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Identification of the pressure-induced phase transition of ZnSe with the positron annihilation method*

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This paper studies the pressure-induced phase transition between zincblende (B3) and NaCl (B1) structure ZnSe by using the hydrostatic pressure first-principles pseudopotential plane wave method. The energy-volume and enthalpy–pressure curves are employed to estimate the transition pressure. It is found that ZnSe undergoes a first-order phase transition from the B3 structure to the B1 structure at approximately 15 GPa derived from the energy-volume relation and 14 GPa based on deduction from enthalpy–pressure data. The pressure-related positron bulk lifetimes of the two ZnSe structures are calculated with the atomic superposition approximation method. In comparison with the 13.4% reduction in volume of ZnSe at the transition pressure, the positron bulk lifetime decreases more significantly and the relative value declines up to 22.3%. The results show that positron annihilation is an effective technique to identify and characterize the first-order phase transition and can give valuable information about changes in micro-scale, such as volume shrinkage and compressibility.

Keywords: high-pressure, phase transition, positron annihilation

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1. Introduction

Phase transition is manifested by the appearance of new properties of materials, it is generally induced by the action from the outside to modify an intensive thermodynamic variable characterizing the system with an extensive variable in the sense of classic thermodynamics.[1] The pressure-induced phase transition has long been studied for ordered materials.[2,3] It is well known experimentally that ZnSe under compression transforms from the B3 structure at low pressure to a high-pressure phase with B1 structure.[4] The properties of the materials are strongly dependent on the interactions between atoms, the applications of high pressure will change the interaction potentials by modifying the density and interatomic distances. Therefore, much more experimental and theoretical efforts are needed to further understand the pressure-dependent properties of ZnSe.

Positron annihilation gives valuable information for the ionic and electronic structures of condensed matter on an atomic scale.[5−8] Within the crystal, the positron could quickly reach thermal equilibrium with the medium and ends up with the spatial distribution. During its diffusion the positron overlaps a lower-than-average density region and has a finite probability of being captured. As a result, the positron lifetime related to the momentum content of the annihilating electron–positron pair in a specific environment could obtain from experimental and theoretical analysis. It has been shown that the positron charge density distribution can yield considerable information of the bonding properties of condensed matter under normal condition and pressure.[9] A typical feature of a first-order phase transition is the abrupt changes of phase volume. However, little work has been done to quantify those phase transitions with positron annihilation techniques.

In this paper, the hydrostatic pressure first-principles method was used to calculate the pressure-induced phase transition of ZnSe. First-principle method has been successfully employed to explain the high pressure phases of materials by using energy-volume calculations and the thermodynamic criterion of equal free energies.[10,11] The calculations of positron annihilation in B3 and B1 structures ZnSe are carried out by employing the atomic superposi-

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tion approximation (ATSUP) method.[12] The variation of the positron bulk lifetime versus pressure shows positron annihilation is a very sensitive probe to characterize the phase transition between the two structures.

2. Method

Pressure-induced phase transition calculations were carried out by using the pseudopotential plane wave method. The non-local ultra-soft pseudopotential was chosen to model the ion–electron interactions.[13] The generalized gradient approximation (GGA) within the scheme due to Perdew–Burke–Ernzerhof was chosen for the exchange–correlation interactions.[14] An energy cutoff of 550 eV was set for the plane wave basis and $5 \times 5 \times 5$ Monkhorst–Pack k mesh grids were chosen for the Brillouin-zone sampling.[15] The chosen plane wave cutoff and number of k points were carefully checked to ensure that the total energy was converged to be smaller than 0.001 eV/atom. All the cell optimization calculations were performed by using the Broyden–Flecher–Goldfarb–Shanno geometry optimization algorithm.[16] With a given external hydrostatic pressure, both the parameters of the unit cell and the internal coordinates of the atoms are all fully relaxed until the maximum force has converged below 0.01 eV/Å (1 Å = 0.1 nm).

Description of the state of a thermal positron in a prefect bulk crystal or that of a positron trapped at a defect requires the solution of the Schrödinger equation. For the ATSUP method, the electron density of the solid is approximated by the superposition of the charge densities of free atoms. The electron density and the positron potential are calculated at each grid point of the three-dimensional mesh. When the potential sensed by a positron is known, the corresponding Schrödinger equation can be solved and thus the spatial distribution of positron density can be obtained. Finally, the positron annihilation rate can be calculated as[12]

$$\begin{aligned}\lambda &= \pi r_0^2 c \int \mathrm{d}r \cdot n_\mathrm{p}(r) \cdot n_\mathrm{e}(r) \cdot \gamma(n_\mathrm{e}) \\ &= \int \mathrm{d}r \cdot n_\mathrm{p}(r) \cdot \mathit{\Gamma}(n_\mathrm{e}),\end{aligned} \tag{1}$$

where r_0 is the classical electron radius, c is the speed of light, n_e is the electron density, n_p is the positron density, $\gamma(n_\mathrm{e})$ is the enhancement factor of the electron density at the positron and $\mathit{\Gamma}(n_\mathrm{e})$ is the positron annihilation rate in a homogenous electron gas with density n_e.

The enhancement factor is a manifestation of electron–positron interactions and it is always a crucial ingredient during calculating the positron lifetime.[17] Many-body calculations for a positron in a homogeneous electron gas have been used to model the electron–positron correlation. For the positron annihilation rate $\mathit{\Gamma}(n_\mathrm{e})$, Boroński and Nieminen gave the following form (BN model):[18,19]

$$\begin{aligned}\mathit{\Gamma}(n_\mathrm{e}) = {}& \pi r_0^2 c n_\mathrm{e}(1 + 1.23 r_\mathrm{s} + 0.8295 r_\mathrm{s}^{1.5} - 1.26 r_\mathrm{s}^2 \\ & + 0.3286 r_\mathrm{s}^{2.5} + (1 - 1/\varepsilon) \cdot (r_\mathrm{s}^3/6)),\end{aligned} \tag{2}$$

where ε is the high-frequency dielectric constant and r_s is the electron density parameter.

3. Results and discussion

3.1. Phase transition

Application of an external hydrostatic pressure to materials will certainly lead to shrinkage in volume and the total free energy of the system will also be affected from the thermodynamic criterion of equilibrium. We computed the structural properties of ZnSe at high pressure by using the first-principle methods at zero temperature. Under this condition, the only information needed to determine the transition pressure is the energy variation with volume.[20] The calculated energy–volume data of the B3 and B1 structures ZnSe are shown in Fig. 1(a). One simple method for obtaining the critical pressure of zero-temperature phase transition from the B3 structure to the B1 structure is applied by using the common tangent of both energy-volume curves.[20,21] Adopting this method, we obtain the transition pressure $P_\mathrm{c} = 15$ GPa. The ratio of the equilibrium volume of the B1 structure to B3 structure ZnSe is 0.84, which is in agreement with previous experimental results.[4]

According to thermodynamics, an exceptionally stable phase structure has the lowest Gibbs free energy within a given high pressure. The B3 structure ZnSe will coexist with the B1 structure ZnSe at a pressure where the Gibbs free energies of the two structures are equal.[20] At zero temperature, the entropic contributions can be neglected and the Gibbs free energies, $G = E + PV - TS$, are equal to the values of enthalpy, $H = E + PV$. To determine the critical pressure for the transition pressure, we also calculated the enthalpies of the B3 structure and the B1 structure ZnSe as a function of pressure, as shown in Fig. 1(b).

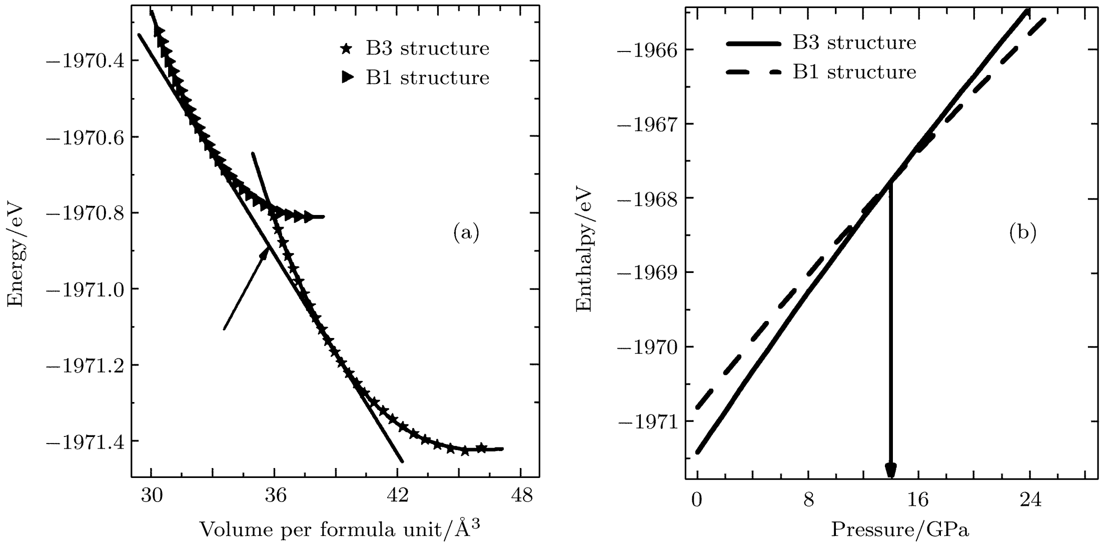

Fig. 1. The calculated results: (a) energy–volume and (b) enthalpy–pressure curves of the B3 structure and B1 structure ZnSe.

The crossing of two curves indicates a phase transition between the two phases. The results show that ZnSe undergoes a first-order phase transition from the B3 structure to the dense B1 structure at approximately 14 GPa. This transition pressure is also in agreement with the experimental values and the values of the previous calculations.[4,22] For comparison, the corresponding results are summarized in Table 1.

Table 1. Theoretical and experimental lattice constants a_0 of B3 and B1 structure ZnSe at $T = 0$ and $P = 0$, together with the critical transition pressure P_c.

		This work	Other calculations	Experiments
a_0/Å	B3	5.692	5.544^a, 5.666^b, 5.669^c, 5.633^d, 5.688^e, 5.674^f	5.669^g, 5.667^h
	B1	5.321	5.172^a, 5.288^b, 5.319^c, 5.303^e, 5.320^i	5.292^h
P_c/GPa		14, 15	20.8^a, 15.2^b, 17^c	13^h

[a] Reference [22] with full-potential linear argumented plane wave method;

[b] Reference [22] with numerical atomic orbital method;

[c] Reference [23] with first-principle plane-wave pseudopotential (PW-PP) method;

[d] Reference [24] with full-potential self-consistent linearized muffin-tin orbital atomic-sphere-approximate method;

[e] Reference [25] with PW-PP method;

[f] Reference [26] with PW-PP method and with the Zn d electrons in the core shell;

[g] Reference [27] which has been measured by the bond method;

[h] Reference [4] which has been measured by X-ray and ^{67}Zn-Mössbauer spectroscopy;

[i] Reference [26] with PW-PP method and with the Zn d electrons in the valence shell.

3.2. Positron annihilation

In this section, the identification of the structural phase transitions with positron annihilation is discussed. Because it is difficult to extract accurate slopes from the common tangent line in Fig. 1(a), the transition pressure obtained from the enthalpy curve crossing is adopted for positron annihilation analysis. The variations of the positron bulk lifetime in B3 and B1 structures ZnSe versus pressure are illustrated in Fig. 2, in which $V_0 = 5.692^3/4$ Å^3 is the zero pressure equilibrium cell volume per formula of B3 structure ZnSe and $\tau_0 = 264.4$ ps is the calculated positron bulk lifetime of the corresponding structure by using ATSUP method. Meanwhile, the observed experimental positron bulk lifetime of the B3 structure ZnSe is 241 ps.[28] The reasons why the calculated positron bulk lifetime τ_0 is not quite fit the experimental results are always accompanied with the selection of calculating method. For high pressure structural optimization, although the GGA approximation usually yields closer agreement with experiment, the lattice constant is slightly overestimated.[29] As listed in Table 1, the calculated lattice constants are approximately 0.4% larger than the experimental value of 5.669 Å. That is one of the reasons why the calculated results are a little bigger than the experimental results.

Clearly shown in our data, the values of $P-V/V_0$ and $P-\tau/\tau_0$ of the B3 structure are all higher than the values of the more dense B1 structure in the entire pressure range. The two $P-V/V_0$ curves are all monotonically decreasing, which indicates a similar compressibility between two structures, and are consistent with other experimental and theoretical high hydrostatic pressure results.[4] Atoms in a crystal approach one another to certain distances at which the crystal is in the state of the highest thermodynamic stability. These distances depend on the interaction forces appearing in crystals.[30] When the solid is compressed, the distances between atoms decrease and the charge distributions of two atoms overlap increase. As a result, the electrostatic repulsive interaction between atoms quickly arises. Thus, with the increase of pressure, the relative value ΔV/GPa of each structure becomes smaller and smaller.

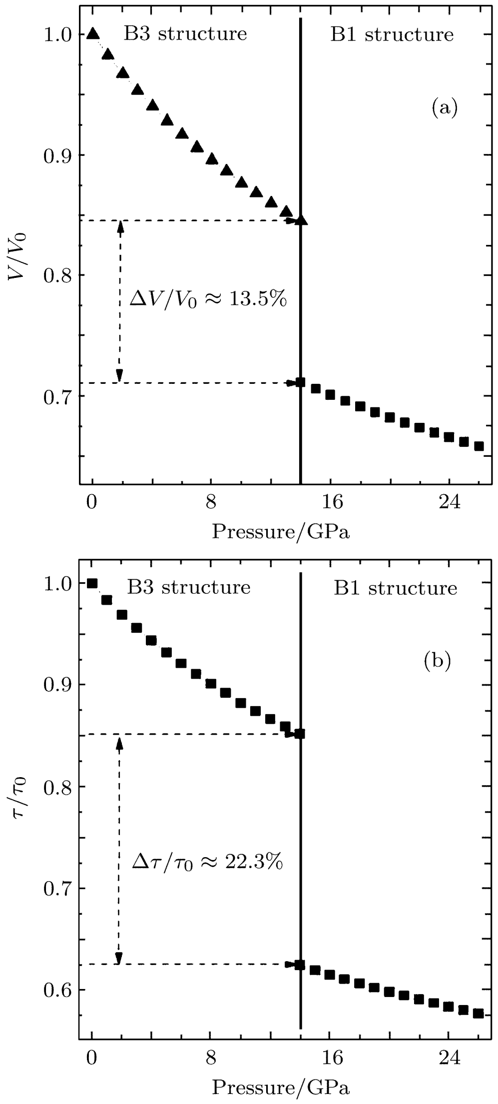

Fig. 2. The calculated results: (a) V/V_0-pressure and (b) τ/τ_0-pressure curves of the B3 structure and B1 structure ZnSe, in which $V_0 = 5.692^3/4$ Å$^3 \approx 46.094$ Å^3 and $\tau_0 = 264.4$ ps.

Along with the decrease of inter-atomic distances and the increase of spatial distribution of electron density, the positron bulk lifetime of each phase decreases quickly. At structural transition pressure $P_c = 14$ GPa, the relative volume difference between the two phases is approximately 13.5%. Under these conditions, the positron bulk lifetime of B3 structure ZnSe is reduced to 223 ps and the corresponding parameter of B1 structure ZnSe is declined to 163 ps. It demonstrates that the relative positron bulk lifetime difference between the B3 structure and B1 structure is reduced up to 22.3%. It proved that positron annihilation is a very sensitive analysis technique for the first order phase transition where the volume and entropy are discontinuous.

4. Conclusion

In this paper, the energy–volume and enthalpy–pressure curves of the B3 structure and B1 structure ZnSe are employed to study the pressure-induced phase transition by using a hydrostatic pressure first-principle pseudopotential plane wave method. The results show that ZnSe undergoes a first order phase transition from the B3 structure to the more dense B1 structure approximately at 14 GPa or 15 GPa with a volume-per-atom decrease at the transition of 13.5%. The pressure-related positron bulk lifetime of ZnSe is calculated by using ATSUP method. The variation of the positron bulk lifetime versus pressure shows that positron annihilation is a very effective analysis technique to identify the first order phase transition of ZnSe.

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