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Pressure-induced structural transitions in partially ionic semiconductors: Self-consistent pseudopotential approach to ZnSe

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We present a self-consistent pseudopotential study of the pressure-induced phase transition from the zinc-blende to the rocksalt structure in ZnSe. Our results for the dependence of the band structures on the lattice constant show that the transition is not accompanied by an insulator-metal transition. The dependence of the various contributions to the total energy on the lattice constant and on the structure is discussed. In agreement with current bond-charge models, we find that the strong dependence of the electron-ion interaction on the lattice constant is responsible for the phase transition.

I. INTRODUCTION

$A^N B^{8-N}$ compounds, when subject to hydrostatic pressure, transform to more dense structures due to the driving term $P\Delta V$ in the expression for the Gibbs free energy. In particular, partially ionic semiconductors, which at atmospheric pressure crystallize in the sphalerite structure with four-fold tetrahedral coordinates, undergo a phase transition to structures with six-fold octahedral coordination, either ideal (rocksalt) or distorted (e.g., white Sn).

Both the transition pressure P_t and the volume ΔV_t are known experimentally only for a few cases. However, a common trend can be recognized[1,2] which consists in an abrupt density change $\Delta V_t / V_t$ of about 20% at the transition pressure. The connection between this structural change and the nature of the chemical bonds has been extensively treated by Phillips[1] and Van Vechten[3] on the basis of their spectroscopic definition of ionicity f_i.

On the other hand, only a rather limited effort has been made[4] so far to describe this phase transition on the basis of full quantum-mechanical calculations. The reason for that is mainly their limited accuracy in predicting the total energy differences involved in the transition, typically of the order of a few tenths of an eV per atom pair (a few percent of the cohesive energy). The problem of accurately calculating equilibrium lattice constants and cohesive energies has been confronted only recently, for simple as well as for transition metals[5] and among semiconductors[6-9] only for the case of Si.

The purpose of quantitatively predicting pressure-induced phase transitions and transition heats $P\Delta V$ is even more ambitious. In this paper, we attempt *for the first time* a self-consistent calculation and apply it to ZnSe, a typical partially ionic semiconductor which most probably transforms from the zinc-blende (zb) structure to the rocksalt (rs) structure at moderate pressure [~100–200 kbars (Refs. 10–12)].

Our approach is based on a self-consistent calculation of the total energy of this system in both structures for various lattice parameters. Our aim is to understand the basic mechanism which drives the transition, in terms of the single contributions to the total energy of the electron-ion system.

Besides the total energy our calculation allows us to discuss:

(i) The energy bands and charge densities in the two different structures for various atomic densities (Sec. II). The former results can be compared to experimental and theoretical values of deformation potentials[13] and to some previous predictions[14] based on the bond-orbital method[15] (BOM). Comparison of the charge densities allows a better understanding of the chemical binding for different structures and atomic densities.

(ii) The reliability and the limitations of soft-core pseudopotentials for the understanding of structural properties.

The balance of the different total-energy contributions which determines the crystal structure is analyzed (Sec. III) and further extensions and improvements of our approach are envisaged (Sec. IV).

II. CHANGE OF ONE-ELECTRON PROPERTIES UNDER PRESSURE

Our calculation is based on the local soft-core pseudopotential models for Zn^{2+} and Se^{6+} ions proposed by Hamann.[16] Their general expression is

$$v_{\mathrm{ion}}(r) = w_1(r) + w_2(r)\,, \tag{1a}$$

where

$$w_1(r) = (v_1 + v_2 r^2)e^{-\alpha r^2} \tag{1b}$$

and $w_2(r)$ is the electrostatic potential of a Gaussian positive-charge distribution

$$\rho(r) = Z(\alpha/\pi)^{3/2}e^{-\alpha r^2}\,. \tag{1c}$$

Z denotes the number of valence electrons. Note that throughout the paper energies are given in Ry.

The Fourier transform of $v_{\mathrm{ion}}(r)$ is

$$v_{\mathrm{ion}}(G) = \frac{2}{\Omega}\left[\frac{8\pi Z}{G^2} + \left(\frac{\pi}{\alpha}\right)^{3/2} v_1 + \left(\frac{\pi}{\alpha}\right)^{3/2} v_2\left(\frac{3}{2\alpha} - \frac{G^2}{4\alpha^2}\right)\right] e^{-G^2/4\alpha}\,. \tag{2a}$$

For later purposes we define

$$\tilde{v}_{\mathrm{ion}}(G) = v_{\mathrm{ion}}(G) + \frac{2}{\Omega}\,\frac{8\pi Z}{G^2}\,, \tag{2b}$$

which describes the ion potential in the presence of a compensating homogeneous negative background. The parameters of the ion pseudopotentials are listed in Table I.

Energy bands and charge densities were calculated self-consistently for both the zb and the rs structures at various lattice constants. Convergence was generally obtained with about 90 plane waves, a typical number for soft-core pseudopotentials. To speed up the self-consistent iteration procedure, we used the Baldereschi point[17] for the calculation of the charge density. The exchange-correlation potential for the system of valence electrons was approximated by the Wigner expression[18]

$$v_{xc}(r) = -2n^{1/3}(r)\left(0.954 + \frac{0.944 + 8.77n^{1/3}(r)}{1 + 12.57n^{1/3}(r)}\right), \tag{3}$$

where $n(r)$ is the electron density.

In Fig. 1(a) the solid line represents the energy bands of ZnSe in the zb structure with the experimental equilibrium lattice constant $a = 5.65$ Å. They compare reasonably well with other nonrelativistic band structures available in the liter-

TABLE I. Pseudopotential parameters for Zn^{2+} and Se^{6+} (Ref. 16). The units used in the expression (1b) are Ry for energies and a.u. for distances.

	Z	v_1	v_2	α
Zn	2	5.7924	−1.8480	0.61
Se	6	4.7656	−3.1002	0.61

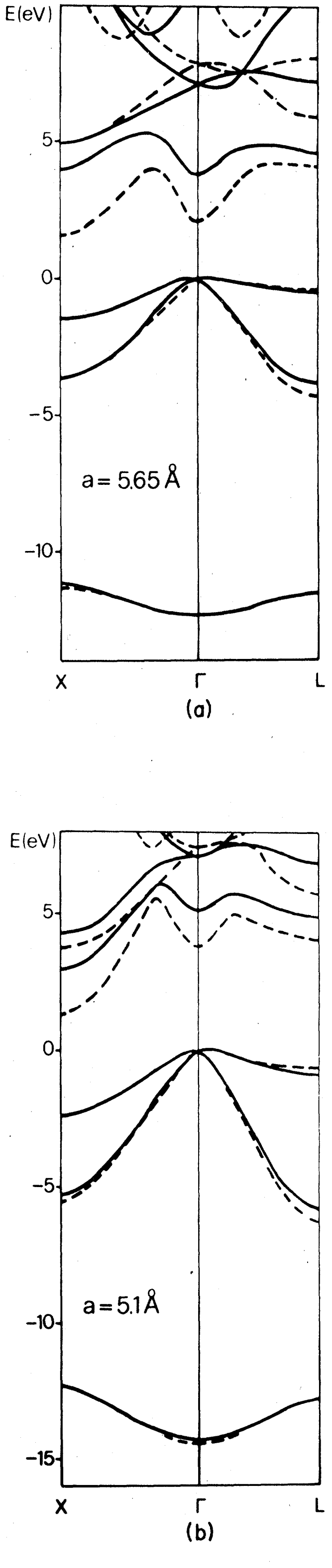

FIG. 1. Band structures of ZnSe for two different values of the lattice constant: (a) $a = 5.65$ Å (b) $a = 5.1$ Å. Solid line = zb structure; dashed line = rs structure.

ature.[19]

The comparison with experimental data is obviously of limited accuracy due to the fact that we do not take into account either nonlocality of the pseudopotential or relativistic effects. Valence-band widths, which are most affected by both effects, can be reasonably compared to photoemission data.[20,21] The worst theoretical result is the energy gap at Γ, for which we obtain 3.8 eV. The experimental value is 2.67 eV.[22] If we subtract the spin-orbit splitting ($\Delta_{so} = 0.43$ eV) (Ref. 23) from our nonrelativistic value, it reduces to 3.66 eV. The gap at L is higher by about 0.16 eV (to be compared to the experimental value 5 eV).[22] Nonlocality of the pseudopotential is expected to be responsible for changes of the order of a few tenths of an eV as has been shown by Chelikowsky and Cohen[24] for GaAs.

In view of the present state of the art of band-structure calculations, our results might appear not accurate enough. However, in this context, we were not interested in the details of the one-electron energies because they are not expected to significantly change our general description of the pressure-induced phase transition. Also, comparison of the energy bands and charge densities in the two different crystal structures and at different lattice constants will not be altered in a significant way.

In Fig. 1(a) the dashed line represents the energy bands of ZnSe in the rs structure at the same equilibrium density ($a = 5.65$ Å). In this configuration, the indirect nature of the material is much more pronounced. Also, the overall character of the band structure is more metallic, both the direct and indirect gaps being smaller. In Fig. 1(b) the two band structures are shown for higher density ($a = 5.1$ Å). The above comparison at lower

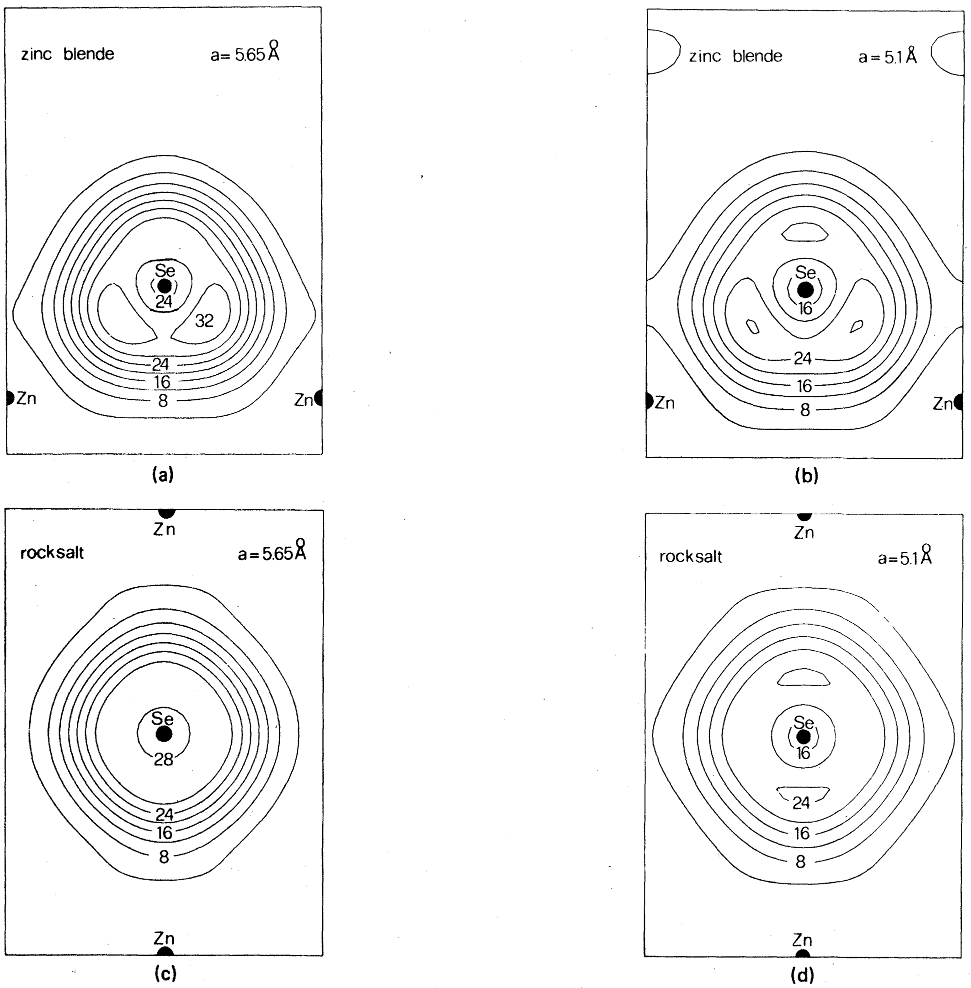

FIG. 2. Valence charge density in ZnSe: (a) zb structure ($a = 5.65$ Å), (b) zb structure ($a = 5.1$ Å), (c) rs structure ($a = 5.65$ Å); (d) rs structure ($a = 5.1$ Å).

density changes in a significant way. While the $\Gamma - \Gamma$ and the $\Gamma - L$ gaps increase with decreasing lattice constant, the indirect $\Gamma - X$ gap strongly decreases in the zb structure and changes only slightly ($\Delta E = 0.01$ eV) in the rs structure. This behavior is in contrast to the non-self-consistent calculation of Ciraci[14] based on the BOM, for ZnSe in the zb structure, which predicts both the indirect gaps at L and X to increase as the lattice constant decreases.

We find that the valence bands are nearly structure independent whereas the conduction bands strongly depend on the structure. This behavior can be qualitatively explained by inspection of the respective charge densities. As shown in Fig. 2, the valence states are essentially localized around the anions and thus only slightly influenced by the relative position of the anion and the cation sublattices. The same argument does not hold for the conduction states, which on the contrary are rather extended in real space.[25]

Both valence and conduction states depend rather strongly on the lattice constant. The density of the valence charge density for the zb structure is also shown in Fig. 2. We notice that the electronic charge density becomes more diluted with increasing atomic density and we observe in particular a decrease of the valence bond charges, which already indicates a destabilization of the zinc-blende lattice.[26,27] We shall discuss this point in more detail in Sec. III.

We have calculated the deformation potentials for the lowest gaps at Γ, X, and L for the zinc-blende structure. These are given in Table II together with the available experimental values and the theoretical values derived by Cerdeira *et al.*[13] in their non-self-consistent Korringa-Kohn-Rostoker approach. Both our values and those of Ref. 13 are calculated with the experimental dependence of the lattice constant on external pressure

$$\frac{1}{a}\frac{da}{dP} = -0.57 \times 10^{-12}\ \text{cm}^2/\text{dyn}$$

(Ref. 28). The agreement is rather satisfactory, in particular if we keep in mind that our band structure differs somewhat from the experimental one as discussed previously.

TABLE II. Calculated and experimental pressure coefficients for ZnSe (in 10^{-6} eV/bar) for various energy gaps. Spin-orbit effects have been neglected in our calculation.

	Γ	X	L
Present calculation	7.5	4.0	−0.1
Theoretical (Ref. 13)	7.3	6.0	
Experimental [a]	10.8		

[a] D. W. Langer, quoted in Ref. 13.

III. CHANGE OF THE TOTAL ENERGY UNDER PRESSURE

A. Formulation

The total energy of the crystal per unit cell (volume Ω) is

$$E_{\text{tot}} = E_{\text{BS}} - E_{ee} + E_{ii}\,, \tag{4a}$$

where E_{BS} is the sum of the one-electron energies discussed in Sec. II

$$E_{\text{BS}} = \frac{2}{\Omega_{\text{BZ}}} \sum_n \int_{\Omega_{\text{BZ}}} d^3k\, E_n(\vec{k})\,, \tag{4b}$$

with Ω = volume of the Brillouin zone and n = band index, running over the valence bands. E_{ii} is the Madelung energy of two ion sublattices of charge Z_ie and Z_je, respectively:

$$E_{ii} = \sum_{i,j,l}{}' \frac{Z_iZ_j}{|\vec{R}_l + \vec{\tau}_i - \vec{\tau}_j|} \tag{4c}$$

and E_{ee} is the interaction energy of the electron system:

$$E_{ee} = E_H + E_{\text{xc}}\,, \tag{4d}$$

namely, the sum of the Hartree (electrostatic) interaction term which depends locally on the electron density $n(r)$:

$$E_H = 2\int_\Omega d^3r \int_{\text{all}} d^3r\, \frac{n(r)n(r')}{|r - r'|} \tag{4e}$$

and of the exchange and correlation interaction terms which are nonlocal in $n(r)$. Within the framework of local density theory,[29] E_{xc} can be reduced to a local form as

$$E_{\text{xc}} = E_{\text{xc}}^{(1)} + E_{\text{xc}}^{(2)}\,, \tag{4f}$$

with

$$E_{\text{xc}}^{(1)} = \int_\Omega v_{\text{xc}}(n(r))n(r)d^3r\,, \tag{4g}$$

$$E_{\text{xc}}^{(2)} = -\int_\Omega n(r)\epsilon_{\text{xc}}(n(r))d^3r\,; \tag{4h}$$

here $\epsilon_{\text{xc}}(n)$ is the exchange-correlation energy density and is related to $v_{\text{xc}}(n)$ through the expression

$$v_{\text{xc}}(n) = \frac{d[n\epsilon_{\text{xc}}(n)]}{dn}\,. \tag{4i}$$

The one-electron term E_{BS} in (4b) can be further decomposed in its single contributions as

$$E_{\text{BS}} = T + E_{ei} + 2E_H + E_{\text{xc}}^{(1)}\,, \tag{5a}$$

where T is the kinetic energy

$$T=\frac{2}{\Omega_{\mathrm{BZ}}}\sum_{n}\int d^{3}k\langle n\vec{k}|\Delta|n\vec{k}\rangle \tag{5b}$$

and E_{ei} is the electron-ion interaction energy

$$E_{ei}=\sum_{l,i}\int_{\Omega}d^{3}r\,n(r)\tilde{v}_{\mathrm{ion}}(\vec{r}+\vec{R}_{l}+\vec{\tau}_{i}). \tag{5c}$$

With Eqs. (5) we can rewrite the total energy as

$$E_{\mathrm{tot}}=T+E_{ei}+E_{H}+E_{ii}-E_{\mathrm{xc}}^{(2)}, \tag{6}$$

which we will use in the later discussion. Since we work in the pseudopotential scheme, $n(r)$ in the above expressions is obviously the pseudodensity of valence electrons and $\tilde{v}_{\mathrm{ion}}$ in (5c) is the ionic pseudopotential given in Sec. II. E_{ii} and E_H can be calculated separately, provided this is done in the presence of a uniform opposite charge distribution that compensates unwanted infinite quantities (see, for instance, Ref. 8).

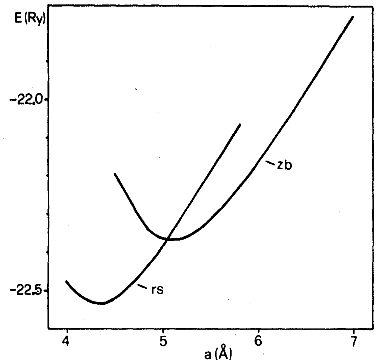

FIG. 3. Total energy of ZnSe in the zb and in the rs structure as a function of the lattice constant [uncorrected $\tilde{v}(q=0)$].

B. Determination of equilibrium lattice constants and transition pressure

In Fig. 3 the total energy $E_{\mathrm{tot}}(a)$ in (4) is shown as a function of the lattice constant in both zb and

TABLE III. Total energy contributions (in Ry) [Eqs. (4) and (5)] for the zinc-blende (above) and the rocksalt (below) structures at different values of the lattice constant (in Å).

a	4.5	4.9	5.1	5.37	5.65	5.8
T	8.251	7.62	7.355	7.054	6.793	6.673
	7.878	7.198	6.945	6.669	6.446	6.348
$2E_H$	2.452	3.546	4.102	4.854	5.630	6.032
	1.974	2.894	3.400	4.115	4.876	5.274
E_{ei}	−2.259	−4.492	−5.474	−6.688	−7.843	−8.413
	−1.248	−3.176	−4.088	−5.270	−6.441	−7.030
$E_{\mathrm{xc}}^{(1)}$	−7.225	−6.934	−6.812	−6.667	−6.536	−6.473
	−7.114	−6.790	−6.661	−6.511	−6.381	−6.320
E_{BS}	1.219	−0.266	−0.829	−1.447	−1.956	−2.181
	1.490	0.126	−0.404	−0.994	−1.500	−1.729
E_H	1.226	1.773	2.051	2.427	2.815	3.016
	0.987	1.447	1.700	2.057	2.438	2.637
$E_{\mathrm{xc}}^{(1)}$	−7.225	−6.934	−6.812	−6.667	−6.536	−6.973
	−7.114	−6.790	−6.661	−6.511	−6.357	−6.320
$E_{\mathrm{xc}}^{(2)}$	5.583	5.364	5.273	−5.165	5.068	5.021
	5.499	5.256	5.159	−5.047	4.950	4.905
E_{ee}	−0.416	0.203	0.512	0.925	1.347	1.564
	−0.628	−0.087	0.198	0.593	1.007	1.222
E_{ii}	−23.829	−21.884	−21.026	−19.969	−18.974	−18.488
	−24.641	−22.629	−21.742	−20.649	−19.620	−19.118
E_{BS}	1.219	−0.266	−0.829	−1.447	−1.956	−2.181
	1.490	0.126	−0.404	−0.997	−1.500	−1.728
E_{ee}	−0.416	0.203	0.512	0.925	1.347	1.564
	−0.628	−0.087	0.198	0.593	1.007	1.222
E_{tot}	−22.194	−22.353	−22.367	−22.341	−22.277	−22.233
	−22.523	−22.416	−22.344	−22.239	−22.127	−22.068

rs structures. For the zb structure, our *ab initio* calculation yields an equilibrium lattice constant which is 10% smaller than the experimental value (~5.1 Å instead of 5.65 Å). Moreover, the absolute minimum of the total energy corresponds to the rs structure, which makes the zb structure metastable at zero pressure.

It is well known that the prediction of crystal stability at the experimental lattice constant from a fully *ab initio* calculation is a very difficult problem, in view of the delicate balance of the bonding forces involved. In order to find the term responsible for the deviation from experiment, we have to study the single contributions to the total energy (4) and (5), and to analyze carefully the assumptions of our calculation.

In Table III we quote the values of all the energy terms in (4), and in Fig. 4 their dependence on a in the zb structure is explicitly shown. It is evident that the most relevant contributions come from the attractive Madelung energy E_{ii} and from the repulsive electron-ion interaction. The latter is essentially caused by its contribution $8[\tilde{v}_{\text{ion}}^{\text{Zn}}(0)+\tilde{v}_{\text{ion}}^{\text{Se}}(0)]$ [see Eq. (2)] which describes the interaction of a uniform electron gas with the ions. Unfortunately, this term depends on the assumed model in a crucial way, as already pointed out by Ihm and Cohen[8] in the case of Si. In full analogy with the remarks of Martin and Wendel,[6] Harris and Jones,[7] and Ihm and Cohen[8] about the Appelbaum and Hamann pseudopotential for Si,[30] we find that also for ZnSe the mean value $\tilde{v}_{\text{ion}}(0)$ of the pseudopotential in Eqs. (1) and (2) is not sufficiently repulsive. This yields an equilibrium lattice constant which is far too small.

Moreover, we notice that it strongly depends on the lattice constant being *linear* in the total density ($\sim 1/a^3$):

$$\tilde{v}_{\text{ion}}^{\text{Zn}}(0)+\tilde{v}_{\text{ion}}^{\text{Se}}(0)=\frac{2}{\Omega}\sum_i\left[v_1^i\left(\frac{\pi}{\alpha}\right)^{3/2}+\frac{3}{2a}\,v_2^i\left(\frac{\pi}{\alpha}\right)^{3/2}+\frac{\pi Z_i}{\alpha}\right]=\frac{C}{a^3}\,.$$

With the potential parameters in Table I, we obtain $C=254.35\ \text{Ry}\,r_B^3$. It is worthwhile to point out that a change in $\tilde{v}_{\text{ion}}(0)$ does not alter either the relative position of the energy bands or the wave functions and charge densities (discussed in Sec. II) and clearly is structure independent.

The other approximation involved in our calculation should be of minor importance, namely, the treatment of local exchange-correlation interaction and other features of the electron-ion pseudopotential model. In particular, the former term, being only slightly dependent on the lattice constant and on the structure, plays a minor role in the relative stability of the structures as will be discussed later. This has already been pointed out by Ihm and Cohen in the case of Si.[8]

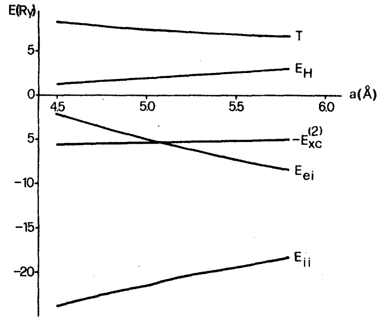

FIG. 4. Individual contributions to the total energy for ZnSe in the zb structure. The notation is the same as in Eq. (6).

We have adjusted the constant C in Eq. (6) to reproduce the equilibrium lattice constant $a_{zb}=5.65$ Å. This choice (correction $\Delta C/C\sim 0.3$) gives the new dependence E_{tot} (a) shown in Fig. 5, here also the zb structure is correctly predicted as the stable one, and the rs structure has a metastable minimum at $a_{rs}\sim 5.3$ Å. This implies that, on passing from zb to rs structure, while the distance between like ions decreases by 6%, the bond length Zn–Se increases by about 8% (from 2.45 to 2.65 Å). This latter corresponds to the transition to a less covalent type of bonding, for increasing density.

The total energy E_{tot} is related to the external hydrostatic pressure P by

$$E_{\text{tot}}=E_0-P\Omega\,, \tag{7}$$

where E_0 is the total energy per unit cell at zero pressure. In Fig. 6 the total energy is plotted as a function of Ω; the external pressure is given by

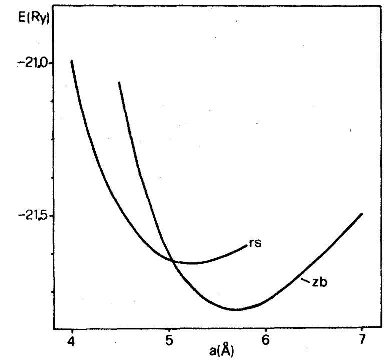

FIG. 5. Total energy of ZnSe in the zinc-blende and in the rs structure as a function of the lattice constant. [corrected $\tilde{v}(q=0)$, see text].

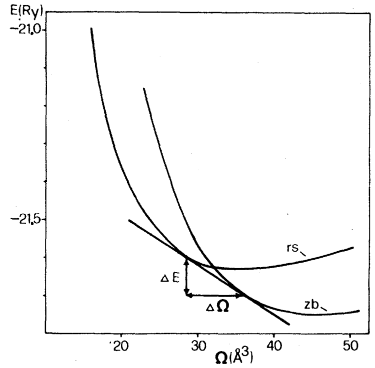

FIG. 6. Total energy of ZnSe in the zb and in the rs structure as a function of the unit-cell volume [corrected $\tilde{v}(q=0)$, see text].

the gradient of $E_0(\Omega)$. For the change of the lattice constant as a function of pressure we obtain $(1/a)(da/dP) = -0.32 \times 10^{-12}$ which can be compared to the experimental value of -0.57×10^{-12} cm²/dyn.[28] The straight line indicates the critical pressure for which the rs and the zb structures coexist. This equals the transition pressure if hysteresis effects can be neglected. From Fig. 6 we obtain a transition pressure of 282 kbars. The lattice constant changes from 5.25 to 4.85 Å during the transition which corresponds to a volume change of 21%. Experimental data[10,12] give a value of 137 kbars for the transition pressure (see, however, Ref. 31) and a volume change of about 20%. The experimental value $a = 5.08 \pm 0.03$ Å for the lattice constant of the rs lattice under pressure, is reported in Ref. 11. It is obvious that the calculated value for the transition pressure depends critically on our choice of $\tilde{v}_{\text{ion}}(0)$: the original value would have given $P_t < 0$. The calculated indirect gap is 3.3 eV just before the transition and 1.1 eV after the transition. Thus, as already mentioned before, the structural phase transition is not accompanied by a semiconductor-metal transition.

C. Mechanism of the structural phase transition

To gain a physical understanding of the mechanism that drives the structural transition, we analyze the relative role played by the individual contributions to the total energy for the two structures. This is done in Fig. 7 where we have plotted the quantities

$$\Delta x = x(\text{rs}) - x(\text{zb}),$$

for each term "x" in the expression of the total energy [Eq. (5d)]. We note that these energy differences are not affected by our choice of $\tilde{v}_{\text{ion}}(0)$. Figure 7 indicates that the electron-ion interaction E_{ei} and the exchange-correlation energy $E_{\text{xc}}^{(2)}$ favor the zb structure whereas the other terms (i.e., the kinetic energy T and in particular the ion-ion interaction E_{ii} and the Hartree energy E_H) favor the rs structure. The exchange-correlation interaction is rather structure independent and can be neglected for the discussion of the relative stability of the two considered lattices.

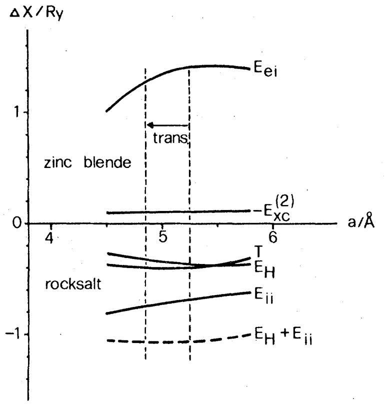

FIG. 7. The difference between the various contributions to the total energy of the rs and the zb structure as a function of the lattice constant.

The covalent interaction energy, which is strongly directional and therefore involves at least three-body forces, is described by the electron-ion interaction E_{ei}. This term, which tends to favor the covalent zb structure, decreases rapidly for increasing atomic densities. This can be easily understood: E_{ei} is strongly determined by the distribution of the valence charge density and in particular by the amount of bond charge Z_b (Refs. 26 and 27) in the case of the zb structure. As shown in Sec. II, our self-consistent electronic charge density becomes more diluted as the lattice constant decreases. The corresponding decrease of bond charge leads to a destabilization of the zb structure for increasing hydrostatic pressure. This can be seen as the microscopic description of the mechanism of the phase transition. The relevance of Z_b for the stabilization of covalent structures and covalent-ionic phase transitions was already emphasized in Refs. 27 and 32.

E_{ii}, E_H, and also the kinetic energy T favor the rocksalt structure: the former because the repulsion of the charges decreases with the nearest-neighbor distance, the latter because the overall electron density is smoother in structures with higher coordination.

The density dependences of ΔE_H and ΔE_{ii} are opposite, the sum of both being roughly constant. This is again a consequence of the density and structure dependence of the valence-electron distribution discussed in Sec. II. It thus appears that the classical Coulomb interaction energies E_H

and E_{ii} are the essential contributions which favor the rs structure against the zb structure. The phase transition itself, however, is driven by the electron-ion interaction E_{ei} which by itself always favors the zb structure, but much less for small lattice constants.

IV. CONCLUDING REMARKS

We have shown that the local-density approach to the total energy of the system is able to describe the basic mechanism which is responsible for pressure-induced phase transitions. In this work, we have considered ZnSe as a prototype of partially ionic semiconductors and studied its transition from a tetrahedrally coordinated to an octahedrally coordinated structure. Such a transition cannot be explained on the basis of simple Born-type phenomenological models of atomic interactions[33] in which only pairwise interatomic forces are considered.[34]

We have shown that the electron-ion interaction plays a key role for the relative stability of the two competitive structures. The density dependence of the electronic charge density shows that the bond charge decreases with increasing atomic density, thus leading to a destabilization of the tetrahedrally coordinated lattice. This behavior of the charge density indicates a density-dependent hybridization of valence states, changing from sp^3 character with increasing atomic density. Bonding Wannier functions,[35] if available, would probably be a useful tool to investigate this point.

In agreement with previous studies of cohesive properties in Si,[6-9] we have found that lack of accuracy in the model pseudopotential for the electron-ion interaction does not allow a quantitative picture of the transition. Fitting of the parameters can be avoided if a totally *ab initio* pseudopotential, which is able to reproduce free-ion energies as well as wave functions, is used. This kind of pseudopotential model starts now to be available.[36] We plan to continue our work along these lines. We believe that the extension of this kind of work to other materials, together with more accurate experimental results, would be of great interest for the understanding of the structural chemistry of semiconducting compounds.

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