

Origin of the unusual dependence of the nonlinear optical susceptibility on bond length for ionic ferroelectrics

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The bond nonlinear polarizability is shown to increase with increasing bond length for covalent compounds but to decrease with bond length for sufficiently ionic compounds. This behavior is shown to explain, for example, the anomalously small value of the d_{31} nonlinear coefficient in LiTaO_3 as compared with the isomorphous LiNbO_3 , as well as the *opposite* signs of d_{33} in the isomorphous BaTiO_3 and PbTiO_3 . The unusually large deviation of $\text{Pb}_3\text{Ge}_3\text{O}_{11}$ from the Jerphagnon relationship between the vector part of Miller's Δ and the spontaneous polarization is also discussed.

I. INTRODUCTION

When an optical field $E(t) = E(\omega) \cos \omega t$ is present in a system which lacks a center of inversion it produces a second-harmonic polarization $P(2\omega)$ given by

$$P_i(2\omega) = d_{ijk} E_j(\omega) E_k(\omega), \quad (1)$$

where d_{ijk} is the tensor second-order nonlinear optical susceptibility. Since d_{ijk} vanishes by symmetry for free isolated atoms, its magnitude and sign in a crystal are intimately related to the formation and properties of the chemical bond¹⁻⁷ (e.g., ionicity f_i and bond length d). Owing to the fundamental importance of these bonds it has proven useful to decompose the macroscopic nonlinear optical susceptibility d_{ijk} into bond contributions β using^{3,6}

$$d_{ijk} = \sum_{\mu} G_{ijk}^{\mu} \beta^{\mu}, \quad (2)$$

where β is the nonlinear optical polarizability of a single bond,⁸ G_{ijk} is the bond geometrical factor (i.e., it is simply a product of the direction cosines between the bond axes and the crystallographic axes), and the sum on μ runs over all the bonds in the crystal.

The magnitude of the bond nonlinearity β has a strong and unusually interesting dependence on the bond length d . The fact that β is indeed a strongly varying function of d can readily be seen in several ways. For example, it is well known both theoretically³⁻⁷ and experimentally⁹ that the nonlinear bond polarizability β is intimately related to the linear susceptibility¹⁰ χ (e.g., Miller's rule⁹ shows $\beta \propto \chi^3$). The linear (L) susceptibility is known to change rapidly with changes in bond length (e.g., via the photoelastic, Raman, or similar effects) and this strong dependence can be represented as a power law,

$$\chi \propto d^{\sigma_L}, \quad (3)$$

where the power-law exponent is given by

$$\sigma_L \equiv \frac{d}{\chi} \frac{\partial \chi}{\partial d}. \quad (4)$$

Thus, from Miller's rule we would also expect the nonlinear susceptibility to change rapidly with d . More directly, experiments¹¹ have shown that d_{ijk} varies with strain (acoustically induced optical harmonic generation) and that lattice contributions to d_{ijk} are important (see, for example, the classic Faust and Henry¹² experiment). A final point worth mentioning is that the zinc-blende semiconductors GaP, GaAs, InAs, GaSb, and InSb all have rather similar properties (e.g., ionicities, etc.) and differ mainly in their increasing bond lengths along the series and their dramatically increasing nonlinear (and linear) susceptibilities. Thus, clearly $\partial \beta / \partial d \neq 0$ and cannot be ignored. In fact, this dependence of the nonlinear (NL) polarizability β on d , which can be expressed [in analogy with Eqs. (3) and (4)] as a power law,

$$\beta \propto d^{\sigma_{NL}}, \quad (5)$$

where the power law exponent is given by

$$\sigma_{NL} \equiv \frac{d}{\beta} \frac{\partial \beta}{\partial d}, \quad (6)$$

will be crucial to understand the unusual behavior of d_{ijk} in ferroelectrics to be discussed later.¹³

The relation between this power-law exponent σ_{NL} and the bond ionicity is expected to show a particularly interesting and unusual behavior from the following considerations. For highly covalent crystals (e.g., GaAs, InSb, etc.) it has been shown theoretically^{3,14} that β is a strongly increasing function of bond length, namely, $\beta \propto d^{+3}$ (i.e., the power dependence is $\sigma_{NL} = +3$). This large positive value for σ_{NL} is required, for example, to quantitatively understand¹⁴ the strain dependence of the crystal nonlinear optical coefficients d_{ijk} . Physically this rapid increase of the bond nonlinearity β is a consequence of the decrease in the

average potential (i. e., the decrease in the average energy gap E_g) for the bonding electrons as the two atoms composing the bond are separated. That is, just as χ increases as E_g decreases,¹⁵ β also rapidly increases as E_g decreases³ (e. g., from Miller's rule $\beta \propto \chi^3$).

However, β clearly cannot continue to increase indefinitely. As the atoms are moved further and further apart, a situation is reached when the bonding between these distant atoms become sufficiently weak so that the decrease of the oscillator strength for the transitions leading to the nonlinear polarizability dominates $\partial\beta/\partial d$. At this point β decreases with increasing bond length d , and vanishes in the limit of completely separated (i. e., spherical) atoms, as of course it must.

This can be seen more quantitatively by considering an extremely ionic "bond" in which essentially all of the valence electrons have been transferred from the cation to the anion, and therefore corresponds to a situation for which both the cation and anion have a nearly spherical charge distribution. The nonlinear optical susceptibility of such an ionic system is of course *not* zero (although it is rather small). It arises from the charged cation polarizing the valence electrons on the anion, and creating various multipole moments¹⁶ (dipole, quadrupole, octupole, etc.). As is well known,¹⁷ the nonlinear susceptibility is approximately proportional to the octupole moment of the ground-state charge distribution $\langle x^3 \rangle$, i. e., $\beta \propto \langle x^3 \rangle / E_g^2$. Since the induced octupole moment will fall off as d^{-4} (where d is the cation-anion distance) and since for such separated atoms the effective gap E_g is expected to be approximately independent of d (is just determined by the anion atomic potentials), we see that for highly ionic systems $\beta \propto d^{-4}$ gives a simple estimate for the dependence of β on d . (This expected constancy of the effective gap for highly ionic crystals will be discussed more fully later.)

To summarize these observations on the interesting ionicity dependence of the exponent of the power-law σ_{NL} , we indicate in Fig. 1(a) that for highly *covalent* strongly bonded systems β *increases* rapidly with d (e. g., $\beta \propto d^{+3}$), whereas, on the contrary, for highly *ionic* weakly bonded atoms, β is expected to *decrease* strongly with d (e. g., $\beta \propto d^{-4}$). Crystals having an intermediate ionicity will have β approximately independent of d (as we will find later for LiTaO_3 , BaTiO_3 , and PbTiO_3) and are therefore especially interesting.

It is important to note that the consideration of this dependence of β on d is only of major importance for ferroelectrics.³ This is simply a result of their nearly centrosymmetric structure and consequent close cancellation between nearly opposing bonds. For example, in BaTiO_3 the use of Eq. (2)

shows that the d_{33} coefficient is proportional to $[\beta(\text{long}) - \beta(\text{short})]$, where $\beta(\text{long})$ and $\beta(\text{short})$ are the two inequivalent Ti-O bonds parallel to the c axis. Clearly, if β were independent of bond length, then d_{33} would be zero. Thus, it is the dependence of β on d which is responsible for this nonzero d_{33} . In fact, using Eq. (5) we can see that $d_{33} \propto \sigma_{NL} \beta$ and thus vanishes if $\sigma_{NL} = 0$. However, in nonferroelectrics, the effect of unequal bond lengths is not usually significant, since there is no near cancellation between the various bonds. This can be clearly seen in the wurtzite structure, for example, where the contribution of the four tetrahedral bonds to d_{33} is proportional to $[\frac{8}{9} + \sigma_{NL} \times (\Delta d/d)]$. The second term, due to the difference in bond lengths Δd , is only a few percent of the first term, which is due to the approximately tetrahedral bond configuration, and hence d_{33} does not vanish if $\sigma_{NL} = 0$.

In the rest of this paper we attempt to quantita-

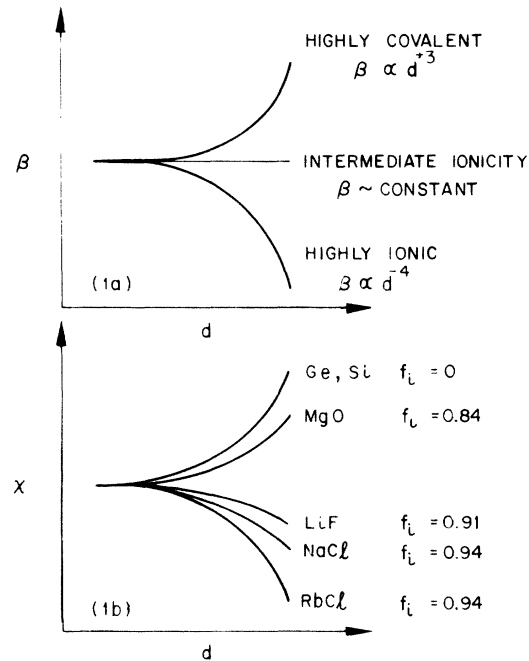


FIG. 1. (a) Schematic representation of the behavior of the bond nonlinearity β on the bond length d . For highly covalent crystals (e. g., GaAs) β increases as d increases ($\beta \propto d^{+3}$), whereas for highly ionic crystals β is expected to decrease rapidly with d ($\beta \propto d^{-4}$). For intermediate ionicities, β will be approximately constant. (b) Schematic representation of the behavior of the linear susceptibility χ . For sufficiently covalent materials (e. g., Ge, Si, MgO), χ increases as d increases, whereas for sufficiently ionic crystals (e. g., LiF, NaCl, RbCl), χ decreases with increasing d . Expressing $\chi \propto d^{\sigma_L}$ the experimental results discussed in Ref. 15 can be given as $\sigma_L = +2.0, +1.6, -1.2, -1.7,$ and -2.6 for Ge, MgO, LiF, NaCl, and RbCl, respectively.

tively understand this transition from $\beta \propto d^{+\sigma_{NL}}$ in covalent bonds, to $\beta \propto d^{-\sigma_{NL}}$ in ionic bonds, and to relate it to the unusual behavior of several ferroelectric crystals. In particular, we will try to explain why LiTaO_3 has an anomalously small¹⁸ d_{31} nonlinear coefficient compared with the similar isomorphous LiNbO_3 . We will also investigate the unusual result that d_{33} has *opposite* signs¹⁹ in the isomorphous compounds BaTiO_3 and PbTiO_3 , and that PbTiO_3 and also $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ (Ref. 20) have two of the largest deviations from the usually accurate Jerphagnon relation²¹ between the spontaneous polarization P_s and the vector part of the Miller's normalized nonlinear susceptibility²² Δ_v (i. e., $\Delta_v \propto -P_s$).

II. LINEAR SUSCEPTIBILITY

Owing to the similarity of Eqs. (3) and (5) it is helpful to begin by discussing the behavior of the linear susceptibility. It is well known²³ that for significantly covalent crystals (e. g., Ge, GaAs, ZnS, MgO, etc.) the linear susceptibility $\chi = (n^2 - 1)/4\pi$ *decreases* under hydrostatic pressure (i. e., $\chi \propto d^{+\sigma_L}$), whereas for highly ionic crystals (e. g., NaCl, LiF, BaF_2 , etc.) χ *increases* with hydrostatic pressure (i. e., $\chi \propto d^{-\sigma_L}$). The close similarity of this linear behavior [illustrated in Fig. 1(b)] with the nonlinear behavior previously discussed [Fig. 1(a)] suggests a common origin for these two phenomena.

In order to examine in detail the dependence of χ on d we use Phillips and Van Vechten's¹⁵ formulation for the linear susceptibility, namely,

$$\chi = (\hbar\Omega_p)^2/E_g^2, \quad (7)$$

where Ω_p is the plasma frequency (including d -band effects if any) and the average energy gap is given by

$$E_g^2 = E_h^2 + C^2, \quad (8)$$

where E_h is the covalent contribution to the total gap,

$$E_h \propto d^{-s} \quad (s = 2.48) \quad (9)$$

and where C is the ionic contribution to the gap, so called since the ionicity is given by

$$f_i = C^2/E_g^2. \quad (10)$$

In terms of the fundamental bond parameters C can be expressed as

$$C = be^{-kr} \left(\frac{Z_\alpha}{r} - \frac{Z_\beta}{r} \right) e^2 \quad (11)$$

(where $r \equiv \frac{1}{2}d$). That is, C is the electronegativity difference between the two bonding atoms (α and β) and vanishes if they are identical. More precisely, C is the difference between the Coulomb potentials Z_α/r of the two atoms composing the bond. The

bare core charges are Z_α and Z_β and these Coulomb potentials are evaluated at the bonding site³ ($r = \frac{1}{2}d$), i. e., at the position of the most mobile electrons, which are those contributing most strongly to χ . Only a small fraction of the electrons are in the bond, however; the remainder screen the ion cores, reducing their charge by the Thomas-Fermi screening factor¹⁵ e^{-kr} (i. e., $Z_{\text{eff}} = e^{-kr} Z_\alpha$). Because the true screening behavior of a solid will be more complex than this simple Thomas-Fermi description a dimensionless correction factor b of order unity is necessary.

Since the Thomas-Fermi screening assumes a free-electron gas it is clearly a more appropriate approximation for covalent semiconductors (e. g., GaAs, etc.) than for highly ionic insulators such as NaCl. To get a feeling for the expected behavior of the prescreening factor b , in a relatively tightly bound crystal such as NaCl, it is instructive to first consider the extreme situation of very tightly bound core electrons, for which atomic, i. e., Slater, screening^{2,24} is appropriate. It is well known² that Slater screening is far less effective than Thomas-Fermi screening and consequently the effective charge Z_{eff} seen by such tightly bound electrons is larger than that seen by loosely bound valence electrons, for which the Thomas-Fermi screening is appropriate, i. e., $Z_{\text{eff}}(\text{Slater}) > be^{-kr} Z_\alpha$. This was also previously² found to be the case for the more tightly bound d electrons. Of course, even rather ionic compounds such as NaCl are much less tightly bound than the atomiclike core electrons just discussed and therefore Slater screening is not really very appropriate. However, the general trend we observed of increasing Z_{eff} , i. e., increasing b , with increasing ionicity would be expected to hold roughly. Physically, this result can be readily interpreted as due simply to the fact that in more covalent bonds the electrons are more mobile and can therefore screen the core Z_α more effectively.

Actually b is most closely related to the average coordination number¹ \bar{N}_c of the compound, and therefore indirectly related to the ionicity. However, this ionicity dependence can be clearly seen, since as f_i is increased (keeping the number of electrons per atom the same) there are phase changes to structures with larger \bar{N}_c . That is, for the ionicity larger than a critical ionicity $f_i > f_{\text{crit}}$ a crystallographic phase change occurs.²⁵ For example, consider the $A^N B^{8-N}$ system. For low ionicity (e. g., Ge, GaAs, ZnSe, etc.) the stable phase is zinc blende, for which $\bar{N}_c = 4$ and $b = 1.6$,¹ for large ionicities ($f_i > 0.79$) the NaCl structure, for which $\bar{N}_c = 6$ and $b = 3.4$,¹ is stable, and finally for extremely large ionicities ($f_i > 0.96$) the CsCl structure, for which $\bar{N}_c = 8$ and $b = 6.1$,¹ is stable.

Van Vechten¹⁵ has shown that the ionic-covalent transition exhibited in Fig. 1(b) can be explained by calculating the bond-length dependence of the linear susceptibility²⁶ using Eqs. (4) and (7)–(11), yielding

$$\sigma_L = (2s - 3) + [2(1 - s) + kr - 2\sigma_b] f_i \quad (12)$$

[with $s = 2.48$ from Eq. (9)], where

$$\sigma_b \equiv \frac{d}{b} \frac{\partial b}{\partial d}, \quad (13)$$

i. e., σ_b is the power-law dependence of the pre-screening factor b on bond length ($b \propto d^{\sigma_b}$). Thus, using Eq. (12) experimental values for σ_b can be determined from the experimental measurements of σ_L . The striking dependence of σ_b on ionicity (determined from the *linear* susceptibility) is shown as full circles in Fig. 2. We have also included the set of cubic crystals CaF_2 , SrF_2 , and BaF_2 (Ref. 27) (the most ionic crystals known¹) as well as the very interesting noble- and transition-metal compounds SiTiO_3 ,²⁸ CuCl ,²⁹ and AgCl .²⁹ SrTiO_3 is the prototype structure for the ferroelectric crystals BaTiO_3 and PbTiO_3 , and as we

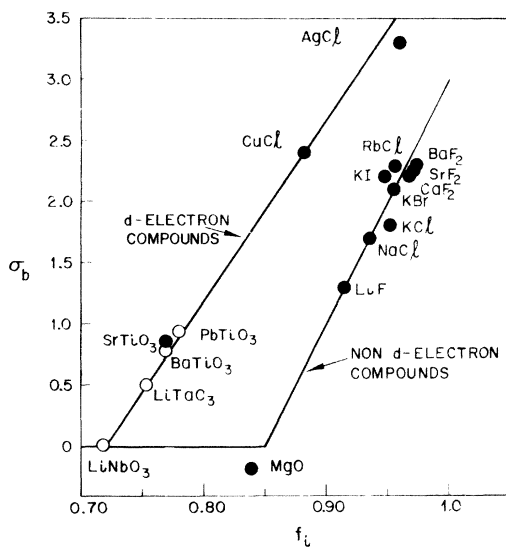


FIG. 2. Plot of experimental values of $\sigma_b \equiv (d/b)(\partial b/\partial d)$ obtained from pressure dependence of the index of refraction [i. e., $\sigma_b(L)$, plotted as filled circles] as a function of ionicity. The lower ionicity curve is for *d*-electron compounds, while the higher ionicity curve is for non-*d*-electron compounds. Note the critical ionicities on both curves ($F_d = 0.72$, and $F = 0.85$) below which $\sigma_b = 0$ and above which σ_b increases rapidly with ionicity. The unfilled circles are obtained from experimental data on the transition-metal bond nonlinearities $\beta(\text{Nb-O})$, $\beta(\text{Ta-O})$, and $\beta(\text{Ti-O})$ [i. e., $\sigma_b(\text{NL})$ from Tables I and II]. Note the good agreement between these two methods of obtaining σ_b .

will see later all these compounds have very similar values of σ_b . Only the full circles (determined from the *linear* susceptibility) are important for the present discussion. The open circles determined from the *nonlinear* susceptibility will be discussed later.

Note that there are *two* best-fit straight lines, drawn through experimental linear-susceptibility results, one for the *d*-electron noble- and transition-metal compounds and the other for non-*d*-electron crystals. (We will shortly discuss the reason for this difference.) Both of these lines result in a critical ionicity F (for the *d*-electron compounds $F_d = 0.72$, while for the non-*d*-electron crystals $F = 0.85$) such that $\sigma_b = 0$ for compounds having $f_i < F$, F_d . (Van Vechten¹⁵ has found that $\sigma_b = 0$ gives a satisfactory description of even less-ionic compounds than those included in Fig. 2.) For the opposite situation, $f_i > F$, F_d , σ_b rises rapidly and reaches values as large as $\sigma_b \sim 3$. This sharp transition from covalent to ionic behavior is similar to that found in a number of other properties.³⁰

The result $\sigma_b = 0$ for the covalent compounds is not unexpected.¹ It means, as discussed before, that the Thomas-Fermi free-electron screening is a good approximation for the highly mobile bonding electrons, and therefore all that is required to correct for the non-free-electron behavior of the bond is a simple multiplicative constant. That is, b is highly constant (as found to be accurately true,¹ within a given crystal structure, for very wide variety of compounds and structures); hence $\partial b/\partial d = 0$, resulting in $\sigma_b = 0$.

It is well known that owing to the strength of covalent bonds, they are significantly shorter than ionic bonds (e. g., the ionicity¹ of the rocksalt crystals MgS and NaCl are 0.79 and 0.94, respectively, while their bond lengths are 4.92 Å and 5.32 Å, respectively). Thus, as the bond length increases this corresponds to a larger ionicity. As discussed above, b increases with ionicity and hence we conclude that b should increase with bond length d for highly ionic compounds, i. e., $\sigma_b > 0$, as is indeed observed in Fig. 2. Another way of saying this is that as d increases it is more difficult for the valence electrons to screen the core charges, and this corresponds to a larger b . This argument may be made more quantitative from the following considerations.¹⁵ In the ionic limit ($f_i \rightarrow 1$) the ionic gap C is expected to be approximately a maximum with respect to the bond length, i. e., $(d/C)(\partial C/\partial d) \sim 0$. The reason for this is that for such highly ionic compounds, this condition minimizes the total energy, since the Madelung energy makes the dominant contribution to the cohesive energy. Thus, assuming $(d/C)(\partial C/\partial d) = 0$, we obtain the following approximate value for

σ_b in highly ionic crystals¹⁵:

$$\sigma_b \approx (1 + \frac{1}{2}kr) \approx 2.5. \quad (14)$$

This estimate is in approximate agreement with the experimental σ_b values for the highly ionic crystals in Fig. 2.

The fact that $F = 0.85$ for the *non-d-electron* crystals, whereas $F_d = 0.72$ for the more complex transition-metal compounds which have *strong d-electron* effects, does not seem unreasonable. This is especially true since, as discussed previously,² the presence of such *d* electrons strongly influences the screening behavior of the bond (i. e., the Thomas-Fermi prescreening factor *b* of the *d*-electron atom) as evidenced by the observation² that $(Z_a^*)_{eff}$ for a noble- or transition-metal atom may be significantly different from the number of valence electrons. Further, we have shown² that the *d* electrons increase χ and hence *decrease* f_i , so that transition-metal compounds have significantly lower ionicities than isomorphous non-*d*-electron analogs. For example, while the ionicity¹ of GeO_2 is $f_i = 0.730$, that of TiO_2 is only² $f_i = 0.686$. An even better example is the comparison between² $f_i(\text{Al}_2\text{O}_3) = 0.80$ and $f_i(\text{Fe}_2\text{O}_3) = 0.68$, where the lowering of the transition-metal ionicity is close to that observed between the critical ionicities (F and F_d) for the transition- and nontransition-metal compounds. Thus, it seems rather appealing that the *d*-electron line, in Fig. 2, can be approximately obtained by simply shifting the non-*d*-electron line to a lower ionicity value. Further, as discussed above, since the *d* electrons are more tightly bound than the *s* and *p* valence electrons, they would be expected to have larger σ_b values.

III. NONLINEAR SUSCEPTIBILITY

A. LiNbO_3 , LiTaO_3

The calculation of the average bond nonlinearities β and Miller's delta,⁹ $\Delta \equiv \beta/\chi^3$, do not require the knowledge of σ_{NL} and can be readily and accurately evaluated using the previously derived³ theoretical expression [written for ABO_3 compounds³¹ in esu, i. e., $(\text{cm}/\text{statvolt})\text{cm}^3$]

$$\beta = \frac{600 be^{-kr}(Z_a + \frac{3}{2}Z_b)\chi_b^2 C}{E_e^2 d^2(q/e)} \text{ esu}, \quad (15)$$

where χ_b is the linear susceptibility of a single bond and where (q/e) is the bond charge³ in units of the electronic charge. By using Eqs. (10) and (11), this expression can be simplified to

$$\beta \propto \chi_b^2 f_i, \quad (16)$$

where we have only exhibited the most significant parameters. Physically the meaning of Eq. (16) is that the nonlinear susceptibility β increases as the linear susceptibility χ_b does (which is reason-

able as discussed earlier) and also that β increases with f_i since this is associated with a larger acentricity in the bond.

We will shortly return to the numerical evaluation of β using Eq. (15) but first we turn to the determination of σ_{NL} [Eq. (6)] using the approach discussed previously.³ That is, by differentiating the theoretical expression for β [i. e., Eq. (15)] we find

$$\sigma_{NL} = \sigma_0 - (6f_i - 2)\sigma_b, \quad (17)$$

where σ_0 is the power dependence found previously³ by assuming $\sigma_b = 0$ and is given by

$$\sigma_0 = (6s - kr - 9) - [6(s - 1) - 3kr]f_i. \quad (18)$$

Equations (15) and (18) were used to calculate³ the nonlinearities for the significantly covalent (i. e., $f_i < F$, F_d) compounds LiNbO_3 , $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$, and GaAs , and excellent agreement with experiment was found. In particular, Eq. (18) accurately predicted both the magnitude and sign of the higher-order acoustically induced optical harmonic coefficient^{11,14} for GaAs , as well as d_{31} for LiNbO_3 , which is directly proportional to σ_0 . Thus confirming, as indicated in Fig. 2, that for covalent compounds the σ_b term in Eq. (17) can be neglected.³² In order to observe its influence we now consider more ionic compounds. We begin with the interesting crystal LiTaO_3 , which is isomorphous to LiNbO_3 but slightly more ionic.

For completeness in calculating d_{ijk} for LiNbO_3 and LiTaO_3 , we include the small contribution of the Li-O bonds. To do this we require the individual contributions of the Li-O, Nb-O, and Ta-O bonds to the linear susceptibility. These can be determined with sufficient accuracy as follows. Following previous work¹⁻³ we decompose LiNbO_3 and LiTaO_3 into their constitutive bond contributions,

$$\chi(\text{LiNbO}_3) = \frac{1}{2} [\chi(\text{Li-O}) + \chi(\text{Nb-O})], \quad (19)$$

$$\chi(\text{LiTaO}_3) = \frac{1}{2} [\chi(\text{Li-O}) + \chi(\text{Ta-O})].$$

Using the ratio of $\chi(\text{Nb-O})$ to that of $\chi(\text{Ta-O})$ determined from the measured long-wavelength indices³³ of Nb_2O_5 and Ta_2O_5 ($n = 2.23$ and $n = 2.13$, respectively) yields $\chi(\text{Nb-O})/\chi(\text{Ta-O}) = 1.12$. Combining this with Eq. (19) and the known³⁴ long-wavelength indices for LiNbO_3 and LiTaO_3 ($n = 2.11$ and $n = 2.04$, respectively) yields the values listed in Table I. We find, as expected, that most of the crystal linear susceptibility (83% in LiNbO_3 and 81% in LiTaO_3) resides in the highly polarizable transition-metal bonds. The other linear and nonlinear parameters obtained following previous work¹⁻³ are also given in Table I.³⁵ The average coordination numbers for the various bonds $\bar{N}_c(A-B)$ were calculated using (for, say, LiNbO_3)

TABLE I. Linear and nonlinear bond parameters for the isomorphous crystals LiNbO_3 and LiTaO_3 . Note that as expected, the nonlinearity of the Li-O bond is negligible. The theoretical nonlinearities of the Nb-O and Ta-O bonds are exactly the same as those determined previously (in Ref. 3) by neglecting the Li-O bonds, and are in good agreement with experiment. For conversion of the experimental results used in Tables I-III to absolute values, we have used the determination of B. F. Levine and C. G. Bethea, Appl. Phys. Lett. 20, 272 (1972). That is, we have multiplied the nonlinear susceptibilities which were measured relative to quartz, by the nonlinear susceptibility of quartz, i. e., $d_{11}(\text{quartz}) = 0.80 \times 10^{-9}$ esu.

	LiNbO_3		LiTaO_3	
	Li-O	Nb-O	Li-O	Ta-O
d (Å)	2.15	2.00	2.18	1.98
$4\pi\chi^\mu$	1.2	5.7	1.2	5.1
χ_b (Å ³)	0.42	2.01	0.42	1.78
Z_α^*	...	6.2	...	5.9
C (eV)	16.4	11.3	16.2	12.9
E_h (eV)	6.0	7.1	5.8	7.3
f_i	0.884	0.717	0.888	0.756
Δ^{calc} (10^{-28} esu)	+0.01	+2.0	+0.01	+1.7
Δ^{expt} (10^{-28} esu)	...	+1.9	...	+1.9
β^{calc} (10^{-30} esu)	+0.03	+6.3	+0.03	+3.9
β^{expt} (10^{-30} esu)	...	+6.0	...	+4.3
σ_{NL}	...	+2.0	...	+0.9
$\sigma_b(\text{NL})$...	≈ 0	...	+0.50
$\sigma_b(\text{L})$...	0	...	+0.50

$$\bar{N}_c(\text{Li-O}) = f_{\text{cat}} N_c(\text{Li}) + f_{\text{an}} N_c(\text{O}), \quad (20)$$

$$\bar{N}_c(\text{Nb-O}) = f_{\text{cat}} N_c(\text{Nb}) + f_{\text{an}} N_c(\text{O}),$$

where, for example, $N_c(\text{Li})$ is the average coordination number of the Li atoms, f_{an} is the atomic fraction of anions in the molecule, and f_{cat} is the atomic fraction of cations.³⁶

Using the linear bond parameters given in Table I together with Eq. (15) results in the bond nonlinearities β and Δ also given in Table I. These values, so obtained, are all rather similar to those previously obtained³ with the neglect of the Li-O bond. In particular, note that $\Delta(\text{Li-O}) \ll \Delta(\text{Nb-O})$ as expected³⁷; further, the calculated bond nonlinearities $\Delta(\text{Nb-O}) = 2.0 \times 10^{-28}$ esu and $\Delta(\text{Ta-O}) = 1.7 \times 10^{-28}$ esu are exactly the same as those obtained previously³ by completely neglecting the Li-O bond, and are in excellent agreement with the experimental value³⁷ $\Delta(\text{Nb-O}) = \Delta(\text{Ta-O}) = 1.9 \times 10^{-28}$ esu.

We have also listed the values for the various σ 's

in Table I. The values of $\sigma_b(\text{NL})$ were obtained from Eq. (17) using the experimental values³⁷ for σ_{NL} , while the values of $\sigma_b(\text{L})$ were obtained from Fig. 2 [i. e., from Eq. (1)] using the known ionicities (also given in Table I). Note that the actual numerical values, for LiTaO_3 , of the linear and nonlinear determinations of $\sigma_b(\text{Ta-O})$ are in good agreement namely, $\sigma_b(\text{L}) = +0.50$ and $\sigma_b(\text{NL}) = +0.50$. That is, the value of $\sigma_b(\text{NL})$ for the Ta-O bond in LiTaO_3 (indicated by an open circle in Fig. 2) lies on the straight line determined from the linear data.

It is also noteworthy that as expected $\sigma_b(\text{Nb-O}) \approx 0$ since $f_i(\text{Nb-O}) < F_d$, while $\sigma_b(\text{Ta-O}) \neq 0$ since $f_i(\text{Ta-O}) > F_d$. This behavior is, in fact, responsible for the anomalously small value of $d_{31}(\text{LiTaO}_3)$ compared with that of $d_{31}(\text{LiNbO}_3)$. That is, the larger σ_b for the Ta-O bond reduces the net power dependence σ_{NL} [see Eq. (17)] and since $d_{31} \propto \sigma_{\text{NL}}$, a small value for d_{31} results.

B. BaTiO_3 , PbTiO_3

The unusual pair of compounds BaTiO_3 and PbTiO_3 gives us a further opportunity to test these ideas. As previously mentioned, d_{33} of BaTiO_3 and PbTiO_3 have opposite signs.¹⁹ Before investigating whether Eq. (17) is related to this unusual behavior, it seems reasonable to first check whether the linear properties of the Pb-O bond are unusual. (The Ba-O and Ti-O bonds have already been discussed^{1,2} and were found to behave as expected.) The bond parameters for PbO_2 , which is isomorphous with GeO_2 , SnO_2 , and TiO_2 , are the following: $\epsilon = 4.1$, $E_h = 6.0$ eV, $C = 12.2$ eV, $b = 1.38$, and $f_i = 0.806$. These are in no way unusual being, in fact, all very similar to the other isomorphous compounds. Thus, the sign difference in d_{33} for BaTiO_3 and PbTiO_3 is not simply related to any peculiar linear properties of the Pb-O bond.

To calculate the nonlinear susceptibilities in these compounds, we first need to determine the linear susceptibilities from^{1,2}

$$\chi(\text{BaTiO}_3) = \frac{2}{3} \chi(\text{Ba-O}) + \frac{1}{3} \chi(\text{Ti-O}), \quad (21)$$

$$\chi(\text{PbTiO}_3) = \frac{2}{3} \chi(\text{Pb-O}) + \frac{1}{3} \chi(\text{Ti-O})$$

(note $\frac{2}{3}$ of the bonds are Ba-O and only $\frac{1}{3}$ are Ti-O). We can determine the susceptibility of the Ti-O bond by making use of the closely related simpler compound TiO_2 . Obtaining $\chi_b(\text{Ti-O})$ from TiO_2 and combining this with Eq. (21) results in the linear susceptibilities given in Table II. In order to evaluate the bond volumes v_b when the average coordination number \bar{N}_c [given by Eq. (20)] for the two bonds μ and ν are unequal we suggest the following simple generalization of the expression used previously^{1,2}:

$$\frac{v_b^\mu}{v_b^\nu} = \left(\frac{d^\mu}{d^\nu} \right)^3 \frac{\bar{N}_c^\nu}{\bar{N}_c^\mu} \quad (22)$$

That is, we have made the reasonable assumption that as the average coordination number \bar{N}_c increases the bond volume decreases. The results for the linear and nonlinear bond properties of BaTiO_3 are given in Table II.^{38,39} The experimental values of $\beta(\text{Ti-O})$ and $\sigma(\text{Ti-O})$ are obtained by neglecting $\beta(\text{Ba-O})$ since the theoretical value of $\beta(\text{Ba-O})$ is only 1% of $\beta(\text{Ti-O})$.

Note that the large magnitude of the Ti-O bond nonlinearity³⁷ $\beta(\text{Ti-O}) > \beta(\text{Nb-O}) > \beta(\text{Ta-O})$ is well accounted for theoretically. A significant contributor to this large β is the large linear polarizability of the Ti-O bond. The reason for the small value of $d_{33}(\text{BaTiO}_3)$ in spite of this large $\beta(\text{Ti-O})$ is that the ionicity of the Ti-O bond is close to the critical ionicity. This results (see Fig. 2) in the unusually small value of $\sigma_{\text{NL}}(\text{Ti-O}) = +0.30$. This small σ_{NL} does not, however, reduce the d_{31} component so that, in fact, $d_{31}(\text{BaTiO}_3) \approx 3d_{31}(\text{LiNbO}_3)$. Thus, new compounds containing the Ti-O bond have promise of having rather large

phase-matchable nonlinearities. Actually this small value of $\sigma_{\text{NL}}(\text{Ti-O})$ is not unexpected since, in fact, it corresponds to a value [from Eq. (17)] of $\sigma_b(\text{Ti-O}) = +0.78$, which is close to that found ($\sigma_b = +0.86$) from the pressure dependence of the linear susceptibility in the similar compound SrTiO_3 (see Fig. 2). This value is also close to $\sigma_b = +0.72$ obtained directly from the d -electron line in Fig. 2 by using the known ionicity $f_i(\text{Ti-O}) = 0.768$ from Table II.

With the aid of the experimentally determined values of β and σ for the Ti-O bond for BaTiO_3 (given in Table II), we can now obtain the experimental values of the Pb-O bond in PbTiO_3 . In order to do this we must take into account (using Fig. 2) the slightly higher ionicity of the Ti-O bond in PbTiO_3 as compared with BaTiO_3 (see Table II). The major effect of this is to cause σ_b to increase somewhat [from $\sigma_b(\text{Ti-O}) = 0.78$ in BaTiO_3 to $\sigma_b(\text{Ti-O}) = 0.93$ in PbTiO_3 as shown in Table II], since as Fig. 2 indicates σ_b increases rapidly with ionicity. Further, this large f_i causes a slight increase of β in PbTiO_3 as Eq. (16) and the $\beta^{\text{calc}}(\text{Ti-O})$ row of Table II show. From these considerations, we can determine the experimental values for $\beta(\text{Ti-O})$, $\sigma(\text{Ti-O})$, and hence also $\beta(\text{Pb-O})$ and $\sigma(\text{Pb-O})$ by obtaining the best fit to the PbTiO_3 experimental d_{33} and d_{31} measurements. These results are given in Table II.⁴⁰ It should be noted that owing to the relatively small value of $\beta(\text{Pb-O})$ the experimentally determined bond parameters β and σ for Pb-O are significantly less accurate (errors of order $\sim 30\%$) than those for the Ti-O bond.⁴¹ As demonstrated in Table II, these experimental bond nonlinearities, $\beta(\text{Pb-O})$ and $\beta(\text{Ti-O})$, are in good agreement with those calculated using Eq. (15). The power dependence $\sigma_b(\text{NL})$ determined from this nonlinear experimental fit are also in good agreement with those, $\sigma_b(\text{L})$, determined from Fig. 2.

In spite of the great similarity between the various linear and nonlinear bond parameters for the Ti-O bond in BaTiO_3 and PbTiO_3 , there is one striking and significant difference between them, namely, that the *net* dependence σ_{NL} of β on the bond length is *positive* for BaTiO_3 and *negative* for PbTiO_3 ; i. e., β increases with d in BaTiO_3 and decreases with d in PbTiO_3 . This remarkable difference in behavior between these two compounds is simply a result of the near cancellation in Eq. (17) between the σ_0 and σ_b contributions. Because of this cancellation, the small increase in σ_b in going from BaTiO_3 to PbTiO_3 (caused by the small ionicity increase) is sufficient to change the sign of the small net σ_{NL} .

In order to see more clearly the role of these parameters in determining the net crystal d_{ijk} coefficients it is helpful to look at the relationship between d_{ijk} and the individual bond β and σ_{NL} val-

TABLE II. Linear and nonlinear bond parameters for the isomorphous crystals BaTiO_3 and PbTiO_3 . Note that the bond nonlinearity β of the Pb-O bond is over five times as large as that of the Ba-O bond, and makes, in fact, a contribution to $d_{33}(\text{PbTiO}_3)$ which is comparable to that of the Ti-O bond. The agreement between the calculated and experimental bond nonlinearities is good. Owing to the small value of $\beta(\text{Pb-O})$ relative to $\beta(\text{Ti-O})$ the experimentally determined Pb-O nonlinear bond parameters are not as accurate as those for the Ti-O bond.

	BaTiO_3		PbTiO_3	
	Ba-O	Ti-O	Pb-O	Ti-O
d (Å)	2.81	2.00	2.84	2.00
$4\pi\chi^\mu$	2.41	7.74	4.17	7.74
χ_b (Å ³)	0.68	2.20	1.19	2.20
Z_α^*	...	7.1	...	7.1
C (eV)	15.5	13.0	10.2	13.4
E_h (eV)	3.1	7.1	3.0	7.1
f_i	0.962	0.768	0.922	0.779
Δ^{calc} (10^{-28} esu)	+0.04	+3.5	+0.11	+1.7
Δ^{expt} (10^{-28} esu)	...	+4.2	+0.09	+2.3
β^{calc} (10^{-30} esu)	+0.2	+17	+1.1	+18
β^{expt} (10^{-30} esu)	...	+21	$\sim +1.5$	+25
σ_{NL}	...	+0.30	-4.0	-0.14
$\sigma_b(\text{L})$...	+0.72	+1.5	+0.89
$\sigma_b(\text{NL})$...	+0.78	$\sim +2$	+0.93

ues. The d_{33} coefficient is especially interesting owing to the comparable contributions of both types of bonds and is given [with the aid of Eq. (2)] by

$$\begin{aligned} d_{33}(\text{PbTiO}_3) \times 10^{21} = & \{- [14 + 5\sigma_{\text{NL}}(\text{Pb-O})] \beta(\text{Pb-O}) \\ & - 2.9\sigma_{\text{NL}}(\text{Ti-O}) \beta(\text{Ti-O})\} \\ = & +18.7 \times 10^{-9} \text{ esu (experiment).} \end{aligned} \quad (23)$$

Note that the Pb-O bond has a rotation contribution in addition to the bond-stretching contribution [proportional to $\sigma_{\text{NL}}(\text{Pb-O})$], whereas the Ti-O bond only has a bond-stretching term. Therefore, if $\sigma_{\text{NL}}(\text{Ti-O})$ were zero (i.e., all bonds has the same nonlinearity β), then the Ti-O bonds would make no contributions to d_{33} .

The above expression, which exhibits the proportionality between the Ti-O bond contribution and $\sigma_{\text{NL}}(\text{Ti-O})$ clearly shows the importance of the sign change in $\sigma_{\text{NL}}(\text{Ti-O})$ between BaTiO_3 and PbTiO_3 , and its direct relationship to the sign change between $d_{33}(\text{BaTiO}_3)$ and $d_{33}(\text{PbTiO}_3)$. Since $\sigma_{\text{NL}}(\text{Ti-O}) < 0$ for PbTiO_3 , the Ti-O bonds make a positive contribution to d_{33} , in agreement with the positive experimental value for d_{33} ; for BaTiO_3 $\sigma_{\text{NL}}(\text{Ti-O}) > 0$ and thus the Ti-O bonds make a negative contribution to d_{33} . The other contributing factor toward making $d_{33}(\text{PbTiO}_3) > 0$ is that $\sigma_{\text{NL}}(\text{Pb-O})$ is large and negative making the factor multiplying $\beta(\text{Pb-O})$ positive. [Since $\beta(\text{Ba-O}) \ll \beta(\text{Pb-O})$, there is no corresponding contribution by the Ba-O bond in BaTiO_3 .] It is noteworthy that this Pb-O contribution to d_{33} is comparable to that of the Ti-O bond in spite of the fact that $\beta(\text{Pb-O}) \ll \beta(\text{Ti-O})$. This is simply a result of the very small value of $\sigma_{\text{NL}}(\text{Ti-O}) \ll \sigma_{\text{NL}}(\text{Pb-O})$ multiplying $\beta(\text{Ti-O})$ in Eq. (23).

The situation is different for the d_{31} coefficient, since as the relation below shows,

$$\begin{aligned} d_{31}(\text{PbTiO}_3) \times 10^{21} = & \{- [3.6 + 2.7\sigma_{\text{NL}}(\text{Pb-O})] \beta(\text{Pb-O}) \\ & - 3.9 \beta(\text{Ti-O})\} \\ = & -88.6 \times 10^{-9} \text{ esu (experiment),} \end{aligned} \quad (24)$$

the Ti-O bond makes a negative contribution to d_{31} which is approximately independent of either the magnitude or sign of $\sigma_{\text{NL}}(\text{Ti-O})$. As can be seen from the above equation, the Ti-O bond makes the dominant contribution to d_{31} [since $\beta(\text{Ti-O}) \gg \beta(\text{Pb-O})$], explaining why d_{31} of both BaTiO_3 and PbTiO_3 have the *same* sign whereas the d_{33} have the *opposite* sign.

These comments also help explain why the value of $\Delta_v \equiv \Delta_{33} + 2\Delta_{31}$ is smaller than expected from the Jerphagnon relation [$\Delta_v \propto (-P_s)$] between the vector part of Miller's delta, Δ_v , and the spontaneous polarization P_s . That is, Δ_v is small in PbTiO_3 because d_{33} is positive (for the reasons discussed

above) and hence this positive d_{33} partially cancels the larger negative value of d_{31} . This does not happen in BaTiO_3 , for which the Jerphagnon relation is well satisfied.

C. $\text{Pb}_5\text{Ge}_3\text{O}_{11}$

$\text{Pb}_5\text{Ge}_3\text{O}_{11}$ is another lead compound which is in poor agreement²⁰ with the Jerphagnon relation.²¹ In fact, it not only disagrees in magnitude (by a factor of ~ 10), but also in sign. Most of the nonlinearity d_{ijk} is due to the Pb-O bonds as can be seen by comparing $\beta(\text{Pb-O}) = +1.5 \times 10^{-30}$ esu (from PbTiO_3) with $\beta(\text{Ge-O}) = -0.3 \times 10^{-30}$ esu (from ${}^3\text{GeO}_2$). Since the geometrical factors for the Pb-O and Ge-O bonds are similar, we can concentrate on just the Pb-O bonds. A good empirical fit to experiment, shown in Table III, is obtained using $\beta(\text{Pb-O}) = +2.4 \times 10^{-30}$ esu and $\sigma_{\text{NL}}(\text{Pb-O}) = -0.5$ [i.e., $\sigma_b(\text{Pb-O}) = +1.15$]. It is noteworthy that $\beta(\text{Pb-O})$ is similar in both $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ and PbTiO_3 despite their rather different structures (e.g., PbTiO_3 has only three Pb-O bond lengths whereas $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ has 24 unequal bond lengths per unit cell). The $\sigma_b(\text{Pb-O})$ value of $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ is in adequate agreement with Fig. 2 since it would correspond to an ionicity of $f_i \sim 0.91$, which seems reasonable compared to $f_i(\text{Pb-O}) = 0.92$ in PbTiO_3 .

It is worth noting that the small values of Δ_{ij} in $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ are simply due to the small "geometrical" (i.e., bond rotation and stretching) factors multiplying $\beta(\text{Pb-O})$ and $\beta(\text{Ge-O})$. That is, the small Δ_{ij} are not due to any near cancellation between the positive $\beta(\text{Pb-O})$ and the negative $\beta(\text{Ge-O})$. Finally the reason for the wrong sign prediction of the Jerphagnon relation is directly related to the negative value of $\sigma_{\text{NL}}(\text{Pb-O})$. That is, by evaluating the geometrical factors for d_{ijk} (just as we did for PbTiO_3), one finds

$$\Delta_v \equiv \Delta_{33} + 2\Delta_{31} = -0.5\sigma_{\text{NL}}(\text{Pb-O}) \beta(\text{Pb-O}) N/\chi^3, \quad (25)$$

TABLE III. Comparison between experiment and an empirical fit using $\beta \propto d^{\text{NL}}$, with $\beta(\text{Pb-O}) = +2.4 \times 10^{-30}$ esu and $\sigma_{\text{NL}}(\text{Pb-O}) = -0.5$. Owing to the lack of absolute x-ray measurements, we cannot relate the fitted absolute signs of d_{11} and d_{22} (predicted to be negative) to the experimental ones (i.e., the handedness of the crystal is unknown). However, the relative experimental signs of d_{11} and d_{22} are the *same*, in agreement with the predictions of the empirical fit.

	$\text{Pb}_5\text{Ge}_3\text{O}_{11}$	
	Empirical fit (10^{-9} esu)	Experiment (10^{-9} esu)
d_{31}	+1.4	+1.3
d_{33}	-2.2	-2.0
d_{11}	-2.4	± 2.4
d_{22}	-3.5	± 3.2

where N is the number of unit cells per cm^3 . In LiNbO_3 , $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$, LiTaO_3 , and BaTiO_3 , for example,⁴² the relevant σ_{NL} is *positive* and Δ_v is *negative*, in agreement with the Jerphagnon relation $\Delta_v \propto -P_s$, which also predicts a negative Δ_v (taking P_s as the positive direction). However, in $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ the power dependence $\sigma_{\text{NL}}(\text{Pb-O})$ is *negative* and as Eq. (25) shows this produces a *positive* Δ_v which is in disagreement with the negative value predicted from $\Delta_v \propto -P_s$.

IV. SUMMARY AND CONCLUSIONS

We have discussed in detail the dependence of the bond nonlinear polarizability β on the bond length d (i. e., $\beta \propto d^{\sigma_{\text{NL}}}$, where σ_{NL} is the power dependence). Physically the reasons for this dependence of β on d are analogous to those for the bond-length dependence of the linear susceptibility χ . That is, for *covalent* bonds as d increases and the atom cores are separated further apart, the effective potential or energy gap E_g acting on the mobile bonding electrons decreases, thereby *increasing* both the linear and nonlinear polarizabilities. However, for highly *ionic* bonds the nonlinearity arises from the induced octupole moment induced in the anion by the charged cation. In this case, as d is *increased*, these induced moments decrease rapidly; hence β *decreases*. This sign change in the power dependence $\sigma_{\text{NL}}(\beta \propto d^{\sigma_{\text{NL}}})$ between covalent and ionic compounds was shown to be closely related to an analogous sign change in σ_L and the pressure dependence of the linear susceptibility (i. e., $\chi \propto d^{\sigma_L}$).

One important reason for this striking difference in behavior for covalent ($\beta \propto d^{+\sigma}$) and ionic ($\beta \propto d^{-\sigma}$) materials was found to be related to the difference

in validity of the free-electron Thomas-Fermi screening in each case. For the relatively loosely bound valence electrons in covalent bonds, the free-electron screening was found to be adequate. However, for the more tightly bound ionic crystals, more atomiclike (and less efficient) screening became appropriate.

These differences in the dependence of β on d (i. e., the ionicity dependence of σ_{NL}) were shown to be crucial to an understanding of the unusual properties of several ferroelectrics. In particular, by using σ values determined from the *linear* susceptibility data we were able to quantitatively account for the small value of $d_{31}(\text{LiTaO}_3)$ as compared with $d_{31}(\text{LiNbO}_3)$, as well as the opposite signs of $d_{33}(\text{BaTiO}_3)$ and $d_{33}(\text{PbTiO}_3)$. The large deviations of PbTiO_3 and $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ from Jerphagnon's relation were also explained. For example, as Eq. (25) shows $\Delta_v(\text{Pb}_5\text{Ge}_3\text{O}_{11}) \propto (-\sigma_{\text{NL}})$. For relatively covalent ferroelectrics (e. g., LiNbO_3 and BaTiO_3) σ_{NL} is *positive* so that $\Delta_v < 0$ as predicted by the Jerphagnon relation. However, $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ is sufficiently ionic so that $\sigma_{\text{NL}} < 0$ and thus we predict $\Delta_v > 0$, in agreement with experiment, but opposite to the prediction of Jerphagnon's relation.

It would certainly be of great theoretical as well as practical interest (e. g., for far-ultraviolet nonlinear devices) to measure d_{ijk} for even more highly ionic, larger band-gap crystals such as fluorides.

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