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Cubic ZnS under pressure: Optical-absorption edge, phase transition, and calculated equation of state

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We have measured the effect of pressure on the energy of the direct-optical-absorption edge (E_0 gap, $\Gamma_{15}^{v}\rightarrow\Gamma_1^c$) of cubic ZnS, covering the full stability range (0–15 GPa) of the tetrahedral phase. The E_0 gap exhibits a sublinear increase under pressure, with the corresponding (linear) gap deformation potential being $-5.0(2)$ eV. X-ray diffraction shows the high-pressure phase of ZnS to have the NaCl-type structure for pressures up to at least 27 GPa. In contrast to earlier reports, this phase is not metallic but shows a broad optical-absorption edge with onset near 2 eV, which is characteristic of an indirect-gap material. Experimental results for the equation of state and band-gap deformation potential are compared with *ab initio* calculations based on local-density theory and the relativistic linear-muffin-tin-orbital method.

I. INTRODUCTION

Zinc chalcogenides in the cubic sphalerite structure are direct-gap semiconductors with $E_0(\Gamma_{15}^{v}\rightarrow\Gamma_1^c)$ gap energies ranging from 2.3 eV (ZnTe) to 3.7 eV (ZnS).[1] Under external pressure these compounds exhibit an increase in direct-gap energy,[1–5] which is the behavior commonly observed in binary tetrahedral semiconductors.[4,5] Recent interest in the high-pressure behavior of zinc chalcogenides has arisen in the context of high-pressure investigations of semimagnetic semiconductors[6] and of strain effects in superlattices.[7] By using diamond-anvil-cell techniques, the effect of pressure on the direct optical gaps of ZnSe (Ref. 8) and ZnTe (Ref. 9) has been investigated for pressures covering the full stability range of the tetrahedral phases. Transitions to high-pressure phases[8–15] occur at about 9.5, 13.7, and 15 GPa in ZnTe,[9,10] ZnSe,[8,10] and ZnS,[11–15] respectively. In the case of ZnS and ZnSe these phases have been identified as rocksalt ($B1$) type[14,15] whereas the 9.5 GPa transition in ZnTe is to a lower-symmetry structure,[16] followed by a second transition[9,16] at slightly higher pressure (~ 11.9 GPa). The high-pressure phases of zinc chalcogenides are commonly assumed to be metallic[10–13] but for the first high-pressure phase of ZnTe this is not confirmed by optical-absorption studies.[9]

In this work we report an optical-absorption and x-ray-diffraction study of ZnS under pressure. The aim is (i) to determine the pressure shift of the direct-gap energy of cubic ZnS over an extended range of pressure up to the phase transition; (ii) to find out from optical measurements if the high-pressure phase of ZnS is indeed metallic as was suggested in several previous studies;[10–13] (iii) to confirm that the high-pressure phase is single-phase $B1$ within the pressure range of the optical measurements and to determine its pressure-volume relation; and (iv) to compare the experimental results with the equation of state and band-gap deformation potentials of ZnS obtained from an *ab initio* calculation based on density-functional theory and the linear-muffin-tin-orbital (LMTO) method.[17]

II. EXPERIMENTAL DETAILS

Samples for high-pressure measurements were prepared from natural single crystals of cubic ZnS. A gasketed diamond-anvil high-pressure cell (DAC) was used for both x-ray-diffraction (XRD) and optical measurements. Samples were embedded in a 4:1 methanol-ethanol pressure medium, and pressures were measured by the standard ruby luminescence method.[18] For XRD investigations the single-crystal material was powdered. The powder pattern was observed down to a d spacing of 130 pm using an angle-dispersive diffraction geometry (Debye-Scherrer method, filtered Mo $K\alpha$ radiation) and a position-sensitive proportional-counter system. Experimental errors in absolute lattice parameters are estimated to be $\sim 0.2\%$. Optical-absorption spectra of ZnS were measured using a micro-optical system. Single-crystal samples were mechanically polished down to thicknesses of 3.5 to 4.5 μm and then broken into pieces of about 100 μm across, which is a typical sample size used in DAC's. A broadband xenon lamp illuminated a 100-μm pinhole, which in turn was imaged onto the sample in the DAC by an achromatic uv lens, forming a 20-μm-diameter focal spot. The transmitted light was imaged onto a second pinhole of 100-μm diameter using a tenfold magnification. In this way the scattered light due to multiple reflections in the pressure cell was considerably suppressed, which is essential for DAC absorption-edge measurements in the near-ultraviolet spectral range. The transmitted light was dispersed by a 0.6 m grating monochromator (dispersion 1.2 nm/mm) and detected by using a cooled GaAs photomultiplier coupled to a fast photon-counting chain. The resolution was about 0.1 nm in the region 280–330 nm.

III. RESULTS AND DISCUSSION

A. Pressure-volume relation and phase transition

Figure 1 shows the pressure-volume (PV) data of ZnS (crosses). Lattice parameters of the $B3$ phase were determined from the (111), (200), (220), and (311) Bragg reflections using least-squares methods. We find excellent agreement with earlier data of Jamieson and Demarest[19] which were obtained from higher-resolution x-ray studies up to 10 GPa. In x-ray diffraction the transition to the high-pressure $B1$ phase is observed at $P_T = 14.7(10)$ GPa. The structural assignment is based on the (111), (200), and (220) reflections. No additional Bragg reflections were observed, and we therefore rule out the admixture of a second phase. The relative total volume change just after the phase transition ($\Delta V/V_0 = 0.27$) is close to the value reported for ZnSe ($\Delta V/V_0 \approx 0.28$, Ref. 14).

The PV data of ZnS can be described by a Murnaghan equation of state:[20]

$$P=(B_0/B_0')[(V_0/V)^{B_0'}-1] . \qquad (1)$$

Here, V_0, B_0, and B_0' are volume, bulk modulus, and its pressure derivative, respectively, at ambient pressure. The parameters obtained from a least-squares fit to the experimental data for the $B3$ and $B1$ phases are given in Table I, together with related experimental[11,19,21] and theoretical[22-24] results.

From visual observation we find the phase transition in *single-crystal* ZnS at $P_T = 15.4(5)$ GPa (increasing pressure), as evidenced by a discontinuous change in color from transparent to dark yellow (sample thickness about 4 μm). The phase-transition pressure of about 15 GPa obtained from x-ray diffraction and optical observation agrees to within 0.5 GPa with experimental transition pressures determined by various methods, e.g., resistivity,[10,13,25] optical transmission,[11,12] and x-ray diffraction.[11,14,15,25] Upon slowly releasing the pressure from about 19.4 GPa the samples become transparent and almost colorless again at 10.3 GPa. Thus, on the time scale of a few hours, the hysteresis in the transition pressure from visual observation is about 5 GPa. The large hysteresis and volume change suggest that the experimental P_T given for increasing pressure corresponds to an *upper limit* for the equilibrium value at room temperature. The optical quality of the sample after back transformation was definitely worse than that of the starting material due to its polycrystalline nature and increased scattering at grain boundaries.

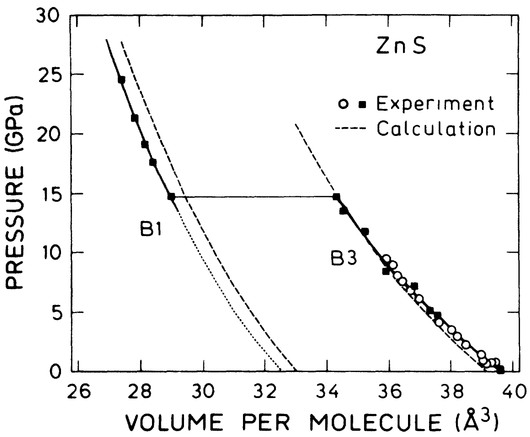

FIG. 1. Pressure-volume relation of ZnS in the zinc-blende ($B3$) and NaCl ($B1$) phase. Crosses refer to present experimental data. Open circles are from Jamieson and Demarest (Ref. 19). The dashed lines correspond to the *ab initio* calculated PV relations.

TABLE I. Summary of parameters describing the pressure-volume relation of ZnS. V_0 is the volume per molecule, B_0 the bulk modulus, and B_0' its pressure derivative, all at zero pressure. V_T/V_0, $\Delta V/V_T$, and P_T refer to relative volume, volume change, and pressure, respectively, at the phase transition from $B3$ (zinc blende) to $B1$ (rocksalt) structure.

Phase	V_0 (Å^3)	B_0 (GPa)	B_0'	V_T/V_0	$\Delta V/V_T$	P_T (GPa)
$B3$ expt.	39.65(30)[a]	75.0(20)[a]	4[a,b]	0.865[a]	0.157[a]	14.7(7),[a]15.4[c]
expt.	39.59[d]	77.1[d]	4[d,b]			15.0,[e]17.4[f]
calc.	39.23[g]	82.0[g]	4.20[g,h]	0.853[g]	0.144[g]	19.5[g]
calc.	34.9[i]	105.7[i]		~0.85[j]		20-23,[j]19.9[k]
$B1$ expt.	32.38(30)[a]	103.6(60)[a]	4[a,b]			
calc.	33.05[g]	100.1[g]	4.05[g,h]			

[a] Present work; powder x-ray data.

[b] B_0' assumed constant during fit.

[c] Present work; visual observation for single-crystal sample.

[d] Reference 19; x-ray diffraction ($P \leq 10$ GPa).

[e] Reference 11; see also Refs. 12, 15, and 25.

[f] Reference 21; shock waves.

[g] Present work; LMTO-LDA total-energy calculation.

[h] From Murnaghan fit to calculated PV data.

[i] Reference 24; *ab initio* pseudopotential calculation.

[j] Reference 22; binding forces in the pseudopotential formalism.

[k] Reference 23; *ab initio* pseudopotential total energy.

In Fig. 2 we compare low-pressure Raman spectra of a ZnS sample measured after loading into the cell and then after taking the sample through the phase transition (maximum pressure was 19.5 GPa) and releasing the pressure again. After undergoing a pressure cycle the Raman spectrum again shows the main peaks characteristic of the zinc-blende phase (for peak assignment see Ref. 26) with only minor broadening of the first-order LO-phonon line near 350 cm^{-1}. Additional structure which would indicate the presence of a second phase like the wurtzite polytype, is not observed from 10 down to 0 GPa. Also, x-ray diffraction did not give any evidence for the admixture of a second phase. Thus, in contrast to group-IV and III-V tetrahedral semiconductors which exhibit a strong tendency to form metastable crystalline phases after undergoing high-pressure phase transitions, the more ionic ZnS appears to be less amenable to the formation of new polytypes by pressure treatment. A similar behavior has been reported for CdS.[27]

The theoretical PV relation of ZnS at $T=0$ K was obtained from *ab initio* calculations within the local-density approximation (LDA). The one-electron wave equation is solved self-consistently by means of the scalar-relativistic (i.e., spin-orbit coupling is omitted) LMTO method.[17] The calculations for both phases $B3$ and $B1$ include "empty spheres."[28,29] The Zn-3d states are taken as fully relaxed band states. The significance of this and other details of the calculation may be found in Refs. 28 and 29.

Numerical results of the calculations are included in Table I and the PV relations for the $B3$ and $B1$ phases are shown in Fig. 1. The calculated PV data for the $B3$ phase show good overall agreement with experimental results including the zero-pressure volume. The bulk modulus (see Table I) is about 7% larger than the various experimental values. The theoretical PV relation of the $B1$ phase lies slightly above the experimental curve (less than 1.5% difference in volume at a given pressure).

The phase transition is calculated at 19.5 GPa, which is close to the result from the total-energy calculation of Chelikovsky[23] but significantly above the experimental transition pressure (14.7 GPa) at 300 K.

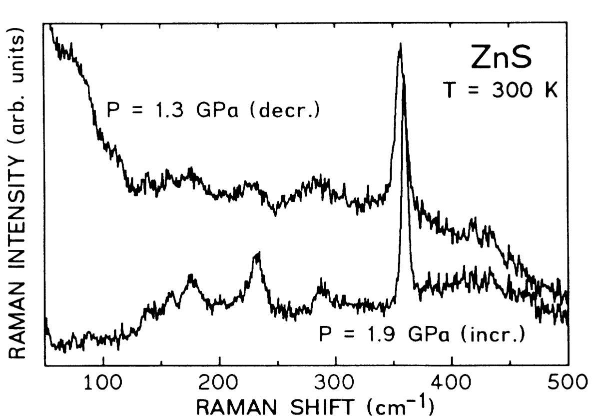

FIG. 2. Low-pressure Raman spectra of ZnS measured before (1.9 GPa) and after (1.3 GPa) taking the sample through the $B3$-$B1$ phase transition.

B. Optical-absorption edge under pressure

Figure 3(a) shows absorption spectra from ZnS at different pressures spanning the stability range of the zinc-blende phase. The intensity $I(\omega)$ transmitted through the sample is normalized to the intensity $I_0(\omega)$ transmitted through a clear area next to it. The thickness d of the sample was estimated from the interference pattern observed at photon energies below the direct absorption edge. In ZnS the E_0 direct absorption edge is expected to be strongly steepened by exciton interactions[30] which manifest themselves in a strong absorption even at 300 K.[31] Thus, the absorption coefficient corresponding to the maxima in Fig. 3(a) is quite large ($\alpha \approx 1.5 \times 10^4$ cm^{-1}). The energy of the direct absorption edge, as indicated by arrows in Fig. 3(a), is taken at the point where the absorption curves bend and become flat which is, at least in part, due to scattered and spuriously transmitted light. This energy is better defined in the actual

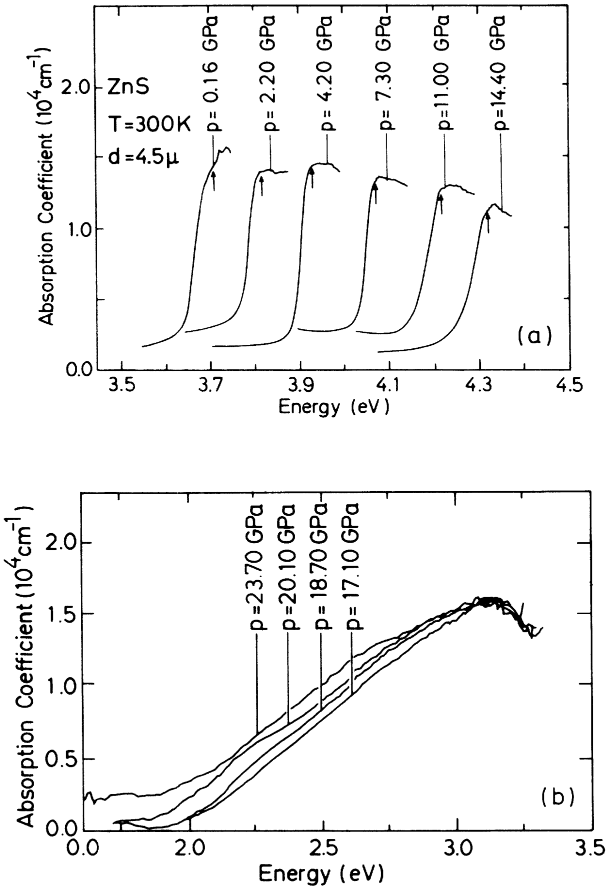

FIG. 3. Absorption spectra of ZnS ($T=300$ K) in the (a) zinc-blende and (b) rocksalt phases at different pressures. The arrows in (a) mark the saturation points taken to represent the gap energy E_0 (see text). The background absorption at low photon energy is an artifact of having neglected corrections due to reflection losses.

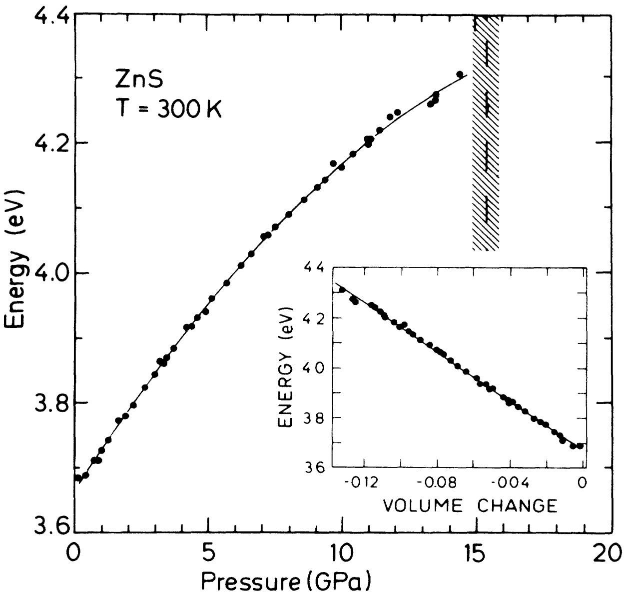

FIG. 4. Energy of the lowest direct absorption edge E_0 of ZnS as a function of pressure. The vertical shaded line refers to the phase-transition pressure from the zinc-blende to the rock-salt structure. The inset shows the energy E_0 as a function of change in relative volume. The solid lines through the data points represent the results of least-squares fits.

intensity-versus-photon-energy curves as compared with the absorption spectra of Fig. 3. Because an indirect gap is not interfering[32] the energy position of the kinks in the absorption curves remain well defined up to pressures just below the phase transition.

The energies of the E_0 direct gap obtained in this way are plotted in Fig. 4 as a function of pressure. For the dependence on pressure we find a weak sublinear behavior. The solid line in Fig. 4 corresponds to the results of a least-squares fit of a second-order polynomial to the experimental data. The linear and quadratic pressure coefficients are given in Table II, together with related experimental[2,30,33–35] and theoretical[3,4,36–39] results. Our linear pressure coefficient is in good agreement with values obtained from, e.g., reflectivity[34] and luminescence[35] measurements at moderate pressures up to 1 GPa.

A comment on possible systematic errors of the experimental absorption edge shift under pressure is in order: The kink in the absorption spectra does not necessarily correspond to the exciton energy, but may be shifted to slightly lower energy due to straylight limitations.[31,40] Apparently, this effect is not important at zero pressure, where our gap value is consistent with literature data (see Table II). However, with the absorption edge shifting further into the uv, straylight effects obviously become more important. For instance, one expects the absorption coefficient to increase with increasing energy gap,[31,40] which is not observed experimentally. As a result, the gap energies at higher pressures are considered to give the lower limit for the true value of the gap. This affects, in particular, the quadratic term c such that its experimental value given in Table II should be considered to be the lower bound for the nonlinear coefficient.

The inset in Fig. 4 shows the dependence of the energy gap on relative change in volume. The energy gap versus volume relation is essentially linear, and the slope corresponds to an average gap deformation potential (in eV):

$$D=\Delta E_0/(\Delta V/V_0)=-5.0(2) .$$

This value of D is close to the results for ZnSe (4.8 eV, Ref. 8) and ZnTe (5.4 eV, Ref. 9), as would be expected due to the small differences in ionicity.

TABLE II. First (b) and second (c) -order pressure coefficients and the deformation potential (D) of the E_0 band gap of ZnS. The second-order polynomial used is $E_0(P)=E_0(P=0)+bP+cP^2$.

	$E_{P=0}$ (eV)	b (meV/GPa)	c (meV/GPa[a])	D (eV)
Experiment ($T=300$ K)	3.666(10)[a] 3.68,[b] 3.66[c]	63.5(7)[a] 57,[d] 63[e] 64[f]	−1.31(5)[a]	−5.0[a]
Theory ($T=0$ K)	2.03[a]	62.2[a] 72[h]	−1.14[a]	−4.53,[a] −2.6[g] −4.0,[i] −3.9[j] −5.0,[k] −6.4[l]

[a] Present work; the theoretical b and c values are calculated in the range -7 to $+7$ GPa using the theoretical pressures.
[b] Reference 33; wavelength-modulated reflectivity.
[c] Reference 30; reflectivity.
[d] Reference 2; optical absorption.
[e] Reference 34; reflectivity.
[f] Reference 35; luminescence.
[g] Reference 36; empirical pseudopotential.
[h] Reference 4; dielectric theory.
[i] Reference 37; *ab initio* calculation, no expB_0 used.
[j] Reference 38; empirical pseudopotential.
[k] Reference 3; Korringa-Kohn-Rostoker method.
[l] Reference 39; local-density-functional pseudopotential formalism.

The deformation potential for ZnS in the $B3$ structure has been calculated for the LDA band structure described above. At zero pressure, the LDA band gap is 2.07 eV which is about 1.6 eV below the experimental value. This reflects the characteristic tendency of the LDA method to yield too small energy gaps. Nevertheless, experience has shown that the LDA method often yields the *variation* of band gaps under pressure in good agreement with experiment. This empirical result has recently been given additional theoretical foundation.[41] The value of the deformation potential obtained from the present calculation ($D=-4.53$ eV) is in fairly close agreement with the experimental result. The pressure coefficient or deformation potential of the E_0 gap in ZnS has been previously calculated by various other methods. For completeness, these results are included in Table II.

In the high-pressure phase of ZnS the absorption edge [see Fig. 3(b)] becomes broad and resembles that of an indirect-gap material with a gap energy near 2 eV. After the phase transition the samples were not homogeneous but developed yellow-brown spots and streaks. Upon further increase in pressure the color changes to dark brown. This tendency continues up to the highest pressure investigated here which is 26 GPa. In the absorption spectra of Fig. 3(b) the broad edge appears to exhibit a small red shift.

At this point we stress that ZnS in the high-pressure phase is not opaque to visible light as reported in Refs. 11 and 12. This apparent discrepancy in experimental observations is presumably due to the fact that rather thick samples were used in the previous investigations. The large drop in resistance at the phase transition[10,13] appears to be due to defects present in the high-pressure phase. Similarly, optical reflectivity measurements of ZnSe under pressure[42] indicate that the first high-pressure phase is not metallic, in contrast to conclusions from resistivity studies (see, e.g., Ref. 13), but in agreement with the theoretical prediction of Ref. 43.

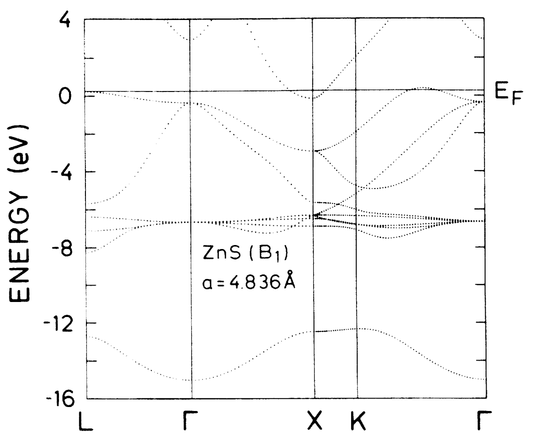

FIG. 5. LMTO-LDA band structure of ZnS calculated in the NaCl phase for $a=4.836$ Å.

The LDA energy bands of ZnS in the NaCl structure, as calculated in the way explained above, are shown in Fig. 5. In this calculation the valence and conduction bands overlap. The band overlap is caused by a drastic lowering of the X_1^c band with respect to the Γ_1^c state and by the trend of the LDA method to produce too small values for energy gaps. In the zinc-blende phase the X_1^c band is well above the conduction-band minimum, but in the $B1$ structure it is shifted to lower energies. This shift appears to increase along the sequence ZnS-ZnSe-ZnTe. As for the valence bands, the presence of the inversion symmetry in the rocksalt structure causes the *p*-*d* interaction to be forbidden at Γ and allowed only away from Γ. Thus, a strong repulsion between *p* and *d* bands takes place off $\mathbf{k}=0$ such that the top of the valence band does not occur at Γ. This effect is clearly manifested in Fig. 5 where the valence band has two nearly degenerate maxima, one almost in the middle of the Σ direction and the other at the L point. The Γ point, contrary to the zinc-blende structure, lies about 1 eV lower than the L point. Therefore, two types of indirect energy gaps, namely $L_3 \rightarrow X_1$ and $\Sigma_4 \rightarrow X_1$, with nearly the same gap value, are possible for the rocksalt ZnS. The LDA calculation predicts very small changes of these gaps (-4 meV/GPa for L-X and 8 meV/GPa for Σ-X). This is in agreement with the qualitative observation from experiment.

IV. SUMMARY

We have measured uv absorption spectra of cubic ZnS under pressure covering the full stability range of the tetrahedral phase. The direct band gap increases at an initial rate of 64 meV/GPA and shows a tendency towards sublinear behavior at higher pressures. The average band-gap deformation potential (-0.5 eV) is similar to the corresponding values for ZnSe and ZnTe. X-ray-diffraction measurements show that the high-pressure phase of ZnS, stable above 15 GPa, is a single-phase rocksalt type up to 27 GPa. A broad adsorption edge in the high-pressure phase with an onset near 2 eV is attributed to an indirect band gap, which is only weakly dependent on pressure. In contrast to earlier reports, the high-pressure phase of ZnS is definitely not metallic. The PV relations of both phases, the volume change at the phase transition, and the pressure dependence of the band gap in the zinc-blende structure have been calculated by an *ab initio* LMTO-atomic-sphere approximation method and are found to be in excellent agreement with the experimental data.

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