a narrow range of βR values and its total three-ion energy is quenched relative to both $B1$ and $B3$.

So far, we have not considered the effect of d electrons in closed shells on crystal stability of RX compounds; R stands for Cu, Ag; Zn, Cd, Hg; Ga, In. In these cases the structures $B1$, $B2$, $B3$, and $B4$ are also observed, often associated with polymorphic transitions.[19] It may also be expected that the crystal stability for compounds of the type RX_2 (fluorite, rutile, $CdCl_2$, CdI_2, etc.) can be explained in terms of three-ion interactions. Such an analysis is at present under way.

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Temperature Dependence of Dielectric Constants of Crystals with NaCl and CsCl Structure

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The dielectric constant and its temperature and pressure dependence have been measured on RbCl, RbBr and CsCl, CsBr, CsI. The values for ϵ, $10^5(\partial\epsilon/\partial T)_p/(\epsilon-1)(\epsilon+2)$ $(°\mathrm{K})^{-1}$ and $10^7(\partial\epsilon/\partial p)_T/(\epsilon-1)(\epsilon+2)$ $(\mathrm{kg/cm^2})^{-1}$ are 5.0, 5.5, −19.4; 4.9, 5.2, −23.5; 7.2, 2.5, −16.3; 6.5, 2.8, −19.1; and 5.7, 3.2, −23.2, respectively. The temperature dependence for compounds with the CsCl structure thus is smaller than for compounds with the NaCl structure. The existence of a structural effect has been verified by measuring RbBr at 4600 $\mathrm{kg/cm^2}$ in both structures. The corresponding quantities as given above are in the NaCl structure 4.65, 4.9, −21 and in the CsCl structure 6.5, 2.1, −17. Analysis of the results shows that the difference is due to a difference in the temperature dependence of the infrared polarizability at constant volume. The theory shows that, whereas there is no difference in the negative contribution from fourth-order anharmonic terms in the potential energy to this temperature dependence of the polarizability in both structures, the positive influence of third-order terms increases as the number of nearest neighbors decreases. By using a simple ionic model a semiquantitative agreement between theory and experiment was obtained.

I. INTRODUCTION

In a previous paper[1] it has been shown that three effects contribute to the temperature dependence of the dielectric constant of a cubic material. For such a material the macroscopic Clausius-Mossotti formula holds:

$$(\epsilon-1)/(\epsilon+2)=\tfrac{4}{3}\pi\alpha_m/V\,, \tag{1}$$

where α_m is the polarizability of a macroscopic, small sphere with a volume V in vacuum.

Differentiation of formula (1) with respect to temperature at constant pressure gives

$$\frac{1}{(\epsilon-1)(\epsilon+2)}\left(\frac{\partial\epsilon}{\partial T}\right)_p=-\frac{1}{3V}\left(\frac{\partial V}{\partial T}\right)_p+\frac{V}{\alpha_m}\left(\frac{\partial\alpha_m}{\partial V}\right)_T\left(\frac{1}{3V}\right)\left(\frac{\partial V}{\partial T}\right)_p+\frac{1}{3\alpha_m}\left(\frac{\partial\alpha_m}{\partial T}\right)_V=A+B+C. \tag{2}$$

The physical processes described by the terms A, B, and C are

A: the decrease in the number of polarizable particles per unit volume as the temperature rises; the direct effect of the volume expansion;

B: an increase of the polarizability of a constant number of particles with the increase of available volume as the temperature rises;

C: a dependence of polarizability on temperature, the volume remaining constant.

The terms A, B and C can be determined separately by measuring the dielectric constant ϵ, its temperature dependence $(\partial\epsilon/\partial T)_p$ and its pressure dependence $(\partial\epsilon/\partial p)_T$, the thermal expansion coefficient $(1/V)(\partial V/\partial T)_p$ and the compressibility $\kappa=-(1/V)(\partial V/\partial p)_T$. The statement of Fuchs[2] that this separation into three terms involves microscopic theories is incorrect, as was already outlined in a previous paper.[3]

In the case of ionic crystals the polarizability α_m of the macroscopic sphere can be separated into $\alpha_m{}^{\mathrm{op}}$, the

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[1] E. E. Havinga, J. Phys. Chem. Solids **18**, 253 (1961).

[2] R. Fuchs, MIT Lab. Ins. Res. Technical Report No. 167, 1961 (unpublished).

[3] A. J. Bosman and E. E. Havinga, Phys. Rev. **129**, 1593 (1963).

TABLE I. The dielectric constant ϵ at 25°C, its temperature and pressure dependence and the contributions A, B, and C to the temperature dependence for a number of compounds with NaCl and with CsCl structure.

Compound	ϵ	$\frac{10^5}{(\epsilon-1)(\epsilon+2)}\left(\frac{\partial\epsilon}{\partial T}\right)_p$ $(°\mathrm{K})^{-1}$	$\frac{10^7}{(\epsilon-1)(\epsilon+2)}\left(\frac{\partial\epsilon}{\partial p}\right)_T$ $(\mathrm{kg/cm^2})^{-1}$	$A\times10^5$ $(°\mathrm{K})^{-1}$	$B\times10^5$ $(°\mathrm{K})^{-1}$	$C\times10^5$ $(°\mathrm{K})^{-1}$
KCl[a]	4.7	5.6	−18.8[c]	−3.8	7.7	1.7
KBr[a]	4.8	5.9	−18.4[c]	−4.0	7.4	2.5
RbCl	5.0	5.5	−19.4	−3.6	6.8	2.3
NaCl[a]	5.6	5.2	−14.8[c]	−4.0	8.2	1.0
LiF[b]	9.3	3.7	−4.5	−3.4	6.4	0.7
MgO[a]	9.8	1.0	−1.8	−1.0	1.9	0.1
CsCl	7.2	2.5	−16.3	−4.5	8.3	−1.3
CsBr	6.5	2.8	−19.1	−4.7	8.6	−1.1
CsI	5.7	3.2	−23.2	−4.9	9.0	−0.9
TlBr[a]	30	−1.0	−5.8[c]	−5.2	7.1	−2.9

[a] See Ref. 3.

[b] See Ref. 5(b).

[c] These values are slightly different from those given in Ref. 3 due to a more correct evaluating procedure of the experimental data.

optical polarizability due to the motion of electrons relative to the ionic nuclei and $\alpha_m{}^{\mathrm{ir}}$, the infrared polarizability, which includes not only the effect of displacements of ions but also that of displacements of electrons thereby induced. The terms B and C then can be written as

$$B=(\alpha_m{}^{\mathrm{op}}/\alpha_m)B^{\mathrm{op}}+(\alpha_m{}^{\mathrm{ir}}/\alpha_m)B^{\mathrm{ir}}, \tag{3}$$

$$C=(\alpha_m{}^{\mathrm{op}}/\alpha_m)C^{\mathrm{op}}+(\alpha_m{}^{\mathrm{ir}}/\alpha_m)C^{\mathrm{ir}}. \tag{4}$$

B^{op}, C^{op} and B^{ir}, C^{ir} are obtained by replacing α_m by $\alpha_m{}^{\mathrm{op}}$ and $\alpha_m{}^{\mathrm{ir}}$, respectively, in the definition formulas of B and C. B^{op} and C^{op} can be determined by measuring the index of refraction and its temperature and pressure dependence.

Results of an experimental determination of the values of A, B, and C for a number of cubic halides and oxides with a broad range of dielectric constants have been reported in a previous paper.[3] It was found that in general the term

$$C=\frac{1}{3\alpha_m}\left(\frac{\partial\alpha_m}{\partial T}\right)_V=\frac{1}{(\epsilon-1)(\epsilon+2)}\left(\frac{\partial\epsilon}{\partial T}\right)_V \tag{5}$$

is negative; positive C values were found only for compounds with a low dielectric constant ($\epsilon<10$). However, the latter compounds all had the NaCl structure. It was suggested that the type of structure might have an influence on the values of the C term, preliminary measurements on CsCl ($\epsilon=7.2$) having indicated that the C term was negative for this compound. In this paper results will be reported of further investigations on the influence of structure on dielectric properties.

II. EXPERIMENTS AND RESULTS

The dielectric constant and its temperature and pressure dependence have been measured on several halides. The measuring techniques have already been described in a previous paper.[3] Values of the thermal-expansion coefficients and compressibilities needed to calculate the factors A, B and C were taken from literature.[4,5] The measurements were made partly on single crystals and partly on pellets pressed from dry powder under high pressure (15 000 kg/cm²). These pellets were clear and transparent and attained a density of about 98% of the x-ray density. KBr was measured in the form of single crystals as well as pellets, and the results showed no significant difference between both types of samples.

The results obtained are presented in Table I together with the results of the previous paper.[3] The compounds are divided into two groups, those having the NaCl structure and those having the CsCl structure. It is seen that halides with the CsCl structure generally have a smaller temperature dependence of the dielectric constant than those having the NaCl structure. This difference originates in the C term, which is positive for the NaCl structure and negative for the CsCl structure. The total volume-dependent contribution $(A+B)$ is almost equal for both structures. A plot of the different C values versus the values of ϵ (Fig. 1) suggests that within one structure the value of C decreases with an increase in the value of ϵ. Probably even negative values of C will occur for those compounds with the NaCl structure that have a high value of ϵ. However, C is always significantly larger for a compound with NaCl structure than for a compound with CsCl structure, both having the same value of ϵ.

In order to investigate whether this difference in the C term really is a structural effect, further measurements were made on RbBr. This compound has at normal conditions the NaCl structure, but at hydrostatic pres-

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[4] (a) W. A. Weyl, Pennsylvania State University and Office of Naval Research Technical Reports Nos. 64, 65, and 66, 1955 (unpublished); (b) M. E. Straumanis and A. Ievens, Z. Anorg. u. Allgem. Chem. **238**, 175 (1938).

[5] (a) F. Birch *Handbook of Physical Constants* No. 86 (Geological Society of America, New York, 1942); (b) S. Mayburg, Phys. Rev. **79**, 375 (1950).

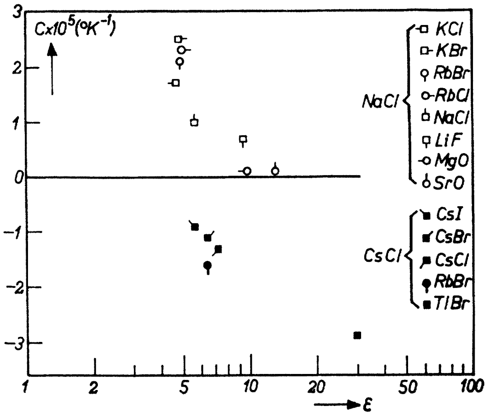

FIG. 1. The temperature dependence of the dielectric constant at constant volume, $C=\{1/(\epsilon-1)(\epsilon+2)\}(\partial\epsilon/\partial T)_V$ as a function of ϵ for a number of cubic compounds at room temperature.

sures above 4600 kg/cm^2 it transforms to the CsCl structure. This transformation has a considerable influence on the dielectric properties, as can be seen from Fig. 2, where the dielectric constant ϵ at room temperature is given as a function of the applied hydrostatic pressure.

The transformation proceeds rather slowly. Therefore the measurements of ϵ are markedly time-dependent. In Fig. 3 the dielectric constant at 5000 kg/cm^2 is plotted as a function of time. It is seen that it takes several weeks to obtain a complete transformation to the CsCl structure at this pressure, which is already 400 kg/cm^2 higher than the minimum pressure at which the transformation starts. However, at 6000 kg/cm^2 the total transformation time is reduced to some hours. The back transformation to the NaCl structure behaves in a similar way; at 3000 kg/cm^2 it is completed in less than one hour.

After back transformation the calculated dielectric constant sometimes differs a few percent from its original value at the same temperature and pressure. This is probably due to minor changes in the geometry of the capacitor that remain after back transformation. As the resistance against shears is notably low during transformation, it is very difficult to avoid shears to such an extent that absolutely no deformations will take place. This effect makes the relative change in capacitance somewhat different from one sample to another. The values of $(C_8-C_6)/C_6$, where C_6 and C_8 are the capacitances at 4600 kg/cm^2, in the NaCl structure and the CsCl structure, respectively, obtained on several samples of RbBr during transformation, are listed in Table II. The mean value is 0.33. As the relative decrease in volume at the transformation is 13.7%,[5(a)] the geometrical form factor f ($\epsilon=fC$) of the disks is 5% larger in the CsCl structure than in the NaCl structure. From $\epsilon=4.9$ for RbBr at 1 atm, and the measured pressure coefficient, the value at 4600 kg/cm^2 in the NaCl structure is calculated to be $\epsilon=4.65$. The value in the CsCl structure at the same pressure is then $4.65\times1.33\times1.05=6.5$.

TABLE II. Change in capacitance at the transformation point for different samples of RbBr.

$\frac{C_8-C_6}{C_6}$ (NaCl → CsCl) (%)	$\frac{C_8-C_6}{C_6}$ (CsCl → NaCl) (%)
31.3	34.3
39.9	35.0
33.2	32.8
29.0	31.3
30.5	31.5

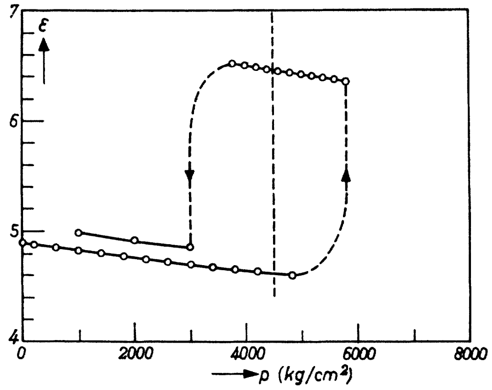

FIG. 2. Variation of the room-temperature dielectric constant of RbBr with pressure.

The pressure dependence of the dielectric constant in both phases follows directly from accurate measurements of the nearly linear parts of the curve in Fig. 2 (see Table III). The temperature dependence of the dielectric constant in both phases was measured in a rather small interval, 15–75°C, at different pressures. The results are shown in Fig. 4, where the temperature dependence of the dielectric constant of some RbBr samples is plotted as a function of the applied pressure. Special care was needed to avoid traces of water in the oil of the pressure vessel; the samples were packed in paraffin and the oil was dried before and during the measurements with a molecular sieve. Nevertheless a small difference remained present between the measurements in gas and those in oil, both at 1 atm. For two samples the temperature coefficient $(1/\epsilon)(\partial\epsilon/\partial T)_p$ in the NaCl structure was measured after a transformation cycle, giving the same values as were found for the fresh samples.

From Fig. 4 it is clear that the change in structure is accompanied by a change not only in the value of the dielectric constant, but also in its temperature dependence. From the values of $(A+B)$ and C, calculated from these measurements (see Table III), we see that whereas the total volume-dependent part $(A+B)$ is nearly equal in both phases, the temperature dependence at constant volume $C=[(\epsilon-1)(\epsilon+2)]^{-1}(\partial\epsilon/\partial T)_V$ is very different in both phases and has even changed sign.

The values of the thermal-expansion coefficient in both phases at 4600 kg/cm^2, needed for calculating the contributions $(A+B)$ and C, are not available in the literature. They were estimated with the use of the Grüneisen relation with some additional assumptions. The value of the Grüneisen constant in the NaCl structure of RbBr, $\gamma=1.4$, is assumed to be independent of pressure, so that the thermal-expansion coefficient changes in the same way as the measured compressibility. The decrease in linear-expansion coefficient from $3.8\times10^{-5}(°\mathrm{K})^{-1}$ at 1 atm down to $3.4\times10^{-5}(°\mathrm{K})^{-1}$ at 4600 kg/cm^2, obtained in this way, seems to be reasonable as compared with changes measured for some other alkali halides.[5(a)] The value of the Grüneisen constant in the CsCl structure was assumed to be $\gamma=1.9$, equal to the value of γ for CsCl, CsBr, and CsI, all having the CsCl structure, and somewhat higher than the values of alkali halides with the NaCl structure ($\gamma=1.4$–1.6). The resulting value for the linear-expansion coefficient is $4.1\times10^{-5}(°\mathrm{K})^{-1}$, leading to $C=-1.5\times10^{-5}(°\mathrm{K})^{-1}$. If it were assumed that γ is equal in either structure of RbBr ($\gamma=1.4$) a value of $3.1\times10^{-5}(°\mathrm{K})^{-1}$ is obtained for the linear expansion coefficient in the CsCl structure, giving a value for C of $-0.6\times10^{-5}(°\mathrm{K})^{-1}$. So the change in the sign of the C term at the transformation certainly is real.

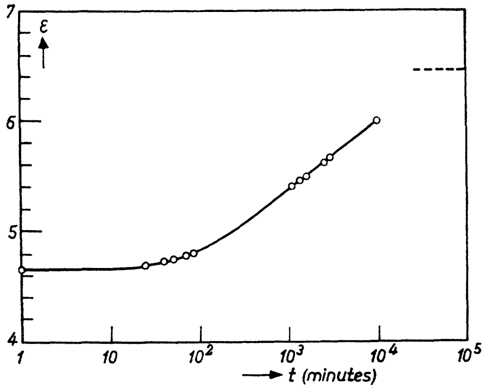

FIG. 3. The room-temperature dielectric constant of RbBr at 5000 kg/cm^2 as a function of the time elapsed since the application of this pressure.

III. DISCUSSION

A. Preliminary Remarks

The main results of the experiments described in this paper can be summarized as follows:

(1) The temperature dependence of the dielectric constant is significantly different for compounds having NaCl structure on one hand and compounds having CsCl structure on the other hand.

(2) This difference is really a structural effect, because it is also found between the two structures of RbBr.

(3) The difference in temperature dependence of the dielectric constant is due to a difference in the C term, describing the change in polarizability with temperature at constant volume.

(4) The dielectric constant of RbBr changes appreciably at the phase transformation.

In the discussion of these results we will first show by a combination with optical data that the difference in temperature coefficient originates in the term C^{ir}. Then it will be shown that the new measurements of the volume-dependent term B^{ir} can also be explained semiquantitatively with the use of the simple ionic model, used in a preceding paper. In the fourth section the jump in dielectric constant of RbBr at the phase transition is considered and the final section is devoted to a discussion of the term C^{ir} and the origin of the structural effect. A calculation of the order of magnitude of C^{ir} is worked out in the Appendix; the results are in reasonable agreement with the experimental values.

B. Combination With Optical Data

In the introduction it was outlined that if the temperature and pressure dependences of the optical polarizability are known, it is possible to separate the contributions from the optical and the infrared polarizability to the factors B and C. Literature data for NaCl structure compounds in all cases lead to a small value of C^{op} (Table IV).[6,7] Its contribution to the C term, being $(\alpha_m^{\mathrm{op}}/\alpha_m)C^{\mathrm{op}}$ can therefore be neglected.

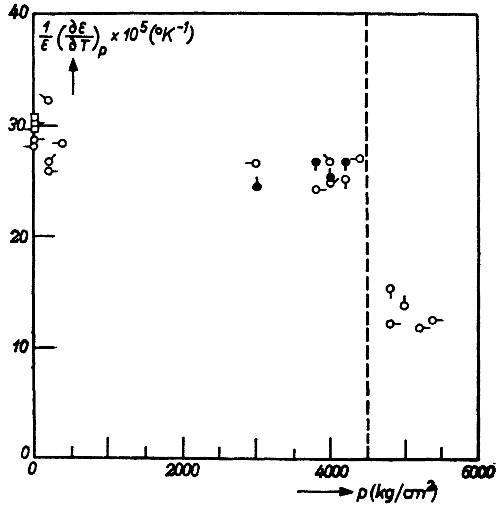

FIG. 4. Temperature coefficient of the dielectric constant of RbBr at different pressures. Squares refer to measurements in a dry gas, open circles to measurements in oil, and black circles to measurements in oil after a transformation cycle.

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[6] (a) R. S. Krishnan, *Progress in Crystal Physics* (Interscience Publishers, Inc., New York, 1958), Vol. I, p. 153; (b) A. Smakula, *Einkristalle* (Springer-Verlag, Berlin, 1961), Appendix.

[7] (a) E. Burnstein and P. L. Smith, Phys. Rev. **74**, 229 (1948). (b) H. Leibssle, Z. Krist. **114**, 457 (1960).

TABLE III. The dielectric constant ϵ at room temperature, its temperature and pressure dependence at different pressures and the contributions A, B and C to the temperature dependence for the compound RbBr.

RbBr	p (kg/cm^2)	ϵ	$\frac{10^5}{(\epsilon-1)(\epsilon+2)}\left(\frac{\partial\epsilon}{\partial T}\right)_p$ (°K)$^{-1}$	$\frac{10^7}{(\epsilon-1)(\epsilon+2)}\left(\frac{\partial\epsilon}{\partial p}\right)_T$ (kg/cm^2)$^{-1}$	$A\times10^5$ (°K)$^{-1}$	$B\times10^5$ (°K)$^{-1}$	$C\times10^5$ (°K)$^{-1}$	$(A+B)\times10^5$ (°K)$^{-1}$
NaCl structure	1	4.9	5.2	−23.5	−3.8	7.2	1.8	3.4
	4600	4.65	4.9	−21	−3.4	6.5	1.8	3.1
CsCl structure	4600	6.5	2.1	−17	−4.1	7.7	−1.5	3.6

Unfortunately, for the compounds with the CsCl structure we have no such direct experimental evidence that the contribution of the optical term to C is also small and negligible, because no strain-polarizability constants $\lambda=(V/\alpha_m^{\mathrm{op}})(\partial\alpha_m^{\mathrm{op}}/\partial V)$ appear to have been measured. Values of λ, calculated with the use of formulas derived previously by one of the authors[8] on the basis of a shell model of the ions, are not trustworthy, because for some compounds with NaCl structure the calculated values of λ differ appreciably from the experimental values; this was also stated by Lawson.[9] However, the following calculation of the order of magnitude of C^{op} will show that its value is very small, irrespective of structure.

The temperature dependence at constant volume of the optical polarizability will be due to density fluctuations. The mean-square fluctuation of the molar volume V is given by the formula[10]

$$\langle(\Delta V)^2\rangle_{\mathrm{av}}=-2RT(\partial V/\partial p)_T. \tag{6}$$

These fluctuations cause a change in the optical polarizability:

$$\Delta\alpha_m^{\mathrm{op}}=\tfrac{1}{2}\langle(\Delta V)^2\rangle_{\mathrm{av}}(\partial^2\alpha_m^{\mathrm{op}}/\partial V^2)_T. \tag{7}$$

If we assume that λ is independent of volume we get

$$C^{\mathrm{op}}=\frac{1}{3\alpha_m^{\mathrm{op}}}\left(\frac{\partial\alpha_m^{\mathrm{op}}}{\partial T}\right)_V=\lambda(\lambda-1)\frac{R\kappa}{3V}, \tag{18}$$

where κ is the isothermal compressibility. For all compounds studied the values of C^{op}, calculated with Eq. (8), turn out to be of the order of -0.1×10^{-5}(°K)$^{-1}$. For compounds with NaCl structure this is within the experimental errors in agreement with the values found experimentally. So it may be concluded that also for compounds with the CsCl structure C^{op} will be negligibly small. Therefore the difference between the experimental C values found for both structures must be ascribed to a difference in C^{ir}.

C. Volume-Dependent Terms

In a preceding paper[3] it was shown that the use of a simple ionic model with a constant effective charge q for the compounds in question leads to a polarizability α_m^{ir} inversely proportional to the force constant $\partial^2\varphi/\partial R^2$. The complete formula can easily be derived (for example by a combination of Eqs. (A5), (A9), and (A10a) of the Appendix and neglecting the temperature-

TABLE IV. Index of refraction n, its temperature dependence (Ref. 6), strain polarizability constants (Ref. 7) $\lambda=(V/\alpha_m^{\mathrm{op}})(\partial\alpha_m^{\mathrm{op}}/\partial V)$, and the three contributions A, B^{op} and C^{op} to the temperature depencence of n^2. Values of C^{op} for CsBr and CsI are assumed. The relative magnitude of α_m^{op} with respect to α_m is given in the last column.

Compound	n_∞	$(\partial n/\partial T)_p\times10^6$ (°K)$^{-1}$	λ	$A\times10^5$ (°K)$^{-1}$	$B^{\mathrm{op}}\times10^5$ (°K)$^{-1}$	$C^{\mathrm{op}}\times10^5$ (°K)$^{-1}$	$\alpha_m^{\mathrm{op}}/\alpha_m$
KCl	1.48	−36	0.55	−3.8	+2.1	−0.2	0.50
KBr	1.53	−40	0.50	−4.0	+2.0	−0.2	0.55
RbCl	1.48		0.45	−3.6	+1.8		0.50
RbBr	1.53		0.55	−3.8	+2.1		0.55
NaCl	1.53	−37	0.60	−4.0	+2.4	−0.3	0.49
LiF	1.39	−16	0.7	−3.4	+2.4	−0.2	0.31
MgO	1.73	+16	1.1	−1.0	+1.1	+0.4	0.52
CsCl	1.62			−4.5			0.52
CsBr	1.67	−79	(0.3)	−4.7	+1.5	~0	0.58
CsI	1.74	−90	(0.4)	−4.9	+1.9	~0	0.64
TlBr	2.30			−5.2			0.65
NH_4Cl	1.63		0.4	−4.9	+2.0		
CaF_2	1.43	−12	0.5	−2.0	+1.0	+0.2	

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[8] E. E. Havinga, Phys. Rev. **119**, 1193 (1960).

[9] A. W. Lawson, *Solids under Pressure*, edited by W. Paul and D. M. Warschauer (McGraw-Hill Book Company, Inc., New York, 1963), p. 35.

[10] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press Ltd., London, 1959), p. 352.

dependent terms) and gives for the polarizability per ion pair

$$\alpha^{\mathrm{ir}}=3q^2e^2/z(\varphi^{\mathrm{II}}+2\varphi^{\mathrm{I}}/R)\,. \qquad (9)$$

Here z is the number of nearest neighbors and φ is the potential energy of the nearest-neighbor repulsive interaction between a pair of ions. Derivatives with respect to a change in the interionic distance R are indicated by the Roman numerals. For φ we may choose for example a Born function $\varphi=aR^{-n}$ or the Born-Mayer function $\varphi=b\exp(-R/\rho)$. Then the volume dependence of the infrared polarizability is given by

$$\frac{B^{\mathrm{ir}}}{A}=\left(\frac{V}{\alpha_m^{\mathrm{ir}}}\right)\left(\frac{\partial\alpha_m^{\mathrm{ir}}}{\partial V}\right)_T=\frac{n+2}{3} \qquad (10)$$

or

$$B^{\mathrm{ir}}/A=(\eta^2-2\eta-2)/3(\eta-2)\,, \qquad (11)$$

respectively. Here $\eta=R_0/\rho$ and R_0 is the equilibrium distance. The experimental values of the compressibility κ can be used to arrive at effective values for n and η at room temperature, because if the energy of the crystal is given by the sum of the Madelung energy $-\mathcal{M}e^2/R$ and a repulsive energy that (for nearest and for next-nearest neighbors) can be described with a single exponent n or a single value of η, the well-known expression holds:

$$n-1=\eta-2=-9R_0V/(\kappa\mathcal{M}e^2)\,. \qquad (12)$$

It can be seen in Table V that the values of B^{ir}/A, calculated in this way, are in good agreement with the experimental values for either potential function.

The volume-dependent part of $(\partial\epsilon/\partial T)_p$ has also been calculated by Fuchs[2] with a formula equivalent with Eq. (11). He compared experimental values of

$$\epsilon^{-1}(\partial\epsilon/\partial V)_T(\partial V/\partial T)_p=(A+B)(\epsilon-1)(\epsilon+2)/\epsilon$$

available in the literature for four compounds, with values obtained from optical data and the calculated values of B^{ir}/A. From the rather bad agreement he concluded that there is an appreciable volume dependence of the effective charge. However, because the differences in the values of B^{ir}/A calculated with either the Born or the Born-Mayer potential are of the same order of magnitude as those between calculated and experimental values (see Table V), we think that this conclusion is not warranted and that the question of the volume dependence of effective charge remains open.

D. Change in ε at the Phase Transformation of RbBr

The dielectric constant of RbBr in the NaCl structure at 4600 kg/cm² is $\epsilon_6=4.65$, whereas in the CsCl structure one has $\epsilon_8=6.5$. This difference leads to a difference of about 18% in the value of α_m/V. However, when the difference in molar volume ($V_8=0.863V_6$) is accounted for, there remains only a small change in total polarizability per ion pair:

$${}^8\alpha_m=0.863\times1.18\,{}^6\alpha_m=1.02\,{}^6\alpha_m\,.$$

TABLE V. Comparison of experimental values of the dependence of the infrared polarizability on volume with values calculated using Eqs. (10) and (11).

Compound	$(V/\alpha_m^{\mathrm{ir}})(\partial\alpha_m^{\mathrm{ir}}/\partial V)_T$ Expt.	Calculated Eq. (10)	Eq. (11)
KCl	3.5	3.6	3.2
KBr	3.5	3.6	3.2
RbCl	3.3	3.6	3.2
RbBr	3.5	3.6	3.2
NaCl	3.4	3.2	2.8
LiF	2.4	2.6	2.1
MgO	2.5	2.2	1.7
CsCl		4.1	3.8
CsBr	~3.9	4.1	3.8
CsI	~4.4	4.3	4.0
TlBr		4.0	3.8

This means that within the experimental errors the change in dielectric constant at the transformation can wholly be ascribed to the change in volume. Of course the fact that the total polarizability remains nearly constant does not prove that the same will hold for the optical and the infrared parts of the polarizability. On the contrary, it will be shown below that the optical polarizability decreases at the transformation and that this effect is more than compensated for by an increase of the infrared polarizability.

The optical polarizability of RbBr in the NaCl structure at 4600 kg/cm² is calculated from the literature data of the index of refraction[11] ($n=1.5283$) and its pressure dependence[7(b)] ($dn/dp=-24.8\times10^{-7}\,\mathrm{atm}^{-1}$). The value $(4\pi/3)({}^6\alpha_m^{\mathrm{op}}/V_6)=0.303$ leaves for the infrared part the difference with the total polarizability: $\frac{4}{3}\pi({}^6\alpha_m^{\mathrm{ir}}/V_6)=0.244$. Unfortunately the refractive index in the CsCl structure of RbBr appears not to have been measured. But literature data[11] indicate that for some cesium halides the optical polarizability per ion pair in the CsCl structure is 3 to 4% lower than that in the NaCl structure. Since for these compounds the difference in molar volume of both phases is 15 to 25% higher than the value found for RbBr at the phase transformation, it is very probable that the optical polarizability of RbBr will diminish by about 3% upon transformation to the CsCl structure. This gives $\frac{4}{3}\pi({}^8\alpha_m^{\mathrm{op}}/V_8)=0.303\times0.97/0.863=0.340$ and leaves for the infrared polarizability $\frac{4}{3}\pi({}^8\alpha_m^{\mathrm{ir}}/V_8)=0.305$. Therefore α_m^{ir} must increase at the transformation by a factor $(0.305/0.244)\times0.863=1.08$.

To calculate the ratio ${}^8\alpha^{\mathrm{ir}}/{}^6\alpha^{\mathrm{ir}}$ from our simple ionic model we will use Eq. (12) and a Born potential $\varphi=aR^{-n}$. The function φ will be a different function of R in both phases, because the value of n, determined from Eq. (12), is about 15% larger in the CsCl structure than it is in the NaCl structure. We therefore eliminate a with the use of the equilibrium condition of the crystal

$$\mathcal{M}e^2/R^2+z\varphi^{\mathrm{I}}+z_2\psi^{\mathrm{I}}=0\,. \qquad (13)$$

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[11] J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. 82, 890 (1953).

Here ψ^{I} is the repulsive force between two next-nearest neighbors that are z_2 in number. After the introduction of $f = z_2\psi^{\mathrm{I}}/z\varphi^{\mathrm{I}}$ we get instead of Eq. (9)

$$\alpha^{\mathrm{ir}} = \frac{3q^2R^3}{\mathfrak{M}} \frac{(-\varphi^{\mathrm{I}}/R)}{(\varphi^{\mathrm{II}} + 2\varphi^{\mathrm{I}}/R)}(1+f). \tag{14}$$

The effective charges q of halides with NaCl and with CsCl structure are not very different.[8] To estimate the order of magnitude of ${}^8\alpha^{\mathrm{ir}}/{}^6\alpha^{\mathrm{ir}}$ it seems therefore reasonable to assume that q has the same value in both structures. Then we have

$$\left(\frac{{}^8\alpha^{\mathrm{ir}}}{{}^6\alpha^{\mathrm{ir}}}\right) = \frac{\mathfrak{M}_6}{\mathfrak{M}_8}\left(\frac{R_8}{R_6}\right)^3 \frac{1+f_8}{1+f_6} \frac{n_6 - 1}{n_8 - 1}.$$

The values of f_6 and f_8 can be estimated with the use of constants tabulated by Fowler[12] for interactions between several ion pairs, which constants were determined with an over-all value of $n = 9$. In the CsCl structure next-nearest neighbor interactions are much more important than in the NaCl structure ($f_8 = 0.28$ and $f_6 = 0.11$). Finally the following result is obtained:

$$\left(\frac{{}^8\alpha^{\mathrm{ir}}}{{}^6\alpha^{\mathrm{ir}}}\right) = \frac{1.747 \times 0.863 \times 1.28 \times 7.7}{1.763 \times 0.770 \times 1.11 \times 9.2} = 1.07.$$

This compares favorably with the value of 1.08 arrived at in the preceding paragraph.

We did not calculate ${}^8\alpha^{\mathrm{op}}$ with the use of the strain-polarizability constant $\lambda = (V/\alpha_m{}^{\mathrm{op}})(\partial\alpha_m{}^{\mathrm{op}}/\partial V)$, although we have stated in Sec. III.B that $\alpha_m{}^{\mathrm{op}}$ is only influenced by the volume. Then we would have arrived at ${}^8\alpha_m{}^{\mathrm{op}}/{}^6\alpha_m{}^{\mathrm{op}} = (V_8/V_6)^{\lambda} \approx 0.93$ instead of the value 0.97 found earlier. However, the ions do not completely fill up the space available; they may be considered as compressible spheres, with some empty regions in between. In the CsCl structure these empty regions will have a smaller volume than they have in the NaCl structure, as can be readily seen. Therefore the ions use a larger portion of the volume in the CsCl structure than they do in the NaCl structure. The effect calculated will thus be too large and the decrease of 3–4% measured in some cesium halides does not contradict the idea that only restraint of volume influences $\alpha_m{}^{\mathrm{op}}$. On the other hand it is clear that such a supposition for the case of of $\alpha_m{}^{\mathrm{ir}}$ leads to completely erroneous results. Therefore we cannot use the simple calculation of C^{op} for C^{ir} also.

E. Dependence of Infrared Polarizability on Temperature at Constant Volume

Szigeti[13] has shown that anharmonic terms in the potential energy as well as anharmonic terms in the dipole moment cause a temperature dependence of the dielectric constant at constant volume. Mitskevich[14] has calculated the magnitude of these effects for NaCl with the use of a rather complicated energy function. His results were in good agreement with the experimental values. It was concluded that the influence of anharmonic terms in the dipole moment is negligible. For a general discussion of the influence of structure on the temperature coefficient and a calculation of its order of magnitude we therefore confine ourselves to anharmonic terms in the potential energy only, and moreover to temperatures above the Debye temperature.

In the previous paper[3] the origin of C^{ir} was discussed with the use of the picture of an ion moving in a potential well. For a parabolic well the force constant does not change with amplitude and the polarizability is thus independent of temperature. Anharmonic terms in the potential give rise to amplitude-dependent force constants and hence to a temperature dependence of the polarizability. As the potential in this model is an even function of the displacements of the moving ion, third-order terms do not enter into the potential, and the value of C^{ir} is determined in first approximation by the fourth-order anharmonic terms only. The main contribution to the fourth-order energy terms stems from the short-range repulsion energy, and for either the Born or the Born-Mayer approximation the force constant increases with growing amplitude, resulting in a negative value of C^{ir}. This model, therefore, is not adequate to explain the occurrence of positive values of C^{ir}.

In a more realistic model one has to look at the influence of the temperature motion on the instantaneous geometry of the whole lattice. The temperature coefficient of polarizability due to fourth-order anharmonic terms in the potential energy clearly becomes twice as large as in the simple well model, because not only the motion of the central ion in a static potential, but also the change in this potential due to the motion of neighboring ions is taken into account. For Born or Born-Mayer interactions the effect remains of course negative.

Third-order terms in the potential energy will have an influence on the free energy because of the presence of fluctuations. They give a positive contribution to the temperature dependence of the polarizability at constant volume. In the Appendix a general formula for the polarizability has been derived [Eq. (A5)], using complex normal coordinates. It is shown in the then following calculation that the origin of the effect of the third-order term is the combined influence of two lattice vibrations with opposite wave vectors and that the greater part stems from combinations of an optical and an acoustic lattice vibration. Let us therefore consider the influence of such lattice vibrations. This can be done most easily in terms of real normal coordinates; the selection rule of opposite wave vector then becomes the

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[12] R. H. Fowler, *Statistical Mechanics* (University Press, Cambridge, England, 1955), 2nd ed., p. 327.

[13] B. Szigeti, Proc. Roy. Soc. (London) **A252**, 217 (1959).

[14] V. V. Mitskevich, Fiz. Tverd. Tela **3**, 3036 (1961) [English transl.: Soviet Phys.—Solid State **3**, 2211 (1962)].

condition that both vibrations have an equal wave vector, but must have a phase difference of $\frac{1}{2}\pi$.

An optical lattice vibration with a nonzero wave vector induces local electric dipole moments, but as the directions of these moments in the different regions of the lattice are opposite, no macroscopic moment results. However, if also deformations (elongation or compression of interionic distances) are present, due to an acoustic lattice vibration with an equal wave vector, but a phase difference of $\frac{1}{2}\pi$, the situation has changed. The amplitude of the optical vibration will increase in dilatated regions and decrease in compressed regions, because of the influence of third-order potential energy terms ($\partial\alpha^{\text{ir}}/\partial V>0$). From the particular choice of wave vectors it follows that local moments in opposite directions are influenced in a different sense: All moments in one direction are at a certain moment in compressed regions and thus reduced, whereas all moments in the other direction are at dilatated regions and thus enenlarged. A macroscopic dipole moment results that oscillates with the frequency of the optical lattice vibrations and fluctuates in maximal amplitude with the frequency of the acoustic lattice vibration.

Now a fluctuating dipole moment is equivalent with a polarizability: configurations with a moment parallel to an applied electric field are stabilized and those with opposite moment destabilized, so that averaged over a long time a dipole moment in the direction of the electric-field results. According to the macroscopic theory of Fröhlich[15] the mean square of such a fluctuating dipole moment is proportional to αkT. Therefore the extra polarizability is, at high temperature, proportional to T, because the amplitude of the fluctuating moment increases as T^2 (it depends on two lattice vibrations simultaneously).

In the Appendix the calculation of this positive contribution to C^{ir} as well as the negative influence of the fourth-order energy terms has been carried out with the assumption that only nearest-neighbor repulsive interactions give rise to these terms. After averaging over the influence of longitudinal and transverse vibrations, which is only justified as a first approximation, the following expression is obtained:

$$C^{\text{ir}}=\frac{1}{3\alpha_m{}^{\text{ir}}}\left(\frac{\partial\alpha_m{}^{\text{ir}}}{\partial T}\right)_V=\frac{kR_0}{\mathfrak{M}e^2}\left(\frac{3.15}{z-1}P-Q\right), \qquad (15)$$

where P and Q are functions of the derivatives of the short-range potential with respect to the separation R:

$$P=\frac{\{(\varphi^{\text{III}})^2+6(\varphi^{\text{II}}/R_0-\varphi^{\text{I}}/R_0)^2\}\varphi^{\text{I}}R_0}{(\varphi^{\text{II}}+2\varphi^{\text{I}}/R_0)^3}, \qquad (16)$$

$$Q=\frac{(\varphi^{\text{IV}}+4\varphi^{\text{III}}/R_0)\varphi^{\text{I}}R_0}{(\varphi^{\text{II}}+2\varphi^{\text{I}}/R_0)^2}. \qquad (17)$$

TABLE VI. Comparison of calculated and experimental values of $C^{\text{ir}}=(1/\alpha_m{}^{\text{ir}})(\partial\alpha_m{}^{\text{ir}}/\partial T)_V$. For each compound the upper row is calculated with the use of a Born potential and the second row with the use of a Born-Mayer potential.

Compound	Debye temperature (°K)	$\frac{3.15}{z-1}P$ Eq. (16)	Q Eq. (17)	$C_{\text{calc}}{}^{\text{ir}}\times10^5$ (°K)$^{-1}$	$C_{\text{expt}}{}^{\text{ir}}\times10^5$ (°K)$^{-1}$
MgO	1000	21.5	10.3	+2.0	+0.1
		16.5	4.0	+2.3	
LiF	770	18.1	11.1	+4.8	+1.0
		14.3	5.6	+6.0	
NaCl	330	16.2	12.5	+3.5	+2.0
		13.3	7.8	+5.3	
KCl	240	15.7	13.5	+2.4	+3.6
		13.2	9.1	+4.4	
KBr	180	15.7	13.6	+2.4	+5.7
		13.2	9.2	+4.5	
RbCl	170	15.7	13.5	+2.5	+4.6
		13.2	9.1	+4.7	
RbBr	140	15.7	13.6	+2.5	+4.6
(6)		13.2	9.2	+4.7	
RbBr		11.3	15.0	−4.4	−3.2
(8)		9.6	10.8	−1.4	
CsCl	170	11.3	15.0	−4.4	−2.4
		9.6	10.8	−1.4	
CsBr	150	11.3	15.0	−4.6	−2.4
		9.6	10.8	−1.5	
CsI	130	11.4	15.4	−5.3	−2.0
		9.7	11.3	−2.1	
TlBr	100	11.3	14.8	−4.0	−8.4
		9.6	10.6	−1.2	

If a Born potential $\varphi=aR^{-n}$ or a Born-Mayer potential $\varphi=b\exp(-R/\rho)$ is substituted, P and Q turn out to depend only on n or on $\eta=R_0/\rho$ (see Appendix). As is well known these coefficients are nearly independent of structure type, but change with the nature of the interacting ions. They may be calculated with Eq. (12). Therefore neither P nor Q depends directly on structure type and where the Madelung energy $-\mathfrak{M}e^2/R_0$ is also about equal for both structures we see that the structural effect is concentrated in the factor $1/(z-1)$ occurring in the third-order terms. The proportionality to $1/(z-1)$ stems from the fact that fluctuations in pairs of bonds are larger, the smaller the number of nearest bonds.

Quantitative results are summarized in Table VI. It is seen that the order of magnitude of C^{ir} is correct for either potential function and especially the experimental difference between C^{ir} of compounds with CsCl structure and NaCl structure is well reproduced by the calculated values. The quantitative agreement is certainly the best for the Born-Mayer potential. The decrease in C^{ir} with increasing values of ϵ (TlBr) is not reproduced, however, probably because of the neglect of long-range polar forces. Due to these forces the frequencies of the transverse optical lattice vibrations with small wave vectors decrease with increasing values of ϵ, whereas the corresponding longitudinal vibrations are hardly influenced by a change in ϵ. Because we did average over both types of polarization, this effect cannot be intro-

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[15] H. Fröhlich, *Theory of Dielectrics* (Clarendon Press, Oxford, England, 1958), 2nd ed.

[16] G. Leibfried and W. Ludwig, Solid State Phys. **12**, 280, 413 (1961).

duced afterwards. Estimates of their separate contributions to P and Q did not yield a clear indication of the direction of the change in C^{ir} to be expected from this effect, because of the occurrence of oppositely directed factors. Another explanation of the decrease of $(\partial\epsilon/\partial T)_V$ with increasing values of ϵ was proposed by Fuchs.[2] He states that in Szigeti's general formula[13] the negative contributions to $(\partial\epsilon/\partial T)_V$ are proportional to $(\epsilon+2)$ whereas the positive contributions are independent of ϵ. However, his argument applies only to part of the influence of nonlinear dipole moments. It leads to contributions to C^{ir} independent of ϵ from the other terms involving nonlinear dipole moments and from those involving anharmonic terms in the potential energy. Therefore the real origin of the decrease in $(\partial\epsilon/\partial T)_V$ with increasing values of ϵ remains as yet uncertain.

The results given in Table VI are rather poor when the Debye temperature exceeds considerably the measuring temperature (LiF,MgO). This was to be expected from the assumptions in the theory. Where the negative contribution (Q term) is only the sum of the influences of separate lattice vibrations it will behave below the Debye temperature as the specific heat C_v. As the positive term (P) essentially is the sum of interactions between a low-frequency acoustic and a high-frequency optical lattice vibration, it will decrease much faster than C_v below the Debye temperature. Hence the calculated values certainly are much too highly positive. Therefore the theoretical explanation given leads to correct answers as to the order of magnitude of C^{ir} for all compounds considered, except TlBr.

APPENDIX: TEMPERATURE DEPENDENCE OF INFRARED POLARIZABILITY AT CONSTANT VOLUME

The macroscopic infrared polarizability α_m^{ir} of a sphere in vacuum is related with M_x^2, the mean square value of the x component of the infrared dipole moment of the body in the absence of a macroscopic electric field [see Ref. 15, Eq. (7.21)]:

$$\alpha_m^{\text{ir}}=\frac{\overline{M_x^2}}{kT}=\frac{\int M_x^2(X)\exp\{-U(X)/kT\}dX}{kT\int\exp\{-U(X)/kT\}dX}. \quad \text{(A1)}$$

In this equation the configuration of the electrical charges within the body is indicated by the general coordinate X; $U(X)$ is the potential energy of such a configuration and the integrations have to be carried out over all possible values of X. From the use of classical mechanics it is clear that results may be significant only above the Debye temperatures of the substances. The general coordinate X may be specialized in terms of the normal coordinates of the lattice $a(\mathbf{k},j)$, corresponding to standing waves. Thus the cyclic boundary condition is adopted, or the influences of temperature motion on the macroscopic dimensions of the sphere are neglected, its volume and form being kept strictly constant. When the sphere contains N unit cells, the wave vector $\mathbf{k}$ can take N different values, and as each unit cell contains 2 ions, for each value of $\mathbf{k}$ there are 6 ways of polarization, labeled with the index j. The linear dipole moment is given by the relation

$$M_x=qa(0,j_0)\sqrt{N}, \quad \text{(A2)}$$

where $a(0,j_0)$ is the normal coordinate of that optical mode with $\mathbf{k}=0$ in which polarization is in the x direction, and q is an effective charge parameter. Nonlinear terms occurring in the general expression for the dipole moment are neglected, as already stated in the discussion. The energy $U(X)$ may be expanded as

$$U(X)=\phi_2+\phi_3+\phi_4, \quad \text{(A3)}$$

with

$$\phi_2=\tfrac{1}{2}\sum_{\mathbf{k},j}\omega^2(\mathbf{k},j)a(\mathbf{k},j)a^*(\mathbf{k},j), \quad \text{(A3a)}$$

$$\phi_3=\frac{1}{3!(2N)^{1/2}}\sum_{\substack{\mathbf{k}\mathbf{k}'\mathbf{k}''\\ jj'j''}}\phi(\mathbf{k},j|\mathbf{k}',j'|\mathbf{k}'',j'')a(\mathbf{k},j)a(\mathbf{k}',j')a(\mathbf{k}'',j''), \quad \text{(A3b)}$$

$$\phi_4=\frac{1}{4!2N}\sum_{\substack{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''\\ jj'j''j'''}}\phi(\mathbf{k},j|\mathbf{k}',j'|\mathbf{k}'',j''|\mathbf{k}''',j''')a(\mathbf{k},j)a(\mathbf{k}',j')a(\mathbf{k}'',j'')a(\mathbf{k}''',j'''). \quad \text{(A3c)}$$

Here $\omega^2(\mathbf{k},j)$ is the eigenfrequency corresponding to the eigenvibration $(\mathbf{k},j)$; $\phi(\mathbf{k},j|\mathbf{k}',j'|\mathbf{k}'',j'')$ indicates the third-order derivative of the potential energy with respect to the normal coordinates and $\phi(\mathbf{k},j|\mathbf{k}',j'|\mathbf{k}'',j''|\mathbf{k}''',j''')$ stands for the fourth-order derivative of the potential energy. The expressions for M_x and $U(X)$ are inserted in Eq. (A1) and the integrals may be evaluated straightforwardly if it is assumed that the anharmonic terms in the potential energy are small with respect to kT, so that the exponentials may be expanded in short power series; the result is

$$\alpha_m^{\text{ir}}=\frac{Nq^2}{\omega^2(0,j_0)}\left[1+\frac{kT}{4N\omega^2(0,j_0)}\left\{\sum_{\substack{\mathbf{k}\mathbf{k}'\\ jj'}}\left(\frac{|\phi(0,j_0|\mathbf{k},j|\mathbf{k}',j')|^2}{\omega^2(\mathbf{k},j)\omega^2(\mathbf{k}',j')}-\frac{\phi(0,j_0|0,j_0|\mathbf{k},j|-\mathbf{k},j)}{\omega^2(\mathbf{k},j)}\right)\right\}\right]. \quad \text{(A4)}$$

Szigeti[13] derived a formula for a slab polarized lengthwise. If we transform this formula to an equation for a sphere by formulas given in Szigeti's paper, and allow for the difference in notation, we also can obtain Eq. (A4).

Differentiation of Eq. (A4) with respect to temperature gives the sought expression:

$$C^{\mathrm{ir}}=(3\alpha_m{}^{\mathrm{ir}})^{-1}(\partial\alpha_m{}^{\mathrm{ir}}/\partial T)_V=(k/12N)(F-G)\,, \tag{A5}$$

with

$$F=\sum_{\substack{\mathbf{kk}'\\ jj'}}\frac{|\phi(0,j_0|\mathbf{k},j|\mathbf{k}',j')|^2}{\omega^2(0,j_0)\omega^2(\mathbf{k},j)\omega^2(\mathbf{k}',j')}\,, \tag{A5a}$$

and

$$G=\sum_{\mathbf{k},j}\frac{\phi(0,j_0|0,j_0|\mathbf{k},j|-\mathbf{k},\,j)}{\omega^2(0,j_0)\omega^2(\mathbf{k},j)}\,. \tag{A5b}$$

In this paper we want to estimate the magnitudes of F and G from simple assumed interionic potentials for compounds having CsCl or NaCl structure. Although these are simple structures, F and G cannot be calculated exactly in closed forms, even assuming nearest-neighbor interactions only, and further approximations have to be made. The evaluation proceeds as follows:

Formulas expressing the derivatives with respect to the normal coordinates in derivatives with respect to the displacements of the ions are, according to Ref. 16:

$$\omega^2(\mathbf{k},j)e_j(\nu|\mathbf{k},j)=\sum_{\mathbf{h},\mu,i}\phi_{ij}(0,\mu|\mathbf{h},\nu)(M_\mu M_\nu)^{-1/2}e_i(\mu|\mathbf{k},j)\,\exp i\mathbf{k}\cdot[\mathbf{R}(\mathbf{h},\nu)-\mathbf{R}(0,\mu)]; \tag{A6a}$$

$$\begin{aligned}\phi(0,j_0|0,j_0|\mathbf{k},j|-\mathbf{k},\,j)=(1/2N)\sum_{\substack{\mathbf{mnpr}\\ \mu\nu\kappa\lambda\\ ijkl}}&\phi_{ijkl}(\mathbf{m},\mu|\mathbf{n},\nu|\mathbf{p},\kappa|\mathbf{r},\lambda)(M_\mu M_\nu M_\kappa M_\lambda)^{-1/2}\\ &\times e_i(\mu|0,j_0)e_j(\gamma|0,j_0)e_k(\kappa|\mathbf{k},j)e_l(\lambda|-\mathbf{k},\,j)\,\exp i\mathbf{k}[\mathbf{R}(\mathbf{p},\kappa)-\mathbf{R}(\mathbf{r},\lambda)];\end{aligned} \tag{A6b}$$

$$\begin{aligned}\phi(0,j_0|\mathbf{k},j|-\mathbf{k}',\,j')=(1/2N)\sum_{\substack{\mathbf{mnp}\\ \mu\nu\kappa\\ ijk}}&\phi_{ijk}(\mathbf{m},\mu|\mathbf{n},\nu|\mathbf{p},\kappa)(M_\mu M_\gamma M_\kappa)^{-1/2}\\ &\times e_i(\mu|0,j_0)e_j(\nu|\mathbf{k},j)e_k(\kappa|\mathbf{k}',j')\,\exp i[\mathbf{k}\cdot\mathbf{R}(\mathbf{n},\nu)+\mathbf{k}'\cdot\mathbf{R}(\mathbf{p},\kappa)].\end{aligned} \tag{A6c}$$

In these equations $e_i(\mu|\mathbf{k},j)$ is a component of the normalized vector $\mathbf{e}(\mu|\mathbf{k},j)$, describing the polarization of the lattice vibration $(\mathbf{k},j)$, and μ indicates the kind of ion considered with mass M_μ. The mean position of an ion μ in its unit cell is given by the vector $\mathbf{R}(0,\mu)$ from the cell origin and its position with respect to the general origin is indicated by $\mathbf{R}(\mathbf{m},\mu)=\bar{\mathbf{A}}\mathbf{m}+\mathbf{R}(0,\mu)$. Here $\mathbf{m}$ is a vector with integer components and $\bar{\mathbf{A}}$ is the matrix constructed from the three basic vectors of the unit cell. The coupling parameters (C.P.'s) $\phi_{ij}\ldots(\mathbf{m},\mu|\mathbf{n},\nu|\cdots)$ are derivatives of the potential energy with respect to displacements of the ion $(\mathbf{m},\mu)$ in the ith direction, the ion $(\mathbf{n},\nu)$ in the jth direction, etc.

The third-order coefficients $\phi(0,j_0|\mathbf{k},j|\mathbf{k}',j')$ obey the selection rule that they are nonzero only if $\mathbf{k}=-\mathbf{k}'$. Namely, a shift of the origin over an arbitrary lattice vector $\mathbf{s}$ does not change the values of the C.P.'s $\phi_{ijk}(\mathbf{m},\mu|\mathbf{n},\nu|\mathbf{p},\kappa)$; irrespective of the value of $\mathbf{s}$ it must therefore hold, in view of Eq. (A6c), that $\exp i\bar{\mathbf{A}}\mathbf{s}(\mathbf{k}+\mathbf{k}')=1$. Since the wave vectors extend only over one Brillouin zone around the origin, this means that $\mathbf{k}=-\mathbf{k}'$.

If we take into account only nearest-neighbor interactions and make use of the relations between the C.P.'s due to the presence of inversion centers at all ionic sites, Eqs. (A6) can be written as

$$\omega^2(\mathbf{k},j)e_j(\nu|\mathbf{k},j)=\sum_i\phi_{ij}(0,\nu|0,\nu)M_\nu{}^{-1}e_i(\nu|\mathbf{k},j)+\sum_{\mathbf{h},i}\phi_{ij}(0,\mu|\mathbf{h},\nu)(M_\mu M_\nu)^{-1/2}e_i(\mu|\mathbf{k},j)\cos\mathbf{k}[\mathbf{R}(\mathbf{h},\nu)-\mathbf{R}(0,\mu)]; \tag{A7a}$$

$$\begin{aligned}\phi(0,j_0|0,j_0|\mathbf{k},j|-\mathbf{k},\,j)={}&\tfrac{1}{2}\sum_{\substack{\mu\\ ijkl}}\phi_{ijkl}(0,\mu|0,\mu|0,\mu|0,\mu)M_\mu{}^{-2}e_i(\mu|0,j_0)e_j(\mu|0,j_0)e_k(\mu|\mathbf{k},j)e_l(\mu|-\mathbf{k},\,j)\\ &+\tfrac{1}{2}\sum_{\substack{\mathbf{h}\\ \mu\neq\nu\\ ijkl}}\phi_{ijkl}(0,\mu|0,\mu|\mathbf{h},\nu|\mathbf{h},\nu)M_\mu{}^{-1}M_\nu{}^{-1}\{e_i(\mu|0,j_0)e_j(\mu|0,j_0)e_k(\nu|\mathbf{k},j)e_l(\nu|-\mathbf{k},\,j)\\ &+e_k(\nu|0,j_0)e_l(\nu|0,j_0)e_i(\mu|\mathbf{k},j)e_j(\mu|-\mathbf{k},\,j)+4e_i(\mu|0,j_0)e_k(\nu|0,j_0)e_j(\mu|\mathbf{k},j)e_l(\nu|-\mathbf{k},\,j)\cos\mathbf{k}[\mathbf{R}(\mathbf{h},\nu)-\mathbf{R}(0,\mu)]\}\\ &+\sum_{\substack{\mathbf{h}\\ \mu\neq\nu\\ ijkl}}\phi_{ijkl}(0,\mu|0,\mu|0,\mu|\mathbf{h},\nu)M_\mu{}^{-3/2}M_\nu{}^{-1/2}\{e_i(\mu|0,j_0)e_l(\nu|0,j_0)e_j(\mu|\mathbf{k},j)e_k(\mu|-\mathbf{k},\,j)\\ &+e_i(\mu|0,j_0)e_j(\mu|0,j_0)e_k(\mu|\mathbf{k},j)e_l(\nu|-\mathbf{k},\,j)\cos\mathbf{k}[\mathbf{R}(\mathbf{h},\nu)-\mathbf{R}(0,\mu)]\};\end{aligned} \tag{A7b}$$

$$\phi(0,j_0|\mathbf{k},j|-\mathbf{k},j')=\frac{i}{2}\sum_{\substack{\mathbf{h}\\ \mu\neq\nu\\ ijk}}\phi_{ijk}(0,\mu|0,\mu|\mathbf{h},\nu)M_\mu^{-1}M_\nu^{-1/2}\sin\mathbf{k}[\mathbf{R}(\mathbf{h},\nu)-\mathbf{R}(0,\mu)]$$
$$\times e_i(\mu|0,j_0)\{e_k(\nu|\mathbf{k},j)e_j(\mu|-\mathbf{k},j')-e_j(\mu|\mathbf{k},j)e_k(\nu|-\mathbf{k},j')\}\,. \qquad \text{(A7c)}$$

In cubic compounds it holds that $\phi_{ijk}(0,\mu|0,\mu|\mathbf{h},\nu)=\phi_{ikj}(0,\mu|0,\mu|\mathbf{h},\nu)$ and instead of the latter factor in Eq. (A7c) we may also write

$$\{e_j(\nu|\mathbf{k},j)e_k(\mu|-\mathbf{k},j')-e_j(\mu|\mathbf{k},j)e_k(\nu|-\mathbf{k},j')\}\,.$$

It is clear that this factor is large only for a combination of an optical vibration $(\mathbf{k},j)$ with an acoustic vibration $(-\mathbf{k},j')$ or conversely; it is exactly zero if both lattice vibrations are of the same branch (e.g., $j=j'$) whereas it is small if they are both optical or both acoustic. Therefore we will make no large error if we replace the numerator of the expression for F by $\omega^2(0,j_0)\omega^2(\mathbf{k},j_{\mathrm{op}})\omega^2(-\mathbf{k},j_{\mathrm{ac}})$ where $\omega^2(\mathbf{k},j_{\mathrm{op}})$ indicates the mean-square value of the frequencies of the three optical lattice vibrations with wave vector $\mathbf{k}$, and $\omega^2(-\mathbf{k},j_{\mathrm{ac}})$ has the analogous meaning. This averaging procedure might introduce serious errors only for lattice vibrations with a very small value of $\mathbf{k}$; however, the contribution of such lattice vibrations to F is not larger than that of others with higher $\mathbf{k}$ values, which outnumber the former vibrations. The denominator of F then can be summed separately over j and j' with the use of the orthogonality and completeness relations and the relation for the optical vibration with zero wave number

$$e_i(\mu|0,j_0)M_\mu^{-1/2}=e_i(\nu|0,j_0)M_\nu^{-1/2}\,. \qquad \text{(A8)}$$

The product $\omega^2(\mathbf{k},j_{\mathrm{op}})\omega^2(-\mathbf{k},j_{\mathrm{ac}})$ is most easily obtained by forming the expression

$$\omega^2(\mathbf{k},j)\omega^2(-\mathbf{k},j')\{e_i(\mu|\mathbf{k},j)e_j(\nu|-\mathbf{k},j')-e_i(\nu|\mathbf{k},j)e_j(\mu|-\mathbf{k},j')\}$$

with the use of Eq. (A7a), and averaging j over the three optical vibrations and j' over the three acoustic vibrations. The value of $\omega^2(0,j_0)$ is obtained from Eqs. (A7a) and (A8):

$$\omega^2(0,j_0)=\tfrac{1}{3}\sum_{\mu,i}\phi_{ii}(0,\mu|0,\mu)M_\mu^{-1}\,. \qquad \text{(A9)}$$

If $\varphi(R)$ stands for the short-range nearest-neighbor potential energy and its derivatives of different orders are indicated by Roman numerals, it follows from the definitions of the C.P.'s, that

$$\sum_i\phi_{ii}(0,\mu|0,\mu)=\sum_j\phi_{jj}(0,\nu|0,\nu)=-\sum_{\mathbf{h},i}\phi_{ii}(0,\mu|\mathbf{h},\nu)=z(\varphi^{\mathrm{II}}+2\varphi^{\mathrm{I}}/R)\,; \qquad \text{(A10a)}$$

$$\sum_{\substack{\mathbf{h}\\ ijk}}|\phi_{ijk}(0,\mu|0,\mu|\mathbf{h},\nu)|^2=z\{(\varphi^{\mathrm{III}})^2+6[(\varphi^{\mathrm{II}}/R)-(\varphi^{\mathrm{I}}/R^2)]^2\}\,, \qquad \text{(A10b)}$$

and, for the calculation of G,

$$\sum_{ij}\phi_{iijj}(0,\mu|0,\mu|0,\mu|0,\mu)=-\sum_{\mathbf{h},ij}\phi_{iijj}(0,\mu|0,\mu|0,\mu|\mathbf{h},\nu)=z(\varphi^{\mathrm{IV}}+4\varphi^{\mathrm{III}}/R)\,. \qquad \text{(A10c)}$$

After averaging over the different directions in real and reciprocal space one gets as a final result

$$F=\frac{36\{(\varphi^{\mathrm{III}})^2+6[(\varphi^{\mathrm{II}}/R)-(\varphi^{\mathrm{I}}/R^2)]^2\}}{z(z-1)(\varphi^{\mathrm{II}}+2\varphi^{\mathrm{I}}/R)^3}\sum_{\mathbf{k}}\frac{\langle\sin^2\mathbf{k}[\mathbf{R}(\mathbf{h},\nu)-\mathbf{R}(0,\mu)]\rangle_{\mathrm{av}}}{\langle\sin^2\tfrac{1}{2}\mathbf{k}[\mathbf{R}(\mathbf{h},\nu)+R(\mathbf{h}',\nu)-2\mathbf{R}(0,\mu)]\rangle_{\mathrm{av}}}\,. \qquad \text{(A11)}$$

The mean square sine in the denominator involves all nearest-neighbor distances; and the mean square sine in the numerator all distances between two cations having the same anion as a neighbor. Moreover, the averaging is over all $\mathbf{k}$ vectors, related by the cubic symmetry. Inspection of the $\mathbf{k}$-dependent part shows already that it must be of the order of N; numerical integrations over the Brillouin zones gives 1.05 N for the CsCl structure as well as for the NaCl structure.

To calculate G, we can combine Eq. (A10c) with Eq. (A7b) which, after averaging as before over longitudinal and transverse vibrations, over all directions of the interionic vectors and allowing for the cubic symmetry of the $\mathbf{k}$

space, gives

$$\phi(0,j_0|0,j_0|\mathbf{k},j|-\mathbf{k},\,j)=\frac{z}{18}(\varphi^{\mathrm{IV}}+4\varphi^{\mathrm{III}}/R)$$
$$\times\big[\{\mathbf{e}(\mu|0,j_0)M_\mu^{-1/2}-\mathbf{e}(\nu|0,j_0)M_\nu^{-1/2}\}^2\{\mathbf{e}(\mu|\mathbf{k},j)\mathbf{e}^*(\mu|\mathbf{k},j)M_\mu^{-1}+\mathbf{e}(\nu|\mathbf{k},j)\mathbf{e}^*(\nu|\mathbf{k},j)M_\nu^{-1}$$
$$-[\mathbf{e}^*(\mu|\mathbf{k},j)\mathbf{e}(\nu|\mathbf{k},j)+\mathbf{e}(\mu|\mathbf{k},j)\mathbf{e}^*(\nu|\mathbf{k},j)]M_\mu^{-1/2}M_\nu^{-1/2}\langle\cos\mathbf{k}[\mathbf{R}(\mathbf{h},\nu)-\mathbf{R}(0,\mu)]\rangle_{\mathrm{av}}\}\big]. \quad (\mathrm{A12})$$

The latter factor in Eq. (A12) is exactly reproduced in the expression that is obtained for $\omega^2(\mathbf{k},j)$ from Eq. (A7a) by an identical averaging procedure. Therefore these factors just cancel in G for each value of $(\mathbf{k},j)$ separately, so one has for the $6N$ lattice vibrations

$$G=\frac{12N(\varphi^{\mathrm{IV}}+4\varphi^{\mathrm{III}}/R)}{z(\varphi^{\mathrm{II}}+2\varphi^{\mathrm{I}}/R)^2}. \quad (\mathrm{A13})$$

When we make use of the equilibrium condition for the crystal $\mathfrak{M}q^2e^2/R^2=z\varphi^{\mathrm{I}}$ [Eq. (16) with $f=0$] and introduce the notation

$$P=\frac{R\varphi^{\mathrm{I}}\{(\varphi^{\mathrm{III}})^2+6(\varphi^{\mathrm{II}}/R-\varphi^{\mathrm{I}}/R^2)^2\}}{(\varphi^{\mathrm{II}}+2\varphi^{\mathrm{I}}/R)^3}\quad\text{and}\quad Q=\frac{R\varphi^{\mathrm{I}}(\varphi^{\mathrm{IV}}+4\varphi^{\mathrm{III}}/R)}{(\varphi^{\mathrm{II}}+2\varphi^{\mathrm{I}}/R)^2},$$

the final result is

$$C^{\mathrm{ir}}=(3\alpha_m{}^{\mathrm{ir}})^{-1}(\partial\alpha_m{}^{\mathrm{ir}}/\partial T)_V=(kR_0/\mathfrak{M}q^2e^2)\{[3.15/(z-1)]P-Q\}. \quad (\mathrm{A14})$$

When a Born potential $\varphi_{\mathrm{B}}=aR^{-n}$ or a Born-Mayer potential $\varphi_{\mathrm{BM}}=b\exp(-R/\rho)$ is assumed, the values of P and Q can easily be calculated; they depend only on n or on $\eta=R_0/\rho$, and not on a or b:

$$P_{\mathrm{B}}=\frac{(n^2+2n+7)(n+2)^2}{(n-1)^3}\quad\text{and}\quad P_{\mathrm{BM}}=\frac{\eta^4+6(\eta+1)^2}{(\eta-2)^2};$$

$$Q_{\mathrm{B}}=\frac{(n+1)(n+2)}{(n-1)}\quad\text{and}\quad Q_{\mathrm{BM}}=\frac{\eta^2(\eta-4)}{(\eta-2)^2},\ \text{respectively.}$$

These formulas have been used in the discussion to calculate the values of C^{ir}. If next-nearest-neighbor interactions had also been taken into account in the equilibrium condition ($f\neq0$) this would only mean that the final result would have had to be multiplied by $(1+f)$. As f is of the order 0.1 to 0.3, and we are only interested in an order-of-magnitude calculation, we have omitted it in the calculation.