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Elastic constants of the perovskite $RbMnF_3$ using a Born model*

E. R. Naimon†

Cryogenics Division, National Bureau of Standards-Institute for Basic Standards, Boulder, Colorado 80302

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The elastic constants of $RbMnF_3$ were calculated using a Born model, which consists of electrostatic and Born-Mayer repulsive interactions. This model has two adjustable parameters; these were determined from the equilibrium volume and one of the three second-order elastic constants. Calculated third-order elastic constants agreed reasonably well with experiment. Also calculated were the electrostatic contributions to the first-, second-, and third-order elastic constants of the cubic perovskite structure for several values of ionic charge. Relationships of these constants to those of the NaCl- and CsCl-type structures are given.

I. INTRODUCTION

Crystals having perovskite structures have been studied extensively because of their phase transitions—electric, magnetic, and structural. Such transitions are often characterized elastically because (i) elastic constants, which are readily measurable, usually behave anomalously at or near phase transitions, and (ii) interatomic forces and potentials can be deduced from elastic constants.

Electrostatic forces affect both the energy of a crystal and, often, its elastic constants. Differentiation of the electrostatic (Madelung) energy with respect to appropriate strains yields the electrostatic contributions to the elastic constants, but such results have been given previously only for crystal structures simpler than perovskites. For perovskites, electrostatic interactions have been considered previously only for determining the electrostatic energy.[1-3]

Short-range forces, such as ion-ion repulsive interactions, may contribute little to the energy but dominantly to higher-order elastic constants, that is, to higher spatial derivatives of the energy. Conversely, because of their long-range nature, electrostatic forces contribute progressively less to higher derivatives of the energy.

In this paper the elastic properties of $RbMnF_3$ are described by a Born model, which contains electrostatic and ion-ion repulsive interactions. $RbMnF_3$ is a cubic perovskite whose second- and third-order elastic constants were measured previously.[4,5] Also reported here are the electrostatic contributions to Brugger-type elastic constants of cubic perovskites; a general method developed recently by Fuller and Naimon[6] was used. Results for first-, second-, and third-order electrostatic constants are given for several values of ionic charge.

II. ELECTROSTATIC CONTRIBUTIONS

The cubic perovskite-type crystal structure has a $Pm3m = O_h^1$ space group and five atoms per unit cell. The structural unit ABX_3 can be visualized as a simple cube with A ions at the corners, a B ion at the body center, and X ions at the face centers. Unlike the case of simpler ionic crystal structures, such as NaCl and CsCl, Madelung constants of perovskites vary with ionic charges. To distinguish structures with different ionic charges, the notation of Templeton[1] is used here. When the ionic charges are +1, +2, and −1 for A, B, and X, respectively, the structure is denoted as 1-2 type; when the ionic charges are +2, +1, and −1, respectively, the designation is 2-1 type. Similarly, the types 1-5, 5-1, and 3-3 can be defined when X has charge −2. The Madelung constants of these perovskite types were determined by Templeton,[1] but his procedure cannot be extended to differentiation of the electrostatic energy with respect to strains to obtain elastic constants.

The method used here is an extension of a procedure developed recently by Fuller and Naimon.[6] In this approach both the Madelung energy and the electrostatic contributions to the Brugger-type[7] elastic constants through third order can be calculated. This procedure is briefly as follows. The Ewald-Fuchs[8,9] method is used to determine the electrostatic energy, per unit initial volume, of a homogeneously deformed lattice of ions. The resulting energy expression contains the atomic volume, the ionic charges, and summations over both the real and reciprocal lattices. The method of homogeneous deformation is then used to obtain derivatives of the electrostatic energy with respect to Lagrangian strains, the results being the electrostatic contributions to the Brugger-type elastic constants. The method is general and is valid for both ionic and metallic structures. Effects on the elastic constants due to internal strains, which occur in nonprimitive lattices when ions are not at centers of symmetry, were also treated by Fuller and Naimon. It is emphasized that the ions of a cubic perovskite are at centers of symmetry. Thus, internal strains and their contributions to elastic constants are irrelevant to the present work.

TABLE I. Madelung energy and electrostatic Brugger-type elastic constants for various types of perovskites. Entries are in units of e^2/a^4, where e is the electronic charge and a is the lattice parameter.

Type:	1-2	2-1	3-3	1-5	5-1
U	−12.377 468	−10.917 700	−44.554 975	−58.535 492	−46.857 351
c_1	4.125 823	3.639 233	14.851 658	19.511 831	15.619 117
c_{11}	−16.495 904	−8.093 657	−51.304 251	−76.412 721	−9.194 747
c_{12}	2.059 218	−1.412 022	3.374 638	8.938 614	−18.831 302
c_{111}	84.989 721	27.705 378	241.617 144	405.846 737	−52.428 008
c_{112}	−1.255 101	6.381 454	7.452 056	−11.891 567	49.200 872
c_{123}	−7.785 887	−5.702 800	−31.777 303	−20.909 936	−4.245 235

Present results for the Madelung energy U and the electrostatic contributions to the first-, second-, and third-order elastic constants are given in Table I. Since electrostatic forces are central forces, the Cauchy relations $c_{12} = c_{44}$, $c_{112} = c_{155}$, and $c_{123} = c_{144} = c_{456}$ hold. The Madelung energies agree to six significant figures with those determined by Templeton.[1] Also, the following calculational checks[6] were obtained among the electrostatic elastic constants:

$$c_1 = -\tfrac{1}{3}U, \tag{1}$$

$$c_{11} + 2c_{12} = U, \tag{2}$$

and

$$c_{111} + 6c_{112} + 2c_{123} = -5U. \tag{3}$$

Relationships among the electrostatic elastic constants of the different perovskite types and those of the NaCl- and CsCl-type structures can be easily developed. Templeton[1] showed that the following identities hold among the Madelung constants α,

$$\alpha(2\text{-}1) = \alpha(1\text{-}2) + \alpha(\text{CsCl}) - \alpha(\text{NaCl}), \tag{4}$$

$$\alpha(3\text{-}3) = 4\alpha(1\text{-}2) + \alpha(\text{CsCl}) - 2\alpha(\text{NaCl}), \tag{5}$$

$$\alpha(1\text{-}5) = 4\alpha(1\text{-}2) + \alpha(\text{CsCl}) + 2\alpha(\text{NaCl}), \tag{6}$$

and

$$\alpha(5\text{-}1) = 4\alpha(1\text{-}2) + 9\alpha(\text{CsCl}) - 6\alpha(\text{NaCl}). \tag{7}$$

In these equations every Madelung constant must have the same scaling factor, taken here to be the unit-cell dimension a. The electrostatic energy per molecule is then $\alpha e^2/a$, and the electrostatic energy per unit volume is

$$U = \alpha e^2/aV_m, \tag{8}$$

where V_m is the molecular volume and e the electronic charge. For cubic perovskites and CsCl-type structures, $V_m = a^3$; for NaCl-type structures, $V_m = \frac{1}{4}a^3$. Thus, when the electrostatic energy density U is in units of e^2/a^4, it follows that

$$U(2\text{-}1) = U(1\text{-}2) + U(\text{CsCl}) - \tfrac{1}{4}U(\text{NaCl}), \tag{9}$$

$$U(3\text{-}3) = 4U(1\text{-}2) + U(\text{CsCl}) - \tfrac{1}{2}U(\text{NaCl}), \tag{10}$$

$$U(1\text{-}5) = 4U(1\text{-}2) + U(\text{CsCl}) + \tfrac{1}{2}U(\text{NaCl}), \tag{11}$$

and

$$U(5\text{-}1) = 4U(1\text{-}2) + 9U(\text{CsCl}) - \tfrac{3}{2}U(\text{NaCl}). \tag{12}$$

Equations (9)–(12) are also valid when the structures involved are subjected to the same homogeneous deformation; both sides of Eqs. (9)–(12) have the same strain dependence. Thus, Eqs. (9)–(12) are true not only for the energy density U, but also for electrostatic elastic constants of all orders. Numerical checks, using the cubic perovskite data of Table I and the NaCl and CsCl tabulations of Fuller and Naimon,[6] verified these relationships for both the energy density and the elastic constants (first, second, and third order).

III. BORN MODEL FOR $RbMnF_3$

In this section the electrostatic interactions will be combined with ion-ion repulsive interactions to determine the elastic constants of $RbMnF_3$, a perovskite for which both second-order[4] and third-order constants[5] have been measured. This type of Born model has proven useful in describing the alkali halides,[10] for example. Because only the static lattice is considered here, the appropriate experimental elastic constants for comparison with theory are obtained by linearly extrapolating the high-temperature constants to 0 K. Thus, for $RbMnF_3$ the "athermal" values of the lattice parameter and of the second-order elastic constants, both determined by Melcher and Bolef,[4] will be used. Third-order elastic constants of $RbMnF_3$ are known only at room temperature[5]; not knowing their temperature dependence prevents determination of "athermal" values. For alkali halides, calculations predict a typical change of 10–20% for third-order constants between room temperature and 0 K.[10]

In $RbMnF_3$ the "athermal" lattice parameter a is 4.209 Å.[4] The closest sets of ions are the Mn-F pairs separated by $\frac{1}{2}a = 2.1045$ Å; the next closest sets are the Rb-F and F-F pairs with spacings of $\frac{1}{2}\sqrt{2}a = 2.976$ Å. The Goldschmidt-ionic radii of

Rb^+, F^-, and Mn^{++} are 1.49, 1.33, and 0.91 Å, respectively.[11] By adding appropriate radii, it is seen that the dominant ionic overlap occurs between Mn and F ions. The Rb-F and F-F overlaps have approximately the same size, but both are considerably smaller than the Mn-F overlap. The ion-ion overlap results in a repulsive potential, assumed here to have the well-known Born-Mayer[12] form

$$\varphi(r) = A e^{-r/b}, \tag{13}$$

where r is the interionic distance, and A and b are adjustable parameters. Because this potential is short range, only nearest-neighbor interactions were considered for the various ion pairs.

Attention is focused first on the Rb-F and F-F interactions. Following Ghate,[10] to minimize the number of parameters, no distinction is made between these interactions. The Rb and F ions then comprise an fcc lattice. The nearest-neighbor distance is $r_0 = \frac{1}{2}a\sqrt{2}$, and the ionic volume is $V_i = \frac{1}{4}a^3$. For this lattice the ion-ion repulsive interactions contribute to the energy and elastic constants as follows[13]:

$$U = (6/V_i)[\varphi(r)]_{r=r_0}, \tag{14}$$

$$c_1 = (2r_0^2/V_i)[D\varphi(r)]_{r=r_0}, \tag{15}$$

$$c_{11} = 2c_{12} = (r_0^4/V_i)[D^2\varphi(r)]_{r=r_0}, \tag{16}$$

$$c_{111} = 2c_{112} = (r_0^6/2V_i)[D^3\varphi(r)]_{r=r_0}, \tag{17}$$

and

$$c_{123} = 0, \tag{18}$$

where $D = (1/r)d/dr$. Because of the central-force nature of the assumed potential $\varphi(r)$, the Cauchy relations hold. Using Ghate's RbF values of $b = 0.333$ Å and $A = 0.1138 \times 10^{-15}$ J [Ghate, Eq. (20)], Eqs. (14)–(17) were evaluated for $RbMnF_3$. These results are listed in the second column of Table II. The first column of Table II lists the electrostatic contributions to the energy and elastic constants of $RbMnF_3$, obtained from Table I with $e^2/a^4 = 0.073\,503 \times 10^{11}$ N/m^2.

The most important ion-ion repulsions, due to Mn-F interactions, can be treated analogously. For these pairs the nearest-neighbor arrangement is the same as for NaCl. Elastic constant contributions from $\varphi(r)$ are thus nonzero only for c_1, c_{11}, and c_{111}.[10,14] It can be easily shown that

$$U = (3/V_i)[\varphi(r)]_{r=r_0}, \tag{19}$$

$$c_1 = (r_0^2/V_i)[D\varphi(r)]_{r=r_0}, \tag{20}$$

$$c_{11} = (r_0^4/V_i)[D^2\varphi(r)]_{r=r_0}, \tag{21}$$

and

$$c_{111} = (r_0^6/V_i)[D^3\varphi(r)]_{r=r_0}, \tag{22}$$

where $V_i = \frac{1}{8}a^3$ and $r_0 = \frac{1}{2}a$. Here the parameters A and b of the potential $\varphi(r)$ are adjusted to the experimental value of c_{11} and to the equilibrium condition that the total calculated value of c_1 be zero. The Mn-F repulsive-potential parameters are then $A = 0.4469 \times 10^{-15}$ J and $b = 0.2033$ Å, with $r_0/b = 10.350$. The contributions to the energy and the elastic constants of $RbMnF_3$ from the Mn-F repulsive interactions are given in the third column of Table II. The total calculated constants and their experimental values are given in the fourth and fifth columns.

TABLE II. Contributions to the energy and elastic constants of $RbMnF_3$. Entries are in units of 10^{11} N/m^2.

	Electrostatic	Rb-F, F-F	Mn-F	Total	Expt.
U	-0.910	0.049	0.046	-0.815	...
c_1	0.303	-0.144	-0.159	0	0
c_{11}	-1.213	0.717	1.802	1.307	1.307[a]
c_{12}	0.151	0.359	0	0.510	0.423
c_{44}	0.151	0.359	0	0.510	0.328
c_{111}	6.247	-3.955	-22.418	-20.13	-18.4 ± 0.4[b]
c_{112}	-0.092	-1.977	0	-2.07	-2.4 ± 0.2
c_{155}	-0.092	-1.977	0	-2.07	-1.8 ± 0.1
c_{123}	-0.572	0	0	-0.57	$+0.4 \pm 0.5$
c_{144}	-0.572	0	0	-0.57	-0.6 ± 0.3
c_{456}	-0.572	0	0	-0.57	-0.5 ± 0.1

[a] Reference 4.

[b] Reference 5.

IV. DISCUSSION

The model used here to describe the elastic constants of $RbMnF_3$ neglects both van der Waals forces and many-body forces. Also, thermal-vibration contributions were omitted in comparing the calculated third-order elastic constants with room-temperature data. Despite these omissions, satisfactory agreement between theory and experiment was found.

As in the alkali halides, the ion-ion repulsion contributes progressively more as higher-order elastic constants are considered. In fact, the third-order constants c_{112} and c_{155} are determined almost entirely by Rb-F and F-F repulsive interactions, while c_{111} is dominated by the Mn-F repulsive interaction. Of special interest is the observation that nearest-neighbor repulsive forces contribute nothing to c_{123}, c_{144}, and c_{456}. Thus, electrostatic contributions to these constants should, and do, compare favorably with experiment.

As mentioned above, Ghate's[10] values for the Born-Mayer parameters were used to describe Rb-F and F-F repulsive interactions. However, choosing a smaller preexponential factor A would improve the agreement of c_{12} and c_{44} with experiment and would not substantially alter agreement of the other constants. This approach would require readjustment of the Mn-F parameters. The observed failure of the Cauchy condition $c_{12}=c_{44}$ cannot be explained by the present model, since it contains only central interatomic forces. A possible explanation is provided by many-body-type forces.[15]

Concerning third-order elastic constants of $RbMnF_3$, the pattern is clear. To a first approximation $c_{111}\neq 0$, and all other $c_{ijk}=0$; as shown in Table II this can be understood by considering the Mn-F repulsive interactions. The constants c_{112} and c_{155} are described by Rb-F and F-F repulsive interactions, and, finally, the constants c_{123}, c_{144}, and c_{456} are determined solely by electrostatic interactions. One expects this pattern to hold also for other cubic perovskite materials. Third-order elastic constants are known for $SrTiO_3$.[16,17] If a scaling factor is chosen such that c_{11} is the same for both $RbMnF_3$ and $SrTiO_3$, then all other elastic constants with the exception of c_{44} and c_{144} are the same within experimental errors. This suggests that the dominant forces should be between the Ti and O ions. Indeed, Cowley[18] indicated that the largest force constants for $SrTiO_3$ are those for the Ti-O interaction. While a calculation for $SrTiO_3$ was not attempted here, it was observed that the electrostatic value of $c_{123}=c_{456}$ agreed with the experimental value of c_{123} within its errors and was only slightly more negative than the experimental value of c_{456}.

Comparison of calculated and experimental elastic constants provides a test of an interatomic potential; the elastic constants describe changes of the energy density with respect to both volume deformations and various shear deformations. That the present model predicts satisfactorily the elastic properties of $RbMnF_3$ gives plausibility to the deduced interatomic potential. This potential provides a possible basis for other calculations, such as thermal vibrations, defect properties, and relative phase stabilities. Addition of vibrational effects might allow the model to describe structural phase transitions, such as those occurring in $SrTiO_3$.

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[†] National Research Council-National Bureau of Standards Postdoctoral Research Associate, 1972–1973.

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