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Pseudopotential plane-wave calculations for ZnS

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We calculate the structural and electronic properties of cubic ZnS using a pseudopotential plane-wave method and compare the results with an all-electron linearized-augmented-plane-wave calculation. The agreement between the two electronic structure methods is excellent, and the calculated structural properties are in good agreement with the experimental results. We find that in both calculations the fundamental band gap is underestimated and that the Zn *d* band is less bound than in experiment. Both effects are due to the use of the local-density approximation.

I. INTRODUCTION

Plane-wave basis sets are very popular for the calculation of the electronic structure of crystals because the mathematical simplicity of the exponential function permits a simpler implementation of the numerical computer codes.[1,2] In particular, the calculation of quantum-mechanical forces,[2] quasiparticle excitations,[3] and the application of electronic-structure calculations to molecular dynamics[4] is much simpler to do with a plane-wave basis set. Of course, electronic wave functions in real crystals are not smooth functions, and for practical applications the core wave functions and the wiggles of the valence wave functions in the core region have to be removed by using the pseudopotential approximation.[1] Even with the pseudopotential approach, the valence *d* wave functions of transition metals are so localized that electronic-structure calculations for crystals containing transition-metal elements have been considered impractical with a plane-wave basis set, and have been performed with basis sets containing more complicated functions.[5,6]

With the development of efficient iterative methods for the diagonalization of large Hamiltonian matrices represented by a plane-wave basis set,[4,7–10] and with the development of particularly smooth pseudopotentials,[11,12] it is now possible to calculate the electronic structure of crystals containing transition-metal elements with a plane-wave basis set. We present here a pseudopotential calculation of the electronic structure of cubic ZnS using a plane-wave basis set. Zinc blende was chosen because Zn has the most tightly bound valence *d* electrons and is therefore the most stringent test for the use of plane waves for transition metals. We compare the pseudopotential plane-wave[2] (PPPW) results with a calculation for the same crystal using the all-electron linearized-augmented-plane-wave[5] (LAPW) method, which is one of the most accurate methods traditionally used in calculations for transition metals. Special care was taken in both calculations to reduce and quantify their numerical inaccuracy. The excellent agreement obtained between the two calculations indicates the high numerical accuracy of both methods.

The calculated structural properties are in good agreement with the experimental results, but we find in both calculations that the fundamental band gap is underestimated by 2 eV and that the Zn *d* band is less bound by 3.5 eV. These discrepancies in the band structure are due to the use of the local-density approximation.

II. COMPUTATIONAL METHOD

The basic procedure used to diagonalize large pseudopotential matrices has been discussed previously,[7] but there are some changes and improvements that should be noticed. We will therefore give a short description of the procedure used in the present work, emphasizing the improvements with respect to the previous work.

The most important aspect of the procedure is that the Hamiltonian matrix H is never explicitly calculated; what is calculated is the result $H\psi$, of operating with the Hamiltonian on a wave vector ψ.[4,7] Let us consider the three contributions to the Hamiltonian: the kinetic energy K, the non-local pseudopotential $V_{\rm NL}$, and the local potential V_L, which includes both the local part of the pseudopotential and the screening potential. It is trivial to operate with the kinetic energy in a plane-wave expansion because the kinetic-energy operator is diagonal in that basis set. For the nonlocal pseudopotential we use the separable form of Kleinman and Bylander.[13] In a plane-wave expansion such an operator can be written as $V_{\rm NL} = A^* B A$, where B is a diagonal matrix and A is a rectangular matrix with one of the dimensions equal to the number of projection operators in the Kleinman-Bylander pseudopotential. Since there is a small number of these operators, eight per atom in the present calculations, the matrix A is much smaller than the matrix V_{NL}, and therefore the calculation of $A^*BA\psi$ is much faster and requires less memory storage than the calculation of $V_{\mathrm{NL}}\psi$. The local potential V_L is diagonal in the position representation, or equivalently, it is a convolution in the momentum representation. The product $V_L\psi$ can therefore be efficiently calculated[4] with the fast-Fourier transform[14] (FFT) algorithm. Both the local pseudopotential and the wave function are Fourier transformed from their momentum representation to a grid $\{\mathbf{r}_i\}$ in real space (position representation),

$$\widetilde{V_L}(\mathbf{G}_j) \longrightarrow V_L(\mathbf{r}_i) \quad \tilde{\psi}(\mathbf{G}_j) \longrightarrow \psi(\mathbf{r}_i)$$

and now we trivially operate with V_L on ψ and transform back to the momentum representation,

$$V_L\psi(\mathbf{r}_i) = V_L(\mathbf{r}_i)\psi(\mathbf{r}_i) \longrightarrow \widetilde{V_L\psi}(\mathbf{G}_j) \ .$$

Mathematically this procedure is exact if the size of the FFT mesh includes all the plane waves up to a maximum momentum of $2G_{\max}$, where $G_{\max}$ is the largest reciprocal-lattice vector included in the expansion of the wave function,

$$\psi(\mathbf{r}_i) = \sum_{\mathbf{G}_j} \tilde{\psi}(\mathbf{G}_j) \exp[i(\mathbf{k} + \mathbf{G}_j) \cdot \mathbf{r}_i] \ . \tag{1}$$

However, in practice we can include only all the plane waves with momentum smaller than $G_{\max}$ in the FFT, and still obtain accurate results.[7] This procedure can be justified if we consider $\tilde{\psi}(\mathbf{G}_j)$ and $\psi(\mathbf{r}_i)$ as the two sides of a dual representation of the wave vector ψ. Notice that the local potential is still calculated up to a maximum momentum of $2G_{\max}$, and that these large momentum components are included in the FFT by wrapping them into the smaller mesh. Contrary to the previous suggestion[7] we have found that reducing the mesh size for the calculation of the charge density using FFT's, although justifiable in principle, and exact for large values of $G_{\max}$ is not always numerically accurate, and we therefore keep a cutoff of $2G_{\max}$ in the calculation of the charge density.

We use a simultaneous iteration diagonalization method that is similar to the *ritzit* procedure,[15] but which was modified to take advantage of the special properties of pseudopotential matrices without compromising its robustness. The iterative algorithm improves an initial guess of the eigensolutions by the repeated application of several relaxation steps followed by a Ritz step until a specified number of eigensolutions with the lowest energy have been determined within the desired accuracy. The relaxation step is designed to yield a fast convergence to the eigensolutions, while the Ritz step assures the orthogonality of the eigensolutions and the fact that we are obtaining those with the lowest eigenvalues. The initial guess is obtained either from the diagonalization of a small submatrix of the Hamiltonian (with a typical size of three times the number of desired eigensolutions) or from the eigensolutions of a previous self-consistent iteration. The relaxation step is the modified Jacobi procedure,[7,8]

$$y \longleftarrow D^{-1}(H - \lambda)y + y \ , \tag{2}$$

where y and λ are the current estimates of an eigensolution, D is the quasidiagonal matrix with diagonal elements $D_{ii} = H_{ii}$, and all the off-diagonal elements are null except for those with indices $i,j \leq M$ where $D_{ij} = H_{ij}$. This modified Jacobi relaxation requires the diagonalization of a small, $M \times M$ matrix, where M is typically three times the number of desired eigensolutions, and therefore much smaller than the original Hamiltonian. The relaxation step is repeated as long as it keeps improving the current estimate of the eigensolutions, and then it is followed by the Ritz step. For the Ritz step we diagonalize the Hamiltonian in the subspace spanned by (i) the initial guesses for the eigensolutions, (ii) the estimations of the eigensolutions obtained from the previous Ritz step (these are obviously absent for the first Ritz step), and (iii) the current estimate for the eigensolutions from the last relaxation step.[9] Furthermore, a random vector is added to the first Ritz step, or when a problem (e.g., two vectors converging to the same eigensolution) occurs in the relaxation step. A Gram-Schmidt orthogonalization is performed before each Ritz step, and linearly dependent vectors are discarded. Finally vectors that are considered to have converged to an eigensolution are spared from further relaxation steps.

This modified *ritzit* procedure is very efficient for the diagonalization of pseudopotential matrices, requiring typically 5 to 15 matrix vector multiplications, but is still very robust. We have tried some of the ill-conditioned matrices that have been proposed in the literature as tough tests for diagonalization procedures,[15] and found out that our procedure could successfully diagonalize those matrices. A big advantage of the robustness is that we can reduce the size of the small matrix used for the relaxation step to one, and still converge to the correct solution. The iterative procedure previously described by one of us[7] could miss some of the eigensolutions if the size of the matrix used in the relaxation step were too small.

We generated first-principles pseudopotentials for Zn and S using a new pseudopotential generation method[11] that gives a very fast convergence of the total energy with respect to basis-set size. We used the core radii of 2.17 bohr for the $4s$, $4p$, and $3d$ wave functions of Zn and the core radii of 1.78 bohr for the $3s$, $3p$, and $3d$ wave functions of S, and the reference configuration was the ground state of the non-spin-polarized atom. The atomic all-electron and pseudopotential wave functions for Zn are shown in Fig. 1. The maximum of the $3d$ wave function is significantly displaced to a larger radius, but since this occurs well inside the core region it should not affect the quality of the pseudopotential.[16] For computational efficiency the pseudopotential was transformed into the separable Kleinman-Bylander form,[13] with the s

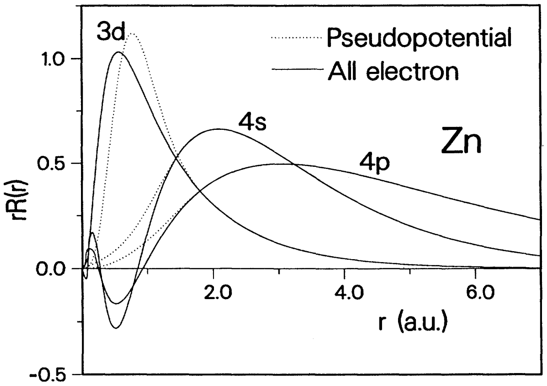

FIG. 1. Comparison of the pseudopotential (dotted line) and all-electron (solid line) radial wave functions for atomic Zn.

pseudopotential chosen as the local component to avoid the appearence of ghost states.[17] The transferability of the pseudopotential in its separable form was checked by calculating the logarithmic derivatives of the all-electron and pseudopotential wave functions. The pseudopotential curves track the all-electron curves for a large range of energies, see Fig. 2, indicating that the transferability of the pseudopotential is excellent. Furthermore, since the calculations were performed with the separable Kleinman-Bylander pseudopotential, Fig. 2 confirms that "ghost states" are not present.[17]

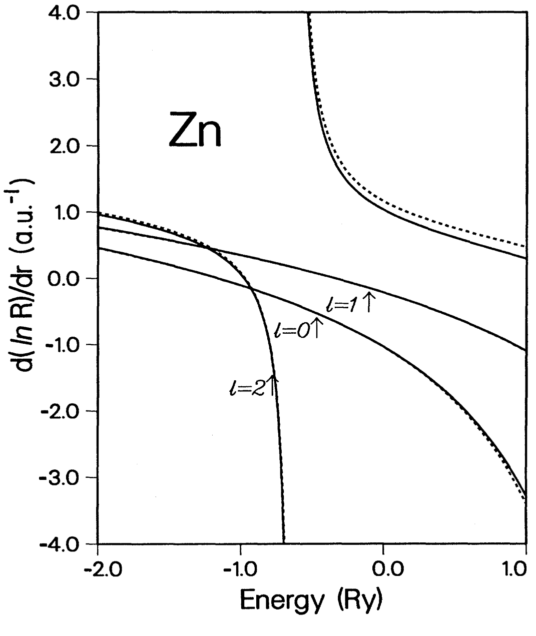

FIG. 2. The logarithmic derivatives of the all-electron (solid line) and pseudopotential (dotted line) radial wavefunctions for atomic Zn are shown at the radius of r=2.2 bohr. The atomic eigenvalues are indicated by the small arrows. The agreement between the two sets of curves displays the high transferability of the pseudopotentials, and the absence of "ghost states" in the Kleinman-Bylander form of the pseudopotential.

Both the LAPW and pseudopotential calculations for cubic ZnS were performed in the framework of the local-density approximation (LDA) of the density-functional formalism.[18] We used the Ceperley-Adler correlation[19] as parametrized by Perdew and Zunger,[20] and two special k points in the irreducible wedge of the Brillouin zone.[21] Increasing the number of k points to 10 decreased the calculated lattice constant by 0.0065 Å, and the total energy by 0.05 eV. The pseudopotential calculations included all plane waves with kinetic energy up to 121 Ry, corresponding to a basis-set sizes of ~ 6000. Increasing the energy cutoff until full convergence was obtained decreased the total energy by only 0.056 eV. The LAPW calculations use ~ 400 wave functions and the total energy was estimated to be converged within 0.01 eV. The muffin-tin radii used in the LAPW calculations were 1.80 and 2.31 bohr radii for S and Zn, respectively. Both calculations were done semirelativistically, a fully relativistic LAPW calculation increased the binding energy by 0.076 eV.

III. RESULTS

The structural properties of cubic ZnS calculated with the PPPW and LAPW methods are in excellent agreement with each other. The calculated binding energy as a function of volume is shown in Fig. 3 and the two curves agree with each other within a few hundredths of an eV. The structural properties derived from a Murnaghan equation-of-state[22] fit to the calculated data points are compared in Table I to the experimental values.[23] The lattice constant and binding energies calculated with the

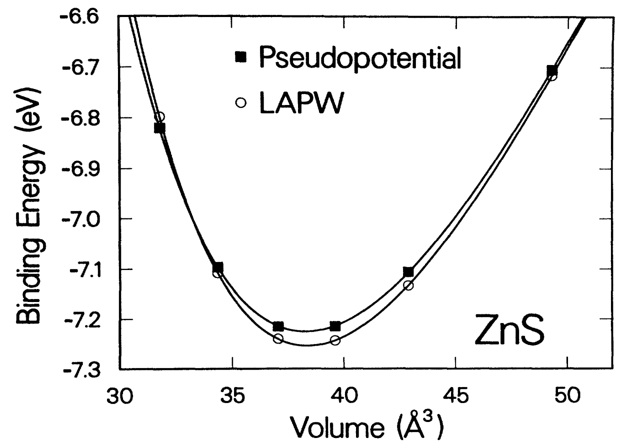

FIG. 3. The calculated equations of state are shown for cubic ZnS. The solid squares and circles are the calculated points with the pseudopotential and LAPW methods, respectively. The solid lines are Murnaghan equation-of-state interpolations.

TABLE I. The structural parameters of cubic ZnS calculated with the pseudopotential (PPPW) and LAPW methods are compared with experiment. The theoretical values of the lattice constant a_0, bulk modulus B_0, pressure derivative of the bulk modulus B_0', and cohesive energy E_c, are obtained with a fit to the Murnaghan equation of state.

	PPPW	LAPW	Experiment[a]
a_0 (Å)	5.349	5.353	5.4041
B_0 (GPa)	82	87	76.9
B_0'	4.6	4.9	4.91
E_c (eV)	7.22	7.25	6.33

[a] See Ref. 23.

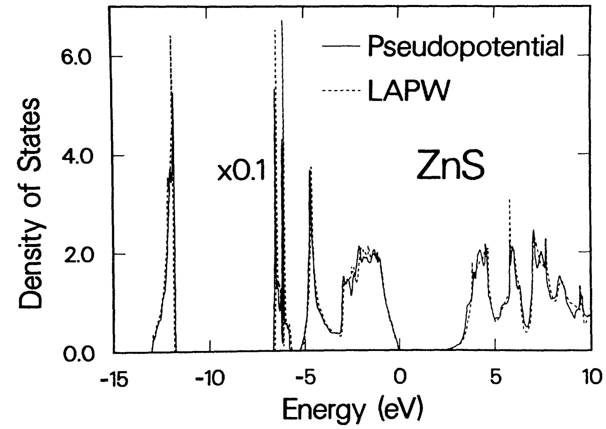

FIG. 4. Densities of states for ZnS calculated with the pseudopotential (solid line) and LAPW (dashed line) are compared. Notice the change of scale for the d band of Zn. The density of states is given in states per eV and per unit cell.

two methods are in excellent agreement with each other and are correspondingly 1% smaller than the experimental lattice constant and 14% larger than the experimental binding energy. This slight underestimate of the lattice constant and overestimate of the binding energy are typical of well-converged local-density calculations. The agreement between the calculated values of the bulk moduli and its pressure derivative is not perfect, but these are high derivatives of the total energy versus volume and are therefore very sensitive to small numerical differences.

The agreement between the two computational methods for the electronic properties is also excellent. The density of states calculated with a tetrahedron method and a mesh of 512 points in the Brillouin zone is shown in Fig. 4 and the eigenvalues calculated at a few high symmetry points and a lattice constant of 10.225 bohr are compared in Table II with experiment.[23] The band structure of ZnS was calculated previously with nonrelativistic methods.[24,25] We verify that the pseudopotential and band-structure calculations agree within ~ 0.04 eV. Most noticeable is the excellent agreement for the 3d bands of Zn, showing that the use of a large core radius for these states is justifiable. The agreement of the local-density band structure with experiment is good except for the band gap and position of the Zn d bands. The fundamental band gap is underestimated by 2.0 eV (~ 50%), and the Zn d bands are at the top of the heteropolar gap instead of the bottom, a difference of ~ 3.5 eV. The problems with the fundamental band gap have been discussed extensively in the literature,[3] but less attention has been given to the position of the d bands. We find that the problem is not with the local density *per se*, but with the interpretation of the eigenvalues as quasiparticle excitation energies.[3,26] The one-electron picture neglects core-hole relaxation effects and other many-body correlation effects. The problem is less severe for more extended states, as evidenced in Table II.

We also generated a pseudopotential for Zn which treats the 3d electrons as part of the core and therefore has only two valence electrons. We found that the calculated structural properties were incorrect, with the predicted equilibrium lattice constant being 4.84 Å, showing that the repulsion of the 3d closed shell is crucial for determining the equilibrium geometry.[27,28] The density of states calculated with that pseudopotential also show that including the 3d electrons in the core has an influence on the band structure similar to that found for other II-VI systems.[27]

TABLE II. The electronic eigenvalues (eV) of cubic ZnS at some high-symmetry points calculated with the pseudopotential (PPPW) and LAPW methods are compared with experiment. Both calculations were performed with the Ceperley-Adler correlation for a lattice constant of a=5.41 Å, and the charge density was converged with two special k points. The number of basis functions used are ~ 6000 and ~ 400 for the PPPW and LAPW calculations.

	PPPW	LAPW	Experiment[a]
Γ_{1v}	−13.07	−13.11	−13.5
Γ_{15d}	−6.63	−6.55	~ −10
Γ_{12d}	−6.16	−6.09	~ −10
Γ_{15v}	0	0	0
Γ_{1c}	1.839	1.814	3.80
Γ_{15c}	6.15	6.19	8.35
X_{1v}	−11.77	−11.84	−12.0
X_{3v}	−4.74	−4.70	−5.5
X_{5v}	−2.29	−2.25	−2.5
X_{1c}	3.19	3.18	
X_{3c}	3.87	3.87	4.9
L_{1v}	−12.10	−12.16	−12.4
L_{1v}	−5.43	−5.38	−5.5
L_{3v}	−0.90	−0.88	−1.4
L_{1c}	3.05	3.05	
L_{3c}	6.75	6.76	

[a] See Ref. 23.

IV. CONCLUSIONS

Our study of cubic ZnS shows that it is now practical to perform pseudopotential plane-wave calculations of the total energy and electronic structure of crystals containing transition-metal elements with tightly bound *d* electrons. The excellent numerical agreement obtained between the pseudopotential calculation and the all-electron LAPW calculation illustrates the high degree of accuracy that is obtained with modern methods of electronic structure theory.

ACKNOWLEDGMENTS

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