

Relationship between atomically related core levels and ground-state properties of solids: First-principles calculations

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A first-principles theoretical study of atomic-related core levels (ARCL's) of atoms in a bond, for 30 binary compounds crystallizing in zinc-blende or rocksalt structures, is presented. It is shown that (i) the ARCL energies of a given element bonded in isostructural compounds are lower for compounds with higher bulk moduli and vice versa, and (ii) in elemental crystals, the minima of ARCL energies calculated as a function of the lattice constants coincide with the equilibrium values corresponding to minima of the total energy of the crystals. In addition, the examples demonstrate that the differences between ARCL's of the same element in different compounds can be applied for the analysis of core-level shifts in the initial-state approximation.

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I. INTRODUCTION

Density functional theory (DFT) is primarily a theory of ground-state electronic structure of atoms, molecules, and solids, considering the electronic density distribution $n(\mathbf{r})$ as a quantity playing the essential role.¹ Within the local density approximation (LDA) to DFT, the ground-state density $n(\mathbf{r})$ of an interacting system can be obtained by the self-consistent solution of the set of Kohn-Sham (KS) equations²

$$(\nabla^2 + V_{\text{eff}}[n(\mathbf{r})])\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}), \quad (1)$$

with

$$n(\mathbf{r}) = \sum_{\mathbf{i}} |\phi_{\mathbf{i}}(\mathbf{r})|^2, \quad (2)$$

where the summation is over occupied KS single-particle orbitals ϕ_i of corresponding single-particle eigenvalues ϵ_i .

The standard application of total energy calculations to a solid usually results in determining the static equilibrium properties, e.g., the equilibrium crystal structure, lattice constant a_0 , bulk modulus B_0 , its pressure derivative B'_0 , elastic constants, etc. In addition, also single-particle KS energies ϵ_i belong to ground-state properties of atoms in a solid that are unambiguously determined by $n(\mathbf{r})$. Basically, they have no rigorous physical meaning, and are considered just as auxiliary quantities in KS equations. In fact, ϵ_i 's form a good approximation for valence band structures of solids; however, they seriously underestimate the energy-band gaps in crystals and removal energies from core levels of tightly bound orbitals.

The solution of the KS equations Eqs. (1) and (2), i.e., eigenvalues, eigenvectors, and the resulting electronic density distribution $n(\mathbf{r})$, is determined by some accompanying boundary conditions for the one-electron wave functions ϕ_i . Both the valence and core states KS eigenvalues ϵ_i , the latter denoted as the core energy levels of the constituent elements, are determined with respect to energy zero of a given solid that depends on the boundary condition for KS equations. Since the periodic boundary condition leaves the additive constant of the electrostatic term in the KS equations undefined, the valence and core eigenvalues ϵ_i calculated for different solids cannot be mutually compared and, e.g., core-

level shifts of the same element in different crystals cannot be studied by direct comparison of calculated core eigenvalues ϵ_i . For such comparison, the crucial point is to relate the energies ϵ_i to some energy zero E_{zero} reasonably defined for a particular atom in particular bonds. For this purpose, a procedure for determining a common reference energy E_{zero} had been developed and applied in Refs. 3 and 4, where the details of this technique are described. We denote the energy levels obtained by means of this technique as atomic-related core levels (ARCL's) and we use the symbol $E_i^{(\text{ARCL})}$ for their values. The purpose of this paper is to demonstrate that these quantities are correlated with important ground-state properties of compounds, and to verify usefulness of the concept of ARCL's in materials with significantly varying bond properties (e.g., ionic or covalent).

The paper is organized as follows: In Sec. II, we describe computational techniques used in this work. In Sec. III, we show correlations between ARCL's and bulk moduli of solids. Section IV deals with the dependence of $E_i^{(\text{ARCL})}$ on the lattice constant a of the crystal and shows that the minimum of $E_i^{(\text{ARCL})}(a)$ corresponds to the equilibrium lattice constant. In Sec. V, we demonstrate good agreement between measured core-level shifts and calculated differences of ARCL's. Finally, we summarize the presented results.

II. COMPUTATIONAL TECHNIQUES

In order to account for the influence of valence wave functions on core levels of atoms in a bond, all-electron methods for solving Kohn-Sham equations have to be employed. In this work, the LDA plane-wave all-electron pseudopotential technique⁵ is used. The technique self-consistently adapts pseudopotentials and corresponding core and valence wave functions to the chemical bond. The plane-wave basis makes no shape approximations to either the valence charge density or the effective potentials.⁶ However, since the present model is not dependent on any particular technique, other sufficiently precise all-electron techniques such as full-potential linearized augmented plane waves (FLAPW) could be used as well.

The exchange-correlation energy is approximated by the Ceperley-Alder functional.⁷ The technical treatment of the

semicore states participating in the chemical bond, of extended valence states, or of a significant charge transfer in alkali chlorides is described in detail in Ref. 8. The lattice constant, bulk modulus, and its volume derivative were obtained by calculating the total energy for different values of the unit-cell volume and by fitting the calculated data to the Murnaghan equation of state.⁹

Concerning the technique for calculations of the atomic-related core energy levels $E_i^{(\text{ARCL})}$, we point out here only the main ideas. For a given atom within a solid, we choose a sphere centered at the atom of interest, the radius of which $R_{Q_{\text{val}}}$ is determined so that the sphere contains exactly the same amount of electronic valence charge (Q_{val}) as a neutral atom does; we define $Q_{\text{val}} = -Q_{\text{N}} - Q_{\text{core}}$, where Q_{N} is the charge of the nucleus and Q_{core} is the total charge of core electrons. In other words, the radius is chosen so that the sphere is electrically neutral as a whole.¹⁰ This condition defines, via charge neutrality, the atomic sphere for the element under study.

Inside of the atomic sphere, we perform an all-electron self-consistent atomiclike calculation where, contrary to a free atom, *boundary conditions* for valence states at $R_{Q_{\text{val}}}$ are taken from the crystal charge density. In order to take into account the nonsphericity affecting the angular-momentum character of valence wave functions in the core region, partial l -projected charges centered at the atomic positions are calculated from the wave functions in a solid in the vicinity of $R_{Q_{\text{val}}}$. The partial charges and corresponding charge densities at $R_{Q_{\text{val}}}$ serve as boundary and normalization conditions for the valence radial wave functions calculated together with their eigenvalues ϵ_i inside the atomic sphere.

An objection can arise concerning the nonsphericity of the charge density at the radius $R_{Q_{\text{val}}}$. Especially for cations in ionic compounds, $R_{Q_{\text{val}}}$ can interfere deeply with the neigh-

boring atom. However, the question about the adequacy of spherical approximation is not appropriate here because, in fact, no assumptions about the sphericity of the charge distribution are necessary at this point. The sphere of $R_{Q_{\text{val}}}$ is used for two purposes: (a) to determine the reference energy E_{zero} by reflecting the slight *relative* variations of the charge density, and (b) to form the potential boundary condition for the reconstruction of core states. The first purpose is independent of the adequacy of the spherical approximation since the scheme can reflect relative charge transfers even for arbitrarily nonspherical charge distribution, assuming that the nonsphericity of the charge distribution is of a similar character for all the compounds in question. The concept of the charge neutrality of the sphere that led to the definition of E_{zero} is not based on any spherical approximation. The second purpose is also independent of the sphericity of the charge at $R_{Q_{\text{val}}}$ since the core states are considered as spherical anyway and, in addition, the relatively localized core states are practically insensitive with respect to potential behavior outside the large sphere.

As mentioned in the Introduction, the crucial point is to find the reference energy zero E_{zero} for a given element in different bonds. Using $R_{Q_{\text{val}}}$ determined above, we *define* the value $E_{\text{zero}} = Q_{\text{val}}/R_{Q_{\text{val}}}$ as the reference value for the atomic-related core energy levels, which is the value of the potential forming, in fact, the natural electrostatic boundary condition for the valence-part Poisson equation.

The atomic-related core energy levels are then defined as $E_i^{(\text{ARCL})} = \epsilon_i - E_{\text{zero}}$.

For a better intuitive understanding, it could be helpful to realize that for a free atom, E_{zero} is what determines the electrostatic boundary condition for the Poisson equation: zero Coulomb potential at infinity. In an analogous way, in a solid E_{zero} corresponds to the electrostatic potential at the surface of the fictitious sphere that contains just enough elec-

TABLE I. Bulk moduli and ARCL's for compounds with zinc-blende structure. The data for each compound are presented in a separate cell, where (i) the ARCL in the upper-right corner of the cell (to the right from the formula of the compound) is related to the element and electronic level symbols in the header of the table, (ii) ARCL in the lower-left corner of the cell (under the formula) is related to the element and electronic level symbols on the left side of the table, and (iii) bulk modulus of each compound is given in bold in the center of the cell. The energies are in hartree units; bulk moduli in GPa. The empty cell in the lower-left corner reflects the fact that BSb does not exist in the zinc-blende structure.

	B (E_{1s})		Al (E_{2s})		Ga (E_{3s})		In (E_{4s})	
N (E_{1s})	BN	-7.6725	AlN	-4.7901	GaN	-6.0280	InN	-4.6942
	391		205		203		163	
	-16.3150		-16.2538		-16.2502		-16.1715	
P (E_{2s})	BP	-7.6190	AlP	-4.7616	GaP	-6.0159	InP	-4.6741
	168		87.1		91.7		73.2	
	-7.9664		-7.9003		-7.9015		-7.8754	
As (E_{3s})	BA _s	-7.6174	AlAs	-4.7567	GaAs	-6.0070	InAs	-4.6711
	148		77.6		76.7		64.2	
	-8.1578		-8.1055		-8.1014		-8.0800	
Sb (E_{4s})			AlSb	-4.7456	GaSb	-5.9977	InSb	-4.6618
			59.6		61.9		52.6	
		-6.1789		-6.1790		-6.1611		

TABLE II. Bulk moduli and ARCL's for rocksalt transition-metal carbides and nitrides. The data presentation is the same as in Table I.

	V (E_{1s})		Nb (E_{2s})		Ti (E_{3s})		Zr (E_{4s})	
N (E_{1s})	VN	-23.2911	NbN	-16.5266	TiN	-20.5088	ZrN	-14.8936
	383		361		331		290	
	-16.2366		-16.2295		-16.2187		-16.2003	
C (E_{1s})	VC	-23.2597	NbC	-16.5101	TiC	-20.4799	ZrC	-14.8825
	356		332		303		253	
	-11.5479		-11.5396		-11.5282		-11.5134	

tronic charge for the full electrostatic screening of the nucleus.

The details and justification of this ansatz are described and discussed in the Appendix of Ref. 4.

III. CORRELATIONS BETWEEN THE ATOMIC-RELATED CORE ENERGY LEVELS AND BULK MODULI OF SOLIDS

Using the computational techniques described above, we carried out the calculations of ARCL's for all the elements in $A^{III}-B^V$ zinc-blende compounds, transition-metal carbides and nitrides, and alkali chlorides in rocksalt structure. These binary compounds with the tetrahedral and octahedral coordinations also represent various types of bonds. The ARCL's were calculated for crystals with equilibrium lattice constants corresponding to minimum total energies.

The results of the calculations are summarized in Tables I–III. The three numbers presented for each system are the bulk modulus of the compound and the atomic-related core energy level of subvalence core orbital for both constituent atoms. The crucial outcome from these tables is the correlation between the bulk moduli and ARCL's that can be expressed by the following rule: *The $E_i^{(ARCL)}$ core energy levels of a given element bonded in isostructural compounds are lower in compounds with higher bulk moduli and vice versa.*

There is no exception from this rule for the 27 compounds shown in Tables I–III. Additionally, we did not find any exception for the group-IV compounds (e.g., C, SiC, and Si), for the II-VI compounds (e.g., ZnS, ZnSe, and ZnTe), and for the series of compounds with hexagonal CdI_2 structure.¹¹

In all tables, we present only the subvalence core s orbitals because all deeper (more inner core) orbitals correlate with the bulk moduli in a similar way as the orbitals presented in the tables.

In Table I we arranged the compounds with zinc-blende structure in rows and columns with respect to atomic num-

bers, i.e., from left to right and from top to bottom, the atomic numbers of the constituent atoms increase. The bulk moduli B_0 of the compounds (bold numbers) decrease in the rows and columns in Table I with two exceptions: $B_0[AlP] < B_0[GaP]$ and $B_0[AlSb] < B_0[GaSb]$. In these two cases, the decrease of bulk moduli when going in rows from left to right is reversed, and also the monotonous behavior of ARCL's of P and Sb is reversed for these compounds, respectively. It should be noted that the calculated relations between bulk moduli including both exceptions mentioned above are in full agreement with experimental data.¹²

The relations between bulk moduli and lattice constants for diamond and zinc-blende solids were studied by Cohen¹³ and Lam *et al.*¹⁴ Both studies present simple empirical formulas demonstrating that for the computation of bulk moduli, only the nearest-neighbor distances are required as an input. Wang and Ye¹⁵ observed the linear relation between the bulk moduli and the inverse of unit-cell volumes for the group IV and III-V zinc-blende materials. All these results nicely correlate with the fact that the unit-cell volumes V_0 of the compounds in Table I increase in columns and rows in the same way as atomic numbers, with only three exceptions: $V_0[AlP] > V_0[GaP]$, $V_0[AlAs] > V_0[GaAs]$, and $V_0[AlSb] > V_0[GaSb]$. Excluding the case of AlAs vs GaAs (where $V_0[AlAs]$ is nearly the same as $V_0[GaAs]$), the approximate relation $B_0 \sim 1/V_0$ is apparent for compounds in Table I.

The remarkable result of our core-level study (30 ARCL's in Table I) is that the core levels correlate with bulk moduli without any exception—even in the three irregular cases mentioned above.

In Table II, the compounds with rocksalt structure are arranged so that the bulk moduli are decreasing from left to right and from top to bottom. As concerns the relation between bulk moduli and the atomic numbers, the trends are reversed with respect to Table I, i.e., atomic numbers of the elements of the same row of the Periodic Table decrease (e.g., V^{23} vs Ti^{22} , Nb^{41} vs Zr^{40} , or N^7 vs C^6). The reason for

TABLE III. Bulk moduli and ARCL's for rocksalt alkali chlorides. The data presentation is similar as in Table I. Both E_{1s} and E_{2s} are listed to illustrate the parallel changes in both energy levels. The core levels for Li, Na, K, and Rb are not listed since the direct comparison of the core levels of different kinds of atoms has no meaning.

	LiCl	39.2	NaCl	33.1	KCl	24.0	RbCl	21.3
Cl (E_{1s})	-101.584		-101.538		-101.533		-101.530	
Cl (E_{2s})	-11.1984		-11.1541		-11.1480		-11.1445	

this difference originates from the different numbers of valence electrons in bonding. Contrary to the materials in Table I, the materials in Table II are not isoelectronic compounds. The compounds with the highest number of valence electrons (VN and NbN) have the highest bulk moduli; the compounds with the lowest number of valence electrons (TiC and ZrC) have the smallest bulk moduli. These results indicate that the additional electrons increase the charge participating in the bonds and strengthen them. Since the ARCL's reflect electron charge distribution, it is plausible to accept a relation between the core energies and the strength of the bonds. We see that the relative differences between bulk moduli in Table II are smaller than in Table I, and the same trend is observed for corresponding ARCL's.

Table III shows the trends for the highly ionic bonds of chlorides. Here, the atomic numbers of the cations are increasing and the bulk moduli decreasing from left to right in the same way as in Table I. The changes of core levels of chlorine follow the changes of bulk moduli.

The rule correlating ARCL's with bulk moduli, demonstrated by the results shown in Tables I–III, has an empirical character. The correlation can be qualitatively understood on the basis of an idea that as the valence charge moves from the core region to the bond region, the strength of the bond increases. Simultaneously, the transfer of valence charge from the core region to the bond region decreases the screening of the nucleus, which results in shifting the core levels to lower energies (i.e., deeper levels). As a consequence, all the ARCL's in Tables I–III are lower than corresponding energies in free atoms.

The bulk moduli, however, depend not only on the strength of the bond but also, e.g., on the numbers and directions of the bonds, i.e., on the structure. At the same time, screening the nucleus by valence electrons depends on pushing the valence charge by directional bonds into the interstitial region, i.e., on the structural coordination. This implies the condition of the isostructurality of compounds in the rule.

As an example of the structural aspect, two structurally different series of nitrides are presented: the tetrahedral series BN, AlN, GaN, and InN in Table I, and the octahedral series TiN, VN, ZrN, and NbN in Table II. The four typical tetrahedral sp^3 bonds in the zinc-blende nitrides undoubtedly screen the nitrogen core differently from the six octahedral $s-p$ bonds in the rocksalt nitrides. This example demonstrates why there is no straightforward link between the ARCL's of nitrogen in Tables I and II.

IV. DEPENDENCE OF THE ATOMIC-RELATED CORE ENERGY LEVELS ON THE LATTICE CONSTANT OF A CRYSTAL

The atomic-related core energy levels $E_i^{(\text{ARCL})}$ presented in Tables I–III were calculated for crystals in equilibrium, i.e., with lattice constants a_{eq} corresponding to minima of total energies E_{tot} . In this section, we study the ARCL's $E_i^{(\text{ARCL})}(a)$ subject to changes of the lattice constant a at the neighborhood of a_{eq} . In that way, by changing the lattice constant, it is possible to simulate both positive and negative pressures.

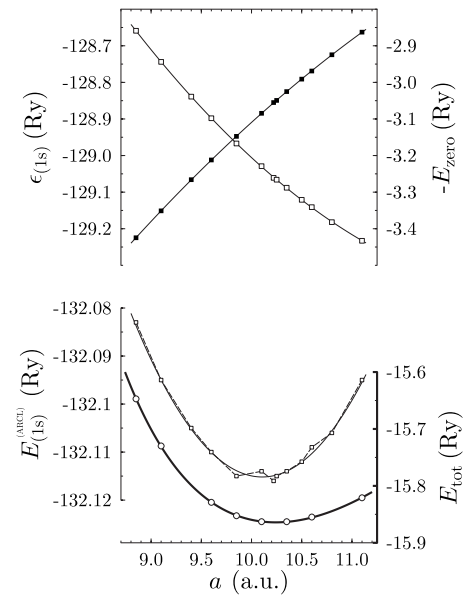


FIG. 1. The upper panel illustrates the opposite trends of 1s eigenvalue $\varepsilon_{(1s)}$ (white squares; scale on the left vertical axis) and the reference energy zero $-E_{\text{zero}}$ (full squares; scale on the right) with the lattice constant a in Si crystal. The negative sign reflects the subtraction of E_{zero} in evaluating the resulting atomic-related core level as $E_i^{(\text{ARCL})(a)} = \varepsilon_i(a) - E_{\text{zero}}(a)$ [$i=(1s)$ in this case]. Values of $E_i^{(\text{ARCL})(a)}$ are depicted in the lower panel as white squares connected with a dashed line. The thin solid line is the least-squares parabolic fit. The bold solid line connecting white circles represents the Murnaghan fit to the calculated values of the total energy (Ref. 9) (scale on the right vertical axis).

Under hydrostatic pressure, the widths of the valence bands tend to increase because of the increased overlap of the wave functions of neighboring atoms. Simultaneously, the increase of the electron density caused by the pressure increases the screening of the nuclear charge, which results in upward shifts of core levels (see, e.g., Ref. 16). On general grounds, one can expect that if a crystal is compressed or stretched (i.e., the positive or negative pressure is applied), the total energy of the crystal is increased by means of exerting an external work and the electron energy levels are shifted upward.

Using the same computational techniques as in the preceding section, we calculated $E_i^{(\text{ARCL})}$ for elemental silicon, diamond, and aluminum crystals (diamond and fcc structure, respectively) at lattice constants close to equilibrium values a_{eq} . The results are presented in Figs. 1–3. The notable result of these calculations is the correlation of the positions of the minima of the $E_i^{(\text{ARCL})}(a)$ curves with a_{eq} . We can see that within the numerical accuracy of the computations, the minima of $E_i^{(\text{ARCL})}(a)$ correspond to the total energy minima of the crystal as a function of the lattice constant a , in agreement with the general arguments mentioned above.

The correlation of the minima of the total energy E_{tot} with $E_i^{(\text{ARCL})}(a)$ in Figs. 1–3 is a result of nontrivial calculations, since the minima of the $E_i^{(\text{ARCL})}(a)$ curves arise as a result of the sum of two counteracting quantities, namely, the refer-

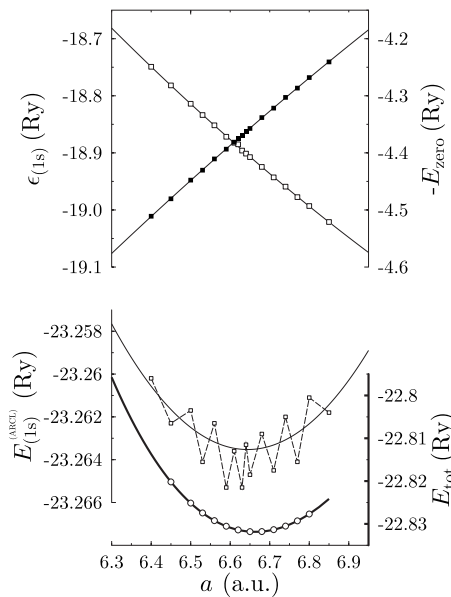


FIG. 2. Plot analogous to Fig. 1 depicting $1s$ eigenvalue, reference energy zero, atomic-related core level, and total energy as a function of the lattice constant for carbon in the diamond structure.

ence energy E_{zero} and the corresponding eigenvalues ϵ_i . In the case of decreasing lattice parameter, the charge density increases. Consequently, the $-E_{\text{zero}}$ goes downward; however, the eigenvalue goes upward (cf. the upper panels of Figs. 1–3). The opposite applies in the case of increasing lattice constant a .

The fluctuations around the least-squares fit to the $E_i^{\text{ARCL}}(a)$ values can be understood by taking into account that just the deviations of the curves in the top part from linear dependence are responsible for forming the minimum

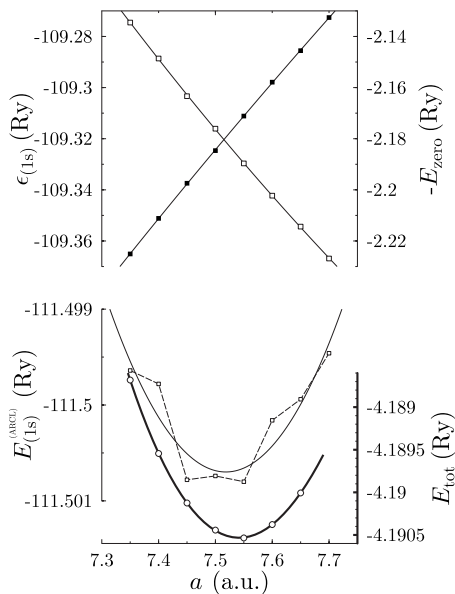


FIG. 3. Plot analogous to Fig. 1 depicting $1s$ eigenvalue, reference energy zero, atomic-related core level, and total energy as functions of the lattice constant for an Al crystal.

and that all the dependencies range in fractions of eV.

Atomic-related core levels in a system of different structures with varying coordination numbers were studied for the case of ScN in Ref. 4. Structural phases of ScN with lower total energy had deeper $E_i^{\text{ARCL}}(a)$'s for both Sc and N atoms, and vice versa, which correspond to the results presented in this section.

V. CORE-LEVEL SHIFTS AND DIFFERENCES OF ATOMIC-RELATED CORE LEVELS

Experimentally measured core-level shifts are interpreted in terms of the initial-state (local charge density) and final-state (core-hole relaxation) effects. Supposing that no external fields are present, the initial-state effects to core levels are fully determined by the local charge density distribution around the atom under study that reflects also the changes due to the bonds to neighboring atoms, e.g., due to their ionicity. Therefore, the calculations based on the self-consistently determined local charge density distribution around an atom are applied.

As mentioned in the Introduction, even though the eigenvalues ϵ_i in the KS equations have no rigorous physical meaning, their differences form a good approximation for valence band structures of solids. The E_i^{ARCL} 's alone also have no rigorous physical meaning. However, contrary to the ϵ_i , their magnitude is now related to a common reference level in different materials. This makes it meaningful to calculate the ARCL's for atoms in different chemical environments and to compare these differences with experimentally measured core-level shifts.

As an example of this approach, we present here several experimental data together with calculations based on differences of E_i^{ARCL} 's.

(i) The core-level shifts in tetrahedrally bonded $\text{Si}_{1-x}\text{C}_x$ ($0 \leq x \leq 1$) were measured by means of photoemission by Fang and Ley.¹⁷ For the limiting cases $x=0$ and $x=1$, the authors obtained a shift of -1.43 ± 0.07 eV for the C $1s$ level (i.e., an upward shift) and a shift of 1.20 ± 0.07 eV for the Si $2p$ levels (i.e., a downward shift). Our calculation, based on the differences between the corresponding E_i^{ARCL} 's, yields the values -1.49 eV for the C $1s$ level and 1.63 eV for the Si $2p$ level.⁵

(ii) Experimental core-level shifts of Si as applied for structural studies of $\text{SiN}_x\text{-H}$ and $\text{SiO}_x\text{-H}$ were presented in Refs. 18 and 19. In these alloys, the silicon atom can be surrounded by four atoms, forming Si-N_4 or Si-O_4 tetrahedra, respectively. As discussed in the references mentioned above, the core-level shifts originate as a consequence of changes of the nearest neighbors of silicon atoms affecting the core states, i.e., they can be considered as an initial-state effect. The measured shift of the Si $2p$ level in SiN_x compounds related to the Si $2p$ level in silicon is 0.78 eV per Si–N bond (see Refs. 20 and 21, and photoemission data). For Si-N_4 tetrahedron, it yields 3.12 eV, in good accordance with the value of 3.2 eV measured by x-ray emission spectroscopy (in Ref. 18). In the case of $\text{SiO}_x\text{-H}$, the measured shift of the Si $2p$ level between Si-Si_4 and Si-O_4 tetrahedra is

4.2 eV (see the photoemission spectroscopic data¹⁹ and x-ray emission spectroscopic data²²). Calculations based on the ARCL differences for Si-N₄ and Si-O₄ tetrahedra with respect to Si-Si₄ yield the core-level shifts of Si 2*p* levels with the value of 3.02 eV for Si-N₄ and 4.24 eV for Si-O₄, in good agreement with the experimental data.

It should be noted that the calculations based on the initial state, neglecting the final-state effects, cannot be used to explain the observed experimental chemical shifts generally. The cases mentioned above have been chosen so that the final-state effect could be considered as equal for the compared cases, as well as the transition matrix elements, in order to demonstrate that our description of the initial-state effects is adequate. The effects of the final state and the particular characteristics of the excitation process in a particular experimental arrangement are not the subject of this paper.

VI. SUMMARY

Correlation between trends in ground-state properties of solids and trends in ARCL's discussed in the present paper is a general feature of calculations based on LDA. In particular, the following were demonstrated:

(i) Atomic-related core levels for a particular atom in various isostructural compounds are lower in the compounds with higher bulk moduli, and vice versa. This correlation rule is demonstrated on 27 compounds crystallizing in zinc-

blende and rocksalt structures with covalent, metallic, and ionic bonds. We studied also other series of materials in various structures. Until now, no exception from the rule was found.

(ii) In elemental solids (Si, Ge, and Al), the positions of total energy minima correlate to the minimum of the $E_i^{(\text{ARCL})}(a)$ curves at the equilibrium lattice constants a_{eq} . The decrease in total energies of ScN was reflected in the ARCL shifts toward higher binding energies.

(iii) Comparing atomic-related core levels $E_i^{(\text{ARCL})}$ of atoms in different tetrahedral bonds can be used to analyze the experimental core-level shifts within the initial-state approximation. For several cases, this approach yields surprisingly good agreement with experiment.

The observed correlations testify *a posteriori* a significant physics of the ARCL's and the E_{zero} concepts, both of which are based on the analysis of the electronic charge density distribution around atoms in bonds. The results indicate that these concepts can provide a tool for the study of the ground-state quantities of solids, such as, e.g., hardness.²³

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