where v is the unit cell volume. The values obtained for CdF_2 and PbF_2 are given in Table I. The values are not very different than those found for the alkaline-earth halides where almost certainly the net charges are the full ionic values.[11] A crude estimate of the distortion effects on the basis of the shell model shows (1) the greater effective charge for PbF_2 reflects not so much greater ionicity but the greater polarizability of the Pb^{2+} ion as compared to the Cd^{2+} ion; (2) the net ion charges must be about 90% of the full ionic values in both cases. This latter conclusion is probably consistent with the observation that the lattice energies of CdF_2 and PbF_2 differ by less than 10% from that calculated using a Madelung attractive potential with full ionic charges.[12]

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Long-Wave Lattice Dynamics of the Fluorite Structure*

J. D. Axe
IBM Watson Research Center, Yorktown Heights, New York

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A simple shell model is used to calculate expressions for the long-wavelength vibrational eigenfrequencies and elastic constants of the fluorite (CaF_2 type) lattice. The concept of effective charge is introduced and expressions analogous to the Szigeti relations for lattices with diatomic unit cells are given. These and other relations between the acoustic and optical properties derived for the dipole shell model are in better agreement with the measured properties of the alkaline-earth fluorides than are those derived for a rigid-ion model. The large deviation from the Cauchy relation $C_{12}=C_{44}$ seems to be largely explainable in terms of the shell-model correction to the internal strain.

I. INTRODUCTION

Recent experimental studies of lattice dynamics, much of it in the form of inelastic slow-neutron scattering,[1,2] have made abundantly clear certain shortcomings in what may be termed the rigid-ion model of a crystal lattice which evolved from the work of Born and others.[3–5] This model, in which nonpolarizable ions interact through long-range electrostatic and short-range repulsive forces, explains reasonably well many properties of simple ionic crystals (e.g., cohesive energies, elastic constants, Debye temperatures), but is quite inadequate in discussing dielectric properties and the detailed dispersion relations of (particularly) longitudinal modes. Of the various attempts to introduce the feature of polarizability correctly into lattice dynamics (complicated by the fact that in addition to being electrically polarizable, ions are also mechanically polarized by the motions of their neighbors[6]), the shell model, introduced in various forms by several workers[7–10] and developed and formalized by Cochran[11] and Cowley,[12,13] has received the most attention recently. Although the theory has limitations, it is physically appealing and even in its simplest form does much to alleviate the discrepancies noted above in simple ionic structures (NaI, KBr)[14] as well as more homopolar ones (Ge, GaAs).[15,16]

Materials having the fluorite structure, only modestly more complicated than the rock-salt or diamond structures mentioned above, are numerous, and experimental data, much of it recent, on the elastic and optical properties of fluorite (CaF_2) and structurally related

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compounds are available.[17–23] The lattice dynamics of fluorite has also been discussed in the rigid-ion approximation.[24–27] However, it seems profitable at this time to re-attempt to correlate existing data, particularly noting to what extent whatever discrepancies that exist can be reconciled by extending the model to one involving dipoles arising from polarizable shells. This will be referred to as the dipole shell model (DSM).

II. THEORY

In the shell model each constituent ion of a crystal is represented as a spherical core made up of the nucleus and inner electrons and a rigid spherical shell of outer electrons coupled together by an isotropic force proportional to their relative displacement. Although both the shell and core retain their spherical symmetry when displaced, a dipole moment is generated by their relative displacement. Equations of motion can be written within the framework of Born–von Karman theory for both the amplitude of the displacement of the κth ion, $U_x(\kappa)$,

$$\omega^2\mathbf{m}\mathbf{U}=(\mathbf{R}+\mathbf{Z}\mathcal{C}\mathbf{Z})\mathbf{U}+(\mathbf{T}+\mathbf{Z}\mathcal{C}\mathbf{Y})\mathbf{W}, \tag{1}$$

and for the relative displacement of the κth shell from its core, $W_x(\kappa)$,

$$0=(\tilde{\mathbf{T}}^*+\mathbf{Y}\mathcal{C}\mathbf{Z})\mathbf{U}+(\mathcal{S}+\mathbf{Y}\mathcal{C}\mathbf{Y})\mathbf{W}. \tag{2}$$

For a lattice with n atoms per unit cell $\mathbf{U}$ and $\mathbf{W}$ are $3n$ vectors and $\mathbf{m}$, $\mathbf{Z}$, and $\mathbf{Y}$ are $3n\times 3n$ diagonal matrices specifying the mass, ionic charge, and shell charge, respectively. The matrices of the interaction coefficients are also of order $3n\times 3n$ and are divided into long-range electrostatic interactions $\mathcal{C}$ and short-range interactions between dipoles $Y_\kappa W_x(\kappa)$, between dipoles and displacements, and between the displacements themselves, and represented by the matrices $\mathcal{S}$, $\mathbf{T}$, and $\mathbf{R}$, respectively. Equations (1) and (2) are just a set of coupled equations of motion for the displacements and dipole moments, and as such have a quantum-mechanical justification.[12] Elimination of $\mathbf{W}$ between Eqs. (1) and (2) leads to a single set of $3n$ equations

$$(\mathbf{M}'-\omega^2\mathbf{m})\mathbf{U}=0, \tag{3}$$

which determine the $3n$ eigen-frequencies $\omega(\mathbf{q})$. Explicit solutions of (3) are in general quite complex. However, if the crystal is "diagonally cubic," i.e., if each atom occupies an equilibrium position with tetrahedral symmetry or higher, considerable simplification results from the fact that in the limit as $|\mathbf{q}|\rightarrow 0$, the electrostatic interaction can be specified by an electric field which is the same at each lattice point in the crystal and is given by the sum of the macroscopic field $\mathbf{E}_M$ and the Lorentz field $\mathbf{E}_L=4\pi\mathbf{P}/3$.[5] Further, Eq. (3) factors into $3n\times n$ equations separately describing the longitudinal and transverse modes. Cochran[14] has shown that under these conditions the interaction matrix is given by

$$\mathbf{M}_T'=\mathbf{R}'^{(0)}-\mathbf{Z}'\mathcal{J}\mathbf{Z}'[4\pi(\epsilon_e+2)/9v], \tag{4}$$

for transverse modes and

$$\mathbf{M}_L'=\mathbf{R}'^{(0)}+\mathbf{Z}'\mathcal{J}\mathbf{Z}'[8\pi(\epsilon_e+2)/9v\epsilon_e], \tag{5}$$

for longitudinal modes. The effective short-range force constants ($\mathbf{q}=0$) are

$$\mathbf{R}'^{(0)}=\mathbf{R}^{(0)}-\mathbf{T}^{(0)}[\mathcal{S}^{(0)}]^{-1}\tilde{\mathbf{T}}^{(0)*}, \tag{6}$$

where $\mathbf{Z}'$ is a diagonal matrix of the effective charges

$$\mathbf{Z}_c'=\mathbf{Z}_c-\mathbf{T}^{(0)}[\mathcal{S}^{(0)}]^{-1}\mathbf{Y}_c, \tag{7}$$

(the subscript c denotes a column vector). $\mathcal{J}$ is a square matrix with each element equal to unity and ϵ_e and v denote the high-frequency (electronic) dielectric constant and unit-cell volume, respectively. The difference in the expressions for the longitudinal and transverse frequencies arises from the fact that the longitudinal motion is accompanied by a macroscopic field $-4\pi\mathbf{P}$ which is not present for a similar transverse motion.[5,28]

While the above discussion is adequate for dealing with long-wavelength optical modes, the low-frequency behavior of the acoustic modes and thus the evaluation of elastic constants is obtained by expansion of Eqs. (1) and (2) as a power series in $\mathbf{q}$ (the method of "long waves").[5] This procedure has been carried through in general form by Cowley.[13] Since the treatment of necessity becomes somewhat involved, the additional material necessary for the evaluation of the fluorite elastic constants in the DSM approximation is relegated to the Appendix.

The fluorite lattice consists of three interpenetrating fcc lattices, one of divalent positive ions M^{2+} and two of nonequivalent negative ions X_1^-, X_2^-, each with a spacing $2r_0$. (The ions will be denoted in the dynamical matrices by $\kappa=1,2,3$. Of course variants on this structure are also possible, e.g., ThO_2 and K_2O both have the fluorite structure where the $\kappa=1$ particle is, in the first instance, a tetravalent positive ion and in the

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second a divalent negative ion.) Each M^{2+} is surrounded by four X_1^- and four X_2^- at alternate corners of a regular cube at a distance of $r_0'=\sqrt{3}r_0/2$. Each X^- has in turn a regular octahedral arrangement of (X_2^-, X_1^-) ions at a distance r_0. Notice that although the structure is diagonally cubic, the X^- sites do not have inversion symmetry, a fact which is consequently felt in the elastic constants. The unit-cell volume is $2r_0^3$.

In most of what is to follow, the assumption will be made that all of the short-range forces act through the shells. In addition to being physically plausible, these assumptions have withstood experimental comparison quite well.[14,16] In this case the interaction coefficients are related by $\mathbf{R}=\mathbf{T}$ and $\mathbb{S}=\mathbf{R}+\delta_{xy}\delta_{\kappa\kappa'}k(\kappa)$, where $k(\kappa)$ is the elastic spring constant coupling the κth shell to its core.[29] Only one set of short-range coefficients then appear and they may be generated from the same set of short-range potentials which are introduced in treating the rigid-ion model. Following Srinivasan's treatment of the rigid-ion problem,[24] the central potentials $\phi_1(r')$ between $(M-X)$ nearest neighbors and $\phi_2(r)$ between $(X-X)$ nearest neighbors are assumed. The cohesive energy per unit cell is

$$\Phi_0=\tfrac{1}{2}\alpha_M Z_1Z_2e^2/r+8\phi_1(r')+6\phi_2(r)\,, \tag{8}$$

where the Madelung constant $\alpha_M=5.818$ is referred to the $(X-X)$ separation. The R matrix is then specified in terms of the derivatives

$$\begin{aligned}(\partial^2\phi_1/\partial r'^2)_{r_0'}&=A_1(e^2/2v)\,,\\ (\partial^2\phi_2/\partial r^2)_{r_0}&=A_2(e^2/2v)\,;\\ (1/r')(\partial\phi_1/\partial r')_{r_0'}&=B_1(e^2/2v)\,,\\ (1/r)(\partial\phi_2/\partial r)_{r_0}&=B_2(e^2/2v)\,.\end{aligned} \tag{9}$$

The complete $\mathbf{R}$ matrix is given in the Appendix. These four derivatives are not independent but at equilibrium are subject to the requirement

$$-(\tfrac{1}{3})Z_1Z_2\alpha_M+B_1+B_2=0\,, \tag{10}$$

obtained by minimizing Eq. (8) with respect to r. A further useful relation involves the compressibility β,

$$\begin{aligned}\beta^{-1}&=(r_0^2/9v)(d^2/dr^2)(\Phi_0)_{r_0}\\ &=\tfrac{1}{3}[A_1+A_2-(\tfrac{2}{3})Z_1Z_2\alpha_M](e^2/2vr_0)\\ &=\tfrac{1}{3}[(A_1+2B_1)+(A_2+2B_2)](e^2/2vr_0)\,.\end{aligned} \tag{11}$$

Consider the solutions of Eq. (3), specifically

$$\begin{vmatrix} M_{11}'-m_1\omega^2 & M_{12}' & M_{12}' \\ M_{12}' & M_{22}'-m_2\omega^2 & M_{23}' \\ M_{12}' & M_{23}' & M_{22}'-m_2\omega^2 \end{vmatrix}=0\,, \tag{12}$$

subject to the restriction $\sum_{\kappa'} M_{\kappa\kappa'}'=0$ imposed by translational invariance. The eigenvalues and eigenvectors are easily shown to be

$$\omega_A^2=0;\quad U_1=U_2=U_3; \tag{13}$$

corresponding to the limiting acoustic mode. For the optic (F_{1u}) modes,

$$\begin{aligned}&\omega_0^2=-M_{12}'(m_1+2m_2)/m_1m_2\,;\\ &\qquad\qquad U_2=U_3=-(m_1/2m_2)U_1\,,\end{aligned} \tag{14a}$$

where Eqs. (4) and (5) are used for the transverse and longitudinal branches, respectively,

$$\begin{aligned}\omega_{\mathrm{LO}}^2&=-(1/\mu_0)[R_{12}'+(8\pi e^2/9v)(\epsilon_e+2)\epsilon_e^{-1}(Z_1'Z_2')]\,,\\ \omega_{\mathrm{TO}}^2&=-(1/\mu_0)[R_{12}'-(4\pi e^2/9v)(\epsilon_e+2)(Z_1'Z_2')]\,,\\ \mu_0&=m_1m_2/(m_1+2m_2)\,.\end{aligned} \tag{14b}$$

For the Raman active (F_{2g}) modes,

$$\begin{aligned}\omega_R^2&=(M_{22}'-M_{23}')(1/m_2)\,;\quad U_1=0;\quad U_2+U_3=0;\\ &=(R_{22}'-R_{23}')(1/\mu_R)\,;\quad \mu_R=m_2\,.\end{aligned} \tag{15}$$

The transverse and longitudinal Raman modes are degenerate because the opposite motions of the X^- ions result in a cancellation of the macroscopic dielectric polarization. Cochran[11] has shown generally that the shell model is compatible with the Lyddane-Sachs-Teller relation, which for a single optically active mode is

$$\epsilon_s/\epsilon_e=(\omega_{\mathrm{LO}}/\omega_{\mathrm{TO}})^2\,, \tag{16}$$

where ϵ_s is the static dielectric constant. This result may be combined with Eqs. (14) to yield a convenient expression relating the effective charges to experimental quantities

$$(\epsilon_s-\epsilon_e)=-(4\pi e^2/9v)(\epsilon_e+2)^2(Z_1'Z_2'/\mu_0\omega_{\mathrm{TO}}^2)\,, \tag{17}$$

which is identical to the expression given by Szigeti[6] for lattices with diatomic unit cells except for the appropriate redefinition of the reduced mass μ_0. This same set of manipulations yields also

$$R_{12}'=-\mu_0\omega_{\mathrm{TO}}^2(\epsilon_s+2/\epsilon_e+2)\,. \tag{18}$$

One further useful relationship (valid for central forces only) can be obtained by using Eqs. (18) and (A5) to rewrite the right-hand side of Eq. (11) to read

$$\frac{1}{\beta}=\left(\frac{1}{12r_0}\right)\left\{2\left(\frac{\epsilon_s+2}{\epsilon_e+2}\right)\frac{\mu_0\omega_{T0}^2}{(1-\gamma_0)}+\frac{\mu_R\omega_R^2}{(1-\gamma_R)}\right\}\,. \tag{19}$$

Equation (19) is similar to the relation between compressibility and TO frequency given by Szigeti[6] for diatomic lattices, but it is more general in that it makes allowances for the effect of distortion polarization on the short-range forces, an effect which was not considered by Szigeti.[30]

III. COMPARISONS AND DISCUSSION

The expressions [Eqs. (A9)] for the two elastic constants together with the equilibrium condition (10) are not sufficient to evaluate the four parameters specifying the $\mathbf{R}$ matrix. Srinivasan's procedure of assuming

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TABLE I. Short-range force constants and cohesive energies of the alkaline-earth fluorides. A_1, B_1 and A_2, B_2 are the short-range force constants between the metal-fluorine and fluorine-fluorine ions, respectively. n_1 and n_2 are the exponents for an assumed inverse r^n potential.

	CaF_2	SrF_2	BaF_2
r_0 (Å) at 0°K	2.722[a]	2.890[b]	3.088[c]
e^2/v (10^4 dyn cm^{-1})	0.572[a]	0.478[b]	0.391[c]
A_1	33.1	34.2	37.9
B_1	-3.75	-3.81	-3.97
n_1	7.83	7.97	8.55
A_2	1.30	0.61	-0.66
B_2	-0.13	-0.06	0.10
n_2	(9)	(9)	(6)
U_{calc} (kcal mol^{-1})	621	585	555
U_{expt}	617[a]	584[d]	549[d]

[a] Reference 17.
[b] Reference 18.
[c] Estimated from room-temperature data in Ref. 18.
[d] Reference 31.

TABLE II. Some quantities relating to the effective charges and elastic properties of the alkaline-earth fluorides. The values of ω, ϵ, α, Y, k, and $R^{(0)}$ are input data for calculating the effective charge Z', the compressibility β, and the Cauchy deviation $\Delta = C_{12} - C_{44}$ for both the rigid-ion (RI) and dipole shell model (DSM).

	CaF_2	SrF_2	BaF_2
ω_{TO} (cm^{-1})[a]	257	217	184
ω_R (cm^{-1})[b]	321	285	244
ϵ_s[a]	6.76	6.6	7.2
ϵ_e[a]	2.04	2.07	2.16
$\alpha(F^-)$ (Å^3)[c]	1.04	1.04	1.04
$\alpha(M^{2+})$ (Å^3)[c]	0.47	0.86	1.55
$Y(F^-)$	-2.35	-2.35	-2.35
$Y(M^{2+})$[d]	-8.7	-9.9	-11.3
$k(F^-)$ (10^4 dyn cm^{-1})	123	123	123
$k(M^{2+})$ (10^4 dyn cm^{-1})	3780	2680	1890
$R_{12}^{(0)}$ (10^4 dyn cm^{-1})	-9.76	-8.48	-7.82
Z_2' (calc)	(-0.833)	-0.869	-0.896
Z_2' (obs)	-0.833	-0.875	-0.896
$\beta_{(\text{obs})}$ (10^{-12} cm^2 dyn^{-1})	1.05[e]	1.325[f]	1.600[f]
$\beta_{(\text{RI})}/\beta_{(\text{obs})}$	1.100	1.076	1.178
$\beta_{(\text{DSM})}/\beta_{(\text{obs})}$	1.012	1.003	1.106
Δ_{RI} (10^{11} dyn cm^2)	0.54	0.60	1.02
Δ_{DSM}	2.50	1.88	1.81
Δ_{OBS}	2.0[e]	1.44[f]	1.94[f]

[a] Reference 19.
[b] Reference 20.
[c] Reference 33.
[d] Reference 9.
[e] Reference 17.
[f] Reference 18.

$\phi_2 = Cr^{-n_2}$ and fixing the value of n_2 is appropriate, since as will be verified, the fluorine-fluorine interaction is much smaller than the metal-fluorine repulsion. For CaF_2 and SrF_2, ϕ_2 is repulsive and $n_2 = 9$ is used as suggested by Pauling's systematics.[5] Because of the increased distance ϕ_2 is attractive in BaF_2 which suggests the use of a van der Waals-type $n_2 = 6$ potential for this case. By using the full formal charges (i.e., $+2$ and -1 for the metal and fluoride ions, respectively) and the measured values for C_{11} and C_{12} the force constants given in Table I are obtained.[31] Also given are the values of n_1 necessary for an inverse r^n dependence for ϕ_1. Using this form of the short-range potentials, it is possible by use of Eq. (8) to calculate the cohesive energies. The comparison with experimental cohesive energies is quite good. Since Madelung energy is ~90% of the total, the conclusions to be drawn are (1) the ions retain essentially their full formal charge, (2) at least insofar as can be determined from the cohesive energies, the approximations made in deriving the **R** matrix from the elastic constants are adequate.

The use of Eq. (17) in conjunction with other data collected in Table II permits the evaluation of the observed effective charges Z'(obs) (by definition $Z_1' = -2Z_2'$). [It should be emphasized that in contrast to the Z parameter introduced by Cribier[25] (see also footnote 32), the effective charges Z' have much more precise physical significance which has been discussed in some detail by Szigeti.[6]] In order to reduce the number of adjustable parameters which occur in Eq. (A6) for Z'(calc), use is made of the following approximate relation between the shell charges and the shell-core coupling constants[29]:

$$\alpha(\kappa) = [Y(\kappa)e]^2 / k(\kappa),$$

where the electronic polarizabilities $\alpha(\kappa)$ of the ions may be obtained from independent sources.[33] Further it is assumed that the shell charges for the positive ions are the same as those deduced by Dick and Overhauser[9] for the isoelectronic rare gases. In this manner only one adjustable parameter, the fluoride shell charge, is retained for the three lattices, and it was fixed by equating the calculated and observed effective charges for CaF_2. (The value $Y_2 = -2.35$ is reasonable and rather closer to the values suggested by Havinga[34] than to those of Dick and Overhauser.) The agreement between the observed effective charges and the ones calculated in this manner for SrF_2 and BaF_2 is quite good.

The next step is then to investigate whether the model which gives good agreement with the observed effective charge improves the situation with respect to effective force constants as well. Perhaps the best single measure of this is obtained through the use of Eq. (19). If overlap polarization were not important in the high-frequency modes, the rigid-ion limit of Eq. (19) ($\gamma_0 = \gamma_R = 0$) should give the compressibility and, in fact, the 10 to 20% discrepancy (see Table II) is about what is observed in the application of the analogous second Szigeti relation in the alkali halides.[6]

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[31] H. J. Harries and D. F. C. Morris, Acta Cryst. **12**, 657 (1959).

[32] A few comments are in order concerning the comparison of the present work with that which has previously appeared. Aside from the inaccuracies which occur in Srinivasan's (Ref. 24) Coulomb sums, his expression (21) for $[xy\ xy]$ ($[xx,yy]$ in our notation) should contain the term $4A_2/r_0$ rather than $2A_2/r_0$. Cribier's (Ref. 25) expressions for the elastic constants aside from the error noted by Ganesan and Srinivasan (Ref. 26) differ from those given above only by a few percent in the numerical values of the Coulomb terms, upon the restriction $Z^2 = \alpha_M/6$ (which follows by imposing the Cauchy condition for central forces). The major inconsistency of Cribier's treatment which is also adopted by Ganesan and Srinivasan, is to ignore this restraint and to treat Z as an adjustable parameter.

[33] L. Pauling, Proc. Roy. Soc. (London) **A114**, 181 (1927).

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Note however that for CaF_2 and SrF_2 this discrepancy is nearly removed when the shell-model corrections are introduced and is reduced by a factor of 2 for BaF_2.[35]

One further important comparison may be made with the data at hand, namely the deviation from the Cauchy relation $C_{12}=C_{44}$. There are, broadly speaking, two possible contributing causes to its failure: (a) the assumed form of the short-range potential is inappropriate, and (b) the "internal strain" contribution. In the first category belong both noncentral two-body interactions and the more "drastic" many-body quantum-mechanical interactions. The (in most cases rather small) deviations which occur in the alkali halides are ascribed to these causes.[5] Internal-strain contributions occur only in lattices in which all particles do not occupy equilibrium positions with inversion symmetry. In the present case certain shear stresses produce a component of "strain" which does not change the macroscopic dimension of the material, but instead involves the translation of the fluoride lattices relative to the metal ion lattice. This so-called internal strain affects only the elastic constant C_{44}, causing a deviation even within the central-force approximation. It is this contribution which is given by Eq. (A11). However, as other workers have observed, it does not seem possible to account for more than about one-third of the observed deviation on the basis of the internal-strain contribution of a rigid-ion model with central forces.[36,37] The situation changes in the shell-model approximation, however. Inspection of Eq. (A11) for $C_{12}-C_{44}$ reveals that the first term in the bracket represents essentially the rigid-ion contribution, whereas the second term represents the shell-model correction and might be supposed to be smaller by a factor of $\sim k_2 v/A_1 e^2 \sim 10$ than the leading term. This reasoning is in fact incorrect because of a near cancellation between the repulsive and Coulombic portions of the numerator of the rigid-ion term. The result is a substantial shell-polarization correction which brings the calculated deviation up to the required magnitude, as can be seen in Table II. It therefore appears likely that the deviations from the Cauchy relation due to noncentral forces may be no larger than for the alkali halides, and that the major effect is one involving the electronic polarization accompanying the relative motion of the constituent sublattices.

IV. SUMMARY

A calculation of the long-wavelength ($\mathbf{q}=0$) optical-mode frequencies, dielectric properties, and elastic constants of the fluorite lattice is performed within the framework of a simple dipole shell model. The concept of effective charge appears naturally and equations analogous to the two Szigeti relations for lattices with diatomic unit cells are developed. These relations are then tested for the alkaline-earth fluorides, with the result that certain key troublesome features which have occurred in previous treatments in the rigid-ion approximation (e.g., the anomalously low "charge" parameter of Cribier[25] and Ganesan and Srinivasan,[26] the large deviation from the Cauchy relation $C_{12}=C_{44}$) tend to resolve themselves in a satisfactory manner. Finally it should be stated that the underlying philosophy has been to show that a minimal number of reasonable shell-model parameters produce significant improvements in the agreement with observations. Any further adjustments of the parameters will surely be more meaningful at such a time when more detailed information of the type provided by inelastic neutron scattering becomes available.

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APPENDIX: I. THE SHORT-RANGE INTERACTION

The elements of the $\mathbf{R}$ matrix are defined in terms of the short-range potential $\Phi^{(R)}$,

$$R_{xy}(\kappa\kappa')=-\sum_{l'}[\partial^2\Phi^{(R)}(l\kappa,l'\kappa')/\partial x\partial y] \times\exp i\{\mathbf{q}\cdot[\mathbf{r}(l'\kappa')-\mathbf{r}(l\kappa)]\}. \quad \text{(A1)}$$

In the notation introduced in Eq. (9)

$$\mathbf{R}_{xx}=\begin{bmatrix} \frac{4}{3}(A_1+2B_1) & -\frac{2}{3}(A_1+2B_1)[C_xC_yC_z-iS_xS_yS_z] & -\frac{2}{3}(A_1+2B_1)[C_xC_yC_z+iS_xS_yS_z] \\ -\frac{2}{3}(A_1+2B_1)[C_xC_yC_z+iS_xS_yS_z] & \frac{2}{3}(A_1+2B_1)+(A_2+2B_2) & -A_2C_{2x}-B_2[C_{2y}+C_{2z}] \\ -\frac{2}{3}(A_1+2B_1)[C_xC_yC_z-iS_xS_yS_z] & -A_2C_{2x}-B_2[C_{2y}+C_{2z}] & \frac{2}{3}(A_1+2B_1)+(A_2+2B_2) \end{bmatrix}(e^2/v) \quad \text{(A2)}$$

and

$$\mathbf{R}_{xy}=\begin{bmatrix} 0 & -\frac{2}{3}(A_1-B_1)[-S_xS_yC_z+iC_xC_yS_z] & -\frac{2}{3}(A_1-B_1)[-S_xS_yC_z-iC_xC_yS_z] \\ -\frac{2}{3}(A_1-B_1)[-S_xS_yC_z-iC_xC_yS_z] & 0 & 0 \\ -\frac{2}{3}(A_1-B_1)[-S_xS_yC_z+iC_xC_yS_z] & 0 & 0 \end{bmatrix}(e^2/v). \quad \text{(A3)}$$

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[35] Some of the discrepancy here and elsewhere may result from the use of low-temperature elastic constants together with room-temperature dielectric constants and mode frequencies.

[36] J. R. Reitz, R. N. Seitz, and R. W. Genberg, J. Phys. Chem. Solids **19**, 73 (1961).

[37] A. K. Rajogopal, J. Phys. Chem. Solids **23**, 317 (1962).

Here $C_x = \cos\pi r_0 q_x$, $C_{2x} = \cos 2\pi r_0 q_x$, and S_x, etc., are the analogous sines. The remaining portions of the matrix are determined by obvious symmetry relations.

Since it is generally true (and as will be verified in the present instance) the dominant terms in the $\mathcal{S}^{(0)}$ matrix are the diagonal terms $k(\kappa)$ coupling the cores and shells, here and in most of what follows the approximation

$$(\mathcal{S}^{(0)})_{xy}{}^{-1} = k(\kappa)^{-1}\delta(\kappa,\kappa')\delta(x,y) \qquad \text{(A4)}$$

is used since it results in considerable algebraic simplification with little loss of rigor. The $\mathbf{R}'$ matrix [Eq. (6)] is then easily evaluated. Two of the resulting relations which will be referred to again are

$$\begin{aligned} R_{12}'/R_{12}^{(0)} &= [1+2R_{12}^{(0)}\{(1/k_1)+(1/2k_2)\}] = (1-\gamma_0)\,, \\ (R_{22}'-R_{23}')/(R_{22}^{(0)}-R_{23}^{(0)}) &= [1-(R_{22}^{(0)}-R_{23}^{(0)})/k_2] \\ &= (1-\gamma^R)\,. \qquad \text{(A5)} \end{aligned}$$

Similarly, evaluation of Eq. (7) gives for the effective charges

$$\begin{aligned} Z_2'-Z_2 &= R_{12}^{(0)}[-(Y_1/k_1)+(Y_2/k_2)] \\ Z_1' &= -2Z_2'\,. \qquad \text{(A6)} \end{aligned}$$

APPENDIX II: THE ELASTIC CONSTANTS

The following expressions[13] are needed in connection with the evaluation of the elastic constants:

$$\begin{aligned} [\alpha\beta,\gamma\lambda] &= (1/8\pi^2 v)\sum_{\kappa,\kappa'}(\mathbf{R}_{\gamma\lambda}{}^{(2)}+\mathbf{Z}\mathcal{C}_{\gamma\lambda}{}^{(2)}\mathbf{Z})_{\alpha\beta} \\ (\alpha\gamma,\beta\lambda) &= -(1/4\pi^2 v)\sum_{\kappa,\kappa'}(\tilde{\mathbf{F}}_\gamma{}^{(1)}[\mathbf{M}^{(0)}]^{-1}\mathbf{F}_\lambda{}^{(1)} \\ &\qquad +\tilde{\mathbf{C}}_\gamma{}^{(1)}[\mathcal{S}^{(0)}]^{-1}\mathbf{C}_\lambda{}^{(1)})_{\alpha\beta}\,. \qquad \text{(A7)} \end{aligned}$$

The notation refers to a power-series expansion, $\mathbf{A}=\mathbf{A}^{(0)}+i\sum_\lambda \mathbf{A}_\lambda{}^{(1)}q_\lambda+\frac{1}{2}\sum_{\lambda,\gamma}\mathbf{A}_{\gamma\lambda}{}^{(2)}q_\gamma q_\lambda+\cdots$. The previously undefined quantities

$$\begin{aligned} \mathbf{F}_\lambda{}^{(1)} &= \mathbf{R}_\lambda{}^{(1)}+\mathbf{Z}\mathcal{C}_\lambda{}^{(1)}\mathbf{Z}-\mathbf{T}^{(0)}(\mathcal{S}^{(0)})^{-1}\mathbf{C}_\lambda{}^{(1)} \\ \mathbf{C}_\lambda{}^{(1)} &= \mathbf{T}_\lambda{}^{(1)}+\mathbf{Y}\mathcal{C}_\lambda{}^{(1)}\mathbf{Z} \qquad \text{(A8)} \\ \mathbf{M}^{(0)} &= \mathbf{R}^{(0)}-\mathbf{T}^{(0)}(\mathcal{S}^{(0)})^{-1}\tilde{\mathbf{T}}^{(0)} \end{aligned}$$

are derivable from the $\mathbf{R}$ matrix and the assumption that all forces act through the shells, with the exception of the Coulomb coefficients $\mathbf{C}_\lambda{}^{(1)}$ and $\mathcal{C}_{\gamma\lambda}{}^{(2)}$. These were evaluated by Srinivasan[24] using Ewald's method. The more precise values given here were derived from Cowley's[13] values for the CsCl and ZnS structures. The relation is similar to that which exists for the Madelung constants $\alpha_M(\mathrm{CaF_2})=\alpha_M(\mathrm{CsCl})+2\alpha_M(\mathrm{ZnS})$.

Of the three independent cubic elastic coefficients two depend only upon rigid-ion interactions and not on the polarizabilities.

$$\begin{aligned} C_{11} &= [xx,xx] = [\tfrac{1}{3}(A_1+2B_1)+A_2 \\ &\qquad -3.05120Z_1Z_2](e^2/2vr_0)\,, \\ C_{12} &= 2[xy,xy]-[xx,yy] = [\tfrac{1}{3}(A_1-B_1) \\ &\qquad +3.46510Z_1Z_2](e^2/2vr_0)\,. \qquad \text{(A9)} \end{aligned}$$

The remaining constant is given by

$$\begin{aligned} C_{44} &= [xx,yy]+(xy,xy) \\ [xx,yy] &= [\tfrac{1}{3}(A_1+2B_1)+B_2 \\ &\qquad +1.52560Z_1Z_2](e^2/2vr_0)\,, \qquad \text{(A10)} \end{aligned}$$

where the last relation follows, as it must for central forces, from the use of Eq. (10). Thus C_{12} and C_{44}, which should obey the Cauchy relation $C_{12}=C_{44}$ for a crystal with inversion symmetry and central forces, differ in this model by an amount

$$\begin{aligned} C_{12}-C_{44} &= -(\alpha\beta,\alpha\beta) \\ &= \left\{\frac{[(A_1-B_1)(1-\gamma_R)+15.087Z_1(Z_2-\gamma_R Y_2)]^2}{[(A_1+2B_1)+3(A_2+2B_2)](1-\gamma_R)}\right. \\ &\qquad \left. +\frac{2}{3}\,\frac{[(A_1-B_1)+15.087Z_1Y_2]^2}{k_2(v/e^2)}\right\}\left(\frac{e^2}{6vr_0}\right). \qquad \text{(A11)} \end{aligned}$$

Note that the formal correspondence of the dipole shell model with the rigid-ion model can be made by letting the shell-core coupling constants $k(\kappa)\to\infty$. Thus all the expressions given here apply for the rigid-ion model in this limit.[32]