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# Anomalies in the pressure dependence of the effective charge in cubic semiconductors

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We have investigated the effect of hydrostatic pressure on the Born effective charge of tetrahedral semiconductors by means of first-principles pseudopotential calculations. In agreement with recent experiments, we find that the effective charge of IV-IV compounds, such as SiC, increases in magnitude with pressure, whereas that of III-V compounds decreases. We explain this behavior in terms of conflicting effects associated with the lattice-constant variation of the long- and short-range components of the crystal potential. We show that an analogous anomaly exists in the pressure dependence of the bond polarity, as measured by the asymmetry of the static valence charge.

A fundamental quantity in the study of the dynamics of crystalline lattices is the Born effective charge $Z^*$ of the ions. For diatomic crystals, the effective charge measures the macroscopic polarization induced by a relative displacement of the cation and anion sublattices.[1] This quantity is thus implicitly related to the bond polarity of the material. The pressure dependence of $Z^*$ was recently measured for a number of III-V zinc-blende crystals.[2,3] The effective charges were found to decrease in magnitude under pressure. This behavior follows the trends generally expected for compressed materials, i.e., an increase in bond metallicity and a decrease in ionicity. Raman measurements, however, showed[4] that the effective charge in zinc-blende SiC ($Z^*_{\mathrm{SiC}}$) has a different behavior, namely, it increases with pressure. The same behavior has been observed in 6H-SiC at low pressure.[5]

The microscopic mechanisms responsible for the observed general trends in $Z^*$ are not well understood. The anomalous behavior of $Z^*_{\mathrm{SiC}}$ is unexplained, and it is unclear whether it also applies to other IV-IV compounds. The unusual pressure dependence of $Z^*_{\mathrm{SiC}}$ has been tentatively assigned to the large difference in the Si and C atomic radii.[4] A decrease in the SiC lattice constant may push more of the Si valence charge into the Wigner-Seitz sphere of C, and therefore increase its Born effective charge.[4] The Born effective charge, however, is a dynamical quantity, and arguments based on static ionic charges should be used with caution. The decrease in $Z^*$ for compressed III-V semiconductors is consistent[3] with the predictions of Harrison's bond orbital model.[6] Unfortunately, this model also predicts[4] a decrease in $Z^*_{\mathrm{SiC}}$ under pressure, in contrast with experiment. Better qualitative predictions can be obtained with the empirical pseudopotential method.[3,4] Within this approach, however, the accuracy of the effective-charge values and especially of their pressure derivative is severely limited.

Quantities that are the derivatives of the macroscopic polarization, such as $Z^*$, are difficult to determine from first-principles calculations.[7] Very recently, King-Smith and Vanderbilt[8] proposed a method based on a Berry phase approach which directly yields macroscopic polarization differences from standard band-structure calculations for perturbed and unperturbed valence Bloch states. Here we exploit this method to investigate the effect of pressure on the effective charge in tetrahedral semiconductors, and quantitatively explain the observed pressure trends of $Z^*$ in III-V and IV-IV compounds.

We will study five III-V compounds: GaAs, AlSb, GaP, InP, and GaN; and two IV-IV compounds, SiC and SiGe. Among these compounds, the first four have as stable crystalline form the zinc-blende structure. Although GaN normally crystallizes in the wurtzite structure, it can also be produced in the zinc-blende structure when grown as a thin film on a substrate with cubic symmetry. SiC exists in numerous polytypes, among which one of the common forms is the zinc-blende phase. SiGe, instead, has not been observed in the zinc-blende structure so far. It occurs as a disordered alloy with diamond structure.

Our calculations were carried out within the local density approximation (LDA) to density-functional theory, using the pseudopotential plane-wave method. We used the exchange-correlation functional of Ceperley and Alder as parametrized by Perdew and Zunger.[9] For GaAs, AlSb, GaP, InP, and SiGe, we used the pseudopotentials by Bachelet, Hamann, and Schluter.[10] For GaN and SiC, to expedite plane-wave convergence, we used pseudopotentials generated with the method by Troullier and Martins,[11] and cast them into the Kleinman-Bylander separable form.[12] The energy cutoffs were 22 Ry for GaAs, 24 Ry for GaP, 26 Ry for InP, 32 Ry for AlSb, 64 Ry for SiC, and 70 Ry for GaN. The $k$-space integrations for the self-consistent charge densities were performed with a (4,4,4) Monkhorst-Pack mesh.[13]

The electronic contribution to $Z^*$ was calculated with the method of King-Smith and Vanderbilt[8] from the polarization induced by a cation sublattice displacement of 0.1% of the bond length along the [1,1,1] direction. The $k$-space integrations for the evaluation of the induced polarization were performed with 13 $k$ points in the plane perpendicular to the [1,1,1] direction obtained by projecting the (4,4,4) Monkhorst-Pack mesh, and using a string of 20 $k$ points for the integrations along the [1,1,1] direction.

In Table I, we compare the zero-pressure effective charges obtained in the present study with the experimental data. By convention, $Z^*$ stands for the cation effective charge (the effective charge of the anion being $-Z^*$). For GaN, as an estimate of the experimental value, we use the average of the

TABLE I. Calculated and experimental (Refs. 2–4 and 19) values of the effective charges in tetrahedral semiconductors.

| | GaAs | AlSb | GaP | InP | GaN | SiC | SiGe |
|---|---|---|---|---|---|---|---|
| $Z^*_{\mathrm{calc}}$ | 2.00 | 1.83 | 2.03 | 2.38 | 2.63 | 2.73 | 0.17 |
| $Z^*_{\mathrm{expt}}$ | 2.18 | 1.91 | 2.04 | 2.55 | (2.71) | 2.70 | |

TABLE II. Calculated and experimental (Refs. 2–4) variation rates of the effective charge as defined in Eq. (1).

| | GaAs | AlSb | GaP | InP | GaN | SiC | SiGe |
|---|---|---|---|---|---|---|---|
| $\partial Z^*_{\mathrm{calc}}$ | 4.9 | 3.1 | 4.2 | 3.9 | 1.1 | -2.1 | -2.2 |
| $\partial Z^*_{\mathrm{expt}}$ | 4.8 | 5.4 | 3 | 4.5 | | -5.4 | |

diagonal elements of the effective charge tensor measured for the wurtzite structure. Good general agreement is found between the LDA predictions and the experimental values. The zero-pressure effective charges of GaAs, AlSb, GaP, InP, and SiC have been computed previously within the LDA-pseudopotential approach by means of a Green's function linear-response method.[14] The results obtained with the two approaches are identical.

For compounds of the same class (III-V or IV-IV), $Z^*$ roughly follows the trend expected from the electronegativity difference[15] of the constituent atoms ($\Delta\epsilon_{sp^3}=$ 0.44, 0.13, 0.51, 0.65, 1.87, 1.09, and $-0.06$ for GaAs, AlSb, GaP, InP, GaN, SiC, and SiGe, respectively). It is interesting to note that Si plays the role of the "cation" with respect to the effective charge in both SiC and SiGe. The result may appear surprising for SiGe, since from its location in the Periodic Table Si is expected to have a higher electronegativity than Ge (consistently with $\Delta\epsilon_{sp^3}$). The expected trend, however, is not followed by the Ge $s$ valence electrons, which are lower in energy than those in Si. Relativistic effects tend to lower the $s$ states of the heavier element Ge with respect to those of the lighter Si.[15] $Z^*$ seems thus to be primarily related to the difference in $s$ electronegativity.

In Fig. 1, we display the calculated pressure dependence of $Z^*$ for GaAs, AlSb, GaP, InP, and SiC together with the experimental derivatives $\partial Z^*/\partial P$ at zero pressure. In agreement with the experimental finding, the theoretical $Z^*$ decreases with pressure for the III-V compounds, and increases for SiC. The experimental slopes at zero pressure are in good general agreement with the calculated curves. The effective charges for the four III-V materials in Fig. 1 have similar pressure dependences over a large pressure range (up to ~30 GPa). The variation with pressure of the effective charge of SiC is qualitatively different as compared to that of the III-V materials. In addition to having opposite sign, the slope is also smaller.[16]

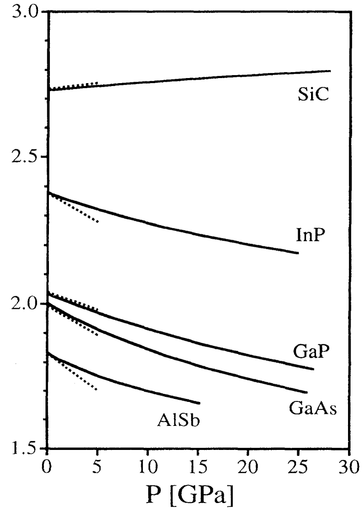

FIG. 1. Pressure dependence of the effective charge in zinc-blende materials. The solid lines are the results of the calculation. The dashed lines show the experimental pressure derivatives of the effective charges at zero pressure (Refs. 2–4) with the origin shifted at the theoretical value of $Z^*$.

In Table II, we present the calculated and experimental variation rate $\partial Z^*$ of the effective charges with the lattice constant, defined by

$$Z^*(a_0+\Delta a)=Z^*(a_0)+\partial Z^*\frac{\Delta a}{a_0}+O((\Delta a)^2). \tag{1}$$

The variation rate is the quantity most often reported in the experimental studies. A positive $\partial Z^*$ indicates a decrease in the effective charge under pressure. The $\partial Z^*$ of GaAs, AlSb, GaP, and InP have similar values. For these materials the calculated and experimental $\partial Z^*$ are $\sim 4\pm 1.5$. The theoretical and experimental $\partial Z^*$ for SiC are both negative, but differ by a factor larger than 2. It should be mentioned, however, that the experimental studies did not measure directly $\partial Z^*$, but rather the splitting between the longitudinal and transverse optic modes (LO-TO) in Raman spectra. The effective charges were then derived from $Z^{*2}=(\epsilon_\infty a^3\mu/16\pi)(\omega_{\mathrm{LO}}^2-\omega_{\mathrm{TO}}^2)$, where $\mu$ is the reduced mass of the two constituent atoms, $a$ the cubic lattice constant, and $\epsilon_\infty$ the electronic dielectric constant. The volume derivative of $\epsilon_\infty$ and the bulk modulus $B_0$, which are needed to determine $\partial Z^*$, are known accurately only in the case of GaAs.

The value of $B_0$ is especially critical to the derivation of $\partial Z^*$, and in the case of SiC a very approximate value of 322 GPa was used.[4] This value, obtained from an average between rather old data in diamond and silicon, is significantly larger than the recently measured value of 224 GPa (Ref. 17) and our calculated value of 227 GPa. Using the experimental value $B_0=224$ GPa, we derive from the Raman data $\partial Z^*_{\mathrm{expt}}=-2.4$, in good agreement with $\partial Z^*_{\mathrm{calc}}=-2.1$. In the case of AlSb, the Raman data show some scattering at low pressure, and a linear fit in $\Delta a/a_0$ was used to derive $\partial Z^*_{\mathrm{expt}}=5.4$.[3] Using instead the value $\partial Z^*/\partial P=2.65\times 10^{-2}$ GPa$^{-1}$ obtained from a quadratic fit in $P$,[3] together with $B_0^{\mathrm{expt}}=55.1$ GPa,[17] one obtains $\partial Z^*_{\mathrm{expt}}=4.4$, in better agreement with our theoretical result.

We also calculated the variation rate for SiGe and GaN, for which no experimental value is available, in order to gain information on the role played by the antisymmetric short-range and long-range components of the crystal potential. The effective charge vanishes in crystals with diamond structure, i.e., in the presence of inversion symmetry with respect to the bond center. The effective charge is thus related to the antisymmetric part of the crystal potential. Both SiC and

TABLE III. Antisymmetric static charge $n^{\mathrm{Asym}}$ and its variation rate with the lattice parameter $\partial n^{\mathrm{Asym}}$.

| | GaAs | AlSb | GaP | InP | GaN | SiC | SiGe |
|---|---|---|---|---|---|---|---|
| $n^{\mathrm{Asym}}$ | 1.9 | 1.6 | 2.2 | 2.9 | 4.2 | 2.4 | 0.1 |
| $\partial n^{\mathrm{Asym}}$ | 2.0 | 2.8 | 2.0 | 0.9 | 0.2 | -1.7 | -0.3 |

SiGe are isovalent zinc-blende materials, and therefore the antisymmetric potential reduces to the short-range component only. GaN, instead, has also a long-range asymmetric potential component associated with the Coulomb tails of the III-V ions. However, in contrast to the other III-V materials investigated, GaN is characterized by an especially large short-range antisymmetric component, since nitrogen is one of the most electronegative elements in the periodic table.

From Table II, we see that the variation rate $\partial Z^*$ in SiGe is negative and similar in magnitude to that of SiC. We have thus a second example of a IV-IV zinc-blende material with negative $\partial Z^*$. Since the ionic radii of Si and Ge are very similar, the result clearly shows that negative values of $\partial Z^*$ are not necessarily related to a large difference in ionic radii, as suggested earlier,[4] but rather to the isovalent character of the material, i.e., to the absence of an antisymmetric long-range component in the crystal potential. The calculated variation rate $\partial Z^*$ for GaN is positive, but significantly smaller than those of the other III-V materials. If one considers the three III-V compounds GaAs, GaP, and GaN, which have the same cation, and are listed here in increasing order of the anion electronegativity, we see that $\partial Z^*$ decreases when the attractive short-range component of the anion potential increases, i.e., when the antisymmetric short-range component of the crystal potential increases.

The trends in $\partial Z^*$ can be explained by considering the effect of a small variation in the lattice constant on the long-range and short-range components of the antisymmetric crystal potential $V^{\mathrm{Asym}}$. The latter produces a coupling between the valence (bonding) states, $\psi_v$, and the conduction (antibonding) states, $\psi_c$, which is responsible for $Z^*$ and to first order in $V^{\mathrm{Asym}}$ is

$$\frac{\langle \psi_c | V^{\mathrm{Asym}} | \psi_v \rangle}{E_v - E_c} = \sum_{G} \frac{V^{\mathrm{Asym}}(\vec{G})}{E_v - E_c} \langle \psi_c | e^{i\vec{G}\cdot\vec{r}} | \psi_v \rangle, \qquad (2)$$

where $V^{\mathrm{Asym}}(\vec{G})$ is the Fourier transform of $V^{\mathrm{Asym}}(\vec{r})$ (a local potential is considered for simplicity). The change in $Z^*$ with pressure results from the variation of this coupling with the lattice constant. For the materials investigated here, the variation of $|E_v - E_c|$ with the lattice constant is mostly kinetic, i.e., $|E_v - E_c| \sim a^{-2}$.[18]

In a IV-IV semiconductor, $V^{\mathrm{Asym}}$ consists only of the short-range component that scales with the lattice constant as $V^{\mathrm{Asym}}(\vec{G}) \sim 1/\Omega \sim a^{-3}$, where $\Omega$ is the unit-cell volume, and consequently

$$\left| \frac{V^{\mathrm{Asym}}(\vec{G})}{E_v - E_c} \right| \sim \frac{1}{a}. \qquad (3)$$

This indicates that in isovalent compounds such as SiC and SiGe, the effective charge should increase under pressure.

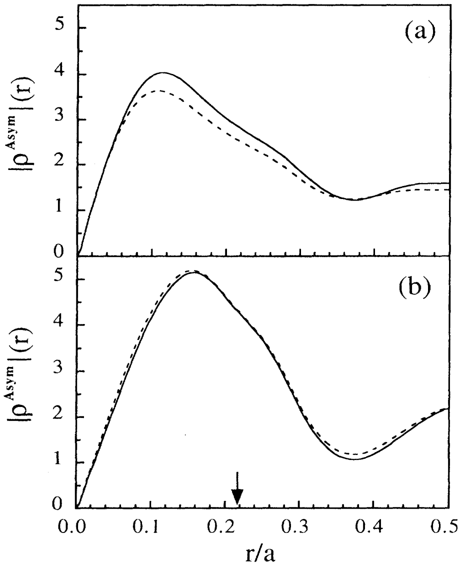

FIG. 2. Radial distribution (in electrons per unit cell) of the modulus of the antisymmetric valence charge-density component, $|\rho^{\mathrm{Asym}}|$, for GaAs (a) and SiC (b). The results at zero pressure and at $P \approx 30$ GPa are indicated by solid and dashed lines, respectively. The origin is at the bond center, and the arrow gives the cation or anion distance.

In III-V semiconductors, we have to consider in addition the long-range Coulomb terms deriving from the valence difference between the anion and the cation, which scale as $V^{\mathrm{Asym}}(\vec{G}) \sim G^{-2}/\Omega \sim a^{-1}$. Therefore for small $G$'s the coupling should scale as

$$\left| \frac{V^{\mathrm{Asym}}(\vec{G})}{E_v - E_c} \right| \sim a, \qquad (4)$$

whereas for large $G$'s, the Fourier components related to the short-range part of the potential should yield the scaling given by Eq. (3), as in the isovalent case. Thus for III-V semiconductors in which the long-range ionic terms dominate with respect to the short-range core potentials the effective charges should decrease under pressure. This applies, in particular, to GaAs, GaP, InP, and AlSb. In GaN, instead, important short-range and long-range antisymmetric potential components coexist, and substantial cancellation between their effects is expected. This accounts for the much smaller $\partial Z^*$ obtained for GaN compared to that of the other III-V materials.

The coupling due to $V^{\mathrm{Asym}}$ is also responsible for the static charge transfer between the cation and the anion, which can be measured by the asymmetry of the charge density. We note that the latter quantity depends only on the modulus of the wave functions, which are obtained by including the coupling, whereas $Z^*$ depends also on their phases. In order to illustrate the change in polarity induced by the variation of the asymmetric component of the ionic potential under pressure, we have analyzed its impact on the asymmetry of the static valence charge. We evaluated the quantity $n^{\mathrm{Asym}}$ obtained by integrating the absolute value of the antisymmetric component of the valence charge density over the whole unit cell. The values of $n^{\mathrm{Asym}}$ and of its variation rate $\partial n^{\mathrm{Asym}}$ [defined similarly to $\partial Z^*$ in Eq. (1)] are listed in Table III. As for the electronegativity difference $\Delta\epsilon_{sp^3}$, $n^{\mathrm{Asym}}$ approximatively reproduces the trends in $Z^*$ within the same class of III-V or IV-IV compounds.

The results for $\partial n^{\mathrm{Asym}}$ show that the asymmetry of the valence charge decreases under pressure in the III-V compounds, whereas it increases in both SiC and SiGe. The changes under pressure in the antisymmetric component of the GaAs and SiC valence charge densities are illustrated in Fig. 2. For the III-V compounds, the decrease under pressure of the antisymmetric charge occurs mainly in the bonding region, whereas the increase in $n^{\mathrm{Asym}}$ for SiC and SiGe comes from annular regions around each atom. Opposite pressure trends in III-V and in IV-IV compounds, resulting from the conflicting effects of the short- and long-range asymmetric potential components, are thus also reflected by the asymmetry of the static valence charge distribution.

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