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Theory of Isotope Effects in Ferroelectrics, Based on the Concept of F-Modes of Lattice Vibration

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On the basis of the concept of *ferroelectric modes* (*F-modes*) of lattice vibration which was introduced in a recent paper by the author, a theoretical investigation is made into the effects of isotopic substitution on the spontaneous polarization at $T=0$, the Curie temperature T_c, the Curie constants in the paraelectric and ferroelectric regions, the coefficient of proportionality of Ω_+^2 to $T-T_c$, and other constants characteristic of a crystal that can become ferroelectric. (T stands for the absolute temperature. "F-mode" mentioned here is conceptually different from "ferroelectric mode" introduced and so named by Cochran, Landauer, and Thomas. Ω_+ is the frequency of the ferroelectric mode in the latter sense.) The elements which undergo isotopic substitution are not restricted to hydrogen, or rather, may preferably be other than hydrogen. The crystal considered is assumed to have a single F-mode of lattice vibration. As a result, the expressions are obtained for computing the rates of change of the matter constants with respect to the mass of an ion when the masses and electric charges of all ions and the constants of the interionic short-range forces are given. Also, a few sum rules are obtained which hold among differential coefficients relating to individual ions. From these formulas, several qualitative conclusions are drawn. For example, it is found that if a certain ion does not move in the F-mode of lattice vibration, the matter constants are unchanged by the isotopic replacement of this ion.

1. INTRODUCTION

In this paper, we examine theoretically the effects of isotopic substitution on ferroelectric properties. The crystal considered is of the same character as that considered in a previous paper[1]; namely, it is (first) an ionic crystal. Its *prototype* is centrosymmetric. (In Ref. 1 we referred to the configuration of the ions which makes $\mathfrak{U}'$ the lowest as the "prototype" of the crystal; here $\mathfrak{U}'$ is that potential-energy term of the Hamiltonian of the crystal which corresponds to the short-range forces among the ions.) The crystal is always kept under the same condition of strain as it prototype. Its ferroelectric phase, if possible, is of the displacement type. Its transition to a paraelectric phase, if possible, is of second order under constant strain.

The crystal is further assumed not to have such a mode of lattice vibration (with zero wave vector) that $(\eta\gamma/v)(S_\sigma/\omega_\sigma)^2$, a dimensionless quantity, is close to unity. (These symbols and most of the symbols which will appear later were also used in Ref. 1 with the same meanings. For these meanings, see Appendix or Ref. 1.) And then the crystal is assumed to possess one, and only one, *ferroelectric* (*F*-) *mode* of lattice vibration. (In Ref. 1 we referred to a mode of lattice vibration as being ferroelectric or paraelectric, according to whether its $(\eta\gamma/v)(S_\sigma/\omega_\sigma)^2 \gg$ or $\ll 1$. Note that this concept of ferroelectric modes is different from that introduced and so named by Cochran[2] and Landauer and Thomas.[3] We shall often abbreviate "ferroelectric mode" in the former sense as "F-mode". This crystal, therefore, necessarily becomes ferroelectric at temperatures below a certain finite temperature T_c, and becomes paraelectric at temperatures above T_c, as was proved in Ref. 1. The qualification that the crystal has a single F-mode implies that its "ferro-paraelectric" phase transition is *primitive*.[4] (We intend, in the future, to deal with crystals which have more than one F-mode. These crystals may be divided into three groups, according to the degree of degeneracy of their F-modes: In group I, any two of the F-modes are not equal in eigenfrequency; in group II, all the F-modes are equal in eigenfrequency; group III is otherwise.)

There are already several experiments and theories reported by other authors concerning the isotope effects on ferroelectric behaviors. But these are all concerned solely with the replacement of hydrogen by deuterium, in contrast with our present work. Let us here write down the main known experimental facts. According to Bantle[5] and Sliker and Burlage,[6] while the Curie temperature of potassium dihydrogen phosphate [KH_2PO_4] is 123°K, that of potassium dideuterium phosphate [KD_2PO_4] is 222°K. (The value of Bantle is 213°K.) Kaminow[7] found, from his experiment on partially deuterated KH_2PO_4, that the Curie temperature varies nearly linearly with the mole fraction of deuterium. (Kaminow distinguished between two terms, "Curie temperature" and "transition temperature." The latter is synonymous with our "Curie temperature.") According to Hablützel,[8] while the upper and lower Curie temperatures of Rochelle salt [$KNaC_4H_4O_6\cdot 4H_2O$] are +24 and −18°C, respectively, those of deuterated Rochelle salt [$KNaC_4H_2D_2O_6\cdot 4D_2O$] are +35 and −22°C. According to Pepinsky *et al.*,[9] deuterated

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methylammonium aluminum sulfate dodecahydrate (MASD) [$CH_3ND_3Al(SO_4)_2\cdot 12D_2O$] has the same Curie temperature, −96°C, and the same spontaneous polarization, 1.0 $\mu C\cdot cm^{-2}$, at the same temperature, −98°C, as nondeuterated MASD [$CH_3NH_3Al(SO_4)_2\cdot 12H_2O$]. According to Waku *et al.*,[10] while the Curie temperature of potassium ferrocyanide trihydrate [$K_4Fe(CN)_6\cdot 3H_2O$] is −24.5°C, that of the deuterated compound [$K_4Fe(CN)_6\cdot 3D_2O$] is −18.0°C. According to Blinc *et al.*,[11] whereas sodium trihydrogen selenite [$NaH_3(SeO_3)_2$] undergoes a ferro-paraelectric phase transition of second order at $T_c=-80°C$, the deuterated compound [$NaD_3(SeO_3)_2$] makes a transition to an apparently antiferroelectric phase at $T_c=-2.5°C$. Blinc and Vovk[12] found, from their experiment on partially deuterated $NaH_3(SeO_3)_2$, that the dependence of the Curie temperature on the mole fraction of deuterium is not linear but hyperbolic.

It is not easy to determine whether a ferroelectric is of the displacement type or of the order-disorder type. The citation of ferroelectrics above has been made irrespective of type.

In our theory, the elements which undergo isotopic substitution are not restricted to hydrogen, or rather may preferably be other than hydrogen for the reasons explained below. Hydrogen atoms often form "hydrogen bonds." In the present theory, we shall assume that the constants of the interionic short-range forces are all unchanged by any isotopic replacement. This assumption is ordinarily considered to be quite reasonable. In the case, however, where the hydrogen atoms which form hydrogen bonds are replaced by deuterium atoms, this assumption may not be valid. Then, what about the hydrogen atoms not forming hydrogen bonds? In the present theory we assume that the change in the mass of any ionic species by isotopic substitution is considerably smaller than the average mass of the ionic species. When hydrogen is replaced by deuterium, this assumption is obviously not valid. (This assumption is, however, for convenience sake rather, and can be withdrawn; for hydrogen, we have only to go back to the system of Ref. 1.)

In Sec. 2, we shall lay the foundation of the theory. In Sec. 3, we shall discuss the effects of isotopic substitution on the Curie temperature and other properties which are mutually equal in their rates of change by isotopic substitution. In Sec. 4, we shall discuss the effects of isotopic substitution on the coefficient of proportionality of $\Omega^{+}{}_2$ to $T-T_c$ and other properties which are mutually equal, but different from the Curie temperature etc., in their rates of change by isotopic substitution. In Sec. 5, we shall summarize the results of the present theory.

2. FOUNDATION OF THE THEORY

It is considered that the following quantities are unchanged by isotopic substitution:

$$C_{\lambda\lambda'},\quad C_{\lambda\lambda'\lambda''\lambda'''},\quad e_\beta,\quad \alpha_\beta,\quad v,\quad \gamma.$$

If ΔM_β and ΔQ are the changes in the masses M_β of the ions and a matter constant Q of the crystal by isotopic substitution, then

$$\Delta Q=\sum_\beta \frac{\partial Q}{\partial M_\beta}\Delta M_\beta+\tfrac{1}{2}\sum_{\beta\beta'}\frac{\partial^2 Q}{\partial M_\beta \partial M_{\beta'}}\Delta M_\beta \Delta M_{\beta'}+\cdots$$

$$\approx\sum_\beta\left(\frac{\partial Q}{\partial M_\beta}\right)\Delta M_\beta,$$

or

$$\Delta Q/Q\approx\sum_\beta \partial \ln Q/\partial M_\beta \Delta M_\beta$$

$$=\sum_\beta(\partial \ln Q/\partial \ln M_\beta)(\Delta M_\beta/M_\beta).$$

In this degree of approximation, the effects of isotopic replacement of the individual ionic species are simply additive. Our primary work hereafter is the calculation of $\partial Q/\partial M_\beta$, $\partial \ln Q/\partial M_\beta$, or $\partial \ln Q/\partial \ln M_\beta$. For convenience we shall assume in almost all that follows that solely the ionic species of $\beta=1$—the first ionic species—undergoes isotopic substitution.

We must first calculate $\partial\omega_\sigma{}^2/\partial M_1$ and $\partial \mathbf{u}_\sigma{}^\beta/\partial M_1$. For this purpose, the following theorem in matrix algebra helps: If A is a real symmetric matrix which depends on a parameter M_1, and if a_σ and x_σ are the σth eigenvalue and σth normalized eigenvector of A, then

$$\partial a_\sigma/\partial M_1=L_{\sigma\sigma} \tag{1}$$

and

$$\frac{\partial x_\sigma}{\partial M_1}=\sum_{\sigma'(\neq\sigma)}\frac{L_{\sigma\sigma'}}{a_o-a_{o'}}x_{\sigma'}, \tag{2}$$

where

$$L_{\sigma\sigma'}\equiv(x_\sigma,[\partial A/\partial M_1]x_{\sigma'})$$

$$=\sum_{\lambda\lambda'}(\partial A_{\lambda\lambda'}/\partial M_1)x_\sigma{}^\lambda x_{\sigma'}{}^{\lambda'};$$

in Eq. (2), the σth eigenvalue must be nondegenerate. [$A_{\lambda\lambda'}$ is the (λ,λ') element of A; $x_\sigma{}^\lambda$ is the λth component of x_σ; the parentheses with a comma (,) containing two vectors mean the scalar product of these vectors.]

In order to evaluate $\partial\omega_\sigma{}^2/\partial M_1$ and $\partial \mathbf{u}_\sigma{}^\beta/\partial M_1$, we have only to put

$$A_{\lambda\lambda'}=(M_\lambda M_{\lambda'})^{-1/2}C_{\lambda\lambda'},\quad a_\sigma=\omega_\sigma{}^2,\quad x_\sigma{}^\lambda=(\sqrt{M_\lambda})u_\sigma{}^\lambda.$$

$L_{\sigma\sigma'}$ is calculated as

$$L_{\sigma\sigma'}=-\tfrac{1}{2}M_1\sum_\lambda \delta_{\beta 1}(u_\sigma{}^\lambda\sum_{\lambda'}C_{\lambda\lambda'}u_{\sigma'}{}^{\lambda'}+u_{\sigma'}{}^\lambda\sum_{\lambda'}C_{\lambda\lambda'}u_\sigma{}^{\lambda'})$$

$$=-\tfrac{1}{2}(\omega_\sigma{}^2+\omega_{\sigma'}{}^2)\mathbf{u}_\sigma{}^1\cdot\mathbf{u}_{\sigma'}{}^1,$$

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since[1]

$$\sum_{\lambda'} C_{\lambda\lambda'} u_\sigma^{\lambda'} = \omega_\sigma^2 M_\lambda u_\sigma^\lambda. \tag{3}$$

Therefore, with the aid of (1),

$$\partial\omega_\sigma^2/\partial M_1 = -\omega_\sigma^2 \|\mathbf{u}_\sigma^1\|^2 \tag{4a}$$

or

$$(\partial/\partial M_1)\ \ln\omega_\sigma^2 = -\|\mathbf{u}_\sigma^1\|^2. \tag{4b}$$

And with the aid of (2),

$$\frac{\partial \mathbf{u}_\sigma^\beta}{\partial M_1} + \delta_{\beta 1}\frac{\mathbf{u}_\sigma^1}{2M_1} = -\tfrac{1}{2} \sum_{\sigma'(\neq\sigma)} \frac{\omega_\sigma^2+\omega_{\sigma'}^2}{\omega_\sigma^2-\omega_{\sigma'}^2} (\mathbf{u}_\sigma^1\cdot\mathbf{u}_{\sigma'}^1)\mathbf{u}_{\sigma'}^\beta,$$

which is rewritten to

$$\frac{\partial \mathbf{u}_\sigma^\beta}{\partial M_1} = -\sum_{\sigma'(\neq\sigma)} \frac{\omega_\sigma^2}{\omega_\sigma^2-\omega_{\sigma'}^2} (\mathbf{u}_\sigma^1\cdot\mathbf{u}_{\sigma'}^1)\mathbf{u}_{\sigma'}^\beta - \tfrac{1}{2}\|\mathbf{u}_\sigma^1\|^2\mathbf{u}_\sigma^\beta, \tag{5}$$

since[1]

$$\sum_{\sigma'} (\mathbf{u}_\sigma^1\cdot\mathbf{u}_{\sigma'}^1)\mathbf{u}_{\sigma'}^\beta = \delta_{\beta 1}\mathbf{u}_\sigma^1/M_1.$$

We must next evaluate $\partial S_f^2/\partial M_1$ and $\partial D_f/\partial M_1$. By means of the definition of $\mathbf{S}_\sigma$ and Eq. (5), obviously,

$$\frac{\partial \mathbf{S}_f}{\partial M_1} = -\sum_{\sigma(\neq f)} \frac{\omega_f^2}{\omega_f^2-\omega_\sigma^2} (\mathbf{u}_f^1\cdot\mathbf{u}_\sigma^1)\mathbf{S}_\sigma - \tfrac{1}{2}\|\mathbf{u}_f^1\|^2\mathbf{S}_f,$$

so that

$$\frac{\partial S_f^2}{\partial M_1} = -2\sum_{\sigma(\neq f)} \frac{\omega_f^2}{\omega_f^2-\omega_\sigma^2} (\mathbf{u}_f^1\cdot\mathbf{u}_\sigma^1)(\mathbf{S}_f\cdot\mathbf{S}_\sigma) - \|\mathbf{u}_f^1\|^2 S_f^2. \tag{6}$$

Also by means of the definition of $D_{\sigma\sigma'\sigma''\sigma'''}$ and Eq. (5),

$$\frac{\partial D_f}{\partial M_1} = -4\sum_{\sigma(\neq f)} \frac{\omega_f^2}{\omega_f^2-\omega_\sigma^2} (\mathbf{u}_f^1\cdot\mathbf{u}_\sigma^1) D_{fff\sigma} - 2\|\mathbf{u}_f^1\|^2 D_f. \tag{7}$$

The matter constants characteristic of a crystal that can become ferroelectric are mainly

$$\langle P\rangle_{T=0}^2,\quad T_c,\quad [\partial\langle P\rangle^2/\partial T]_{T=T_c-0},\quad C_{\text{para}},$$
$$C_{\text{ferro}},\quad \Omega_+^2/(T-T_c),\quad \Omega_-^2/(T_c-T),\quad \Delta T_c/\omega^2.$$

Here, $\langle P\rangle_{T=0}^2$ is the square of the spontaneous polarization at 0°K (the brackets mean the statistical expectation value); C_{para} and C_{ferro} are the Curie constants in the paraelectric and ferroelectric regions, respectively; the meanings of the other symbols are given in the Appendix. According to Ref. 1, $\Omega_+^2 \sim T-T_c$ right above T_c; $\Omega_-^2 \sim T_c-T$ right below T_c; $\Delta T_c \sim \omega^2 (\omega<\omega_f)$. Therefore, $\Omega_+^2/(T-T_c)$, $\Omega_-^2/(T_c-T)$, and $\Delta T_c/\omega^2$ mean the coefficients of proportionality. In Secs. 3 and 4 we shall investigate the effects of isotopic substitution on these matter constants.

3. ISOTOPE EFFECTS ON $\langle P\rangle_{T=0}^2$, T_c, C_{para}, AND C_{ferro}

From Eq. (36) of Ref. 1, we see that

$$\left[\frac{\partial\langle P\rangle^2}{\partial T}\right]_{T=T_c-0} = -\frac{\eta k}{\gamma v(1-J_0^2/3J_1^2)}.$$

All of the factors appearing on the right-hand side are unchanged by isotopic substitution. Hence, $\partial\langle P\rangle^2/\partial T$ at T just below T_c is unchanged by isotopic substitution.

From Eqs. (28), (34), (41), and (42) of Ref. 1, it is seen that

$$\begin{aligned}(\partial/\partial M_1)\ \ln\langle P\rangle_{T=0}^2 &= (\partial/\partial M_1)\ \ln T_c \\ &= (\partial/\partial M_1)\ \ln C_{\text{para}} = (\partial/\partial M_1)\ \ln C_{\text{ferro}} \\ &= 2(\partial/\partial M_1)\ \ln S_f^2 - (\partial/\partial M_1)\ \ln D_f.\end{aligned} \tag{8}$$

Thus, the rates of change of the matter constants $\langle P\rangle_{T=0}^2$, T_c, C_{para}, and C_{ferro} by isotopic substitution are all equal. It is convenient to use the same symbol, say G, for any of these matter constants:

$$G = \langle P\rangle_{T=0}^2,\quad T_c,\quad C_{\text{para}},\quad \text{or}\quad C_{\text{ferro}}.$$

From Eqs. (6), (7), and (8), we obtain

$$\frac{\partial}{\partial M_1}\ln G = 4\sum_{\sigma(\neq f)} \frac{\omega_f^2}{\omega_f^2-\omega_\sigma^2}(\mathbf{u}_f^1\cdot\mathbf{u}_\sigma^1) \times (D_{fff\sigma}/D_f - \mathbf{S}_f\cdot\mathbf{S}_\sigma/S_f^2). \tag{9}$$

This formula enables us, in principle, to compute $\partial\ \ln G/\partial M_1$ when the atomic constants M_β, e_β, $C_{\lambda\lambda'}$, and $C_{\lambda\lambda'\lambda''\lambda'''}$ are given. [Before applying Eq. (9), we must calculate the eigenvalues and eigenvectors of the matrix $(M_\lambda M_{\lambda'})^{-1/2}C_{\lambda\lambda'}$.] We see as a qualitative corollary of Eq. (9) that if $\mathbf{u}_f^1=0$, i.e., if the first ion does not move in the F-mode of lattice vibration, G is unchanged by the isotopic replacement of the first ion. Also, we find, in the case of $\mathbf{u}_f^1\neq 0$, that individual modes of lattice vibration contribute additively to the change of G, but that the following modes make no contribution:

(a) the three acoustic modes,
(b) optical modes in which the first ion does not move,
(c) optical modes in which the first ion moves perpendicularly to the direction along which the first ion moves in the F-mode,
(d) optical modes whose eigenfrequency is considerably higher than that of the F-mode,
(e) optical modes such that $\mathbf{S}_f\cdot\mathbf{S}_\sigma/S_f^2 = D_{fff\sigma}/D_f$.

For (a), it should be noticed that $\mathbf{S}_\sigma$ and $D_{fff\sigma}$ are zero for the acoustic modes. The reasons for (b)–(e) may be obvious. The condition in (e) is rather accidental.

We consider two special cases: case A, where all of the paraelectric optical modes have a considerably higher eigenfrequency than that of the F-mode, and case B, where only one of the paraelectric optical modes has a lower or slightly higher (but unequal) eigenfrequency than that of the F-mode. We apply Eq. (9) to these cases. In case A, obviously,

$$\partial \ln G/\partial M_1 \approx 0;$$

hence G is unchanged by the isotopic replacement of *any* ionic species. (The equation, as such, says that G is unchanged by the isotopic replacement of *the first* ionic species. It should, however, be noticed that *any* ionic species can become "the first" ionic species.)

In case B, Eq. (9) reduces to

$$\frac{\partial}{\partial M_1}\ln G \approx \frac{4\omega_f^2}{\omega_f^2-\omega_\sigma^2}(\mathbf{u}_f^1\cdot\mathbf{u}_\sigma^1)\frac{D_{fff\sigma}}{D_f}. \tag{10}$$

(Whereas $\omega_\sigma \lesssim \omega_f$, in order that the mode σ should be paraelectric, it is necessary that $S_\sigma \ll S_f$.) We can determine the senses (*not* directions) of the vectors u_f and u_σ (in the matrix-algebraical sense) as we please. The sign of $D_{fff\sigma}$ depends on the choice of the senses of u_f and u_σ. We agree to choose these senses so that $D_{fff\sigma}>0$. (D_f is positive independently of the choice of the sense of u_f.) Then, from Eq. (10), we can make a qualitative statement that $\partial G/\partial M_1$ is positive or negative according to whether the signs of $\omega_f-\omega_\sigma$ and $\mathbf{u}_f^1\cdot\mathbf{u}_\sigma^1$ are the same or different.

Equation (10) can be rewritten as

$$\frac{1}{\mathbf{u}_f^1\cdot\mathbf{u}_\sigma^1}\frac{\partial G}{\partial M_1}\approx G\frac{4\omega_f^2}{\omega_f^2-\omega_\sigma^2}\frac{D_{fff\sigma}}{D_f}.$$

Since the right-hand side is not particularly concerned with the first ion, it is evident that

$$(\mathbf{u}_f^\beta\cdot\mathbf{u}_\sigma^\beta)^{-1}\partial G/\partial M_\beta: \quad \text{independent of } \beta. \tag{11}$$

Now, suppose that the second ion undergoes isotopic substitution in place of the first ion. From (11) it follows that the signs of $\partial G/\partial M_1$ and $\partial G/\partial M_2$ are the same or different according to whether the signs of $\mathbf{u}_f^1\cdot\mathbf{u}_\sigma^1$ and $\mathbf{u}_f^2\cdot\mathbf{u}_\sigma^2$ are the same or different. [Once we have determined the sign of $D_{fff\sigma}$, the signs of $\mathbf{u}_f^\beta\cdot\mathbf{u}_\sigma^\beta(\beta=1, 2, \cdots)$ are all definite. It is possible that the signs of $\mathbf{u}_f^1\cdot\mathbf{u}_\sigma^1$ and $\mathbf{u}_f^2\cdot\mathbf{u}_\sigma^2$ may be different.]

We try to estimate the order of magnitude of $\partial \ln G/\partial \ln M_1$ in case B. If

$$\omega_\sigma/\omega_f=\tfrac{1}{10},\quad D_{fff\sigma}/D_f=\tfrac{1}{5},\quad M_1\mathbf{u}_f^1\cdot\mathbf{u}_\sigma^1(\approx M_1\|\mathbf{u}_f^1\|^2)=\tfrac{1}{4},$$

then, by means of Eq. (10),

$$\partial \ln G/\partial \ln M_1=\tfrac{1}{5}.$$

Let us consider the case where $G=T_c$. Rewriting the above relation to

$$\Delta T_c/T_c=\tfrac{1}{5}(\Delta M_1/M_1),$$

if we put

$$M_1=16,\quad \Delta M_1=1,\quad T_c=400°\text{K},$$

then we have

$$\Delta T_c=5°\text{K}.$$

If the second ion (and only the second ion) is the same element as the first ion, and is situated similarly to the first ion in the structure of the crystal, we cannot perform isotopic substitution on the first ion exclusively, but on both the first and second ions simultaneously. In this case, therefore,

$$\begin{aligned}\frac{\Delta T_c}{T_c}&=\frac{\partial \ln T_c}{\partial \ln M_1}\frac{\Delta M_1}{M_1}+\frac{\partial \ln T_c}{\partial \ln M_2}\frac{\Delta M_2}{M_2}\\&=2\left(\frac{\partial \ln T_c}{\partial \ln M_1}\right)\left(\frac{\Delta M_1}{M_1}\right)\\&=\tfrac{2}{5}(\Delta M_1/M_1).\end{aligned}$$

Hence,

$$\Delta T_c=10°\text{K}.$$

ΔT_c is positive because we have assumed that $\mathbf{u}_\sigma^1$ makes an *acute* angle with $\mathbf{u}_f^1$, and that $\Delta M_1>0$.

We come back from the special cases A and B to the general case. It may be obvious that Eq. (9) holds also if M_1, $\mathbf{u}_f^1$, and $\mathbf{u}_\sigma^1$ are replaced by M_β, $\mathbf{u}_f^\beta$, and $\mathbf{u}_\sigma^\beta$ with arbitrary β, respectively. If we multiply both sides of this variation of Eq. (9) by M_β and take the sum with respect to β, then

$$\begin{aligned}&\sum_\beta M_\beta(\partial \ln G/\partial M_\beta)\\&\quad=4\sum_{\sigma(\neq f)}\frac{\omega_f^2}{\omega_f^2-\omega_\sigma^2}\Big(\sum_\beta M_\beta\mathbf{u}_f^\beta\cdot\mathbf{u}_\sigma^\beta\Big)\frac{D_{fff\sigma}}{D_f}\frac{\mathbf{S}_f\cdot\mathbf{S}_\sigma}{S_f^2}\\&\quad=0\end{aligned}$$

(because $\sum_\beta M_\beta\mathbf{u}_f^\beta\cdot\mathbf{u}_\sigma^\beta=0$ for $\sigma\neq f$). Hence, we obtain the sum rule

$$\sum_\beta M_\beta(\partial G/\partial M_\beta)=0. \tag{12}$$

This suggests that all $\partial G/\partial M_\beta$ ($\beta=1, 2, \cdots$) cannot take arbitrary values independently of one another. We find as a qualitative corollary of (12) that if, among $\partial G/\partial M_\beta$ ($\beta=1, 2, \cdots$), there is a positive (or negative) one, there is necessarily a negative (or positive) one.

4. ISOTOPE EFFECTS ON $\Omega_+^2/(T-T_c)$, $\Omega_-^2/(T_c-T)$, AND $\Delta T_c/\omega^2$

From Eqs. (59), (63), and (66) of Ref. 1, it is seen that

$$\frac{\partial}{\partial M_1}\ln\frac{\Omega_+^2}{T-T_c}=\frac{\partial}{\partial M_1}\ln\frac{\Omega_-^2}{T_c-T}=-\frac{\partial}{\partial M_1}\ln\frac{\Delta T_c}{\omega^2}$$

$$=(\partial/\partial M_1)\ln\omega_f^2-(\partial/\partial M_1)\ln T_c. \tag{13}$$

[Incidentally, it should be noted that $(T_c-T)/\Omega_-^2$: $(T-T_c)/\Omega_+^2$:$\Delta T_c/\omega^2=1:2:3$.] The rates of change of the matter constants $\Omega_+^2/(T-T_c)$, $\Omega_-^2/(T_c-T)$, and $\omega^2/\Delta T_c$ by isotopic substitution are all equal. For convenience, we shall use the same symbol, say K, for any of these matter constants:

$$K=\Omega_+^2/(T-T_c),\quad \Omega_-^2/(T_c-T),\quad \text{or}\quad \omega^2/\Delta T_c.$$

From Eqs. (13), (4b), and (9), we obtain

$$(\partial/\partial M_1)\ln K=-\|\mathbf{u}_f^1\|^2 -4\sum_{\sigma(\neq f)}\frac{\omega_f^2}{\omega_f^2-\omega_\sigma^2}(\mathbf{u}_f^1\cdot\mathbf{u}_\sigma^1)\left(\frac{D_{fff\sigma}}{D_f}-\frac{\mathbf{S}_f\cdot\mathbf{S}_\sigma}{S_f^2}\right). \tag{14}$$

This is the formula for computing $\partial\ln K/\partial M_1$ when the atomic constants M_β, e_β, $C_{\lambda\lambda'}$, and $C_{\lambda\lambda'\lambda''\lambda'''}$ are given. From (14), just as for G, we find as qualitative corollaries that if the first ion does not move in the F-mode of lattice vibration, K is unchanged by the isotopic replacement of the first ion, and, in the case of $\mathbf{u}_f^1\neq 0$, that individual modes of lattice vibration contribute additively to the change of K, but that the modes (a)–(e), which are given in Sec. 3, make no contribution.

We consider the special cases A and B which were introduced in Sec. 3. In case A, Eq. (14) reduces to

$$\partial\ln K/\partial M_1\approx-\|\mathbf{u}_f^1\|^2. \tag{15}$$

It is seen that only the magnitude of $\mathbf{u}_f^1$ takes part in $\partial\ln K/\partial M_1$. It is further found that

$$-1\leqq\partial\ln K/\partial\ln M_1\leqq 0 \tag{16}$$

(since $M_1\|\mathbf{u}_f^1\|^2\leqq\sum_\beta M_\beta\|\mathbf{u}_f^\beta\|^2=1$). This shows the limits of value of $\partial\ln K/\partial\ln M_1$.

In case B, Eq. (14) reduces to

$$\partial\ln K/\partial M_1\approx-\|\mathbf{u}_f^1\|^2-\frac{4\omega_f^2}{\omega_f^2-\omega_\sigma^2}(\mathbf{u}_f^1\cdot\mathbf{u}_\sigma^1)\frac{D_{fff\sigma}}{D_f}. \tag{17}$$

From this we get the following qualitative information. Let the senses of the vectors u_f and u_σ be chosen so that $D_{fff\sigma}>0$. Then, if the signs of $\omega_f-\omega_\sigma$ and $\mathbf{u}_f^1\cdot\mathbf{u}_\sigma^1$ are the same, $\partial K/\partial M_1$ is negative; while if the signs of $\omega_f-\omega_\sigma$ and $\mathbf{u}_f^1\cdot\mathbf{u}_\sigma^1$ are different, $\partial K/\partial M_1$ is not necessarily negative.

We come back to the general case. Equation (14) holds also if M_1, $\mathbf{u}_f^1$, and $\mathbf{u}_\sigma^1$ are replaced by M_β, $\mathbf{u}_f^\beta$, and $\mathbf{u}_\sigma^\beta$ with arbitrary β, respectively. If we multiply both sides of this variation of Eq. (14) by M_β and take the sum with respect to β, then

$$\begin{aligned}\sum_\beta M_\beta\partial\ln K/\partial M_\beta &=-\sum_\beta M_\beta\|\mathbf{u}_f^\beta\|^2-4\sum_{\sigma(\neq f)}\frac{\omega_f^2}{\omega_f^2-\omega_\sigma^2}\\ &\quad\times\Big(\sum_\beta M_\beta\mathbf{u}_f^\beta\cdot\mathbf{u}_\sigma^\beta\Big)(D_{fff\sigma}/D_f-\mathbf{S}_f\cdot\mathbf{S}_\sigma/S_f^2)\\ &=-1.\end{aligned} \tag{18a}$$

This sum rule can also be written as

$$\sum_\beta\partial\ln K/\partial\ln M_\beta=-1 \tag{18b}$$

or

$$\sum_\beta M_\beta\partial K/\partial M_\beta=-K. \tag{18c}$$

From (18c), a qualitative corollary follows that at least one of $\partial K/\partial M_\beta$ ($\beta=1, 2, \cdots$) is nonzero and negative. (There is not necessarily a positive one.) If we denote by n the total number of ions per unit cell, we notice from (18b) that the value of $\partial\ln K/\partial\ln M_\beta$ is $-1/n$ on the average.

5. SUMMARY OF RESULTS

We now summarize the results obtained in the preceding sections.

(1) $\partial\langle P\rangle^2/\partial T$ at $T=T_c-0$ is unchanged by isotopic substitution.

(2) The rates of change of $\langle P\rangle_{T=0}^2$, T_c, C_{para}, and C_{ferro} by isotopic substitution are all equal.

(3) $\partial\ln G/\partial M_1$ can (in principle) be evaluated by means of Eq. (9) when the atomic constants M_β, e_β, $C_{\lambda\lambda'}$, and $C_{\lambda\lambda'\lambda''\lambda'''}$ are given. [$G=\langle P\rangle_{T=0}^2$, T_c, C_{para}, or C_{ferro}.]

(4) If the first ion does not move in the F-mode of lattice vibration, G is unchanged by the isotopic replacement of the first ion.

(5) Individual modes of lattice vibration contribute additively to the change of G.

(6) The modes (a)–(e) [see Sec. 3] make no contribution to the change of G.

(7) A sum rule, Eq. (12), holds among $\partial G/\partial M_\beta$ ($\beta=1, 2, \cdots$).

(8) Among $\partial G/\partial M_\beta$ ($\beta=1, 2, \cdots$), if there is a positive (or negative) one, there is necessarily a negative (or positive) one.

(9) In case A [see Sec. 3], G is unchanged by the isotopic replacement of any ionic species.

(10) In case B [see Sec. 3], $\partial\ln G/\partial M_1$ can be evaluated by means of Eq. (10) a simpler formula than Eq. (9).

(11) In case B, $\partial G/\partial M_1$ is positive or negative, according to whether the signs of $\omega_f-\omega_\sigma$ and $\mathbf{u}_f^1\cdot\mathbf{u}_\sigma^1$ are the same or different. [Here, the senses of the vectors u_f and u_σ (in the matrix-algebraical sense) are assumed to be chosen so that $D_{fff\sigma}>0$.].

(12) In case B, $(\mathbf{u}_f^\beta\cdot\mathbf{u}_\sigma^\beta)^{-1}\partial G/\partial M_\beta$ is independent of β.

(13) In case B, $\partial G/\partial M_1$ and $\partial G/\partial M_2$ are the same or different in sign, according to whether $\mathbf{u}_f^1\cdot\mathbf{u}_\sigma^1$ and $\mathbf{u}_f^2\cdot\mathbf{u}_\sigma^2$ are the same or different in sign.

(14) The rates of change of $\Omega_+^2/(T-T_c)$, $\Omega_-^2/(T_c-T)$, and $\omega^2/\Delta T_c$ by isotopic substitution are all equal.

(15) $\partial\ln K/\partial M_1$ can (in principle) be evaluated by means of Eq. (14) when the atomic constants M_β, e_β,

$C_{\lambda\lambda'}$, and $C_{\lambda\lambda'\lambda''\lambda'''}$ are given. [$K=\Omega_+^2/(T-T_c)$, $\Omega_-^2/(T_c-T)$, or $\omega^2/\Delta T_c$.]

(16) If the first ion does not move in the F-mode of lattice vibration, K is unchanged by the isotopic replacement of the first ion.

(17) Individual modes of lattice vibration contribute additively to the change of K.

(18) The modes (a)–(e) make no contribution to the change of K.

(19) A sum rule, Eq. (18), holds among $\partial K/\partial M_\beta$ ($\beta=1, 2, \cdots$).

(20) At least one of $\partial K/\partial M_\beta$ ($\beta=1, 2, \cdots$) is nonzero and negative.

(21) The value of $\partial \ln K/\partial \ln M_\beta$ is $-1/n$ on the average. [n is the total number of ions per unit cell.]

(22) In case A, $\partial \ln K/\partial M_1$ can be evaluated by means of Eq. (15), a much simpler formula than Eq. (14).

(23) In case A, the value of $\partial \ln K/\partial \ln M_1$ is between 0 and -1.

(24) In case B, $\partial \ln K/\partial M_1$ can be evaluated by means of Eq. (17), a simpler formula than Eq. (14).

(25) In case B, if the signs of $\omega_f-\omega_\sigma$ and $\mathbf{u}_f^1\cdot\mathbf{u}_\sigma^1$ are the same, $\partial K/\partial M_1$ is negative; if the signs of $\omega_f-\omega_\sigma$ and $\mathbf{u}_f^1\cdot\mathbf{u}_\sigma^1$ are different, $\partial K/\partial M_1$ is not necessarily negative. [Here, the senses of the vectors u_f and u_σ are assumed to be chosen so that $D_{fff\sigma}>0$.]

APPENDIX

Most of the symbols used in this paper were also used with the same meanings in Ref. 1. These meanings are as follows (For details see Ref. 1.):

β is the number assigned to each of the ions composing the basis of the crystal;

i is the number assigned to each of the rectangular coordinate axes;

λ is a single index standing for the double index (i,β);

M_β is the mass of the βth ion;

e_β is the electric charge of the βth ion;

α_β is the electronic polarizability of the βth ion;

α is the sum of all α_β, i.e., the electronic polarizability of the unit cell;

v is the volume of the unit cell;

γ is the constant of the internal electric field;

$\eta\equiv(1-\gamma\alpha/v)^{-1}$;

$\mathbf{q}_\beta$ is the displacement of the βth ion;

U' is the potential energy per unit cell causing the short-range forces among the ions;

$C_{\lambda\lambda'}$ are the coefficients in the second-order terms of U';

$C_{\lambda\lambda'\lambda''\lambda'''}$ are the coefficients in the fourth-order terms of U'

$$\Big(U'=\tfrac{1}{2}\sum_{\lambda\lambda'} C_{\lambda\lambda'}q_\lambda q_{\lambda'}+\tfrac{1}{4}\sum_{\lambda\lambda'\lambda''\lambda'''} C_{\lambda\lambda'\lambda''\lambda'''}q_\lambda q_{\lambda'}q_{\lambda''}q_{\lambda'''}\Big);$$

σ is the number assigned to each mode of lattice vibration;

ω_σ is the eigenfrequency of the σth mode;

$\mathbf{u}_\sigma^\beta$ is the relative displacement of the βth ion in the σth mode of lattice vibration [The σth eigenvalue and the λth component of the σth normalized eigenvector of the matrix whose (λ,λ') element is $(M_\lambda M_{\lambda'})^{-1/2}C_{\lambda\lambda'}$ are put equal to ω_σ^2 and $(\sqrt{M_\lambda})u_\sigma^\lambda$, respectively.];

$$D_{\sigma\sigma'\sigma''\sigma'''}\equiv\sum_{\lambda\lambda'\lambda''\lambda'''} u_\sigma^\lambda u_{\sigma'}^{\lambda'}u_{\sigma''}^{\lambda''}u_{\sigma'''}^{\lambda'''}C_{\lambda\lambda'\lambda''\lambda'''};$$

D_f is an abbreviation of the symbol D_{ffff} (The F-mode of lattice vibration is referred to as the mode of $\sigma=f$.);

$\mathbf{S}_\sigma\equiv\sum_\beta e_\beta \mathbf{u}_\sigma^\beta$;

P is the dielectric polarization (per unit volume);

T is the (absolute) temperature;

T_c is the Curie temperature;

k is the Boltzmann constant;

$$J_n\equiv\int_{-\infty}^{\infty} x^{2n}\exp(-\tfrac{1}{4}x^4)dx;$$

ω is the frequency of the external alternating electric field;

χ is the dielectric susceptibility;

Ω_+ is the resonance frequency for χ at $T>T_c$, associated with the F-mode of lattice vibration, or the frequency of the Cochran-Landauer-Thomas ferroelectric mode of vibration;

Ω_- is the resonance frequency for χ at $T<T_c$, associated with the F-mode of lattice vibration;

ΔT_c is the difference between the two temperatures, T_{c+} and T_{c-}, at which χ becomes maximum for $\omega=\text{const}$ ($T_{c+}=T_{c-}=T_c$ when $\omega=0$).

The following two symbols did not appear in Ref. 1, but their meanings are written down:

C_{para} is the Curie constant in the paraelectric region;

C_{ferro} is the Curie constant in the ferroelectric region.