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Determination of the fluorine-fluorine potential in fluoroperovskites and prediction of phonon dispersion curves

S. Salaün and M. Rousseau
Equipe de Physique de l'Etat Condensé, U.R.A. No. 807, Université du Maine, Av. O. Messiaen, 72017 Le Mans Cedex, France

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A simple, unified form of the fluorine-fluorine interionic potential is deduced from the modelization of many fluoroperovskites through a rigid-ion model. The Born-Mayer potential appears to be the most convenient description ($V_{\text{F-F}}=\lambda e^{-r/\rho}$ with $\rho=0.582$ Å and $\lambda=481$ nm^{-1} Å^2). The short-range force constants deduced from this potential enabled the prediction of phonon-dispersion curves and density of states in perovskite-type compounds for which very few experimental data are available.

INTRODUCTION

In the past few years, considerable progress has been made in molecular-dynamics simulation (MDS) of ordered or disordered systems. There have been many developments in several domains such as the study of glasses, the resolution of problems associated with relaxation around impurities or ionic mobility in crystals. The MDS technique is potentially efficient for fluoride materials which generally involve weakly polarizable ions. In order to minimize the number of adjustable parameters that are necessary to model the dynamics of fluoride compounds, it appears to be of the highest importance that one works out a simple unified form of a F^--F^- interionic potential which would be easily transferable from one kind of structure to another one.

Various potentials have been proposed by several authors: (i) Born-Mayer or Buckingham potentials in alkali halides,[1] in MF$_3$ compounds,[2] in KMnF$_3$ and KZnF$_3$,[3] (ii) spline potential by Catlow, Diller, and Norgett,[4] (iii) *ab initio* pair potentials by Boyer and Hardy.[5]

The most relevant description is undoubtedly the one deduced from *ab initio* pair potentials. Nevertheless it seems to be clear presently that available potentials are not fully satisfying because they are not consistent one with another.

In this paper we attempt to give a simple unified form of the F^--F^- interionic potential which is deduced from the dependence of the force constants on the internuclear separation derived from a rigid-ion model (RIM) applied to many AMF$_3$ compounds. It is shown how the parameters of a RIM determined from the experimental phonon-dispersion curves of some fluoroperovskites enable the estimation of a fluorine-fluorine interionic potential that is valid over a wide range of interionic distances. The proposed F-F potential is applied to estimate the RIM parameters of others AMF$_3$ compounds for which very few experimental data are available.

I. MODEL AND APPROXIMATIONS

The fluoroperovskites of general formula AMF$_3$ where A and M are, respectively, monovalent and divalent ions, are mainly ionic in character. Thus the crystal stability is assumed by the competition between electrostatic long-range interactions and short-range forces.

When a high degree of accuracy is needed in the representation of the phonon-dispersion curves, a shell model is much more convenient than a RIM. But, our purpose here being the determination of transferable force constants which would be valid for various structures, the shell model is less useful because it is less tractable than the RIM due to the great number of adjustable parameters. Thus, as is usually done, we use the RIM throughout this work to describe the lattice dynamics of fluoroperovskite compounds.

Following Cowley,[6] the short-range potential energy is considered as a sum of two-body axially symmetric interactions limited to nearest neighbors. For each pair of interacting ions, two parameters are needed to specify axially symmetric forces and they are chosen to be the second derivative of the corresponding short-range potential V_i, parallel and perpendicular to the line joining relevant ions. These two parameters (in SI units: N m^{-1}) are then classically defined by

$$A_i=\left.\frac{\partial^2 V_i}{\partial r_{i\parallel}^2}\right|_0, \quad B_i=\left.\frac{\partial^2 V_i}{\partial r_{i\perp}^2}\right|_0,$$

where the 0 subscript stands for the equilibrium position and the suffix i ($i=1$, 2, or 3) refers, respectively, to A-F, M-F, or F-F interaction.

The electrostatic long-range interactions are defined by only two independent parameters: Z_A and Z_F (the remaining ionic charge Z_M is given by the charge neutrality condition). According to Szigeti,[7] the substitution of the nominal charges Z_i by effective charges Z_i^* can account partially for the electronic polarizabilities of the atoms. With the aim of finding a general form for the interionic potential we decided to impose the same ratio Z_i^*/Z_i on all of the ions involved in these fluoride compounds.

Macroscopically, the electronic polarizability is characterized by the relative dielectric constant ε_∞ ($\varepsilon_\infty=n^2$) determined in the near-infrared range of wavelength. Finally, the effect of the ionic polarizabilities can

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be taken into account either by ε_∞ in a continuous medium, or by the effective ionic charges Z_i^* in a microscopic model. In order to get a rough estimate of these charges, one can write in a first approximation

$$\frac{Z_i Z_j e^2}{4\pi\varepsilon_0\varepsilon_\infty r^2} \approx \frac{Z_i^* Z_j^* e^2}{4\pi\varepsilon_0 r^2} \ .$$

With the previous assumption, the ratio Z_i^*/Z_i may be estimated to be roughly equal to $\sqrt{1/\varepsilon_\infty}$ which is lying between 0.63 and 0.72 in many fluoroperovskites according to the values reported in Table I.

Actually the effective ionic charges deduced from the RIM include phenomenological polarizabilities, shell deformation, and dipole-dipole interactions. Indeed the effective ionic charges of the fluorine ion calculated in various compounds with a RIM lie in a narrow range, i.e., from -0.73 to -0.82 in units of $|e|$.[20] Owing to all these arguments we have chosen to impose Z_i^*/Z_i to the mean value 0.77 for every fluoride compound.

In the perovskite structure, since each ion is located at a center of symmetry, the polarizabilities do not affect the elastic constants which may be hereby introduced explicitly in the model[6]

$$C_{11} = \frac{1}{2a}(2A_1 + 2B_1 + A_2 + 2A_3 + 2B_3) + \frac{2e^2}{aV}F_{11}(Z_A^*, Z_M^*, Z_F^*) \ ,$$

$$C_{12} = \frac{1}{2a}(A_1 - 5B_1 - B_2 + A_3 - 5B_3) + \frac{2e^2}{aV}F_{12}(Z_A^*, Z_M^*, Z_F^*) \ ,$$

$$C_{44} = \frac{1}{2a}(A_1 + 3B_1 + B_2 + A_3 + 3B_3) + \frac{2e^2}{aV}F_{44}(Z_A^*, Z_M^*, Z_F^*) \ .$$

The electrostatic contributions F_{ij} were calculated by Cowley,[6] a is the lattice parameter, V the volume of the unit cell and the force constants are expressed in N m^{-1}. When the elastic constants are known experimentally, there are three fewer variable parameters in the model since, thanks to the previous relations, the short-range force constants A_i and B_i may be expressed in terms of C_{ij} and F_{ij}.

II. DETERMINATION OF THE FLUORINE-FLUORINE POTENTIAL

As discussed in the Introduction, the large number of fluoroperovskites for which experimental data are available (Table I) enables to calculate the fluorine-fluorine interaction over a wide range of interionic distance (2.8 to 3.2 Å). For the determination of this potential, only the compounds which have been studied by means of inelastic neutron scattering have been considered in order to have as large a number of experimental data as possible.

The fitting is carried out, in the cubic domain of temperature of each compound, for the low-frequency zone-boundary modes in the main symmetry directions and the resulting short-range force constants are reported in Table II. In the fitting procedure, the effective charges are fixed as defined previously and the elastic constants at their experimental values.

The F-F short-range potential energy between a pair of ions interacting with central forces might be expressed in the Buckingham form as

$$V_{\text{F-F}} = \lambda e^{-r/\rho} - \frac{C}{r^6} - \frac{D}{r^8} \ ,$$

where r is the fluorine-fluorine distance and λ, ρ, C, D are constants characteristic of this ionic pair. Since they are defined as the second derivative of the potential, the short-range force constants $A_{\text{F-F}}$ and $B_{\text{F-F}}$ are linked to these four parameters, namely,

TABLE I. Crystallographic data, infrared-active experimental phonon frequencies, measured elastic constants, and relative dielectric permittivity for fluoroperovskites.

Compound	References (see text)	a (Å) at 300 K	Cubic domain of temperature	C_{11} (GPa)	C_{12}	C_{44}	TO1 (cm^{-1})	LO1	TO2	LO2	TO3	LO3	ε_∞
$KMgF_3$	8,9,10	3.973	Remains cubic	132±1.5	39.6±1.5	48.5±0.6	168	197	299	362	458	551	2.04
$BaLiF_3$	11,22	3.995	Remains cubic	130±1	46.5±0.5	48.7±0.5	142	240	332	339	382	509	2.25
$KNiF_3$	8,9	4.010	Remains cubic	158.2±0.5	48.5±1	40.2±0.2	150	165	246	310	445	517	2.30
$KZnF_3$	8,9,12,13	4.054	Remains cubic	134.5±1	52.7±0.5	38.1±0.2	141	149	200	292	410	474	2.20
$KCoF_3$	8,9,14	4.069	$T > 114$ K	132±2	52±2	35±2	140	156	224	293	430	512	2.25
NH_4ZnF_3	15	4.118					165		275		420		
$KMnF_3$	8,9,13	4.190	$T > 184$ K	115±1	39.5±1	27.4±1	119	144	193	270	399	483	2.10
$RbMnF_3$	8,9	4.239	Remains cubic	117.4±0.2	42.1±0.4	31.9±0.1	114	124	198	272	372	435	2.53
NH_4MnF_3	15	4.242					163		250		390		
$KCaF_3$	9,19	4.46 (748 K)	$T > 560$ K	110±20	35±5	20±5	108	140	204	246	388	479	
$RbCaF_3$	12,16,17	4.455	$T > 193$ K	102±1	24.6±0.5	21.5	87.5	115	192	249	402	486	1.90
$CsCaF_3$	12	4.526	Remains cubic	102±1	25.3±0.5	25.5±0.5	98	115	192	250.5	374	449	2.10
$TlCdF_3$	18	4.395	$T > 191$ K	102.8±0.6	38.5±0.5	17.7±0.1							
$RbCdF_3$	18	4.399	$T > 124$ K	109.6±0.2	37.3±0.5	20.4±0.2							
$CsCdF_3$	18	4.465	Remains cubic	107.8±0.2	40.5±0.5	25.0±0.2							
$RbCoF_3$	18	4.127	$T > 101$ K	129.6±0.6	55.4±1	41.5±0.2							

TABLE II. Calculated short-range force constants A_i and B_i expressed in $\mathrm{N\,m^{-1}}$. Index $i=1$ (respectively, 2,3) is used for A-F interaction (respectively, M-F and F-F interactions). Electric charges have been fixed to $Z_A=-Z_F=0.770$, $Z_M=1.540$ in units of $|e|$. The adjustment quality factor is defined by, $F=\sum_i[(\omega_{i\mathrm{calc}}-\omega_{i\mathrm{exp}})^2/\omega_{i\mathrm{exp}}^2]$.

Compound	$KMgF_3$	$BaLiF_3$	$KZnF_3$	$KCoF_3$	$KMnF_3$	$KCaF_3$	$RbCaF_3$	$CsCaF_3$
$d_{\mathrm{F\text{-}F}}$ (Å)	2.809	2.825	2.866	2.877	2.963	3.153	3.150	3.200
A_1 (N/m)	12.23	29	14.72	13.64	8.94	8.88	6.209	9.87
B_1	−0.305	−2.90	−1.47	−1.36	−1.78	−1.77	−0.62	−0.493
A_2	112.95	77.48	113.46	113.43	109.75	112.04	113.93	101.36
B_2	−8.50	−3.85	−12.55	−13.85	−12.32	−7.30	−8.24	−5.76
A_3	12.23	8.70	11.04	10.91	9.39	6.22	6.209	5.43
B_3	−1.22	−0.87	−1.10	−1.09	−0.23	−1.244	−0.62	−1.08
Adjust. quality	7.08	4.26	6.93	6.88	19.11	25.96	12.28	1.91

$$A_{\mathrm{F\text{-}F}}=\frac{\partial^2 V_{\mathrm{F\text{-}F}}}{\partial r^2}=\frac{\lambda}{\rho^2}e^{-r/\rho}-\frac{42C}{r^8}-\frac{72D}{r^{10}}$$

and

$$B_{\mathrm{F\text{-}F}}=\frac{1}{r}\frac{\partial V_{\mathrm{F\text{-}F}}}{\partial r}=-\frac{\lambda}{r\rho}e^{-r/\rho}+\frac{6C}{r^8}+\frac{8D}{r^{10}}\ .$$

Figure 1 shows a plot of $\ln(A_{\mathrm{F\text{-}F}})$ versus the fluorine-fluorine distance. It appears that data points (solid circles) fit a straight line where the slope, determined by a mean-square analysis, yields following values for the potential's parameters:

$$\rho=0.582\ \text{Å}\ ,$$

$$\lambda=481\ \mathrm{N\,m^{-1}}\,\text{Å}^2\ .$$

The parameters C and D turn out to be negligible. Consequently, the short-range potential is restricted to the well-known Born-Mayer form.

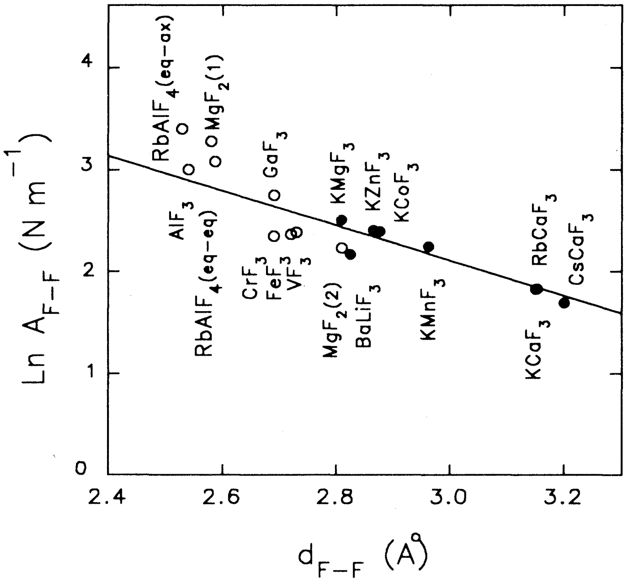

FIG. 1. Plot of $\ln[A_{\mathrm{F\text{-}F}}(\mathrm{N\,m^{-1}})]$ vs the F-F distance. The solid line represents a mean-square treatment including values of F-F short-range force constants of AMF_3 compounds (filled circles). Previous results obtained in other fluoride compounds are also reported (open circles).

It also appears that if the inverted perovskite $BaLiF_3$ is left out completely, the rest of the AMF_3 data points fall almost perfectly on a straight line, defined by the parameters $\rho=0.51$ Å and $\lambda=785\ \mathrm{N\,m^{-1}}\,\text{Å}^2$ which are somewhat different from the former ones. Nonetheless, since the aim of this work is to obtain an empirical F-F pair potential as general as possible and hence tractable in other types of fluoride ionic compounds, we have decided to keep the $BaLiF_3$ data point in the fitting procedure.

The value we obtain for ρ is fairly different from those determined by Daniel[2] in MF_3 compounds ($\rho=0.26$ Å) in a much more restricted area of interionic distances, or by Tosi[1] in alkali halides ($\rho=0.282$ to 0.338 Å) where the electronic configurations are those of rare gas, as in the F^--F^- interaction. Moreover, within the considered interval of F-F distances, the ratio $d_{\mathrm{F\text{-}F}}/\rho=-A_{\mathrm{F\text{-}F}}/B_{\mathrm{F\text{-}F}}$ varies from 4.36 to 5.50, marking a significant deviation from the usual approximation for this sort of compound where $A_{\mathrm{F\text{-}F}}/B_{\mathrm{F\text{-}F}}\cong-10$.

Nonetheless our results agree fairly well with previous data obtained in $RbAlF_4$,[20] MgF_2,[21] and MF_3 compounds[2] as shown in Fig. 1 where these data have been reported (open circles). It is important to note that, in all of these compounds, the effective ionic charges remain free during the fitting procedure, and the Z_F values obtained by the authors are really close to the one we imposed during this work. Concerning $RbAlF_4$, it must be noticed that we only took into account the so-called F_{eq}-F_{eq} and F_{ax}-F_{eq} interactions[20] because both ions of each pair belong to the same octahedron. The good agreement between all those data and our empirical potential confirms the choice we made in keeping, together with the others fluoroperovskites, the $BaLiF_3$ data point.

III. APPLICATION TO SOME FLUORIDE PEROVSKITES

As shown in the Introduction, it is worthwhile to predict the phonon-dispersion curves and the phonon density of states in AMF_3 compounds. Some of the fluoroperovskites, such as $KMnF_3$, $KZnF_3$,[13] $KCaF_3$,[9] $RbCaF_3$,[17] $KMgF_3$,[10] and $BaLiF_3$ (Ref. 22) have been studied by means of inelastic neutron scattering and IR

TABLE III. Lattice parameter a, elastic constants (in GPa), and short-range force constants (in $\mathrm{N\,m^{-1}}$) in AMF_3 compounds: the quantities in italics have been fitted, the others have been imposed. The A_3 and B_3 parameters have been taken from our fluorine-fluorine potential with the appropriate F-F distances.

Compound	a (Å)	C_{11} (GPa)	C_{12}	C_{44}	A_1 (N/m)	B_1	A_2	B_2	A_3	B_3
$KNiF_3$	4.010	158.2	48.5	40.2	*13.10*	*−0.61*	*137.08*	*−9.45*	10.89	−2.24
$KCoF_3$	4.069	132	52	35	*13.50*	*−1.35*	*117.18*	*−10.07*	10.14	−2.05
$RbMnF_3$	4.239	117.4	42.1	31.9	*13.25*	*−0.87*	*105.91*	*−9.25*	8.25	−1.60
$CsCaF_3$	4.526	102	25.3	25.5	*9.87*	*−0.16*	*99.88*	*−7.19*	5.82	−1.06
NH_4ZnF_3	4.118	*122.4*	*40.2*	*37.8*	*10.51*	*−1.05*	115.05	−6.23	9.58	−1.92
NH_4MnF_3	4.242	*109.3*	*39.6*	*29.9*	*10.45*	*−1.05*	105.0	−9.16	8.21	−1.59

reflectance measurements. Their respective phonon-dispersion curves have already been published. Henceforth we have focused our attention on AMF_3 compounds with less experimental data. Nevertheless, insofar as the calculation of the short-range force constants requires a minimal number of experimental frequencies to achieve a meaningful fitting procedure, we studied fluoroperovskites with experimental frequencies for infrared-active optical modes.

A. Parameters of the RIM

The fluorine-fluorine potential developed in the previous paragraph (with the appropriate F-F distances) yields values for the short-range force constants A_3 and B_3

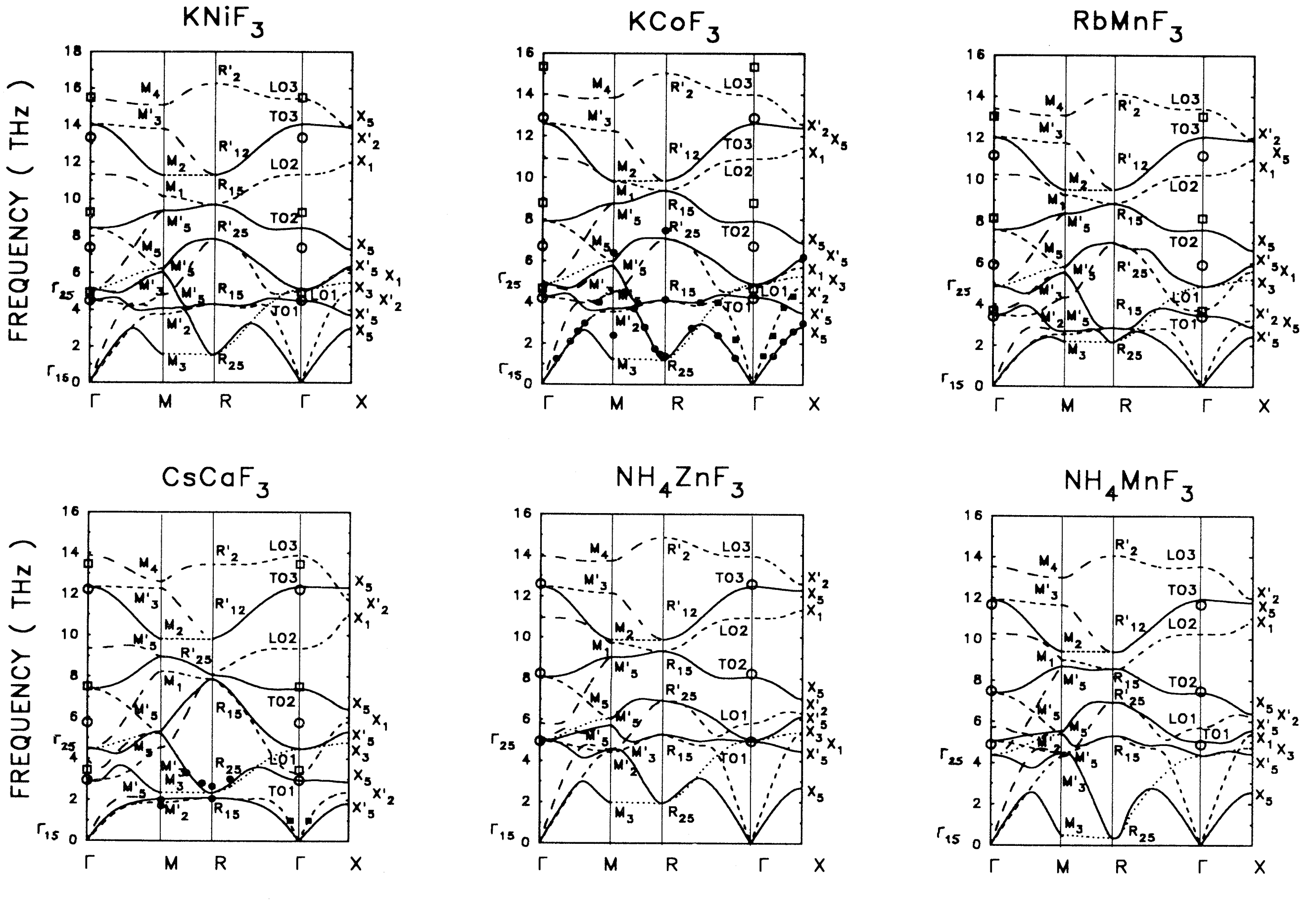

FIG. 2. Calculated phonon-dispersion curves in AMF_3 compounds together with experimental data points: IR results (○ TO, □ LO) and inelastic neutron-scattering results (● transverse modes, ■ longitudinal modes). The vibration modes of the different high-symmetry lines are represented as follows: Solid line, $\Sigma_3(\Gamma M)$, $T_5(MR)$, $\Lambda_3(R\Gamma)$, $\Delta_5(\Gamma X)$; Long dash, $\Sigma_1(\Gamma M)$, $T_2'(MR)$; Medium dash, $\Sigma_4(\Gamma M)$, $T_1(MR)$, $\Lambda_1(R\Gamma)$, $\Delta_1(\Gamma X)$; Short dash, $T_1'(MR)$; Dotted line, $\Sigma_2(\Gamma M)$, $T_2(MR)$, $\Lambda_2(R\Gamma)$, $\Delta_2(\Gamma X)$.

which will be used as input constants during the fitting procedure. Moreover the effective charges Z_A^* and Z_F^* will be held, respectively, at 0.77 and -0.77 as previously. Hence the number of adjustable parameters is reduced to 4. All the compounds studied in this part of our work may be classified in two different classes: those for which experimental elastic constants data are available and those for which they are not known.

1. Fluoroperovskites with experimental elastic constants

In so far as Z_A^*, Z_F^*, A_3, B_3, C_{11}, C_{12}, and C_{44} are imposed, there is only one adjustable parameter left which is chosen to be the short-range force constant A_1 relative to the A-F interaction. This constant is fitted to obtain calculated frequencies as close as possible to the experimental ones at the Γ point of the Brillouin zone. The results for $KNiF_3$, $KCoF_3$, $RbMnF_3$, and $CsCaF_3$ are reported in Table III.

2. Fluoroperovskites without experimental elastic constants: NH_4ZnF_3 and NH_4MnF_3

For both of these compounds, the short-range force constants A_2 and B_2 which characterize the Zn-F or Mn-F interaction, have been estimated from previous studies on $KZnF_3$, $KMnF_3$, and $RbMnF_3$ in which the interionic distances are close to those encountered in NH_4ZnF_3 and NH_4MnF_3, respectively. The fitting is carried out for the three transverse optical modes measured by Bartholomé *et al.*[15] The elastic constants have been deduced (see Table III).

The calculations concerning NH_4MnF_3 predict the existence of a soft mode at the R point. Indeed the squared frequency of the soft mode, which eigenvectors involve MF_6 octahedra rotations around $\langle 100 \rangle$ axes, may be expressed in terms of parameters of the RIM:[17]

$$\omega^2(\mathbf{q}_R)=\frac{e^2}{M_F V}\left[\frac{2V}{e^2}(A_1+B_1+B_2+4B_3)-14.461Z_F^{*2}+5.779Z_A^*Z_F^*-13.596Z_M^*Z_F^*\right].$$

In this expression, the calculations lead to a negative short-range contribution whereas the long-range one is positive and fixed because we imposed the effective ionic

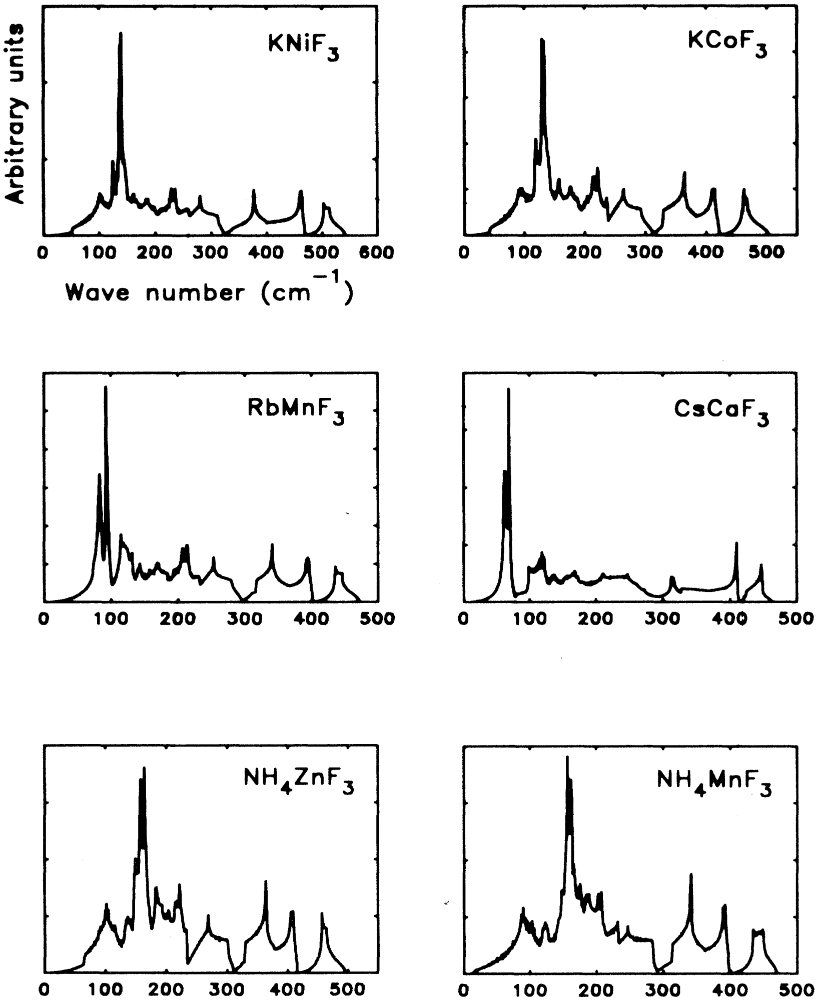

FIG. 3. Calculated phonon density of states of AMF_3 compounds.

charges. Then a very slight variation in the short-range forces leads $\omega^2(\mathbf{q}_R)$ to zero. The set of force constants we proposed in Table III lead to a slightly positive value for the squared frequency of the soft mode.

B. Deduced phonon-dispersion curves and density of states

Previous results allow in every case the calculation of phonon-dispersion curves along MR, ΓM, $R\Gamma$, and ΓX lines. For each $AM\mathrm{F}_3$ compound, the irreducible representations are labeled according to a choice of origin at the A site. The calculated phonon-dispersion curves are plotted in Fig. 2 together with experimental data. The experimental points we report are quite numerous in the case of $\mathrm{KCoF_3}$, but the dispersion curves that have previously been published were only guides to the eye. As clearly shown in the corresponding graph, $\mathrm{CsCaF_3}$ exhibits an interesting behavior, i.e., the calculated and measured R_{25} and R_{15} vibration modes are inverted in comparison with all the other fluoroperovskites. It is worth noticing that there is in every case a very good agreement, for such rough a model, between calculated and measured low-frequency phonons.

The one-phonon density of states have been calculated using a mesh of 10^6 independent **q** vectors in the irreducible section of the Brillouin zone with a frequency step of 1 cm^{-1}. The resulting curves are plotted in Fig. 3. All of the calculated cutoff frequencies are in the vicinity of 500 cm^{-1} as generally observed in fluoride compounds.

CONCLUSION

From inelastic neutron scattering, ultrasonic and infrared data we have deduced a short-range potential for the fluorine-fluorine interactions. The large range of interionic distances (2.5 to 3.2 Å) for which this potential is available makes it a useful tool for molecular-dynamics simulation and lattice-dynamics calculations in fluoride compounds. The best function consistent with experimental data turns out to be the simple Born-Mayer form $V=\lambda\exp(-r/\rho)$. The strong correlation between the parameters A and ρ explains the discrepancy between the values proposed by different authors for both of these parameters. As mentioned before, the validity of our potential lies essentially in its wide range of applicability.

Additionally, we have used this potential to calculate the phonon-dispersion curves of some fluoroperovskites for which few experimental data are available. In this way, we are now using this potential to investigate the dynamical properties of compounds with a different structural arrangement such as $\mathrm{LiYF_4}$ and $\mathrm{Li}L\mathrm{F_4}$ ($L=$Ho, Er, Tm, or Yb) which crystallize in the scheelite structure where new fluorine-fluorine distances are encountered. Both lattice-dynamical calculations and neutron-scattering experiments in the laser matrix $\mathrm{LiYF_4}$ are in progress.

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