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Ab initio high-pressure structural and electronic properties of ZnS

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The total energy of ZnS as a function of unit-cell volume has been calculated for the zinc-blende and rocksalt structures by the first-principles Hartree-Fock linear-combination-of-atomic-orbitals method. The calculated structural properties of both phases and the transition pressure between them agree very well with experiment. The band structure of the high-pressure phase is obtained and discussed in relation to zinc-blende ZnS and other IIB-VIA semiconductors.

ZnS is the prototype IIB-VIA semiconductor. Its cubic form, which occurs naturally as a mineral, has given the name zinc blende to the structure (also known as sphalerite or B3) in which most IIB-VIA and IIIA-VA semiconductors crystallize at zero pressure, provided they are not too ionic. At high temperature the hexagonal wurtzite structure, which also has tetrahedral fourfold coordination, is the equilibrium phase and may occur as a metastable form of ZnS at room temperature, as can various polytypes that are intermediate between wurtzite and zinc blende. There has been relatively little work on the properties of ZnS at high pressure, but it is known experimentally[1] that at a pressure in the range 15–18 GPa (150–180 kbar) ZnS adopts the rocksalt (NaCl or B1) structure with the sixfold octahedral coordination typical of ionic solids. This transition, which occurs at sufficient pressure for most binary semiconductors, has been treated theoretically for ZnS in some empirical[2] and semiempirical work[3] and in a density-functional calculation[4] by Ves *et al.*, and has been studied experimentally in two recent papers.[4,5]

We will study the equation of state and zinc-blende-to-rocksalt transition of ZnS by the first-principles Hartree-Fock (HF) method. We use the program CRYSTAL developed by Dovesi, Pisani, and Roetti *et al.*[6] which employs linear combinations of Gaussian orbitals multiplied by spherical harmonics to construct a localized atomic basis from which Bloch functions are constructed by a further superposition. All basis functions in our calculation are atom centered, but the outermost orbitals have a mean radius comparable to the nearest-neighbor bond length, so that partially covalent bonds can be represented. This approach has been extensively tested and found to give good results[7] for ground-state structural properties of many systems, especially insulators and semiconductors. Excited-state properties, on the other hand, are known to be poorly predicted by the HF approach, with binding energies of occupied states being somewhat overestimated relative to photoemission data, and band gaps greatly overestimated (by a factor of 2–3) relative to optical data. Approximate or phenomenological correlation corrections have been proposed for HF eigenvalues,[8] but these will not be considered here. More accurate correlation corrections for the total energy may be calculated from a correlation-only density functional, but we will not include these since they are likely to have only a small effect on the energy differences between solid phases (though the effect on absolute cohesive energies is much larger). Our focus in this work will primarily be on the ground-state properties.

In the linear-combination-of-atomic-orbitals (LCAO) method the results can be quite sensitive to the choice of Gaussian basis-set exponents [denoted by α_i where the ith basis function has a radial factor of the form $\exp(-\alpha_i r^2)$] and to the linear-combination coefficients used to form the atomic orbitals. There is, however, a clear variational criterion for the construction of a basis set: the lower the HF total energy of the system, the better is the basis set in terms of the quality of the resulting HF wave function. The energy can always be lowered by increasing the variational freedom of the wave function, but increasing the number of independent basis functions beyond a certain point results in excessive computational costs or linear dependence problems. We begin with basis sets that have been optimized for isolated atoms, and add a small set of additional Gaussian basis functions (usually one each of s, p, and d symmetry). We then systematically optimize the exponents of these virtual (i.e., initially unoccupied) orbitals by calculating the total energy of the solid for a set of values for each exponent. A similar optimization has been applied to the outermost Gaussians of the initial atomic set. We started from the 5333/533/5 basis given by Huzinaga[9] for the Zn ion, and the standard Pople[10] 6621* basis for sulfur; the outer exponents of our final basis set for zinc-blende ZnS with the experimental lattice constant $a = 5.41$ Å are given in Table I.

In principle, our basis set must be reoptimized for the rocksalt structure, and for each value of the lattice constant. To examine the effect of the change in coordination between the two phases, we perform energy versus Gaussian exponent calculations for the virtual and outer valence orbitals for the rocksalt structure with lattice constant $a = 5.00$ Å. It was found that only small

TABLE I. Gaussian exponents α_i of the outermost basis orbitals for the two crystal structures considered, in a.u.$^{-2}$. All other basis functions are taken from the Huzinaga 5333/533/5 and Pople 6621* basis sets as described in the text.

Orbital	Exponent (zinc blende)	Exponent (rocksalt)
Zn 4*s*	0.1354	0.1400
Zn 4*p*	0.1900	0.2130
Zn 3*d*	0.5225	0.5225
S 3*sp*	0.1511	0.1443
S 3*d*	0.6500	0.6500

changes in the exponents were needed to reoptimize the basis in the rocksalt structure; the revised exponents for this structure are also included in Table I. We see that in going from the zinc-blende to the rocksalt structure, the outer *s* and *p* exponents of the Zn atom increase (so that the orbitals contract) while the common exponent of the outer *s* and *p* orbitals of the S atom decrease (the orbitals expand). This behavior is consistent with the effects of ionic charge transfer and screening: as will be seen from our Mulliken population analysis below, electronic charge is transferred from the Zn to the S atom in going to the rocksalt structure, so that the outer orbitals of Zn are less shielded from its nuclear charge, resulting in a contraction of the orbitals, with the opposite effect occurring on S. The optimized exponent of the outer *d* orbital on Zn was found not to change with the crystal structure, reflecting its corelike character; it is, however, treated in the same way as the other band states in our all-electron calculation.

Earlier studies using CRYSTAL have shown that reoptimizing the basis for each value of the lattice constant is unnecessary if the calculation is performed at a high enough level of precision. The precision is controlled by cutoff parameters that determine how small the Coulomb, exchange, and overlap integrals between basis orbitals on different atomic sites must be before they can be treated approximately or neglected altogether. Standard values for the cutoff parameters have been defined[6] corresponding to "fair," "good," and "very good" levels of precision, with cutoff values decreasing by roughly one order of magnitude per level. The level of precision is important because when the lattice constant is changed at constant precision settings, certain integrals may switch from the exact to the approximate or approximate to neglected region, so that the accuracy of the calculation changes from one lattice constant value to the next. This effect is manifested in a total energy versus lattice constant curve which is ragged in appearance. However, if the precision is high enough then the neglected and approximate terms are small in any case, so the energy curve is smooth. We tested these effects in ZnS by calculating the total energy versus volume at approximately ten volumes for good tolerance settings, then repeating the calculations at a few volumes using very good settings. For the zinc-blende structure a smooth energy-versus volume curve was obtained at the lower precision, and the changes in going to the higher precision were negligible (structural parameters changing by approximately 1%, energy eigenvalues by less than 0.1 eV) indicating that good precision is already sufficient for to calculate the equation of state for ZnS in this structure with fixed precision tolerances. For the rocksalt structure, the energy-volume curve at good precision was noticeably rough (on a scale of about 0.1 eV) and the changes on going to very good precision were larger than for the less closely packed zinc-blende structure. Accordingly, we recalculated the total energy over the entire volume range at the higher precision, and obtained a smooth energy-volume curve from which to calculate the structural parameters of the rocksalt phase.

We have fitted the energy-volume curves to the Vinet[11] universal equation of state to obtain the structural parameters (equilibrium lattice constant and binding energy, and bulk modulus and its pressure derivative at zero pressure) for the two phases given in Table II. The transition pressure from zinc blende to rocksalt is found from the common tangent construction: it is the negative slope of the line tangent to both curves sketched in Fig. 1. The zero of energy (per primitive unit cell) is taken to be the sum of the energies of an isolated Zn and an isolated S atom, calculated by CRYSTAL using the same atomic basis set before modification for the crystalline environment. In this way our total energy becomes an estimate

TABLE II. Present results for structural parameters for the zinc-blende (B3) and rocksalt (B1) phases of ZnS, compared with other calculations and with experiment. We give (in order) the B3 phase lattice constant, bulk modulus and pressure derivative at zero pressure, the cohesive energy, the lattice constant at the transition pressure, the relative volume change through the transition, the transition pressure, and analogous quantities for the B1 phase.

	HF (present work)	LDA	Experiment
Zinc-blende phase			
a_0 (Å)	5.58	5.39,[a] 5.35[b]	5.41[c]
B_0 (GPa)	75.9	82.0[a,b]	76.9[c]
dB/dp	4.7	4.2,[a] 4.6[b]	4.9[c]
$E_{\rm coh}$ (eV)	4.66	7.22[b]	6.33[c]
a_T (Å)	5.31	5.11[a]	5.16[a,f]
$\Delta V/V_T$	0.160	0.144[a]	0.157[a]
p_T (GPa)	16.1	19.5[a]	18.1,[d] 15.0–16.2,[e] 14.7–15.4[a]
Rocksalt phase			
a_0 (Å)	5.21	5.09[a]	5.06,[a] 5.21,[g] 5.13[h]
B_0 (GPa)	83.1	100.1[a]	103.6,[a] 47.5,[g] 85.0[h]
dB/dp	10.0	4.05[a]	6.2[g]
a_T (Å)	5.01	4.86[a]	4.87,[a] 4.99[c]

[a] Reference 4.

[b] Reference 11.

[c] Reference 12.

[d] Reference 1.

[e] Reference 15.

[f] Reference 5.

[g] Reference 5, extrapolation from high pressure using the Vinet equation (Ref. 9).

[h] Reference 5, extrapolation from high pressure using the third-order Birch-Murnaghan fit.

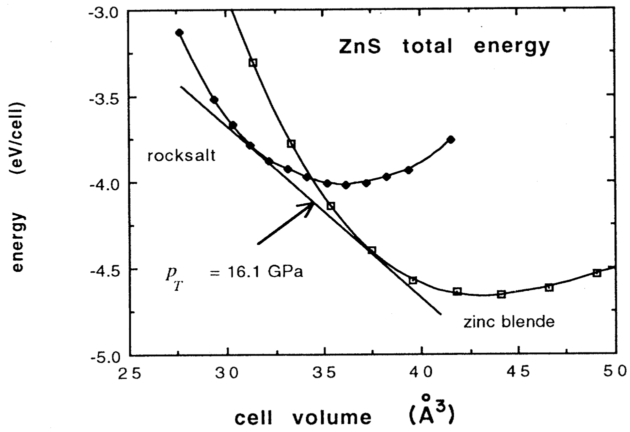

FIG. 1. Total energy (per primitive unit cell) vs volume for the zinc-blende (B3) and rocksalt (B1) phases of ZnS according to the present calculation. The zero of energy is taken as the sum of total energies of an isolated neutral Zn and an isolated neutral S atom, calculated by the same method using the atomic limit of the same basis sets as for the solid.

of the cohesive energy of the solid. In Table II we also include experimental data[4,5,12] and the results of earlier calculations[4,13] on the zinc-blende phase, while our predictions for the low-temperature equation of state are shown in Fig. 2 along with experimental p-V data.[4,5,14]

The cohesive energy of the zinc-blende phase is found in our calculation to be 4.66 eV per formula unit, which is 26% smaller than the experimental value of 6.33 eV. This result is typical of HF calculations and can be accounted for by the correlation energy. This correction, however, is largely independent of crystal structure and hence has little effect on energy differences between structures. We also find that our prediction for the lattice constant of the zinc-blende phase is about 3% higher than experiment, while the local-density approximation (LDA) results are 0.5–1 % lower. Again, our discrepancy from experiment is fairly typical of uncorrelated HF calculations and could be corrected using a correlation functional, but is small enough to begin with that this is not necessary. Our predictions of the bulk modulus and its pressure derivative are seen to agree well with experiment, somewhat better in fact than do the LDA results.

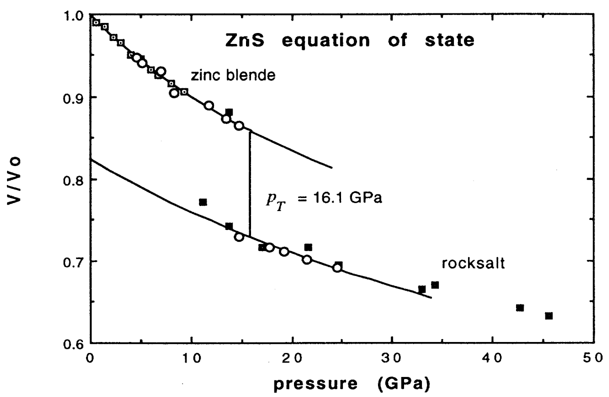

FIG. 2. Pressure vs normalized unit-cell volume for the same phases as the previous figure. The solid curves are obtained from the total energies calculated in this work by fitting to the Vinet universal equation of state (Ref. 9). Plot symbols are experimental data from Ref. 4 (circles), Ref. 5 (dark squares), and Ref. 14 (light squares).

We compare our results for the high-pressure rocksalt (B1) phase of ZnS to experiment[1,4,5,12,15] and to the *ab initio* LDA results of Ves *et al.*[4] We find that the lattice constant of the rocksalt phase at the transition pressure (5.01 Å) agrees well with experiment[12] (4.99 Å). More important, our predicted value of the transition pressure (16.1 GPa) agrees very well with measured values (18.1 GPa in early experiments,[1] 14.7–16.2 GPa in most later measurements[4,15]). We find that the lattice constant of the zinc-blende phase at the transition (5.16 Å in our calculation) disagrees with experiment (5.31 Å) by the same 3% margin as the equilibrium (zero pressure) lattice constant, so that the change in volume over this pressure range is accurately predicted, as is the fractional change in volume as the transition occurs (see Table II). It should be noted that the experimental zero-pressure properties of the B1 phase are very uncertain since they can only be found by extrapolation from higher pressure. Also, strictly speaking, our calculation applies only to $T=0$ while the experimental data was taken at room temperature; however, finite-temperature corrections to the structural parameters mentioned above would only be on the order of 1%. All results mentioned above are included in Fig. 2 and Table II.

The HF band structure of the zinc-blende phase at the experimental lattice constant is plotted in Fig. 3(a). It is in qualitative agreement with LDA calculations, but we see from Table III that there are significant quantitative disagreements with experimental excitation spectra, as expected in calculations of this type (and as also found in LDA calculations, though in the opposite direction). Band gaps, in particular, are always overestimated in HF theory and underestimated in LDA calculations, but these errors are close to being constant shifts of band energies, so that the variation of energy differences with wave vector, pressure, or other parameters can still be ac-

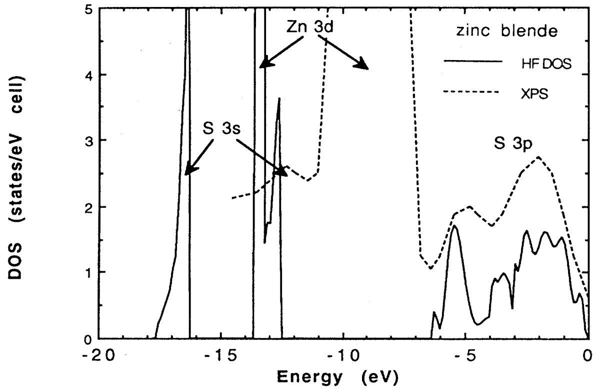

FIG. 3. Band structure for the zinc-blende (a) and rocksalt (b) phases of ZnS, at lattice constants of 5.41 and 5.00 Å, respectively. Space-group representation labels are shown for the eigenvalues given in Table III.

TABLE III. Band eigenvalues from the present work compared to earlier theory and experiment. The zero of the single-particle energy has been shifted to the valence-band maximum to facilitate comparison.

Zinc blende, $a=5.41$ Å	HF	LDA[a]	Experiment[b]
Γ_{15v}	0.00 eV	0.00 eV	0.00 eV
L_{1v}	−7.62	−5.43	−5.5
Γ_{12d}	−13.10	−6.16	−10.0
Γ_{1v}	−17.65	−13.07	−13.5
Γ_{1c} (Band gap)	11.45[c,d]	1.84,2.07[e]	3.8
X_{1c}	13.82	3.19	

[a] Reference 13.

[b] Reference 12.

[c] Zinc-blende phase at transition pressure ($a=5.31$ Å); band gap is 12.01 eV (direct, Γ_{15v} to Γ_{1c}).

[d] Rocksalt phase at transition pressure ($a=5.00$ Å); band gap is 8.51 eV (indirect, ΓK line to X_{1c}).

[e] Reference 4.

curately predicted. Thus in our case the ordering of the valence bands agrees well with experiment, as shown by the valence-band total density of states which is compared with x-ray photoemission-spectroscopy (XPS) data of Ley *et al.*[16] in Fig. 4. Furthermore the relative positions of the first few conduction bands are realistically represented; in particular, the lowest band at the X point is 2.37 eV above the conduction-band minimum at Γ, making the gap direct in agreement with experiment. Our conduction-band results depend sensitively on the Gaussian exponents for the outermost basis orbitals, especially those on the cation, because these orbitals form the basis for the unoccupied conduction states, but still affect the total energy because they also form part of the basis for the occupied states. Evidently their optimization with respect to the total energy is important for the realistic treatment of the lowest conduction bands because this optimization improves the accuracy of the valence-band states, to which the conduction-band states must be orthogonal. We find that the conduction-band minimum at Γ shifts upward with pressure at 0.066 eV/GPa relative to the valence-band maximum, in good agreement with the experimental values 0.064 and 0.057 eV/GPa,[4,17] and the LDA value[4] of 0.062 eV/GPa. The energy of the lowest band at the X point is almost independent of pressure and near the phase transition is only 1.68 eV above the Γ minimum; these minima would become degenerate (making the gap indirect) at a pressure around 44 GPa if the transition to the rocksalt structure did not occur.

The band structure of the high-pressure rocksalt (B1) phase of ZnS at a volume corresponding to the transition pressure is shown in Fig. 3(b). This band structure is qualitatively similar to that of ambient pressure CdO, which occurs naturally in the rocksalt structure because it is more ionic than the other IIB-VIA materials. A characteristic difference from the zinc-blende case is that the valence-band maximum shifts away from the Γ point towards the L and K points as a result of p-d hybridization effects, as discussed in detail elsewhere.[4,8] The X-point conduction-band minimum is 3.12 eV below the Γ-point minimum, and moves up at 0.014 eV/GPa relative to the valence-band maximum with increasing pressure while the conduction minimum at Γ shifts upwards at 0.073 eV/GPa. We predict the band gap of the rocksalt phase at the transition pressure to be about 2.9 eV smaller than the gap of the zinc-blende phase at zero pressure; since the latter is about 3.8 eV experimentally, we predict that the rocksalt phase is a semiconductor and not a metal, in agreement with experiment.[4,5] The LDA band structure for the high-pressure phase calculated by Ves *et al.*[4] is in reasonable agreement with ours; in particular, they found that the lowest gap in the B1 phase was −0.5 eV, which is 2.6 eV smaller than in the B3 phase (2.1 eV) so that they would also have obtained a positive gap for the B1 phase were it not for the usual band-gap error in the LDA.

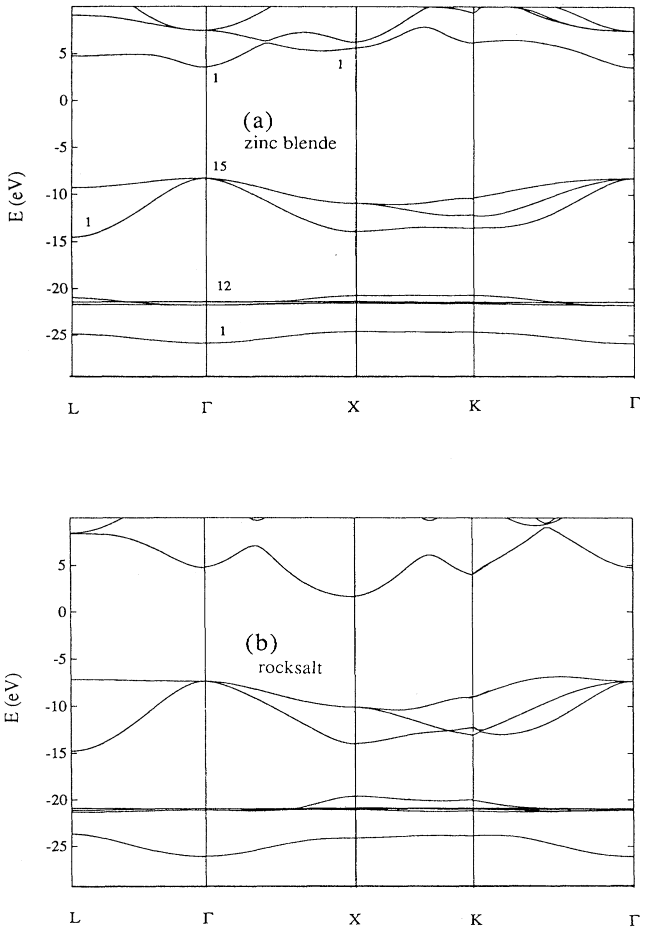

FIG. 4. Calculated valence-band single-electron density of states for the zinc-blende phase of ZnS (solid curve) compared to x-ray photoemission spectroscopy data of Ref. 16 (dashed curve). The vertical scale of the XPS data is arbitrary, and it contains a background signal that increases with the binding energy. The data also exaggerate the amplitude of the Zn 3d peak and broaden the width of all peaks. The Hartree-Fock calculation exaggerates the binding energy of the S 3s and Zn 3d bands but is otherwise in good agreement.

A detailed theoretical study of the electronic charge-density distribution in ZnS will not be attempted here, but we note that a Mulliken population analysis indicates the presence of mixed ionic-covalent bonding, with effective ionic charges close to $Zn^{+1}S^{-1}$ for the zinc-blende phase and $Zn^{1.3+}S^{1.3-}$ for the more ionic rocksalt phase.

In summary, we find that the *ab initio* HF-LCAO method gives a very realistic account of the electronic and structural properties of ZnS. The equations of state of both the high- and low-pressure phases and the transition pressure between them are in excellent agreement with experiment. Also, the qualitative features of the valence bands and the lowest few conduction bands are correctly reproduced despite the expected overestimation of band gaps and binding energies, and the pressure derivatives of the principal gaps are in reasonable agreement with experimental values where the latter are known. No difficulty is encountered in including the Zn 3*d* bands in the calculation, and the high-pressure phase is found to have a band structure similar to that of CdO, where *p*-*d* hybridization effects are important. An interesting feature of our calculation is that we can predict the properties of phases which are metastable or unstable experimentally; for example, we find that the conduction-band minimum of the rocksalt phase would remain at the *X* point at pressures all the way down to $p=0$, while the zinc-blende phase would continue to be a direct gap material up to $p=44$ GPa if no phase transition occurred.

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