

## Dependence of Compton $B(\mathbf{r})$ -Functions on Electronic Bonding Character in the Series of Ge-GaAs-ZnSe

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### Ge-GaAs-ZnSe 系列におけるコンプトン $B(\mathbf{r})$ 関数 の電子結合依存性

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A real-space function  $B(\mathbf{r})$  is a quantity defined as the Fourier inversion transform of the distribution function of electron momentum density  $\rho(\mathbf{q})$  and is well known as a very powerful intermediate for highly accurate calculation of  $\rho(\mathbf{q})$  in solids. As shown previously on the basis of a pseudopotential-theoretical approach to  $\rho(\mathbf{q})$  via  $B(\mathbf{r})$  for the series of semiconductors Ge, GaAs and ZnSe, the systematic increase of ionicity in valence electronic bond is well reflected on the contour maps of  $\rho(\mathbf{q})$ , corresponding to the distribution shift of electrons from the III or II atomic site to the V or VI site.

A possibility that the  $B(\mathbf{r})$ -function itself may be related directly to some spatial characteristics in electron distribution has been tested for the prototype semiconductor series. It has been found that values of the first deep valley and the second peak structures of  $B(\mathbf{r})$  are well connected with a degree of ionicity or a difference in electronegativity between the two constituting atoms which relates closely to the ionicity. Beyond the nature of mathematical intermediate, the  $B(\mathbf{r})$ -function is a physical quantity with a possibility of providing us with useful information on properties of electronic bond.

A density distribution function  $\rho(\mathbf{q})$  of electron momentum  $\mathbf{q}$  is one of fundamental quantities for investigating electronic properties of solids. Experimentally, Compton scattering data provide us with various aspects of the function  $\rho(\mathbf{q})$  through the energy and momentum transfer of high energy photons scattered from electrons. Analyzing the results theoretically, we can discuss details of electron occupation in electronic states, charac-

teristics of electronic bond, origin and mechanism of high-momentum transfer, crystalline structures in bulk and surfaces of solid, and so on.

In recent papers<sup>1)~5)</sup> on momentum density distribution of the valence electrons in semiconductors, pseudopotential-theoretical treatments are developed for discussion of quantum mechanical core-orthogonalization effect of valence electrons on  $\rho(\mathbf{q})$  and of reflection of

the covalent and ionic characters in valence electronic bond on  $\rho(\mathbf{q})$ . In these treatments, a  $B(\mathbf{r})$ -function formalism<sup>1)</sup> plays an essential role for calculation of  $\rho(\mathbf{q})$  in quantitatively high accuracy. The function  $B(\mathbf{r})$  of the valence electron system is defined as the Fourier inversion transform of  $\rho(\mathbf{q})$ :

$$B(\mathbf{r}) = \sum_{\mathbf{q}} \rho(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{r}) / \Omega, \quad (1)$$

where  $\Omega$  is the crystal volume. In the framework of usual energy band theory for valence electronic states,  $\rho(\mathbf{q})$  is given by

$$\rho(\mathbf{q}) = 2 \sum_n \sum_{\mathbf{k}} \left| \int \Psi_{n\mathbf{k}}(\mathbf{r}) \exp(-i\mathbf{q} \cdot \mathbf{r}) d^3r / \sqrt{\Omega} \right|^2, \quad (2)$$

where  $\Psi_{n\mathbf{k}}$  is the wave function of the valence electron with wave vector  $\mathbf{k}$  in the  $n$ -th occupied energy band. Advantages of  $\rho(\mathbf{q})$  calculation via the mathematical intermediate  $B(\mathbf{r})$  combined with adoption of the so-called special point scheme<sup>6)</sup> was discussed in detail in references 7 and 8. In reference 8, the merit is explained in the analogous case of  $A(\mathbf{r})$ -function formalism for the electron-positron annihilation.

In references 3 and 5, it is shown for the samples of Si and Ge that an image of one of the intra-unit-cell atoms appears clearly on the contour maps of  $B(\mathbf{r})$ , as a result of orthogonalization effect between the valence and the atomic core electrons. The fact can be explained by considering that the  $B(\mathbf{r})$ -function is represented in terms of spatial autocorrelation function of valence electron wave functions<sup>9)10)</sup>. This is an example showing that  $B(\mathbf{r})$  is not only a mathematical intermediate but a physical quantity. In the semiconductor series of Ge (diamond structure), GaAs and ZnSe (zinc-blende structure) composed of the fourth row elements in the periodic table, an ionic charac-

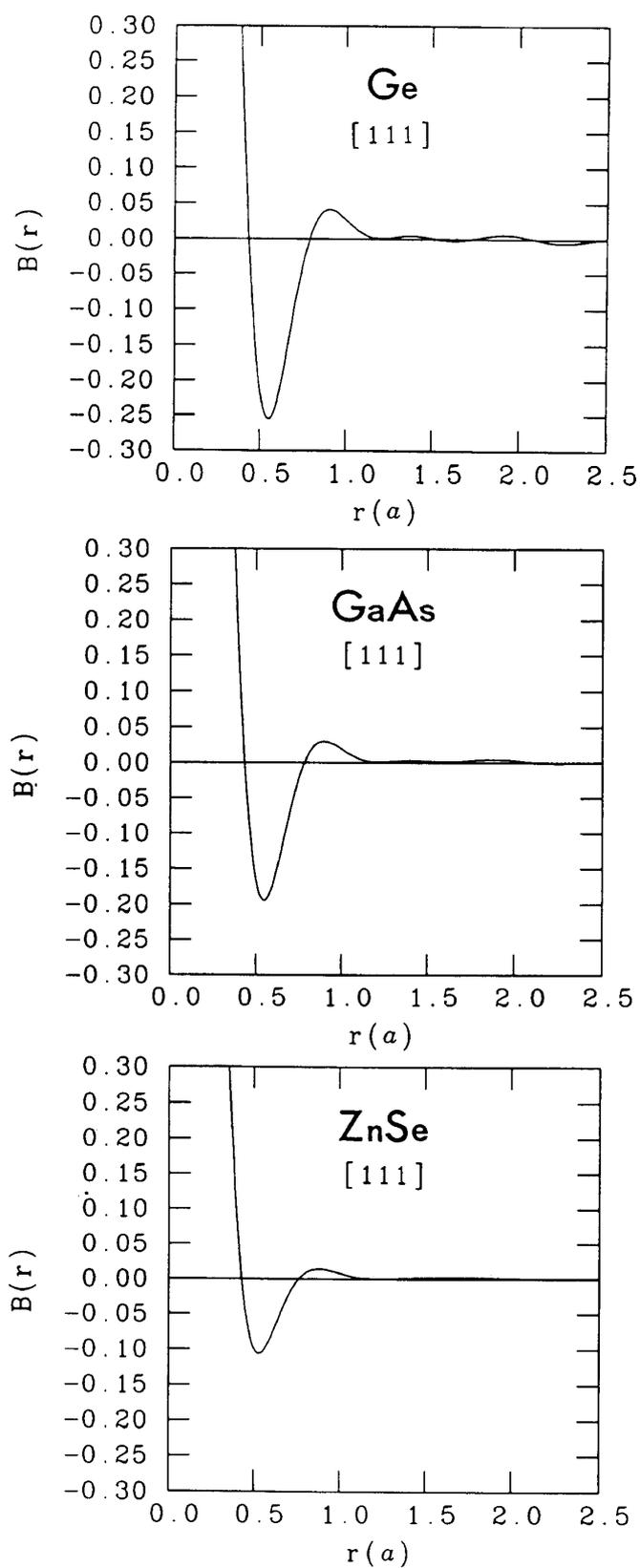
ter in valence electronic bond increases in the order of the material series, putting the base on the case of Ge of purely covalent character. As shown and discussed in detail in reference 4, the increase of the ionic character leads to a decrease of anisotropy in momentum distribution. The effect is reflected sensitively on the distribution pattern of the  $\rho(\mathbf{q})$  contour map. It will be, therefore, expected that the character in electronic bond may be reflected also sensitively on the corresponding  $B(\mathbf{r})$ .

The purpose of this short note is to show that a systematic trend concerning with ionic character in the electronic bond is clearly found in structure of  $B(\mathbf{r})$  for the series of Ge, GaAs and ZnSe: Values in depth or height of main structures in  $B(\mathbf{r})$  depend sensitively on the degree of ionicity in the electronic bond or equivalently on the difference in electronegativity between the two constituting atoms. We will obtain another example of physical aspect of the function  $B(\mathbf{r})$  beyond the quantity of mathematical convenience.

Nonlocal pseudopotentials for the electronic states in Ge, GaAs and ZnSe, the method of pseudopotential energy band calculation to determine the electron pseudo-wave functions and the method of the  $B(\mathbf{r})$  calculation are the same as those adopted in reference 4. Description of them is not repeated in this short note. Directional variations of  $B(\mathbf{r})$  in the fundamental [001], [112], [111], [221] and [110] directions are calculated for Ge, GaAs and ZnSe.

In Fig. 1, results in the most interesting [111] direction along the bond axis are shown. Values of  $B(\mathbf{r})$  are given in units of  $1/\Omega_a$ . Here, the atomic volume  $\Omega_a$  is a half of the primitive unit cell volume  $a^3/4$  of the corresponding diamond and zinc-blende crystalline structures, where  $a$  is the lattice constant.

Electronic Bonding Character in Compton  $B(\mathbf{r})$ -Function



**Fig. 1.** Behaviours of the  $B(\mathbf{r})$ -function of Ge, GaAs and ZnSe in the  $[111]$  direction along the valence electronic bond.

The values of  $a$  are 10.67715 a.u. (Ge), 10.68338a.u. (GaAs) and 10.70908 a.u. (ZnSe). The distance parameter  $r$  is given in units of  $a$ .

As can be seen in Fig. 1, the  $B(\mathbf{r})$ -function shows the first bulk peak around the origin at  $r=0$ , the first valley around  $r\sim 0.55$  and the second peak around  $r\sim 0.90$ . Because the integration of  $\rho(\mathbf{q})$  over  $\mathbf{q}$  gives the total number of valence electrons, the value of  $B(\mathbf{r})$  at  $r=0$  should be equal to the fixed value of uniform density of valence electrons, namely, 4.0 in units of  $\Omega_a^{-1}$ . The first valley shallows its depth  $B_v$  in the order of Ge, GaAs and ZnSe;  $B_v$ 's are  $-0.25522$  at  $r=0.55$  for Ge,  $-0.19497$  at  $r=0.55$  for GaAs and  $-0.10602$  at  $r=0.53$  for ZnSe. Similarly, the second peak decreases its height  $B_p$  as 0.04017 at  $r=0.90$  for Ge, 0.02985 at  $r=0.90$  for GaAs and 0.01386 at  $r=0.88$  for ZnSe. Let us define  $\Delta B_v(M)$  and  $\Delta B_p(M)$  as

$$\Delta B_v(M) = B_v(M) - B_v(\text{Ge}), \quad (3)$$

$$\Delta B_p(M) = B_p(M) - B_p(\text{Ge}), \quad (4)$$

where M refers to a material Ge, GaAs or ZnSe. Then, we have the following values :

$\Delta B_v$		
Ge	GaAs	ZnSe
0	+0.06025	+0.14920

$\Delta B_p$		
Ge	GaAs	ZnSe
0	-0.01032	-0.02631

We notice that the material dependent change in the absolute values of  $\Delta B_v(M)$  and  $\Delta B_p(M)$  seems to be closely relating to the order in ionicity or in the difference in electronegativity of the two constituting atoms. In the valence electronic bond, electrons tend to be attracted toward the atom with larger electronegativity and then the concept of

ionicity is formulated<sup>11)12)</sup>. In the tetrahedrally coordinated materials of Ge, GaAs and ZnSe, the main bonding character is covalent. Due to the electron transfer between the atoms, a ratio of ionic character increases. Since in the elemental semiconductor Ge the electronic bond is purely covalent, the ionicity is of course zero. The Pauling's ionicity<sup>11)</sup> is famous and is directly related to the difference in electronegativity between the two constituting atoms. However, it is a little empirical. Modern concept of ionicity based on the energy band theory is proposed by Phillips<sup>12)</sup>. As discussed in reference 12 in detail, it is more suitable for materials with the tetrahedral  $sp^3$ -type hybridized electronic states which we consider here.

Electronegativities  $X$  with Phillips' definition and with Pauling's one (in parentheses) for the constituting atoms are listed below :

Zn	Ga	Ge	As	Se
0.91	1.13	1.35	1.57	1.79
(1.6)	(1.6)	(1.8)	(2.0)	(2.4)

Then, the differences in electronegativity between the constituting atoms,  $\Delta X$ , are obtained as follows :

Ge	GaAs	ZnSe
0	0.44	0.88
(0)	(0.4)	(0.8)

On the other hand, the values of ionicity with Phillips' definition  $f_i$  are as follows :

Ge	GaAs	ZnSe
0	0.310	0.630
(0)	(0.28)	(0.57)

By comparison among these data, we can find that the structural quantities  $\Delta B_v$  and  $\Delta B_p$  are in a good proportional dependence on the electron transfer parameter  $\Delta X$  and then to the ionicity parameter  $f_i$ . Figure 2(a) and (b) show the relations of  $\Delta B_v$  and  $|\Delta B_p|$  to Phillips'  $\Delta X$

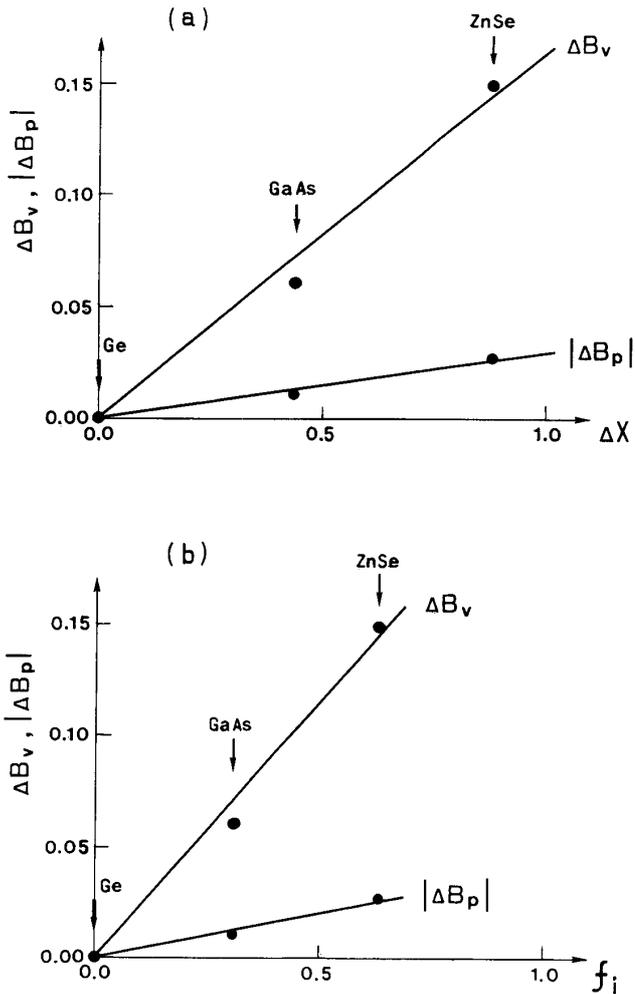


Fig. 2. (a)  $\Delta B_v$  and  $|\Delta B_p|$  vs Phillips'  $\Delta X$ , and (b)  $\Delta B_v$  and  $|\Delta B_p|$  vs  $f_i$ .

and to  $f_i$ , respectively. Our observation is consistent with discussions given for systematic decreases of anisotropy in  $\rho(\mathbf{q})^4$  for Ge, GaAs and ZnSe and in Compton profile function  $J(q_z)^{13}$ , which corresponds to a one-dimensional Fourier transform of  $B(0, 0, z)$  [see eq. (29) in reference 8], for the semiconductor groups of Si, (Ge, GaAs, ZnSe) and (Sn, InSb, CdTe). Actually, preliminary calculations of  $B(\mathbf{r})$  for the fifth-row group (Sn, InSb, CdTe) also show a systematic trend similar to one mentioned above for the fourth-row group. Therefore, these simple structural parameters in  $B(\mathbf{r})$  such as  $\Delta B_v$  and  $\Delta B_p$  provide us with a

quantitatively useful probe to estimate electronic character of valence bonds of compound semiconductors. Theoretical basis of the problem can be given more precisely by using the autocorrelative nature of  $B(\mathbf{r})$ -function<sup>9)10)</sup>, as was employed in discussion for appearance of atomic image in  $B(\mathbf{r})$ <sup>3)5)</sup>. Experimental developments in high resolution measurements in Compton scattering and in reconstruction procedures for  $B(\mathbf{r})$  are desirable. Theoretical and experimental Compton  $B(\mathbf{r})$ -functions can work in resolving many difficulties in X-ray analysis of electron charge distribution.

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