Prediction of the Pressure-Induced Phase Transition in GaAs by the Positron Affinity

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Abstract

The thermalized positron charge distribution is calculated as a function of pressure variation in GaAs. Calculations have been carried out via the independent particle method (IPM) coupled with the empirical pseudopotential method (EPM). Initial results show a clear asymmetrical positron charge distribution relative to the bond center. From this positron affinity we have calculated the ionicity character with respect to the pressure variation using our empirical formula. Our results show an agreement with the thermochemical phase diagram proposed by Phillips.

Key Words: Positron affinity, phase transition, band structure, semiconductor.

1. Introduction

Hydrostatic pressure has been proved to be a valuable tool for studying the influence of the band-structure parameters on the electronic properties of semiconductors, bulk crystals, or two dimensional systems [1–4].

Perhaps the most remarkable aspect of tetrahedrally coordinated structures is their low density. The openness of these semiconductors is highlighted by the fact that, for the homopolar members, the ratio of the volume of touching atom spheres to that of the unit cell is 0.34, less than half for the close-packed element structure (0.74). It is not surprising, therefore, that under pressure tetrahedrally coordinated semiconductors can be transformed to structure with higher density [5]. Many methods of calculations have been used to confirm these results. One of them is to relate the high pressure behavior of these semiconductors to the type of chemical bond between the nearest atoms by examining the electronic charge density evolution, which has been correlated to the empirical qualitative concept as ionicity [6, 7].

Inherent in defining ionicity of the covalent bonds is the difficulty in transforming a qualitative or verbal concept into a quantitative mathematical formula. In the physics and chemistry of matter, many methods were

used for the calculation of the ionicity character where every definition involves some assumptions. Pauling [8] made use of thermochemical arguments to quantify the ionic character of molecular bonds and was able to develop an electronegativity scale for the elements. Coulson, Redei, and Stocker [9] used a molecular-orbital approach for the study of the tetrahedrally coordinated octet binary compounds $A^N B^{8-N}$. Phillips [5, 10] introduced a dielectric model of the chemical bond in $A^N B^{8-N}$ crystals which is based on two band gap parameters (homopolar and heteropolar gaps). One of the most remarkable features of Phillip's ionicity scale is the existence of a critical value of ionicity that separates fourfold-coordinated from sixfold-coordinated compounds. Christensen [11] performed self-consistent calculations to establish the ionicity scale. Garcia [12] has establish an unambiguous procedure to compute numerical values for the ionicity using a measure of the asymmetry of the valence charge distribution in $A^N B^{8-N}$ compounds.

In recent years several investigations have been reported in which the positron was used as a probe for studying the electronic properties of solids [13]. It has been shown that the positron charge density can yield considerable information of the bonding properties of simple and binary semiconductors at normal pressure and under pressure [14–17]. Within the crystal the positron reaches thermal equilibrium with the lattice (state k=0) and ends up spatially distributed. During its diffusion the positron overlaps a lower-than-average density region, such as a vacancy, a dislocation or a micro void. It has a finite probability of being captured and thus being localized in such region. The positron affinity for such region is due to the repulsion between the positron and positive atomic cores. Due to this repulsion, the positron charge densities were distributed asymmetrically relative to the bond center. These considerations lead us to state that the positron distribution seem to be able to give information about the ionicity character of the studied solids.

The aim of the present work is to propose an alternative way to calculate the ionicity character from a quantitative analysis of the positron charge density in GaAs with respect to the pressure variation using our empirical formula, discussed extensively elsewhere [18]. The choice of the GaAs compound is due to the abundant existence of the theoretical and experimental data. Comparison has been given between our results and the Phillips ionicity scale.

2.   Calculations

The crystal potential experienced by a positron differs from that experienced by an electron. Assuming that there is only one positron for many electrons (IPM), there can be no exchange because there is no positron-positron interaction. The positron potential is purely coulombic in nature. There is a repulsive ion core potential and an attractive Hartree potential. In addition to these two forces, there is a third which originates from the electron-positron correlation. The total positron potential can thus be expressed as:

$$V_+ = V_i + V_e + V_{ep} \tag{1}$$

where V_i is the potential due to the ion core, V_e is the potential due to the valence electrons and V_{ep} is the electron-positron correlation potential. The electron-positron potential is a slow function of the electron density. It is generally flat in interstitial regions and swamped by V_i and V_e in the ion core regions. Hence it is negligible. Since the crystal ion core potential is periodic and the zincblende structure involves non-primitive lattice translation, it can always be written in terms of an atomic equivalent:

$$V_i = \sum \sum v_i(r - R_n - T_i) \tag{2}$$

where R_n denotes the set of all Bravais lattice vectors and T_i is a non-primitive vector of a two-atom basis. If we choose the origin of coordinates to be halfway between the two atoms of the unit cell with a positron plane wave basis set $\varphi_+(r)$

$$v_i(G) = v_s(G)\cos(G \cdot \tau) + iv_a(G)\sin(G \cdot \tau) \tag{3}$$

where v_s and v_a are symmetric and antisymmetric contributions of the atomic potentials and G is a reciprocal lattice vector, $\tau = \frac{1}{8}(1,1,1)$ in units of the lattice constant. In the ion-core approximation:

$$v_i(r) = \frac{Ze^2}{r} \tag{4}$$

$$v_1(G) = \frac{2N}{\Omega}\frac{4\pi Z_1 e^2}{|G|^2} \tag{5}$$

$$v_2(G) = \frac{2N}{\Omega}\frac{4\pi Z_2 e^2}{|G|^2} \tag{6}$$

where $v_1(G)$ and $v_2(G)$ are the contribution of the cation and the anion respectively, with $Z_1 e$ and $Z_2 e$ as charges, and Ω is the unit cell volume in which

$$2V_s(G) = v_1(G) + v_2(G) \tag{7}$$

$$2V_a(G) = v_1(G) - v_2(G) \tag{8}$$

In the case of the diamond semiconductors, the antisymmetric part of the potential is equal to zero. On the other hand, the electron-positron Coulomb potential is expressed as

$$V_e(r) = -e^2 \int \frac{\rho_e(r')}{|r - r'|}d^3r \tag{9}$$

The positron wave function was solved with the ionic potential taken in the point-core approximation. With the potential diverging at the ion core region the wave function is expected to need a lot of plane waves in order to converge. However, the situation is simplified because of the fact that the positron gets pushed away from the ion core region into the interstitial positions, with its wave function vanishing at the ion core. This smooth structure of the positron wave function, which has no oscillations in the ion core region, lends itself very well to a representation in terms of a relatively small number of plane waves. The wave function for positron becomes

$$\varphi_+(r) = \frac{1}{\sqrt{\Omega}}\sum A(G)e^{iGr} \tag{10}$$

The coefficients $A(G)$ is found by solving the equation

$$\sum \left[\left|G^2 - E\right|\delta_{GG'} + V + (|G - G'|)\right].A(G') = 0. \tag{11}$$

The resulting wave functions are used to compute the positron charge density:

$$\rho_p(r) = |\varphi_+(r)|^2. \tag{12}$$

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The conversion from pressure dependence to the relative lattice change is performed using Murnaghan's equation of state [19]:

$$p = \frac{B_0}{B_0'}\left[\left(\frac{a_0}{a}\right)^{3B_0'} - 1\right], \tag{13}$$

where a is the lattice constant at pressure p, B_0 the bulk modulus equal to 74.8 GPa [20]; and B_0' is its pressure derivative, equal to 3.36 [21].

The linear and quadratic pressure coefficients of GaAs for different transitions are taken from [22]. All the parameters used for this calculation are listed in Table 1.

Table 1. The adjusted symmetric and ant symmetric form factors (in Rydberg units), and the lattice constants a_0 (in atomic units) for different pressure in the GaAs.

Pressure (kbar)	a_0	$V_S(3)$	$V_S(8)$	$V_S(11)$	$V_a(3)$	$V_a(4)$	$V_a(11)$
0	10.6885	-0.24242	0.01	0.06351	0.06436	0.05	0.01
20	10.59768	-0.24427	0.01	0.07047	0.05773	0.05	0.01
40	10.51473	-0.24603	0.01	0.07664	0.05092	0.05	0.01
60	10.43845	-0.24776	0.01	0.08489	0.04387	0.05	0.01
80	10.36788	-0.24943	0.01	0.09244	0.03662	0.05	0.01
100	10.30226	-0.25103	0.01	0.10022	0.02918	0.05	0.01
120	10.24097	-0.25258	0.01	0.10823	0.02152	0.05	0.01
140	10.1835	-0.25406	0.01	0.00647	0.01366	0.05	0.01
160	10.1294	-0.25549	0.01	0.12494	0.00559	0.05	0.01
175	10.09083	-0.25652	0.01	0.13145	-0.00058	0.05	0.01
190	10.05383	-0.25752	0.01	0.13808	-0.00068	0.05	0.01

3. Results and Discussions

In the first step of our calculations, we have computed the pressure dependence of the form factors using the empirical pseudopotential method (EPM). This method has been proved to be largely sufficient to describe qualitatively the realistic charge densities [23–25]. Hence, the quadratic fit expressions of the resulting form factors (the symmetric and the antisymmetric parts) as a function of the pressure are

$$V_S(3) = -0.242428 - 9.34398 \times 10^{-5}P + 7.35984 \times 10^{-8}P^2$$
$$V_S(11) = 0.0636179 + 3.37313 \times 10^{-4}P + 2.87525 \times 10^{-7}P^2$$
$$V_A(3) = -0.064367 - 3.26126 \times 10^{-4}P - 2.57397 \times 10^{-7}P^2.$$

The form factors $V_S(8)$, $V_A(4)$ and $V_A(11)$ are not affected by the pressure variation. These form factors are used as input to compute the Fourier coefficients of the valence charge densities required to construct the electron-positron Coulomb potential. The resulting Fourier coefficients (the symmetric and the antisymmetric parts) are used to calculate the corresponding positron wave function using the IPM.

Figure 1 displays the positron charge densities at the Γ_1 point at normal pressure (solid line) and under 190 kbar (dashed line). The exclusion of the positron from both the ion cores and from the regions of the

valence bonds is clear. There is a clear asymmetrical positron distribution relative to the bond centre, whereas the charge is symmetrically distributed in the elemental semiconductors. Between the two atomic cores, the situation is different since the charge distribution is less significant. The positron is repelled by the positively charged atomic cores and tends to move in the interstitial regions.
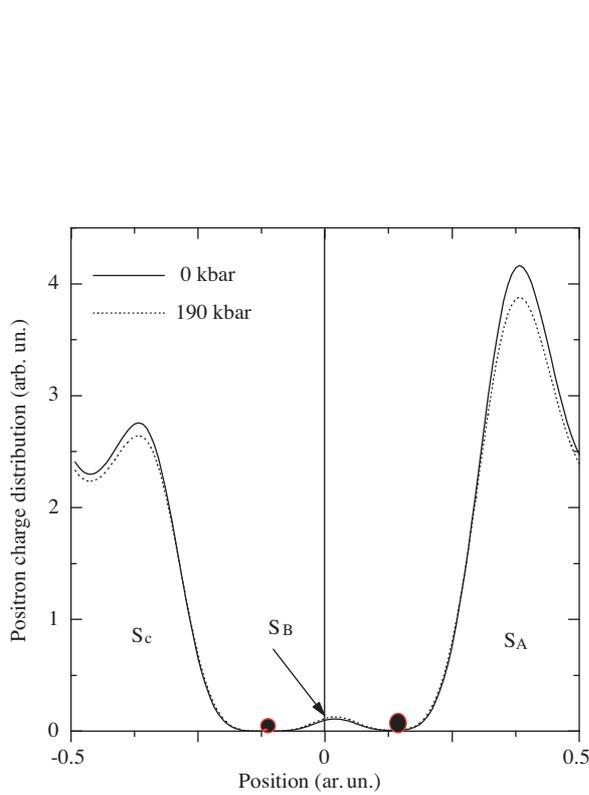
Figure 1. The positron charge densities along the $\langle 111 \rangle$ direction at Γ_1 point in GaAs at normal pressure (solid line) and under 190 kbar (dashed line).
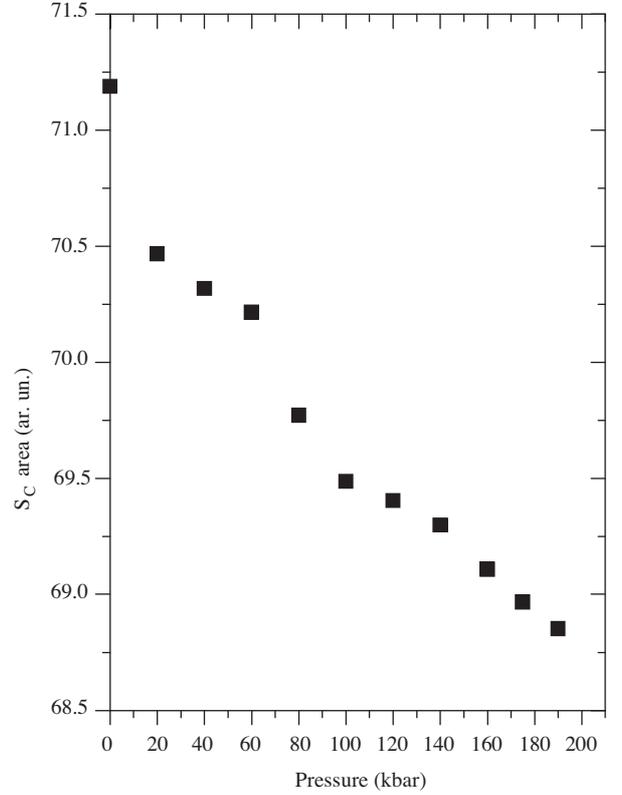
Figure 2. The variation of the S_c area with respect to the pressure variation in GaAs.

From the quantitative point of view, there is a difference of charge in the interstitial regions. The positron distribution is more pronounced in the neighborhood of the As anion than in that of the Ga cation. This behavior could be explained by a charge transfer from the cation to the anion interstitial site and therefore a strong affinity for the latter.

We denote by S_C the area below the curve of the thermalized positron charge distribution from the cation interstitial region towards the cation site, S_B the area between the two atomic cores and S_A the area from the anion site to the anion interstitial region. In Figure 2, we have plotted the variation of the S_C area versus the pressure (from atmospheric pressure to 190 kbar). We notice that the effect of increasing the pressure leads to a decrease of the S_C area. The same situation was seen for the S_A area (Figure 3) with a more qualitative difference. These plots show two quasi linear decreases from 0 to 60 kbar and from 80 to 190 kbar. The discontinuity observed could be attributed to the behavior of the lattice when the pressure is applied. The consequence is the inversion of the Γ_1^c and X_1^c minima which lead to the transition from the direct to indirect gap in GaAs. The situation is quite different for the S_B area which increases as well as the pressure increase

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(Figure 4). The explanation of this phenomenon is the positron charge transfer from both the cation and the anion interstitial sides to the ion cores leading to the positron trapping in the internuclear spacing.
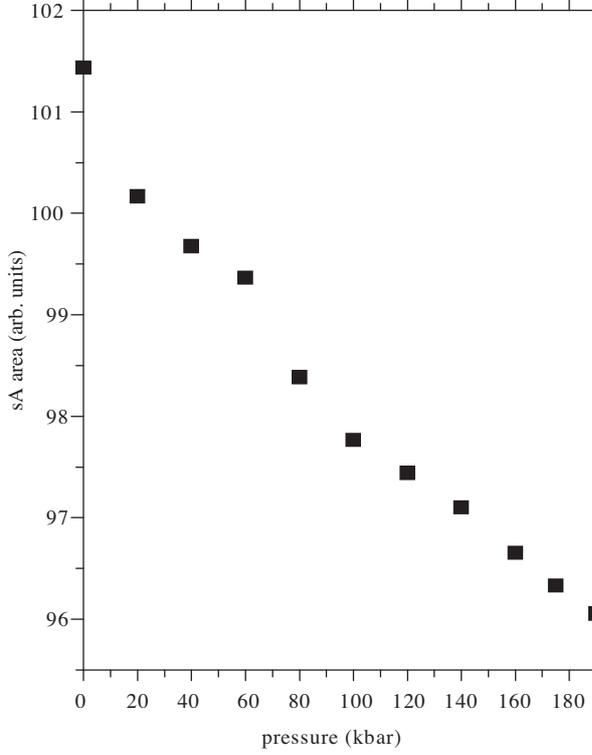
Figure 3. The variation of the S_A area with respect to the pressure variation in GaAs.
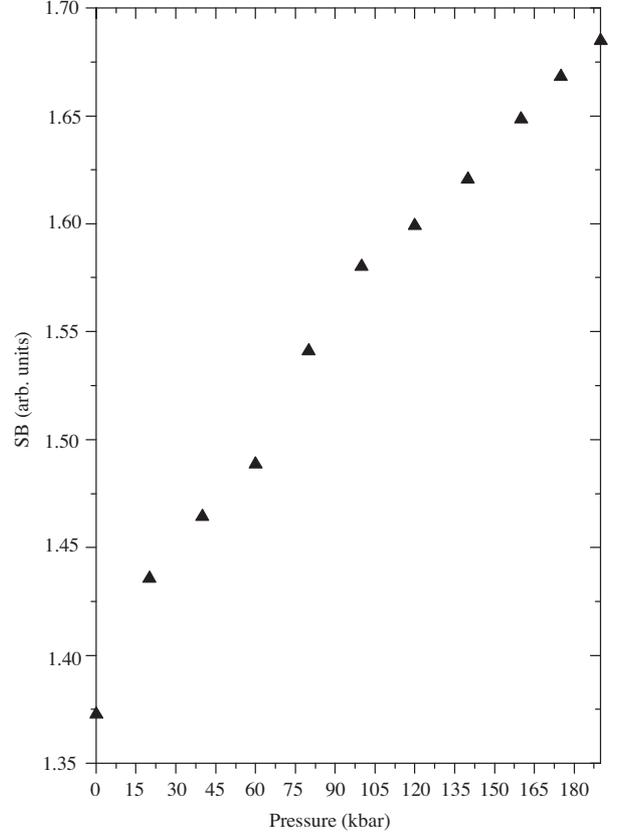
Figure 4. The variation of the S_B area with respect to the pressure variation in GaAs.

The behavior of the positron charge distribution when the pressure is applied will be explained in more detail by considering the ionicity character of the bonds, which allowed us to give a comparison between our results and the thermochemical phase diagram. Hence, the ionicity character is calculated using our empirical formula defined in [18]:

$$f_i^= \left(\frac{S_A}{S_A + S_B + \beta S_C} \right)^{\beta}, \tag{14}$$

where β is an empirical parameter separating the strongly ionic elements from weakly ionic ones. In our case, β =-1 for the III-V group and β =+1 for the II-VI group. Table 2 gives the calculated ionicity for different pressure. At atmospheric pressure, the ionicity value is 0.3117 in agreement with the Phillip's value ($f_i = 0.310$). At zero pressure, the GaAs is fourfold coordinated ($N_c = 4$). The reason that the density is so low is that nearest neighbors are found together through overlapping hybridized orbitals, whose are the well-known sp^3 hybrids. For the low pressure GaAs is still partially ionic since the relative stability of the zinc blende phase against the β-Sn phase before transition results from the fact that the covalent electronic contribution (to the total energy) favoring the zinc blende phase more than compensates the Ewald contribution favoring the β-Sn

phase. The structural transition occurs when the Ewald contribution dominates over the covalent electronic contribution. Hence, for the high pressure, a transition to a denser structure occurs which is metallic ($N_c = 6$). For this phase, there are four neighbors, displaced from the xy plane toward tetrahedral sites, and two slightly more distant (+5%) neighbors along the z axis. This is a consistent with the thermochemical phase diagram (pressure versus ionicity) found by Phillips (Figure 5), the same results were confirmed by Chelikowsky [26]. The experimental pressure transition to the β-Sn phase was found to be between 160 kbar. and 190 kbar [27, 28].

Table 2. The calculated ionicity character using equation (4) for different pressure in GaAs.

Pressure (kbar)	Ionicity value
0	0.3117
20	0.3108
40	0.309
60	0.307
80	0.3065
100	0.3053
120	0.3041
140	0.303
160	0.302
175	0.3013
190	0.3007
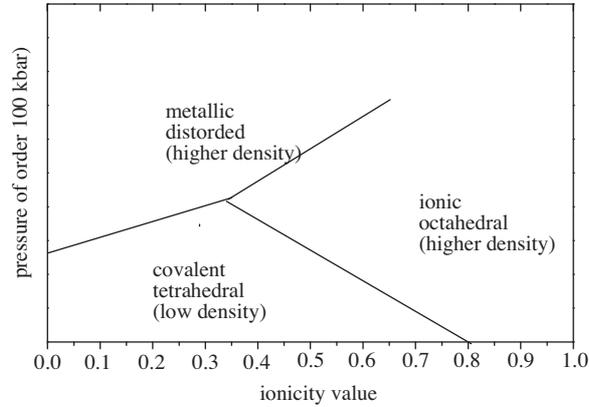
Figure 5. Schematic thermochemical (P versus f_i) phase diagram showing the covalent, ionic, and metallic structures of $A^N B^{8-N}$ compounds.

4. Conclusion

In conclusion, we have shown that from an empirical formula of a qualitative concept as ionicity, one can predict the pressure- induced phase transition of semiconductors compounds. From the positron distribution in the GaAs compound, we have found a relationship between spectroscopic crystal ionicity and spatial structure

which is consistent with a microscopic point of view. Therefore, the relative positron affinity for GaAs under pressure is different from that at normal pressure. This result allows us to state that the positron will annihilate differently in GaAs when pressure is applied. Further work is in progress.

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