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Role of Coulomb interactions in semicore levels Ga d levels of GaX semiconductors: Implication on band offsets

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ABSTRACT

The positions of the semicore Ga d levels in GaX semiconductors (X = N, P, and As) are underestimated in density functional calculations using either the local density approximation LDA or the generalized gradient approximation GGA for the exchange functional. Correcting for this inaccuracy within LDA + *U* calculations with an on-site Coulomb interaction *U* on the semicore d-states results in a modest enhancement of the band gap. We show that this modest enhancement of the band-gap energy comes from the movement of the valence-band maximum alone, thus not affecting the conduction-band states. Further, the localization of the charge on Ga d states with *U* leads to a regulation of charge on Ga. This yields a shift of 1–2 eV of the core levels on the Ga atom while the anion core levels remain unchanged.

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1. Introduction

Enormous progress has been made over the years in the development of realistic theories of materials starting from a first-principles approach [1]. A popular method in this direction is the Kohn-Sham formalism of density functional theory (DFT). The Hohenberg-Kohn theorem [2] states that the ground state energy can be written as an exact functional of the density. Unfortunately the exact form of the functional is not known, and approximations such as the original local density approximation (LDA) [3,4] as well as various types of the generalized gradient approximations (GGA) [5,6] have been used quite successfully in describing the ground state properties of a wide variety of systems. See Ref. [7] for pros and cons of the DFT.

The limitations of the approximated exchange functionals (incorrect self interaction and the neglect of correlations effects) directly affect the electron energy states, especially excited properties such as the band-gap energy. For s–p bonded semiconductors, the GW approximation [8] has been enormously successful in improving the gap energy by partially or fully self-consistently solving the Dyson equation. However, another contributory factor to the LDA band-gap error is the cation d position [9,10], especially for shallow d states. The reason is that the LDA d-levels are not deep enough to be chemically inert, and so they interact with the valence-band states leading to a reduction of the gap energy. To correct this LDA error, without degrading the computational time, an on-site correction potential *U* has been proposed [11]. The correction potential is chosen to be dependent on the atom and angular momentum projected density operator [12,13], therefore the correction will affect mainly the semicore states. Within this LDA + *U* model, the potential correction thus pushes the semicore/valence states to deeper energies and thereby modifies the valence-band maximum position as a result of the modified semicore/valence interaction. In this work, we examine the modification of the energy of the valence-band maximum and the consequent change in the band gap arising from an incorrect position of the semicore d states on the cations in binary GaX semiconductors (X = N, P, and As). The belief has been that the t_2 states on the semicore cation d states interact with the states comprising the valence-band maximum with the same symmetry pushing them up. As a result, the band gap is reduced. A recent paper [14] has questioned this model, and has proposed that a part of the shifts come from modified screening effects which result in a movement of the conduction-band minimum also. Re-examining this proposition we demonstrate that the opening of the band gap with a *U* correction on the semicore d states is due to a movement of the valence-band maximum alone. In addition there is a reorganization of charge on the Ga atoms and this results in large shifts of ∼1–2 eV of the core levels on Ga while those on the anion remain unchanged.

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Table 1
Calculated lattice constants in units of Å of GaN, GaP and GaAs using the VASP/PAW and WIEN2k/FPLAPW methods. $U = 11$, 10 and 9 eV for GaN, GaP and GaAs, respectively.

	LDA		LDA + U	
	VASP	WIEN2k	VASP	WIEN2k
GaN	4.46	4.46	4.24	4.45
GaP	5.39	5.40	5.27	5.37
GaAs	5.61	5.61	5.49	5.58

2. Methodology

We have carried out ab initio calculations within the local spin density approximation of the DFT. A full potential linearized augmented plane wave (FPLAPW) implementation in the WIEN2k code [15] was used by us in our calculations. We considered the systems GaN, GaP and GaAs in the zinc-blende structure. The radii for the muffin tin spheres used were $R_{MT} = 1.20$, 1.16 and 0.96 Å for both Ga and X in GaAs, GaP and GaN, respectively. In the calculations we use $G_{MAX} = 14$ and $|K| < 9/R_{MT}$. The LDA approximation to the exchange functional was used. The number of **k**-points used was 8 × 8 × 8 for the self-consistency and in the evaluation of the density-of-states (DOS). The tetrahedron method of integration was used for the DOS calculation. An additional potential within the LDA + U [13] formalism was introduced on the Ga d states, and the changes in the electronic structure were calculated as a function of U. Superlattices of the form $(GaX)_5/(Ga(U)X)_5$ were constructed to determine the valence- and conduction-band offsets introduced by U with respect to the $U = 0$ eV result. A **k**-points grid of 8 × 8 × 1 was used for the superlattice.

The equilibrium lattice constants of these materials were found to be 4.46, 5.40 and 5.61 Å (Table 1), respectively, in the absence of any U on the Ga d states. The value of U applicable for each system was determined by comparing the energy of the semicore d states with that determined from photoemission experiments [16,17], yielding $U = 11$, 10 and 9 eV for GaN, GaP and GaAs respectively. Using these values, the equilibrium lattice constants were determined to be slightly smaller, namely 4.45, 5.37 and 5.58 Å, respectively. The results are given in Table 1. In order to make a proper comparison with earlier published work [14] which was performed with a plane wave pseudopotential implementation, we calculate the equilibrium lattice constant also by using projector augmented-wave (PAW) potentials [18] within the VASP package [19].

In order to obtain the band lineup between the LDA and LDA+U calculations, the following prescription was followed. First, we performed bulk calculations using WIEN2k for GaX within LDA and LDA + U separately at its equilibrium lattice constant, and we determined the valence-band maximum and the conduction-band minimum with respect to the corresponding X anion 1s core level (E_{v_0} and E_{c_0} respectively). As the value of energy by itself has no meaning, we cannot compare the energy corresponding to the valence-band maximum/conduction-band minimum between two different calculations. Threfore, we constructed superlattices of the form $(GaX)_5/(Ga(U)X)_5$ and the relative separations of the two core X 1s levels in the bulk-like regions on both sides, far away from the interface, were determined. This was used to construct the band lineup. The optimized lattice constants of GaX were different from Ga(U)X, and therefore the superlattice was constructed using the average of the lattice constants obtained by the LDA and LDA + U methods. Thereafter, we incorporated the effects of strain on the band lineup, by using the literature values of the hydrostatic deformation potentials for the valence band and conduction band [20]. The strained valence-band maximum (E_v) and conduction-band minimum (E_c) were related to the unstrained values E_{v_0} and E_{v_0} by the two expressions:

$$E_v = E_{v_0} + a_v \frac{(V - V_0)}{V_0},$$

$$E_c = E_{c_0} + a_c \frac{(V - V_0)}{V_0}$$

where, V_0 was the volume of the unit cell in its equilibrium lattice constant within LDA or LDA + U while V was the volume of the unit cell at the averaged lattice constant. a_v and a_c were the hydrostatic deformation potentials for the valence-band maximum and conduction-band minimum. The procedure followed in Ref. [14] was similar except that they used the averaged electrostatic potentials instead of core levels for the definition of an absolute energy scale.

3. Results and discussion

In Fig. 1 we have plotted the Ga d and As p partial density of states for GaAs for the cases without a U on the Ga d states [panel(a)] and with a U on the Ga d states [panel(b)]. The most notable change seems to be a movement of the Ga d states from −15 eV to −18.5 eV with a U of 9 eV. There are changes in the conduction band as well as in the valence band which are not evident on the energy scale at which Fig. 1 is plotted. In order to examine the changes in the valence-band/conduction-band, we first align with respect to the As 1s core level in both the systems. The zero of energy has been chosen to be the valence-band maximum of the zero U calculations. The conduction bands of the two calculations line up and the shifts are in the valence band alone. As is evident one has an increase of the band gap. Using the value of U determined to be appropriate for each material, we find that the increase in the band gap is found to be 0.23 eV for GaN, by 0.28 eV for GaP and 0.20 eV for GaAs.

The mechanism for the opening up of the gap has been discussed in the literature in another context [21]. Wei and Zunger [21] examined the role of semicore d states in the valence-band offsets of lattice matched common anion semiconductors. The belief was that, for the first approximation, the valence-band maximum in the common anion semiconductors should be aligned. Additional interactions were responsible for the observed offsets. For instance, here, these were found to arise from an interaction between the d states with t_2 symmetry on the cation with the corresponding states with the same symmetry comprising the valence-band maximum. This interaction pushes the valence-band maximum into the band gap, reducing it from the value in the system which has no semicore states. An incorrect position of the semicore states closer to the valence-band maximum results in an enhancement of the effective p–d interaction coupling the two interacting states, and therefore a reduction in the band gap.

Recent work by Janotti et al. [14] have examined the mechanism of the increase in the band gap with U on the semicore states. Their approach involved determination of the band offsets between the GaX and the Ga(U)X calculations using the procedure described in the methodology. They found shifts in both the valence-band maximum as well as the conduction-band minimum. The former could be understood by the model described earlier. The shift in the conduction band minimum was understood in terms of modified screening arising from a U on the semicore states.

Our analysis presented in Fig. 1 assumes that the X 1s core level are aligned in the two systems. This is not the case and a superlattice geometry is used to determine the relative shifts of the X 1s core level. In addition, Ref. [14] suggested a different equilibrium lattice constant for GaX and Ga(U)X, while analysis of Fig. 1 was carried out with the same lattice constant with and without U. We examined the theoretical equilibrium lattice constant within both VASP and WIEN2k with and without potential correction U. We expect small changes due to modified interactions

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