

Dependence of Linear Electro-optic Coefficient on Difference in the Atomic Sizes in Zinc Blende Crystals

Dongfeng Xue and Siyuan Zhang¹

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

Received September 18, 1996; accepted January 7, 1997

Covalent radii of the bonding elements have strong effects on the linear electro-optic coefficients of zinc blende crystals; these effects can be quantitatively determined by investigating the relation between the difference in the atomic sizes ρ and the magnitude of the linear electro-optic tensor coefficient r_{41} . It is interesting to note that for the same cation Zn^{2+} , Ga^{3+} , or In^{3+} the magnitude of r_{41} increases with increased covalent radius of the bonded anion r_{β} . Especially with the increasing tendency of the parameter ρ , the magnitude of r_{41} of crystals that have a same cation will increase suddenly when the value of r_{β} becomes larger. © 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 and Ω is below the latter. Tetrahedrally coordinated zinc blende semiconductors are the simplest accentric crystals, which show a nonvanishing linear electro-optic effect. With macroscopic equations between polarization, ion displacement, and electric field, Kelly (1) found an expression for the coefficient of zinc blende crystals. The electrostatic point-charge model and dielectric theory were used to determine the electro-optic coefficients of III–V compounds (2) and II–VI compounds (3) by Flytzanis. Recently, a simple model was derived for calculating the electro-optic coefficient of diatomic crystals by Shih and Yariv (4). Unfortunately, the effect of the covalent radii of the bonding elements on the magnitude of the linear electro-optic tensor coefficient in zinc blende crystals has never been considered. A systematic and quantitative calculation of the linear electro-optic tensor coefficient has been presented for zinc blende and wurtzite crystals, including seven zinc blende crystals (GaP, GaAs, ZnS, ZnSe, ZnTe, CdTe and

CuCl) and four wurtzite crystals (ZnO, ZnS, CdS and CdSe) (5). The results calculated show that different sets of covalent radii have a strong effect on the magnitude of the linear electro-optic tensor coefficient r_{41} , and some values of covalent radii of the bonding elements in the most reliable tabulations (6, 7) would lead to quite large deviations in the calculation of the linear electro-optic tensor coefficients of zinc blende crystals. Therefore it is necessary to investigate the effects of the covalent radius of the magnitude of r_{41} .

The purpose of this paper is to determine the dependence of the magnitude of r_{41} on the differently coordinated elements for the same cations Zn^{2+} , Ga^{3+} , and In^{3+} in zinc blende crystals including ZnS, ZnSe, ZnTe, GaP, GaAs, GaSb, InP, InAs, and InSb. The dependence can be obtained by investigating the effects of the difference in the atomic sizes ρ on the magnitude of r_{41} . Hopefully, these effects will serve as a guide for “predicting” the electro-optic behavior of new diatomic crystals.

THEORY

The electro-optic effect can be separated into two contributions, a purely electronic part r^e (where $r^e = r_{ijk}(C) + r_{ijk}(E_h)$) produced by the applied electric field acting directly on the electrons, and an ionic part $r(\text{ionic})$ produced by coupling between the field-induced ionic displacements and the electrons. In the previous paper (5), a detailed expression for the linear electro-optic tensor coefficient r_{ijk} was presented as

$$r_{ijk} = r_{ijk}(\text{ionic}) + r_{ijk}(C) + r_{ijk}(E_h) \quad [1]$$

$$r_{ijk}(\text{ionic}) = \left[-1/(\epsilon'_i \epsilon'_j q N r_0) \right] \chi \epsilon_0 (\epsilon'_{dck} - \epsilon'_{\infty ck}) \times \left[G_{ijk} f + \sum_{\mu} \frac{1}{2} (\alpha_{\mu}^i(\lambda) \delta_{jk} + \alpha_{\mu}^j(\lambda) \delta_{ik}) \right] \quad [2]$$

$$r_{ijk}(C) = \left[-2/(\epsilon'_i \epsilon'_j q N E_g^2) \right] G_{ijk} \chi^2 b e^2 \exp(-k_s r_0) (Z_{\alpha} + Z_{\beta}) C / r_0^2 \quad [3]$$

¹ To whom correspondence should be addressed.

$$r_{ijk}(E_h) = [1/(\epsilon'_i \epsilon'_j q N)] \chi^2 G_{ijk}(-4)s \times (2s-1) [r_0/(r_0 - r_c)]^2 f_c \rho / d, \quad [4]$$

where $\rho = (r_\beta - r_\alpha)/(r_\alpha + r_\beta)$ is the difference in the atomic sizes. The summation is over all the bonds in the unit cell, and $\alpha_i^\mu(\lambda)$ is the direction cosine with respect to the i th coordinate axis of the λ th bond of type μ in the unit cell. ϵ'_i or ϵ'_∞ is the relative optical permittivity, q is the bond charge (its expression can be written as $q/e = n_v(1/\epsilon_\infty + f_c/3)$, where n_v is the number of valence electrons per bond) (8), N is the number of bonds per unit cell, and ϵ'_{dc} is the relative dielectric constant. G_{ijk} is a geometrical factor,

$$G_{ijk} = \sum_{\lambda} \alpha_i^\mu(\lambda) \alpha_j^\mu(\lambda) \alpha_k^\mu(\lambda), \quad [5]$$

in which the sum on λ is over all bonds of type μ in the unit cell. χ is the bond linear susceptibility along the bond direction which is same for a given type of bond.

f is the bond ionicity factor given as $f = (k_s r_0 / 2 - 1.48) f_i - 0.02$, containing k_s , the Thomas–Fermi wave factor. δ_{jk} is the Kronecker delta function.

E_g is the average energy gap, which can be separated into homopolar (E_h) and the heteropolar (C) parts, namely, $E_g^2 = E_h^2 + C^2$. The generalized expressions used in the evaluation of E_h and C has been given as (8,9)

$$E_h^{-2} = (39.74/d^s)^{-2} [(r_\alpha - r_c)^{2s} + (r_\beta - r_c)^{2s}] / 2(r_0 - r_c)^{2s}, \quad s = 2.48 \quad [6]$$

$$C = b e^2 \exp(-k_s r_0) [Z_\alpha / r_0 - Z_\beta / r_0], \quad [7]$$

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 $r_0 = d/2$.

b is a correction factor and is proportional to the square of the average coordination number. Z_α and Z_β are the numbers of valence electrons of α and β atoms, respectively.

The ionicity f_i and covalency f_c of the individual bonds are defined as $f_i = C^2/E_g^2$, $f_c = E_h^2/E_g^2$ (9).

RESULTS AND DISCUSSION

By using the given values for covalent radii of the bonding elements (5), we have calculated the linear electro-optic tensor coefficients of zinc blende crystals including ZnS, ZnSe, ZnTe, GaP, and GaAs. In this paper, following a similar rule proposed previously (5), we have calculated other zinc blende crystals including GaSb, InP, InAs, and InSb. All calculated results are given in Table 1 and agree satisfactorily with the experimental data, except those that have not yet been observed experimentally. At the same time, the important chemical bond parameters in the calculation of the linear electro-optic tensor coefficients of zinc blende crystals are also listed in Table 1. In the calculation, the introduced values of the relative optical permittivity ϵ'_i and the relative dielectric constant ϵ'_{dc} were from Refs. 11 and 12.

The cancellation between $r_{ijk}(C)$ and $r_{ijk}(E_h)$ for crystals except GaSb and ZnTe is particularly pronounced especially for the crystals InP and InAs in which the cancellation is practically complete. It is obviously desirable to avoid such near cancellations when searching for new linear electro-optic materials having large coefficients.

To show the dependence of the linear electro-optic tensor coefficient on the difference in the atomic sizes (also the covalent radii $r_{\alpha,\beta}$ of the bonding elements) in the simplest

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 Experiment

Crystal	GaP	GaAs	GaSb	InP	InAs	InSb	ZnS	ZnSe	ZnTe
a_0^a	5.4505	5.6537	6.118	5.8687	6.036	6.4782	5.4093	5.6676	6.089
d	2.3601	2.4481	2.6492	2.5412	2.6137	2.8051	2.3423	2.4511	2.6366
E_h	4.7246	4.3145	3.5473	3.9331	3.6680	3.0783	4.8141	4.3014	3.5895
C	2.9977	2.5685	2.0964	3.3735	2.8908	2.1535	5.2733	4.9065	3.4329
f_c	0.7130	0.7383	0.7411	0.5761	0.6169	0.6714	0.4546	0.4346	0.5223
ρ	-0.0412	-0.0244	0.0526	-0.1094	-0.0909	-0.0141	-0.0417	-0.0364	0.0385
q/e	0.6834	0.6632	0.6319	0.5936	0.5802	0.5751	0.6306	0.5724	0.5563
$r_{41}(C)$	-2.4601	-2.5898	-3.2649	-4.8419	-4.9520	-5.1619	-2.1733	-2.8769	-3.1385
$r_{41}(E_h)$	1.4639	1.0357	-2.8591	4.1823	4.2118	0.8633	0.8771	0.9358	-1.5339
$r_{41}(\text{ionic})$	-0.1096	-0.0056	-0.0365	-0.2038	-0.1458	-0.0786	-0.2734	-0.2532	-0.0399
$r_{41}^{\text{calc.}}$	-1.11	-1.61	-6.16	-0.86	-0.89	-4.38	-1.57	-2.19	-4.71
$r_{41}^{\text{expt. } b}$	-1.07	-1.6	—	—	—	—	1.6	2.0	4.45

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

^a Ref. 10.

^b Ref. 11.

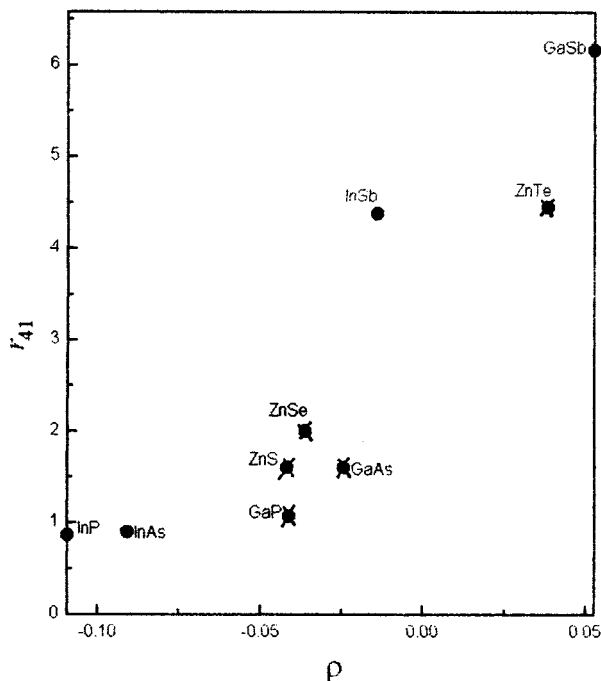


FIG. 1. Dependence of the linear electro-optic coefficient r_{41} on the difference in the atomic sizes ρ in zinc blende crystals. \times Experimental values (Ref. 11); \bullet theoretical prediction (this work).

diatomic crystals, the relationship between the parameter ρ and the magnitude of r_{41} is expressed explicitly in Fig. 1 by using the tabulated values for the parameter ρ and the observed and theoretically calculated linear electro-optic coefficients r_{41} in Table 1. Considering the purpose of this paper, which could lead to a powerful method for predicting the linear electro-optic effects of new diatomic crystals, the measured linear electro-optic coefficients were introduced. Because these have not yet been determined experimentally, the theoretical results were used instead here.

In Fig. 1, we can see similar increasing tendencies in diatomic crystals for the same cation, In^{3+} , Zn^{2+} , or Ga^{3+} , bonded with different elements. The magnitude of r_{41} in these zinc blende crystals also increases as the parameter ρ increases; that is to say, with the increase of the covalent radius of the bonded anion, r_{β} , the magnitude of r_{41} increases at the same time. When the cation In^{3+} , Zn^{2+} , or Ga^{3+} is bonded with elements in periods 3 and 4 of the periodic table, the magnitude of r_{41} increases slowly with increase in r_{β} ; however, the magnitude of r_{41} of the three crystals InSb, GaSb, and ZnTe has a sudden increase, because of the much larger values of r_{Sb} and r_{Te} . On the other hand, because of the large value of the covalent radius of the element In (which is situated in the next period from the elements Ga and Zn), the magnitude of r_{41} for the three crystals InP, InAs, and InSb is smaller than for the corresponding crystals which have a Ga cation, GaP, GaAs, and

GaSb. Therefore, we can conclude that with increased covalent radius of the atom β , the magnitude of the electro-optic coefficient r_{41} increases obviously.

In Fig. 1, we can see similar increasing tendencies in the crystals GaP, GaAs, ZnS, and ZnSe. The case has been determined by experimental data, and the increasing tendency formed by our calculated results accords with that determined by experiment: slow increase of r_{41} in InP and InAs, and rapid increase of r_{41} in InSb and GaSb crystals, like that in ZnTe crystal. The good agreement of calculated results and experimental data shows us that our theoretical method could give us a useful method to predict the linear electro-optic effects when searching for new linear electro-optic crystals. From the points in Fig. 1, we can see that GaSb, ZnTe, and InSb crystals are good candidates to be used as linear electro-optic materials, because of the large values of covalent radii of the bonded elements Sb and Te, and these values are so large that they approach or exceed those of the corresponding cations In^{3+} , Zn^{2+} , and Ga^{3+} bonded with them. Finally, these values would lead to the minimum cancellation between $r_{ijk}(C)$ and $r_{ijk}(E_h)$. Strictly speaking, InP, InAs, and InSb crystals would not be good candidates for use as linear electro-optic materials, because the value of r_{β} is not larger than that of r_{α} , and that would lead to the strong cancellation between $r_{ijk}(C)$ and $r_{ijk}(E_h)$. In contrast, for GaSb and ZnTe crystals the value of r_{β} is much larger than that of r_{α} , and the magnitude of r_{41} is quite large; therefore, they are good candidates to use in the search for new linear electro-optic materials.

CONCLUSION

By investigating the calculation of the linear electro-optic coefficients in zinc blende crystals, which have the same cation In^{3+} , Zn^{2+} , or Ga^{3+} bonded with different anions, the dependent relationship between the magnitude of r_{41} and the parameter ρ has been explicitly presented. The interesting thing in this paper is that the effects of the covalent radii of the bonding elements on the linear electro-optic coefficients r_{41} of the zinc blende crystals will serve as a guide for predicting the electro-optic behavior of new crystals.

ACKNOWLEDGMENT

This research was supported by the State-Key Program of Basic Research of China.

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. D. F. Xue and S. Y. Zhang, *J. Solid State Chem.* in press.
6. J. A. Van Vechten and J. C. Phillips, *Phys. Rev. B* **2**, 2160 (1970).
7. A. B. Dai and M. C. Shen, "Periodic Table of the Elements." Scientific Technology Press, Shanghai, 1981. [In Chinese].
8. B. F. Levine, *Phys. Rev. B* **7**, 2600 (1973).
9. J. A. Van Vechten, *Phys. Rev.* **182**, 891 (1969); *Phys. Rev.* **187**, 1007 (1969).
10. R. W. G. Wyckoff, "Crystal Structures," 2nd ed., Vol. 1. Wiley, New York, 1963.
11. I. P. Kaminow and E. H. Turner, in "Handbook of Lasers" (R. J. Pressley, Ed.), p. 453. Chemical Rubber Co., Cleveland, 1971.
12. T. S. Moss *et al.*, "Semiconductor Opto-electronics," p. 330. Butterworths, Stoneham, MA, 1973.