STUDY OF STRUCTURAL PHASE TRANSITION IN MgSe

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Total energy of MgSe as a function of unit cell volume has been calculated for the
wurtzite, zinc-blende, and rocksalt phases by the periodic Hartree-Fock method. The
calculated results suggest the crystallization of MgSe in the wurtzite phase at ambient
conditions. No phase transition from wurtzite to zinc-blende is predicted which is
found to be about 0.05 eV higher than wurtzite at equilibrium volume. For the phase
transition to the rocksalt phase, the transition pressure comes out to be about 60 GPa.
Analysis of electronic structure at equilibrium volume shows the minimum band gap
to be indirect in the high-pressure phase of MgSe.

There has been recent interests in Magnesium
Selenide as a cladding layer for ZnSe-based diode lasers and
as a key component in large band-gap semiconductor alloys
having both n and p type doping ability. It has also been
suggested that MgZnSe alloy lattice can easily be matched
with III-V alloy substrates for device applications. [1, 2] In
these studies, the crystal structure of MgSe was taken to be
either zinc-blende with a=5.45 Å [3] or rocksalt with
a=5.463 Å [4] . However, thin films of MgSe have also
been shown to crystallize in the wurtzite phase with lattice
constant of 4.145 Å and c/a of 1.622.[5] This ambiguity
about the crystallization of MgSe at ambient conditions has
led us to study its phase equilibria involving wurtzite, zinc-
blende and rocksalt phases from theoretical standpoint.

Our theoretical approach is based on the *ab initio*
periodic Hartree-Fock (HF) approximation which uses linear
combinations of Gaussian orbitals to construct a localized
atomic basis from which Bloch functions are constructed by
a further linear combination with plane-wave phase factors.
These Bloch functions are the basis in which the Fock
operator is diagonalized and in terms of which its
eigenvectors are expanded.[6] In this work, Gaussian basis

sets consisting of two sp shells have been used to describe
valence electrons and effective core pseudopotentials for core
electrons of Mg and Se.[7, 8] This periodic pseudopotential
HF approach implemented in CRYSTAL 92 program has
shown to predict accurate structural properties for III-V and
IV-IV semiconductors. [9] For the basis set, the exponents
of the innermost shell are obtained by the atomic
optimization while the outermost exponents are optimized in
the crystalline state yielding the sp exponents of 0.3 and
0.13 for Mg and Se respectively. It is to be noted here that
we have used the same basis set for the wurtzite, zinc-blende
and rocksalt phases and a relatively high precision level for
calculations.

We begin with a calculation of total energy as a
function of unit cell volume. Both the zinc-blende and
rocksalt phases can be characterized by a single structural
parameter, the cubic lattice constant a with the primitive unit
cell volume of $a^3/4$. For the hexagonal wurtzite phase, there
are three parameters: the basal plane lattice constant a, the
uniaxial lattice constant c and the internal coordinate u that
determines the relative position of the anion and cation
sublattice along the c-axis. We therefore minimize the total
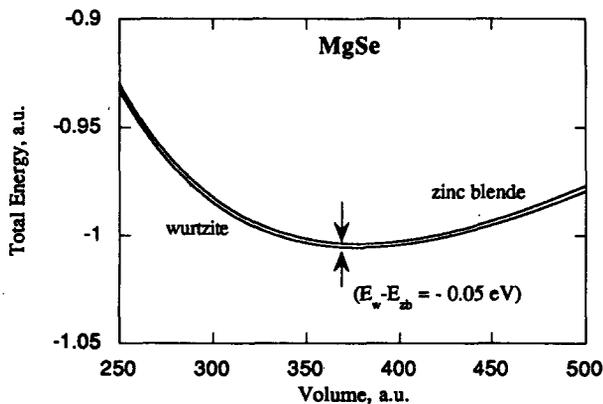
Fig. 1 : Total energy (per formula unit) vs. volume per
formula unit for the wurtzite and zinc-blende phases of
MgSe.
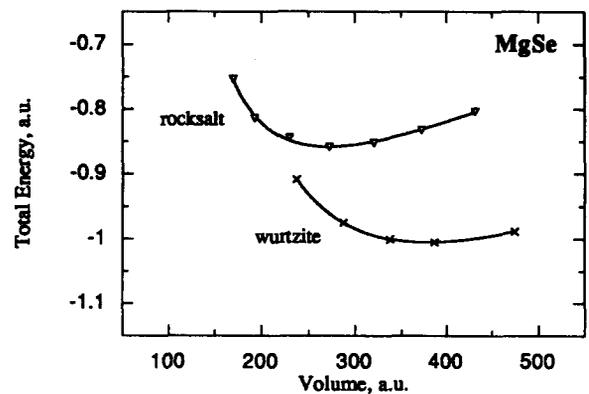
Fig. 2 : Total energy (per formula unit) vs. volume per
formula unit for the wurtzite and rocksalt phases of MgSe.

Table I

Structural properties of the wurtzite, zinc-blende and rocksalt phases of MgSe. All extensive quantities are per formula unit.

	Wurtzite	Zinc blende	Rocksalt
Experiment			
a (Å)	4.145[a]	5.89[b]	5.463[c]
c/a	1.622	---	---
Present work			
a (Å)	4.319	6.072	5.434
c/a	1.602	---	---
u	0.38	---	---
ΔE [d](eV)	---	0.05	5.41
B_0 (GPa)	56	58	68
B'	3.07	2.89	4.04

[a]Ref. 5
[b]Ref. 2, extrapolation from ZnMgSe alloy.
[c]Ref. 4
[d]Energy difference between wurtzite and zinc-blende / rocksalt phases at equilibrium volume.

energy with respect to c/a and u at fixed volume ($3^{1/2}a^2c/4$ per formula unit) for each volume we consider. (The details of this optimization procedure are the same as in the reference 10.) The equilibrium structural parameters (total energy, lattice constant, bulk modulus and its pressure derivative) are found by fitting the energy-volume data to the Murnaghan equation [11]

Figs. 1 and 2 show the calculated total energy as a function of the volume (both per formula unit) of wurtzite

and zinc-blende and wurtzite and rocksalt phases respectively. The equilibrium volume and bulk modulus of the zinc-blende phase are predicted to be similar to those of the wurtzite phase while the total energy is 0.05 eV less, consistent with wurtzite being the ground state. No high-pressure phase transition from wurtzite to zinc-blende is predicted. From the common tangent, the phase transition from wurtzite to rocksalt is predicted to occur at about 60 GPa accompanied by a volume contraction of about 19%.
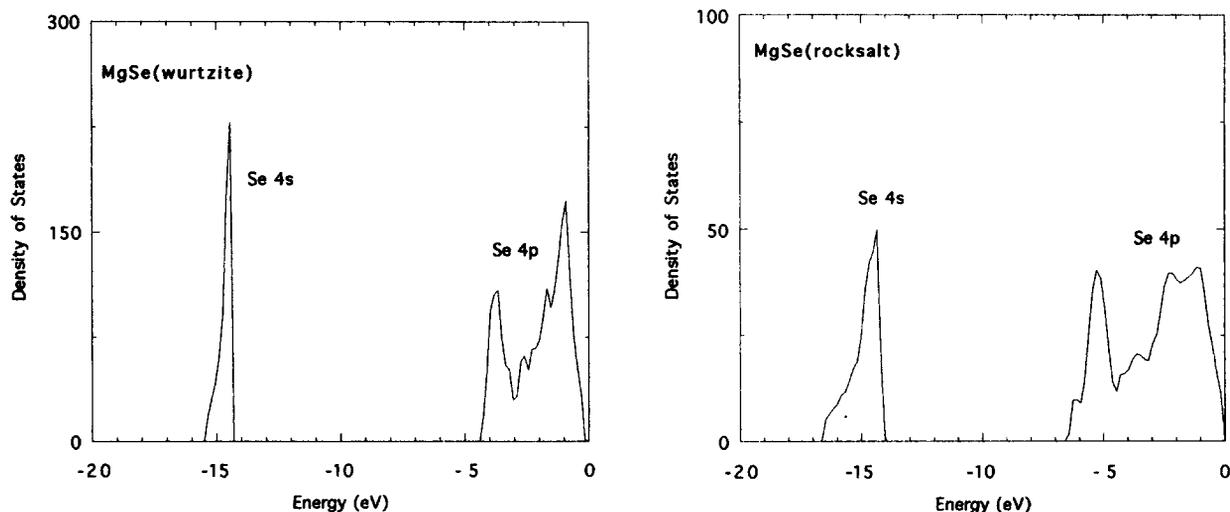
Fig. 3 : Density of States of MgSe in the wurtzite and rocksalt phases.

The lattice constant in the zinc-blende phase has been reported to be 5.45 Å. [3] However, it comes out to be 5.862 Å when we assume the density of zinc-blende to be the same as of the wurtzite. The extrapolation of the lattice constant from ZnMgSe alloy yields the value of 5.89 Å [2] whereas Table 1 shows the calculated value of 6.072 Å. For the rocksalt phase, the calculated value of a is 5.434 Å in comparison to the reported values of 5. 463 Å [4] or 5.449 Å. [12]

Next we briefly comment on the electronic structure of MgSe. In all the three phases considered here, the valence-band maximum occurs at Γ. The calculated band structure is similar to one reported earlier using Hartree-Fock approximation with the mixed basis. For the rocksalt phase, the direct gap at Γ was found to be about 9.9 eV. The conduction band minimum was at X with the indirect gap of 4.1 eV.[13] Note that Hartree-Fock approximation is known to overestimate band gaps relative to optical data. The density of states are shown in Fig. 3. The upper valance bandwidth is 4.1 and 6.3 eV in the wurtzite and rocksalt phases respectively. The larger bandwidth in the (denser) rocksalt phase is the result of more overlap between neighboring atoms.

In summary, we have provided a theoretical basis for understanding the phase equilibrium of MgSe. Our calculations predict the crystallization of MgSe in the wurtzite phase at ambient conditions. Its transition to the rocksalt phase is predicted about 60 GPa. It is hoped that this study will provide a stimulus for experimental investigations which will result in the full exploitation of such an important material for device applications.

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