

Theoretical study on the high-pressure phase transformation in ZnSe

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The high-pressure phase transition in ZnSe has been examined with full-potential linear augmented plane wave and numerical atomic orbital band structure calculations within the local-density approximation. At ambient pressure, ZnSe is a direct band gap semiconductor with the zinc-blende structure. Under compression, the direct band gap at Γ increases and eventually is replaced by the indirect gap at X . At about 15 GPa, the zinc-blende structure becomes unstable and transforms into the rock salt structure, which is metallic in nature. Theoretical results fully substantiate the recent experimental observation of the metallization of ZnSe at pressures higher than 13 GPa.

I. INTRODUCTION

The electronic structure of ZnSe under high pressure has been a subject of great interest for almost three decades. A phase transition at about 12–20 GPa has been characterized by both x-ray diffraction and electrical resistivity measurements. At the transition, ZnSe transforms from a four-coordinated zinc-blende (ZB) structure to a six-coordinated rock salt (RS) structure. This transformation is accompanied by a drastic drop in the electrical resistivity, which strongly suggests that the RS phase may be metallic. The nature of the high-pressure phase had been a subject of controversy until very recently, when its metallic character was confirmed unequivocally.¹

This experimental observation, however, is in contradiction with a theoretical study² which found the high-pressure transition is associated with the formation of a new semiconductor phase. This earlier calculation is based on soft-core pseudopotential plane wave method. The results showed that the band structures for the ZB and RS phases are very similar at high-pressure. Both remain semiconducting with an indirect band gap with the band gap for the RS structure smaller than that of the ZB structure. Without an empirical correction to the electron-ion interaction term, this calculation seriously underestimated the equilibrium lattice constant of the ZB phase and predicted that the ZB structure is metastable with respect to the RS structure. These observations are rather surprising. In particular, comparison with the electronic structure of the well known type IV-VI semiconductors with the rock salt structure would suggest that the electron deficient ZnSe RS phase should behave like a metal.

In view of the discrepancy in the experimental evidence with the previous theoretical study and the recent development of accurate total energy calculation methodologies, the structural and electronic properties of ZnSe at high-pressure are reexamined in this study. The results here give excellent structural parameters as compared to experiment and substantiate the experimental observation that ZnSe with the RS structure is indeed metallic.

II. COMPUTATIONAL DETAILS

Both the full-potential linear augmented plane wave (FLAPW) method³ and numerical atomic orbital (NAO) method⁶ were used to calculate the electronic structure and the total energy of ZnSe in the zinc-blende and rock salt phases in a wide range of pressures. In contrast to pseudopotential calculations, Zn 3d states are treated as band states because of their proximity to the valence band.

The FLAPW method places no restrictions on the form of crystalline potential and is known to yield reliable structural parameters for metals, semiconductors, and insulators. Relativistic effects are included via the scalar-relativistic treatment for valence electrons and the fully relativistic one for the core. The calculations are performed using a Hedin-Lunqvist⁴ parametrization of the exchange-correlation potential in the local-density approximation (LDA). Plane wave cutoff was chosen from the condition $R_{\text{MT}}K_{\text{max}} = 7.0$ Å sufficiently dense k -point grid was used to achieve a convergence of total energy to better than 1 mRy.

The NAO calculations are performed within the linear-combination-of-atomic-orbital (LCAO) approximation with the atomic basis sets obtained from a Herman-Skillman-type calculation for a spherically symmetric solution of the atom. The core levels up to the 2p level and to the 3d level for Zn and Se atoms, respectively, were kept frozen. To improve accuracy, the NAO basis set is augmented with an additional set of Slater-type orbitals (STO's) for each of the valence s , p , and d levels. A highly efficient and accurate tetrahedron scheme is used for the k -space integration.⁷ The gradient corrections (GC's) to the electron density were evaluated in a perturbative manner using the self-consistent LDA density. The Becke correction⁸ for the exchange energy and the Perdew correction for the correlation energy⁹ were employed. It has been shown previously that the NAO method is as accurate as the FLAPW method.⁶

III. RESULTS AND DISCUSSION

The total energy of the ZB and RS phase of ZnSe as a function of the lattice parameter calculated with differ-

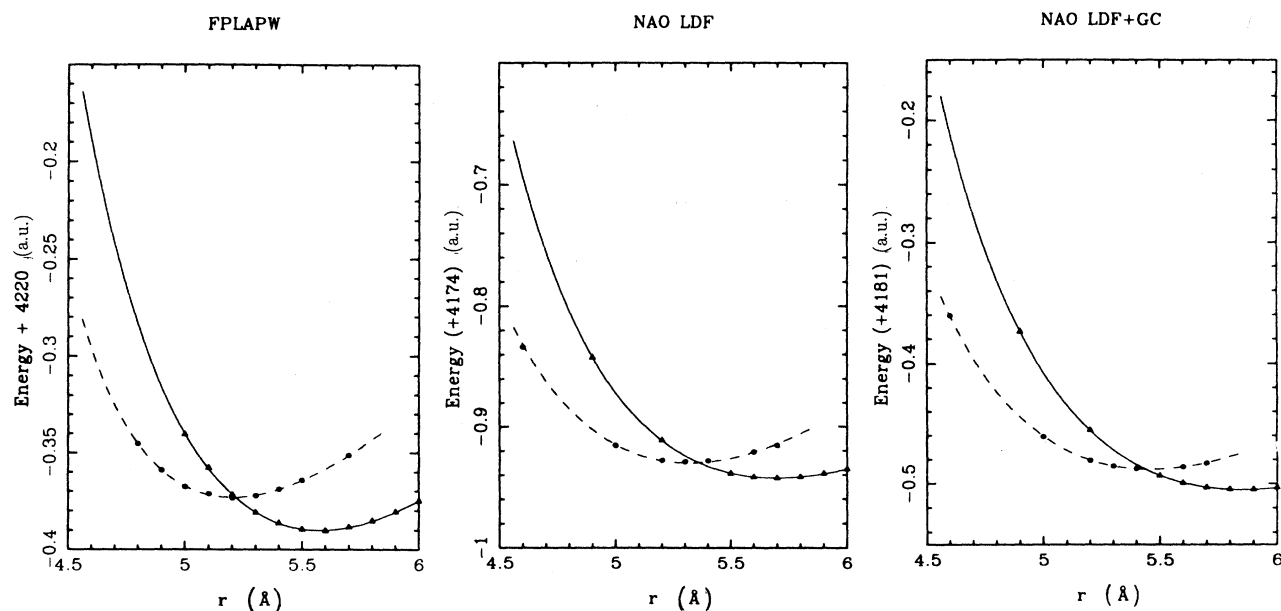


FIG. 1. The total energy curve for the zinc-blende (full line) and rock salt (dashed line) structure of ZnSe. (a) FLAPW calculation; (b) numerical atomic basis set augmented with localized Slater-type orbitals calculations; (c) addition of gradient corrections to (b).

ent approaches are shown Fig. 1. All three calculations reproduced the expected trend that the ZB structure is more stable than the denser RS structure. The calculated energy difference is about 8–11 kcal/mol. A summary of the calculated bulk properties obtained by fitting the calculated total energy to the Murnaghan equation of state¹⁰ is tabulated in Table I. For the ZB ZnSe phase where experimental values are available for comparison the calculated results are in reasonable agreement. The FLAPW predicted lattice parameter of 5.544 Å is only 2% shorter and the bulk modulus of 72.44 GPa is slightly higher than the observed values of 5.65 Å and 62.5 GPa, respectively. In comparison, at the LDA level, the results obtained from the NAO calculations are almost in quantitative agreement with experiment. The nonlocal corrections to the LDA increase the lattice constant significantly to 5.82 Å and gave a smaller bulk modulus of 52.92 GPa. It is apparent that the nonlocal corrections generally overestimate the lattice constant but under-

estimate the bulk modulus. This behavior is consistent with recent studies on the effect of gradient corrections to the local-density functional in both the metallic¹¹ and semiconductor¹² systems.

The theoretical transition pressure for the transformation from the ZB to RS structure, obtained by equating the Gibbs free energy of the two phases by common-tangent construction, occurs in the range 15–20 GPa (Table I) is well within the experimental estimate of 12–20 GPa. It is interesting to note that in all the calculations the phase transition is predicted to be very close to the energy minimum of the RS structure. This observation shows that the reverse transformation back to the ZB structure when the pressure is relieved does not have a significant activation barrier. Consequently the ZB → RS transformation is reversible, a fact that has already been established by experiments. At the NAO calculated transition pressure of 15.2 GPa the ZB phase with a lattice constant of 5.38 Å transforms into the RS

TABLE I. Theoretical and experimental structural parameters of ZnSe.

	FLAPW	NAO	NAO+GC	Expt.
Zinc blende				
B_0 (GPa)	72.44	62.45	52.92	62.5 ^a
B'	4.02	4.05	3.81	
a_0 (Å)	5.544	5.666	5.820	5.65 ^b
Rock salt				
B_0 (GPa)	90.72	92.16	74.16	
B'	4.92	3.47	3.55	
a_0 (Å)	5.172	5.288	5.426	
Transition pressure (GPa)	20.8	15.2	16.9	12 – 20
$\Delta E(\text{ZB-RS})$ (kcal/mol)	-10.4	-7.9	-10.7	

^aReference 19.

^bReference 20.

structure with a lattice constant of 5.10 Å. The volume decrease associated with the transition is 14.8%. The predicted values are in substantial agreement with recent experimental measurements of the lattice constant before (ZB)¹³ and after (RS)¹⁴ the transition at 5.308 Å and 5.04 Å, respectively, with a volume change of 15%.¹

The band structures calculated with FLAPW and NAO methods are very similar and, therefore, in the ensuing discussion only the FLAPW results will be presented. Electronic structure of ZnSe for two different lattice constants in two phases is shown in Fig. 2. At equilibrium [Fig. 2(a)] the calculated direct band gap at Γ is $E_g = 1.2$ eV, significantly smaller than the experimental value $E_g = 2.7$ eV, which is a well-known limitation of LDA. Note that the band gap obtained in the pseudopotential calculation² is actually greater than experimental value, which is unusual, since local-density-functional-based methods tend to underestimate the value of the band gap. As the pressure increases, the direct band gap at Γ increases also, whereas the indirect band gap at X decreases [see Fig. 2(b)], so that they are both equal to $E_g = 2.25$ eV at $a = 5.2$ Å. The direct band gap has the pressure coefficient 5.3 meV/kbar, whereas the pressure coefficient for the indirect gap is -2.6 meV/kbar. This behavior is consistent with an empirical rule governing the pressure coefficients of the energy gaps of semiconductors.⁵ It should be stressed that the ZB phase remains semiconducting up to the transition pressure.

Metallization occurs when ZnSe is transformed into the RS phase [Fig. 2(c)], rather than as a result of the band closure. The present result is in contradiction with the earlier work² which suggested the RS phase is semiconducting. The cause of this discrepancy is unknown. However, a survey of the well-known band structure of the IV-VI semiconductors with the RS structure, such as PbTe, PbSe, etc., shows that all these materials have 10 *sp* valence electrons and exhibit small energy gaps at the L point. In comparison, ZnSe, with only 8 *sp* electrons, will therefore be metallic due to the partially filled fifth band. The energy difference between the L point and X point is calculated to be -1.06 eV. The present results are in agreement with a recent LDA calculation on the isostructural CdSe where the corresponding RS structure was also found to be metallic¹⁵ with the energy of the upper valence band at L and the energy of the lower conduction band at X of -0.1 eV. It should be noted that CdSe becomes a semiconductor with an indirect band gap of 0.7 eV after correction to the quasiparticle excitation energies with the *GW* approximation.¹⁶ In view of the similarities in the geometrical and electronic structures between these two compounds, it is reasonable to apply a similar quasiparticle correction energy in RS CdSe (0.8 eV) to ZnSe. For example, the quasiparticle corrections to the direct band gap in the ZB structure in ZnSe and CdSe are 1.39 and 1.25 eV,¹⁷ respectively. The RS structure of ZnSe will still be metallic even after the correction. Furthermore, the energy difference between the L and X points in RS ZnSe is also found to increase with pressure, indicating the metallic character

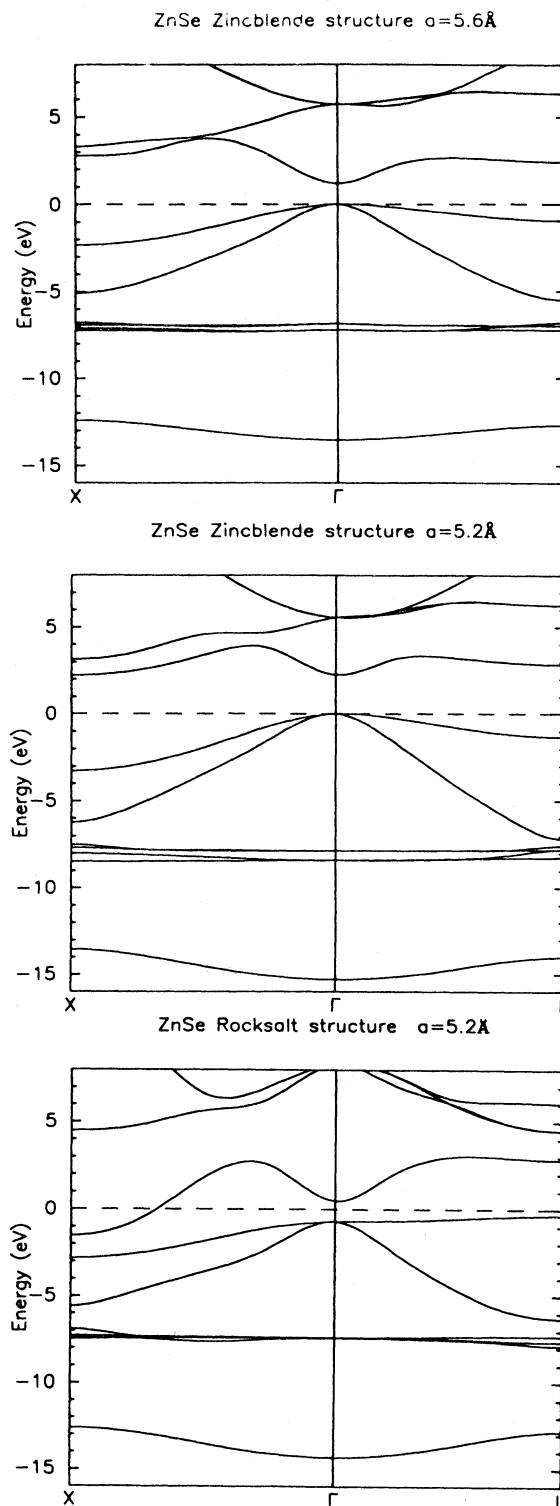


FIG. 2. The electronic band structure for ZnSe at selected volumes. For semiconducting phase, zero of energy corresponds to the top of the valence band. For metallic phase, zero is equal to E_F .

will prevail at high pressures.

In passing, it is interesting to note that many metallic transition metal carbides, nitrides, and oxides crystallize in the RS structure. They have relatively high superconducting transition temperatures ($T_c \approx 20\text{--}30$ K) due to the strong covalent-ionic bonding, which leads to the enhancement of the electron-phonon coupling.¹⁸ It is conceivable that ZnSe in the RS phase would have high T_c too. Unfortunately, experimental data¹ on the resistivity of ZnSe exist only to $T = 50$ K.

IV. CONCLUSIONS

We have performed electronic structure and total energy calculations for ZnSe in a wide region of pressure. Our calculations are in good agreement with experimental data on equilibrium lattice constants, transition pressure, and bulk modulus. We have shown that the high-pressure RS phase of ZnSe is metallic, so that recently observed metallization is caused by the the phase transition from a semiconducting into metallic phase rather than by the band closure under pressure.

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