the transitions. In the framework of a rigid-ion model, lattice dynamics in the cubic phase of MF$_3$ compounds involves only a small number of parameters. These parameters are A_1, B_1, A_2, B_2, Z_F, Z_M where A_1,B_1 (respectively, A_2,B_2) correspond

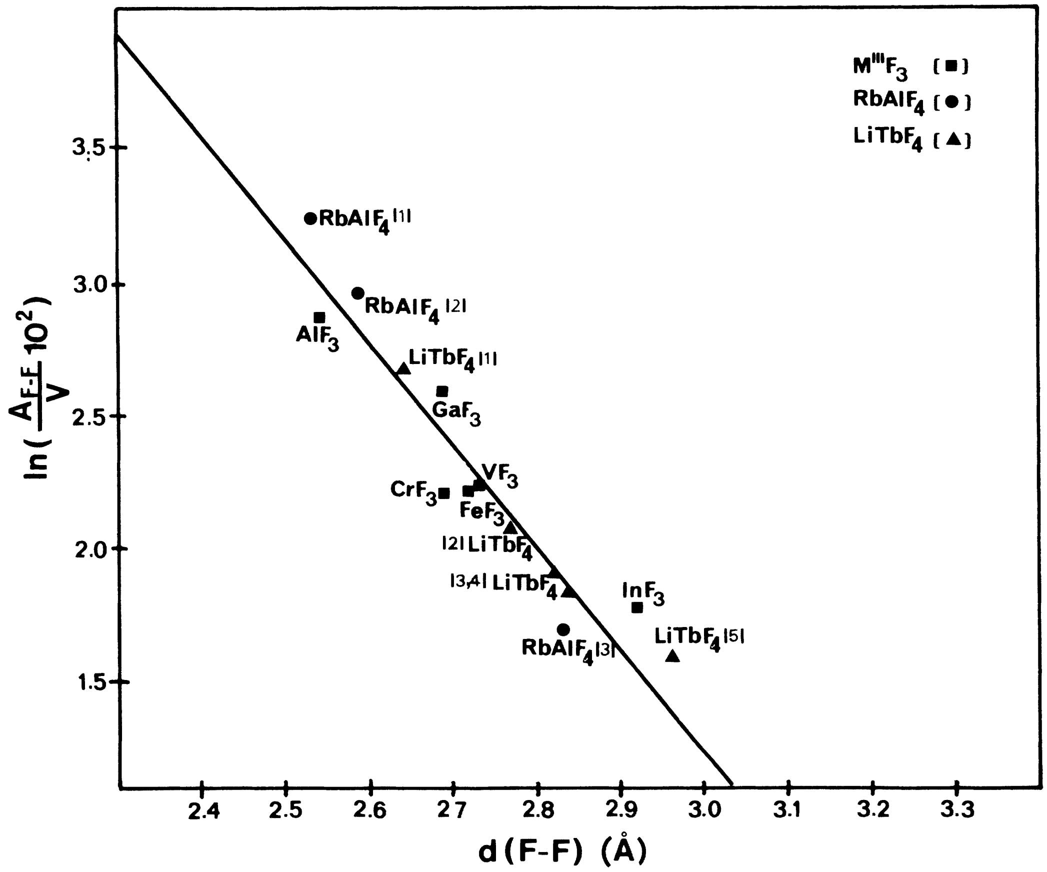

FIG. 4. Plot of $\ln[(A_{\text{F-F}}/V)10^2]$ vs the F-F distance, where V is the volume of the cubic cell. The solid line represents a mean square treatment including values of F-F force constants of MF$_3$ compounds, RbAlF$_4$ and LiTbF$_4$. Numbering associated to RbAlF$_4$ and LiTbF$_4$, on the figure corresponds to the different F-F interactions in these compounds.

to interaction constants parallel and perpendicular to M—F bond (respectively, F—F bond) and Z_F, Z_M the electric charges of the ions. Therefore assuming as a first approach that $B_1 = -A_1/10$ as in alkali-metal halides,[26,27] and $Z_F + 3Z_M = 0$ (electric neutrality), it is shown that the model requires three independent parameters (A_1, A_2, Z_F) and then the experimental Raman data are sufficient to determine the constants of the model and make possible *estimation* of the whole phonon spectrum. Such calculations are performed in the cubic phase while experimental data are collected in the rhombohedral phase. Actually R_3 and R_4 modes of the cubic phase are almost temperature independent. Furthermore the R_5 soft mode, which gives rise in the low-temperature phase to A_{1g} and E_g, is low frequency fixed to 50 cm^{-1}; indeed the A_i interactions are weakly affected by the value of this R_5 mode. Results for the calculated A_1, A_2, Z_F parameters are presented in Table III; the F-F constant in case of InF_3 is determined within a similar attribution of Raman lines (R_5 soft mode fixed to 50 cm^{-1}, $R_4 = 266$ cm^{-1}, $R_3 = 428$ cm^{-1}). It was verified that the A_i constants are weakly dependent on the value of the R_5 mode.

Neglecting van der Waals interactions, the short-range potential energy between a pair of ions interacting with central forces might be expressed in the Born-Mayer form by

$$V_i = \lambda_i e^{-r_i/\rho_i} , \tag{1}$$

where r_i is the interionic distance and λ_i, ρ_i are constants characteristic of the pair of ions. So the parameters A_i, B_i defined in terms of second derivative of V_i are linked to λ_i, ρ_i (in SI units: N/m) by

$$A_i = \frac{\lambda_i}{\rho_i^2} e^{-r_i/\rho_i} , \tag{2}$$

$$B_i = -\frac{\lambda_i}{r_i \rho_i} e^{-r_i/\rho_i} . \tag{3}$$

Thus, it seems natural to have an interest to study the evolution of F-F interaction constants versus the F-F distance. In Fig. 4 we have plotted $\ln[(A_{\text{F-F}}/V)10^2]$ versus d(F-F) for MF_3 compounds; on this curve previous data on $RbAlF_4$ (Ref. 6) and $LiTbF_4$ (Ref. 28) are also report-

TABLE IV. Calculated mode frequencies at high symmetry points of the first cubic Brillouin zone. These calculations were obtained from parameters of the rigid-ion model in the cubic phase determined with experimental Raman frequencies. The degeneration of high symmetry modes is given in parentheses in the first column near their designations. Corresponding symmetry coordinates of all modes are reported in Ref. 1. cm^{-1} unit is used.

		AlF_3	CrF_3	GaF_3	VF_3	FeF_3
Γ	$\Gamma_9(3)$	219	180	194	170	171
	$2\Gamma_{10}(3)$					
	LO	765	718	553	566	585
	TO	641	650	513	509	530
	LO	481	415	392	366	371
	TO	378	295	278	267	267
X	$X_1(1)$	570	606	498	481	503
	$2X_4(1)$	661	522	420	434	436
		278	249	210	210	213
	$X_8(1)$	231	194	204	180	182
	$X_9(2)$	252	211	223	197	198
	$3X_{10}(2)$	639	648	506	506	527
		325	249	244	229	229
		104	71	75	70	68
M	$M_1(1)$	622	640	544	518	539
	$M_3(1)$	51	51	51	51	51
	$2M_4(1)$	637	647	501	504	525
		218	139	132	133	129
	$M_5(1)$	481	540	418	415	438
	$M_7(1)$	398	347	351	313	318
	$M_9(2)$	250	209	221	195	196
	$2M_{10}(2)$	540	421	320	343	344
		254	222	206	196	199
R	$R_1(1)$	669	672	585	551	571
	$R_3(2)$	481	540	418	415	440
	$R_4(3)$	383	330	338	300	304
	$R_5(3)$	50	50	50	50	50
	$R_{10}(3)$	487	265	265	303	304

ed. It is evident that data points fit a straight line where slope, determined by a mean square analysis, induces $\rho=0.26$ Å. This value is close to the ones given by Tosi[27] in alkali-metal halides (0.282 Å $\leq \rho \leq 0.338$ Å); moreover, within the considered interval of F-F distances [2.5 Å, 3.0 Å], the ratio r_i/ρ is situated between -9.5 and -11.5 in good agreement with the hypothesis $A_i/B_i=-10$. However, this evolution of F-F constants in MF_3 compounds is fairly different from the one observed in fluoroperovskites[29] where force constants are estimated with much more experimental data. Actually such calculations bring a first approximation that will be improved in the future with the straight study of lattice dynamics in the rhombohedral phase. Note that an identical exponential law is not evident for M-F interaction constants as a function of the M-F distance.

Estimation of interaction constants of the model makes it possible to calculate the whole phonon spectrum; particularly, it becomes possible using a standard program to determine frequencies of vibration modes at high symmetry points of the first Brillouin zone in the high-temperature phase. These values are very useful in the framework of a study of interaction electron phonon.[30] Table IV shows calculated phonon frequencies at $X(\frac{1}{2},0,0)$, $M(\frac{1}{2},\frac{1}{2},0)$, $R(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, and $\Gamma(0,0,0)$. Note that frequency values of the infrared active modes at Γ and R points of the cubic phase are also in good agreement with experimental data recently collected in case of AlF_3. It can be noted that in all cases the R_5-M_3 line is flat. Then the transitions in MF_3 compounds could be explained by a similar model as the I-II phase transition in $RbAlF_4$ (Ref. 31) and the cubic phase could be disordered over a wide temperature range. This hypothesis is consistent with the fact that the squares of the soft-mode frequencies are linear in temperature (Fig. 3) in spite of the strong first-order character of the transitions.

The phonon density of states can be also directly determined in the cubic phase from values obtained for the force constants. Calculation is performed using a mesh of 10^6 q vectors in the $\frac{1}{16}$ volume of the first Brillouin zone with a frequency interval of 1 cm^{-1}. The result is plotted in Fig. 5 for all the MF_3 compounds studied in this work (except InF_3). Note a great similarity between the density of states curves, especially in case of FeF_3 and VF_3 of which Raman spectra are very closed. Moreover, an abrupt change in the vicinity of 50 cm^{-1} is observed. It corresponds to the value of the R_5 soft-mode frequency. Then the soft mode plays a major role in the density of states and therefore, could be deduced from inelastic neutron studies. Furthermore, in all compounds an intense peak (AlF_3: 639 cm^{-1}, CrF_3: 648 cm^{-1} GaF_3: 506 cm^{-1}, VF_3: 505 cm^{-1}, FeF_3: 527 cm^{-1}) is noticed. Such facts can be attributed to the existence of a flat phonon branch along the line Γ_{10}-Σ_4-M_4-Z_3-X_{10}-Δ_5-Γ_{10} and indeed in the whole $\Gamma XM\Gamma$ plane corresponding to vibration of M^{3+} with respect to F_6 octahedra.[10]

CONCLUSION

It has been shown that the structural phase transition which occurs at high temperature in all MF_3 compounds is of first-order character with the existence of a large hysteresis.

The low-temperature Raman spectra of AlF_3, CrF_3, GaF_3, VF_3, FeF_3 are consistent with rhombohedral $R\bar{3}c$ symmetry, and the Raman lines have been attributed on the basis of a group-theory analysis in the cubic phase. The temperature study of the Raman spectra shows the presence of two soft modes and indicates that the transition can be attributed to the condensation of the triple

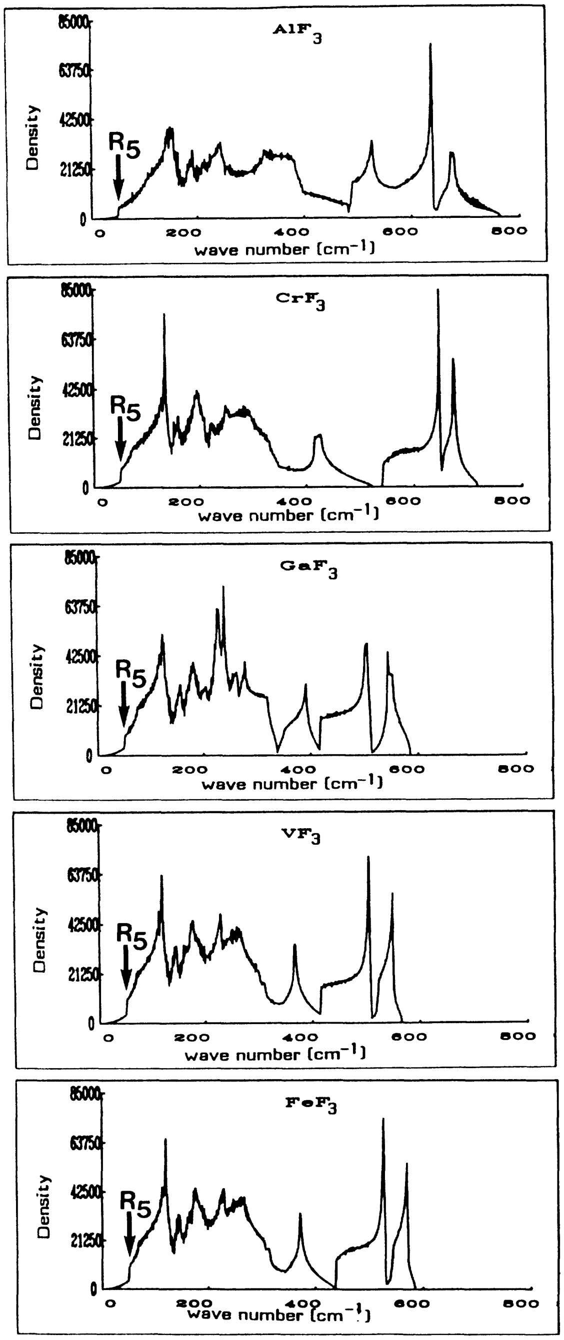

FIG. 5. Calculated phonon density of states of AlF_3, CrF_3, GaF_3, VF_3, and FeF_3 in the cubic phase.

degenerate R_5 soft mode of the cubic phase. On the other hand InF_3 exhibits more lines than expected for $R\bar{3}c$ symmetry, and its structure should be reinvestigated.

The Raman data appear to be sufficient to calculate interionic force constants and to estimate the whole phonon spectrum in the high-temperature phase. These force constants are in fairly good agreement with the ones obtained in alkali-metal halides and tetrafluoroaluminates but differ slightly from available data in fluoroperovskites. Investigations are in progress to conclude whether this discrepancy is due to the nature of the M cations or must be connected to the way of determining force constants. Such force constants are useful data to predict the phonon spectra of layered AMF_4 compounds and have already been used to describe successfully the vibrational properties of $RbFeF_4$.[32] Furthermore, these results should be useful to investigate the vibrational properties of amorphous MF_3 compounds. The whole phonon spectra of MF_3 in their cubic phase are also deduced together with the one-phonon density of states. This information throws some light on the mechanism of the transition and indicates that the soft mode in the cubic phase could be obtained easily from the one-phonon density of states.

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