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Bond-Charge Calculation of Electro-Optic Coefficients of Diatomic Crystals

Dongfeng Xue and Siyuan Zhang[1]

Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, Jilin, People's Republic of China

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A theoretical method has been set up to calculate the electro-optic tensor coefficients r_{ijk}, based on the Phillips–Van Vechten (PV) dielectric theory and the Levine bond charge model. Starting from the crystal structure data and only introducing the experimentally determined optical permittivity and dielectric constant, the electro-optic tensor coefficients r_{ijk} can be quantitatively predicted. The theoretical calculations are in good agreement with experiment in the case of zinc blende and wurtzite crystals. For zinc blende crystals, the effects of covalent radii on the linear electro-optic coefficients are discussed. © 1997 Academic Press

INTRODUCTION

The linear electro-optic (Pockels) effect may be regarded as the second-order polarization $P_i^{(\omega+\Omega)} = r_{ijk}E_j^{(\omega)}E_k^{(\Omega)}$ induced in the crystal under the action of a high-frequency field $E_j^{(\omega)}$ and a low-frequency field $E_k^{(\Omega)}$, where ω is a frequency well below the optical absorption but above the lattice resonance while Ω is below the latter. Physically, the applied static field $E_k^{(\Omega)}$ can be viewed as causing a change of the optical susceptibility of the medium, and consequently, the index of refraction at a frequency Ω. This causes the optical field to acquire sidebands at $\omega \pm n\Omega$. The large interest in this physical property is due in part to its wide application in light modulators and numerous laser devices.

The comprehensive theoretical understanding of the electro-optic effect must lead to the discovery of synthesis of the ideal material for a certain application in the scientific method. Several theoretical attempts to understand the electro-optic effect have been carried out since the late 1960s. Kelly (1) found an expression for the coefficient of zinc blende crystals, but the results was only applied to CuCl and ZnS with satisfactory agreement with measurements. The electrostatic point-charge model and dielectric theory were used to determine the electro-optic coefficients of III–V compounds (2) and II–VI crystals (3) by Flytzanis. Lately, a simple model was derived for calculating the electro-optic coefficient of diatomic crystals by Shih and Yariv (4). Unfortunately, each part of the contribution to the total electro-optic coefficient has not yet been quantitatively calculated to this day. One of the motivations in this work is to solve this problem; at the same time, a new simple and systemic model has been set up to deal with the calculation of electro-optic coefficients of diatomic crystals.

The simplest accentric crystals are the tetrahedrally coordinated zinc blende and wurtzite semiconductors showing a nonvanishing linear electro-optic effect, which has two contributions, the ionic contribution r_{ijk}(ionic) and the pure electronic contribution $r_{ijk}(C)$ and $r_{ijk}(E_\mathrm{h})$. In the present work we shall give a theoretical method derived from the localized bond-charge model of PV (5, 6), which can be applied to the calculation of r_{ijk} in these compounds.

THEORY

When the frequency of the applied electric field ω is high enough, the linear susceptibility will have a very simple expression

$$\chi(\infty) = (h\Omega_\mathrm{p})^2/E_\mathrm{g}^2 \qquad [1]$$

where Ω_p ($\Omega_\mathrm{p}^2 = 4\pi N_e e^2/m$) is the plasma frequency and E_g is the average energy gap, which can be separated into homopolar (E_h) and heterpolar (C) parts, namely, $E_\mathrm{g}^2 = E_\mathrm{h}^2 + C^2$. It is proposed that the generalized expressions used in the evaluation of E_h and C are (6, 7)

$$E_\mathrm{h}^{-2} = (39.74/d^s)^{-2}[(r_\alpha - r_\mathrm{c})^{2s} + (r_\beta - r_\mathrm{c})^{2s}]/2(r_0 - r_\mathrm{c})^{2s}, \quad s = 2.48 \qquad [2]$$

$$C = be^2 \exp(-k_s r_0)[Z_\alpha/r_0 - Z_\beta/r_0], \qquad [3]$$

where d is the bond length, $r_{\alpha,\beta}$ are the covalent radii of atoms α and β, r_c is the average core radius, and $r_0 = d/2$.

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[1] To whom correspondence should be addressed.

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When the low-frequency field $E_k^{(\Omega)}$ is applied to a crystal in the k direction, a relative displacement of atoms Δx_k will be induced; just as shown in Fig. 1d of Shih and Yariv (4), it induces a displacement of the bond charge Δx_k^q, a variation of the bond length Δd, and a bond rotation $\Delta\theta$.

The displacement Δx_k will induce a change in both Ω_p ($\Delta\Omega_p$) and E_g (ΔE_g) causing χ to change by $\Delta\chi^{(\Omega)}$, and the displacement Δr_α will produce a change in both E_h (ΔE_h) and C (ΔC) causing χ to change by $\Delta\chi^{(\omega)}$. From Eq. [1] we can write it as

$$\begin{aligned}\Delta\chi &= \Delta\chi^{(\Omega)} + \Delta\chi^{(\omega)}\\ &= h^2\Delta(\Omega_p)^2/E_g^2 - (\chi/E_g^2)[\Delta(E_h)^2 + \Delta(C)^2]_1\\ &\quad - (\chi/E_g^2)[\Delta(E_h)^2 + \Delta(C)^2]_2. \qquad [4]\end{aligned}$$

The second term on the right-hand side of Eq. [4] is caused by the variation of the bond length Δd; the last term is caused by the displacement of the bond charge Δr_α caused by the high-frequency field $E_j^{(\omega)}$.

$$\Delta(\Omega_p)^2 = -3\Omega_p^2\Delta d/d \qquad [5]$$

$$[\Delta(E_h)^2 + \Delta(C)^2]_1 = -[(k_s/2 + 2/d)f_i + sf_c/d]\Delta d \qquad [6]$$

$$\begin{aligned}[\Delta(E_h)^2 + \Delta(C)^2]_2 = \{&-4s(2s-1)[r_0/(r_0 - r_c)]^2E_h^2\rho/d\\ &-2be^2\exp(-k_sr_0)[Z_\alpha + Z_\beta]C/r_0^2\}\Delta r_\alpha, \qquad [7]\end{aligned}$$

where the ionicity and covalency of the bond are defined as $f_i = C^2/E_g^2$, $f_c = E_h^2/E_g^2$ (5, 6), and $\rho = (r_\alpha - r_\beta)/(r_\alpha + r_\beta)$ is the difference in the atomic sizes.

The linear macroscopic susceptibility tensor χ_{ij} can be expressed as

$$\chi_{ij} = V^{-1}\sum_\mu \chi^\mu\alpha_i^\mu(\lambda)\alpha_j^\mu(\lambda), \qquad [8]$$

where V is the volume of unit cell, $\alpha_i^\mu(\lambda)$ is the direction cosine with respect to the ith coordinate axis of the λth bond of type μ in the unit cell, and the sum on μ is over all bonds of type μ in the unit cell.

Further, we have

$$\Delta\chi_{ijk} = \Delta\chi_{ijk}^{(\Omega)} + \Delta\chi_{ijk}^{(\omega)}, \qquad [9]$$

where

$$\Delta\chi_{ijk}^{(\Omega)} = \chi/(Vr_0)\left[fG_{ijk} + \sum_\mu 1/2(\alpha_i^\mu(\lambda)\delta_{jk} + \alpha_j^\mu(\lambda)\delta_{ik})\right]\Delta x_k^q, \qquad [10]$$

where $f = (k_sr_0/2 - 1.48)f_i - 0.02$, and δ_{jk} is the Kronecker delta function (4).

$$\begin{aligned}\Delta\chi_{ijk}^{(\omega)} = \chi G_{ijk}/V\{&-4s(2s-1)[r_0/(r_0 - r_c)]^2f_c\rho/d\\ &- 2be^2\exp(-k_sr_0)[Z_\alpha + Z_\beta]C/(r_0^2E_g^2)\}\Delta r_\alpha, \qquad [11]\end{aligned}$$

where G_{ijk} is the geometrical factor,

$$G_{ijk} = \sum_\lambda \alpha_i^\mu(\lambda)\alpha_j^\mu(\lambda)\alpha_k^\mu(\lambda), \qquad [12]$$

in which the sum on λ is over all bonds of type μ in the unit cell.

The relative displacement of the bond charge Δx_k^q is related to the dielectric constant of the crystal by

$$Nq\Delta x_k^q = \varepsilon_0(\varepsilon'_{\mathrm{dc}k} - \varepsilon'_{\infty k})E_k^{(\Omega)}, \qquad [13]$$

where N is the number of bonds per unit cell, q is the bond charge (7), $\varepsilon'_{\mathrm{dc}}$ is the relative dielectric constant, and ε'_∞ is the relative optical permittivity. The bond charge q can be obtained by (7)

$$q/e = n_v(1/\varepsilon_\infty + f_c/3), \qquad [14]$$

where n_v is the number of valence electrons per bond.

The displacement Δr_α is related to the macroscopic measured susceptibility χ

$$Nq\Delta r_\alpha = \chi E_j^{(\omega)}. \qquad [15]$$

It is conventional to define the coefficient r_{ijk} in terms of change of $1/n_{ij}^2$, namely,

$$r_{ijk}E_j^s = \Delta(1/n^2)_{ij} = -\Delta\chi_{ijk}/\varepsilon'_i\varepsilon'_j. \qquad [16]$$

From Eqs. [9], [10], [11], and [16], it is a straightforward procedure to obtain

$$r_{ijk} = r_{ijk}(\text{ionic}) + r_{ijk}(C) + r_{ijk}(E_h), \qquad [17]$$

where

$$\begin{aligned}r_{ijk}(\text{ionic}) = {}&[-1/(\varepsilon'_i\varepsilon'_jqNr_0)]\chi\varepsilon_0(\varepsilon'_{\mathrm{dc}k} - \varepsilon'_{\infty k})\\ &\times[G_{ijk}f + \sum_\mu 1/2(\alpha_i^\mu(\lambda)\delta_{jk} + \alpha_j^\mu(\lambda)\delta_{ik})], \qquad [18]\end{aligned}$$

$$r_{ijk}(C) = [-2/(\varepsilon'_i\varepsilon'_jqNE_g^2)]G_{ijk}\chi^2be^2\exp(-k_sr_0)(Z_\alpha + Z_\beta)C/r_0^2, \qquad [19]$$

$$\begin{aligned}r_{ijk}(E_h) = {}&[-1/(\varepsilon'_i\varepsilon'_jqN)]\chi^2G_{ijk}(-4)s(2s-1)\\ &\times[r_0/(r_0 - r_c)]^2f_c\rho/d. \qquad [20]\end{aligned}$$

TABLE 1

Parameters and Calculated Results of the Electro-optic Coefficients for Zinc Blende Crystals and Comparisons of the Theoretical Prediction for r_{41} with Experimental Data

Crystal	GaP	GaAs	ZnS	ZnSe	ZnTe	CdTe	CuCl
a_0[a]	5.4505	5.6537	5.4093	5.6676	6.089	6.480	5.4057
d	2.3601	2.4481	2.3423	2.4511	2.6366	2.8059	2.3407
E_{h}	4.7246	4.3145	4.8141	4.3014	3.5895	3.0762	4.8222
C	2.9977	2.5685	5.2733	4.9065	3.4329	4.0408	8.2116
f_{c}	0.7130	0.7383	0.4546	0.4346	0.5223	0.3669	0.2564
ρ	0.0412	0.0244	0.0417	0.0364	− 0.0385	0.0000	0.0417
q/e	0.6834	0.6632	0.6306	0.5724	0.5563	0.4926	0.7250
$r_{41}(C)$	− 2.4601	− 2.5898	− 2.1733	− 2.8769	− 3.1385	− 5.0863	− 1.2827
$r_{41}(E_{\mathrm{h}})$	1.4639	1.0357	0.8771	0.9358	− 1.5339	0.0000	0.3213
r_{41}(ionic)	− 0.1096	− 0.0056	− 0.2734	− 0.2532	− 0.0399	− 0.1652	− 0.8127
$r_{41}^{\text{Calc.}}$	− 1.11	− 1.61	− 1.57	− 2.19	− 4.71	− 5.25	− 1.77
$r_{41}^{\text{Expt.}\,b}$	− 1.07	− 1.6	1.6	2.0	4.45	5.0	2.20

Note. All coefficients are in units of $10^{-12}\,\mathrm{mV}^{-1}$. $r^{\text{expt.}}$ are measurements with clamped crystals. Their signs are not yet determined, unless so specified.

[a] Ref. (9).

[b] Ref. (10).

Equation [18] is the final working expression for the ionic component of the electro-optic tensor r_{ijk}^{ion} presented by Shih and Yariv (4). The summation of the terms on the right-hand side of [19] and [20] is identical to the purely electronic contribution obtained from the coefficient of the second harmonic generation (SHG) (8), that is,

$$r_{ijk}(C) + r_{ijk}(E_{\mathrm{h}}) = -4d_{ijk}/\varepsilon_i'\varepsilon_j'. \qquad [21]$$

TABLE 2

Parameters and Calculated Results of the Electro-optic Coefficients for Wurtzite Crystals and Comparisons of the Theoretical Prediction for r_{33} with Experimental Data

Crystal	ZnO	ZnS	CdS	CdSe
a_0[a]	3.2495	3.811	4.1348	4.30
d	1.9809	2.3300	2.5320	2.6330
E_{h}	7.2947	4.8774	3.9686	3.6017
C	8.2656	5.7301	5.7407	5.2931
f_{c}	0.4378	0.4201	0.3234	0.3165
ρ	0.2874	0.0417	0.1098	0.0684
q/e	0.7356	0.6368	0.5904	0.5436
$r_{33}(C)$	− 1.6207	− 2.5898	− 3.7282	− 4.5769
$r_{33}(E_{\mathrm{h}})$	4.2172	0.8906	2.2736	1.6857
r_{33}(ionic)	− 0.6549	− 0.6549	− 1.0158	− 0.8960
$r_{33}^{\text{Calc.}}$	1.94	− 2.15	− 2.47	− 3.79
$r_{33}^{\text{Expt.}\,b}$	1.9	− 1.8	2.4	4.3

Note. All coefficients are in units of $10^{-12}\,\mathrm{mV}^{-1}$. $r^{\text{expt.}}$ are measurements with clamped crystals. Their signs are not yet determined, unless so specified.

[a] Ref. (9).

[b] Ref. (10).

Using Eqs. [18], [19], and [20], we have calculated the electro-optic coefficients of seven zinc blende crystals and four wurtzite crystals; the calculated values of r_{ijk} are compared with experimental data and are shown in Tables 1 and 2, respectively. The experimental data introduced in this paper are all from Ref. (10).

RESULTS AND DISCUSSION

Starting from the PV dielectric theory, just as Shih and Yariv had done (4), and the Levine bond-charge model, we have derived a general expression for the electro-optic coefficient of diatomic crystals, which shows clearly the quantitative relationship between the crystal structure and the crystal electro-optic property. From the calculated results in Tables 1 and 2, it can be seen that the most parts of contributions to the total electro-optic coefficient exist in $r_{ijk}(C)$ and $r_{ijk}(E_{\mathrm{h}})$, and the ionic contribution is quite small. This is in good agreement with the experimental observation (11) and the previous prediction (4). Therefore, it is reasonable to neglect the ionic contribution to the total electro-optic coefficient, experimentally. In our calculation, the relative signs of r_{ijk}^{ion} and $r_{ijk}^{\text{elec.}}[r_{ijk}(C) + r_{ijk}(E_{\mathrm{h}})]$ are same (both are negative); therefore, there is no cancellation of the two parts. The opposite signs of $r_{ijk}(C)$ and $r_{ijk}(E_{\mathrm{h}})$ lead to their partial cancellations, especially in GaP and GaAs. The only exception is ZnTe, because of the negative sign of ρ. In the calculation of Shih and Yariv (4), only the ionic contribution r_{ijk}(ionic) was quantitatively calculated, however, the electronic contribution, the major contribution to the total linear electro-optic coefficient r_{ijk}, was obtained directly from the experimentally determined SHG coefficient, and

TABLE 3

Comparisons of the Different Sets of Values of Covalent Radii for Zinc Blende Crystals

	Ref. (12)		Ref. (13)		This work	
Crystal	r_A	r_B	r_A	r_B	r_A	r_B
GaP	1.225	1.128	1.26	0.947	1.225	1.128
GaAs	1.225	1.225	1.26	1.20	1.26	1.20
ZnS	1.225	1.127	1.25	0.944	1.225	1.127
ZnSe	1.225	1.225	1.25	1.076	1.238	1.151
ZnTe	1.225	1.405	1.25	1.295	1.25	1.35
CdTe	1.405	1.405	1.48	1.295	1.405	1.405
CuCl	1.225	1.127	1.17	0.994	1.225	1.127

TABLE 4

Comparisons of Experimental Data and Calculated Results, Which Were Obtained by Using the Different Sets of Values of Covalent Radii in Calculating the Linear Electro-optic Coefficients of Zinc Blende Crystals

		Calc.		
Crystal	Expt. r_{41}[a]	r_{41}[b]	r_{41}[c]	r_{41}[d]
GaP	−1.07	−1.11	2.47	−1.11
GaAs	−1.6	−2.65	−1.61	−1.61
ZnS	1.6	−1.57	0.49	−1.57
ZnSe	2.0	−3.13	−1.2	−2.19
ZnTe	4.45	−5.91	−3.88	−4.71
CdTe	5.0	−5.25	−2.97	−5.25
CuCl	2.20	−1.77	−1.47	−1.77

[a] Ref. (10). Their signs are not yet determined, unless so specified.
[b] Values were obtained by using the covalent radii of Ref. (12).
[c] Values were obtained by using the covalent radii of Ref. (13).
[d] Values were obtained by using the covalent radii of this work.

the two parts had the opposite signs. This is one of the main reasons that encouraged us to derive quantitatively the detailed expression for r_{ijk} by using the unified bond-charge expression formula (7).

To evaluate the value of ρ, covalent radii were introduced (12, 13). The values (12) are suitable for wurtzite crystals, but not all of them are applied to the zinc blende crystals. Results calculated by using the different sets of values of covalent radii in Table 3 show that covalent radii of the bonding elements have strong effects on the linear electro-optic coefficients of zinc blende crystals; these calculated results are presented in Table 4.

In Table 3, we have listed the different sets of covalent radii in the calculation of the linear electro-optic coefficients of zinc blende crystals. Using the given values we have calculated the linear electro-optic tensor coefficients of zinc blende crystals; the calculated results showed that the fixed values (12, 13) of the same element in different compounds (e.g., the covalent radius of Zn atom r_{Zn} is 1.225 Å (12) or 1.25 Å (13) in ZnS, ZnSe, and ZnTe) could not meet the required precision in calculations of the linear electro-optic coefficients r_{41} of zinc blende. The values given by us came from the two tabulations, either the originals or the averaged values of the originals, and our values showed us that, for the same bonding element in different compounds, the value of the covalent radius of the element increases with the same tendency as the bond length. For example, the value of r_{Zn} is 1.225, 1.238 (the averaged value of 1.225 and 1.25), and 1.25 Å in ZnS ($d = 2.34$ Å), ZnSe ($d = 2.45$ Å), and ZnTe ($d = 2.64$ Å), respectively, instead of the fixed value 1.225 or 1.25 Å. In our case, there is a similar rule in GaAs, GaP, ZnS, and ZnSe, that is $[r_{\mathrm{As}}(\mathrm{GaAs}) - r_{\mathrm{P}}(\mathrm{GaP})] \approx 2[r_{\mathrm{Ga}}(\mathrm{GaAs}) - r_{\mathrm{Ga}}(\mathrm{GaP})]$, and $[r_{\mathrm{Se}}(\mathrm{ZnSe}) - r_{\mathrm{S}}(\mathrm{ZnS})] \approx 2[r_{\mathrm{Zn}}(\mathrm{ZnSe}) - r_{\mathrm{Zn}}(\mathrm{ZnS})]$. Because the values given in Ref. (12) are only for the tetrahedrally coordinated atoms, especially for the diatomic semiconductors, and Ref. (13) is the popularized *Periodic Table of the Elements*, we selected the two tables as our references when the covalent radius $r_{\alpha,\beta}$ was introduced. From the results listed in Table 4, we can see our selection of covalent radii was reasonable.

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REFERENCES

1. R. L. Kelly, *Phys. Rev.* **151,** 721 (1966).
2. C. Flyzanis, *Phys. Rev. Lett.* **23,** 1336 (1969).
3. C. Flyzanis, *Phys. Lett. A* **34,** 99 (1971).
4. C. Shih and A. Yariv, *Phys. Rev. Lett.* **44,** 281 (1980).
5. J. C. Phillips, *Phys. Rev. Lett.* **20,** 550 (1968).
6. J. A. Van Vechten, *Phys. Rev.* **182,** 891 (1969); **187,** 1007 (1969).
7. B. F. Levine, *Phys. Rev. B* **7,** 2600 (1973).
8. A. Yariv, “Quantum Electronics,” 2nd ed., Wiley, New York, 1975.
9. R. W. G. Wyckoff, “Crystal Structures,” 2nd ed., Vol. 1. Wiley, New York, 1963.
10. I. P. Kaminow and E. H. Turner, *in* “Handbook of Lasers” (R. J. Pressley, Ed.). Chemical Rubber Co., Cleveland, 1971.
11. W. L. Faust and C. H. Henry, *Phys. Rev. Lett.* **17,** 1265 (1966).
12. J. A. Van Vechten and J. C. Phillips, *Phys. Rev. B* **2,** 2160 (1970).
13. A. Dai and M. Shen, “Periodic Table of the Elements,” Scientific Technology Press, Shanghai, 1981. [in Chinese]