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Phase transition and thermodynamic properties of SrS via first-principles calculations*

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The phase transition of SrS from NaCl structure (B1) to CsCl structure (B2) is investigated by means of ab initio plane-wave pseudopotential density functional theory, and the thermodynamic properties of the B1 and the B2 structures are obtained through the quasi-harmonic Debye model. It is found that the transition phase from the B1 to the B2 structures occurs at 17.9 GPa, which is in good agreement with experimental data and other calculated results. Moreover, the thermodynamic properties (including specific heat capacity, the Debye temperature, thermal expansion and Grüneisen parameter) have also been obtained successfully.

Keywords: phase transition, thermodynamic properties, SrS
PACC: 6740K, 7115M

1. Introduction

Recently, the developments in computer simulations have shown an interesting possibility in investigating electronic and structural properties of condensed matters from first-principles calculations. For example, it is now possible to explain and predict properties of solids which were previously inaccessible to experiments. As one of alkaline earth chalcogenides, SrS forms an important closed shell ionic compound crystallizing into NaCl structure (B1) in an ambient condition, it is proposed that this material be used as host materials for device applications such as multicolour thin-film electroluminescent and magneto-optical devices. So, it is extensively investigated both experimentally[1] and theoretically.[2−7]

X-ray diffraction experiment [1] showed that SrS underwent a first-order phase transition from the B1structure to CsCl structure (B2) at a pressure of 18 GPa and its equation of state (EOS) was obtained up to 35 GPa. Cortona *et al* [2] reported the results for the electronic property and found the transition pressure to be 23 GPa. Khenata *et al* [3] found the structural phase transformation to occur at 18 GPa, and presented the elastic constants in B1 in an ambient condition. Rached *et al* [4] investigated the elastic constants at zero pressure in the B1 and the B2 structures. The electronic band structure and the optical property of SrS are mainly discussed in Refs.[5–7].

In this work, we focus on investigating the structural phase transition of SrS from the B1 structure to the B2 structure by means of the plane-wave pseudopotential density functional theory using the Cambridge Serial Total Energy Package (CASTEP) program.[8,9] Moreover, we also obtain the thermodynamic properties of the B1 and the B2 structures of SrS through the quasi-harmonic Debye model.[10]

2. Theoretical methods

In the investigation of electronic structure, the ultrasoft pseudopotentials introduced by Vanderbilt[11] are employed for all the ion-electron interactions, the generalized gradient approximation (GGA) exchange-correlation function[12] is represented by the Perdew–Wang (PW) formula. A plane wave basis set with an energy cut-off of 600 eV is applied. Pseudo atomic calculations are performed for S $3s^2 3p^4$ and Sr $4s^2 4p^6 5s^2$. For the Brillouin-zone sampling, we use the 8×8×8

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Monkhorst–Pack mesh, where the self-consistent convergence of the total energy is at 10^{-6} eV/Atom.

To investigate the thermodynamic properties, we apply the quasi-harmonic Debye model, [10] where the non-equilibrium Gibbs function $G^*(V;P,T)$ of SrS is in the form of

$$G^*(V;P,T) = E(V) + PV + A_{\rm Vib}(V;T), \quad (1)$$

where $E(V)$ is the total energy per unit cell for SrS, PV corresponds to the constant hydrostatic pressure condition, and the vibrational contribution $A_{\rm Vib}$ is written as[13,14]

$$A_{\rm Vib}(\Theta;T) = nkT\left[\frac{9}{8}\frac{\Theta}{T} + 3\ln(1-{\rm e}^{-\Theta/T}) - D(\Theta/T)\right], \quad (2)$$

in which the $\Theta(V)$ is the Debye temperature, $D(\Theta/T)$ represents the Debye integral, and n is the number of atoms per formula unit. For an isotropic solid with Poisson ratio σ= 0.21,[15] Θ is expressed as

$$\Theta = \frac{\hbar}{k}\left[6\pi^2 V^{1/2} n\right]^{1/3} f(\sigma)\sqrt{\frac{B_{\rm S}}{M}}, \quad (3)$$

where M is the molecular mass per formula unit, $B_{\rm S}$ is the adiabatic bulk modulus, $f(\sigma)$ and $B_{\rm S}$ are given in Refs.[16,17]. For both the B1 and the B2 phase structures of SrS, n=2, M =19.85×10^{-26}kg, and $f(\sigma)$= 0.932944. Then the non-equilibrium Gibbs function $G^*(V;P,T)$, as a function of $(V;P,T)$, can be minimized with respect to volume V

$$\left(\frac{\partial G^*(V;P,T)}{\partial V}\right)_{P,T} = 0. \quad (4)$$

Thus one could obtain the thermal EOS by solving Eq.(4). The heat capacity C_V is given by

$$C_V = 3nk\left[4D(\Theta/T) - \frac{3\Theta/T}{{\rm e}^{\Theta/T}-1}\right], \quad (5)$$

$$\alpha = \frac{\gamma C_V}{B_{\rm T} V}, \quad (6)$$

$$\gamma = -\frac{{\rm d}\ln\Theta(V)}{{\rm d}\ln V}. \quad (7)$$

Applying this method above, we can successfully investigate the structural phase transitions and thermodynamic properties of GaAs,[18] BN[19] and AlB_2.[20]

3. Results and discussion

For the B1 and the B2 structures of SrS, a series of different values of lattice constant a are set to calculate the total energy E and the corresponding volume V, and then the calculated $E-V$ data are fitted to the natural strain equation of state (EOS) developed by Poirier and Tarantola. [21] The obtained values of lattice constant a, bulk modulus B_0, pressure derivative of bulk modulus B_0' and elastic constants for the B1 and the B2 structures of SrS at zero pressure are listed in Table 1. Our calculated values of lattice constant a and bulk modulus B_0 range between those from Ref.[3] and Ref.[22]. Compared with other theoretical results presented by Khenata *et al* from the GGA method,[3] our results slightly approach to the experimental data.[1] For the B1 structure, our elastic constants (except C_{44}) are relatively close to other results.[3] We have obtained a negative value of the elastic constant C_{12} in the B2 structure. This is indicative of the metastability of SrS in the B2 structure. The pressure dependences of the primitive cell volume at 300 K and 1200 K are illustrated in Fig.1. It is noted that the volume decreases with pressure increasing, and increases with temperature rising, which accords well with experiments.[1]

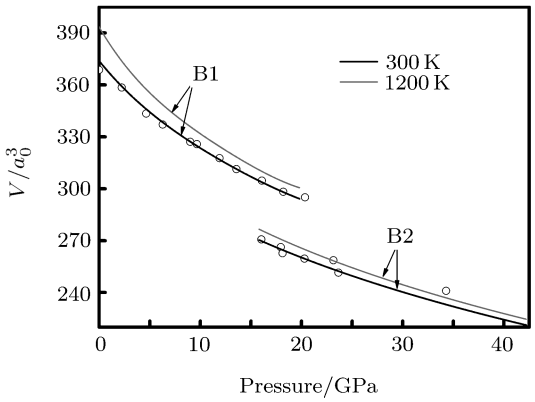


Fig.1. The volumes as a function of pressure for SrS at two different temperatures, where the open circles represent the experimental data, a_0 is the Bohr radius.[1]

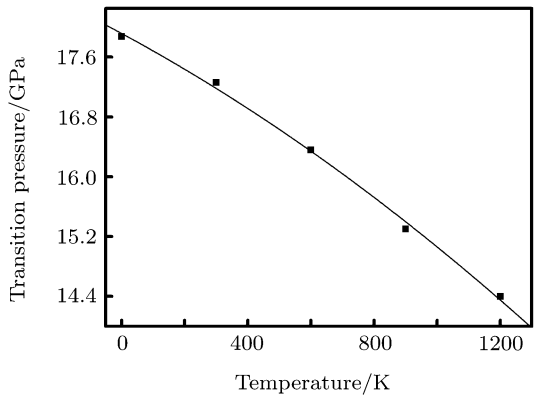


Fig.2. Phase transition pressure as a function of temperature for SrS.

Table 1. Lattice constants (in Å), bulk modulus (in GPa) and its pressure derivative, as well as elastic constants C_{ij} (in GPa) of SrS in the B1 and the B2 structures at zero pressure.

		$a/10^{-1}$nm	B_0/GPa	B_0'/GPa	C_{11}/GPa	C_{12}/GPa	C_{44}/GPa
B1 structure	Present results	6.024	53.9	4.66	113.9	19.4	30.3
	Exp.[1]	6.024	58.0				
	Others	6.076[a], 5.774[b]	47.0[a] , 62.0[b]	4.19[a]	141.0[c]	17.2[c]	62.5[c]
B2 structure	Present results	3.646	50.6	4.50	207.8	–1.2	5.19
	Experiment	3.61					
	Others	3.68[a], 3.481[b]	50.0[a], 67.3[b]	3.88[a]	147.6[c]	1.20[c]	88.1[c]

[a]Ref.[1], [b]Ref.[22], [c]Ref.[3].

The transition pressure between the B1 structure and the B2 structure of SrS may be estimated from the usual condition of equal Gibbs energy, i.e. when temperature is constant, the values of pressure P, at which Gibbs energy $G(V,P,T) = E(V) + PV + A_{\rm vib}(V,\ T)$,[10] for both phases are the same. The obtained $P-G$ data for the B1 structure and the B2 structure of SrS are fitted to the second-order polynomial, and the results are shown in Table 2. It is found that at temperatures of 0, 300, 600, 900, and 1200 K, the obtained transition pressures are 17.9, 17.3, 16.4, 15.3, and 14.4 GPa, respectively. The obtained zero-temperature transition pressure is in good agreement with the experimental value 18 GPa,[1] and also with the calculated value in Ref.[3].

Table 2. Calculated pressure (in GPa) coefficients of Gibbs energy (in Hartree) for SrS in the B1 and the B2 structures, where $G(P)=a+bP+cP^2+dP^3+eP^4$.

T/K	Structure	a	b	$c/10^{-5}$	$d/10^{-6}$	$e/10^{-9}$
0	B1	–41.31588	0.01175	–4.26009	1.004	–1.0200
	B2	–41.2933	0.01044	–3.82208	1.0003	1.0000
300	B1	–41.33554	0.01257	–9.38785	1.16886	–8.02763
	B2	–41.31277	0.01117	–8.3339	1.0253	–7.01951
600	B1	–41.36097	0.01273	–9.89428	1.27251	–8.8812
	B2	–41.33828	0.01132	–8.80749	1.12145	–7.80609
900	B1	–41.38953	0.1291	–1.04757	1.39477	–9.90192
	B2	–41.36693	0.01149	–9.35092	1.23467	–8.74588
1200	B1	–41.42019	0.1311	–1.11463	1.53918	–11.1226
	B2	–41.39768	0.01168	–9.99443	1.37361	–9.92353

In Table 3, we list the values of heat capacity C_V, Debye temperature Θ, thermal expansion α and Grüneisen parameter γ at several temperatures (0, 300, 600, 900, and 1200 K) and several pressures (0, 8, 16, 22, 30, and 40 GPa). It is found that for the B1 structure, when the applied pressure increases from 0 to 16 GPa, the heat capacity C_V decreases by 0.0%, 5.3%,1.4%, 0.6%, and 0.4%, the Debye temperature Θ increases by 33.4%, 34.8%, 37.0%, 39.8%, and 43.2%, the thermal expansion α decreases by 0.0%, 53.8%, 54.7%, 57.7%, and 61.7%, and the Grüneisen parameter γ decreases by 20.5% 21.3%, 22.2%, 23.4%, and 25.6% at 0, 300, 600, 900, and 1200 K, respectively. Correspondingly, for the B2 structure, when the pressure increases from 22 to 30 then to 40 GPa, the heat capacity decreases by 0.0%, 4.2%, 1.1%, 0.5%, and 0.2% , the Debye temperature increases by 15.6%,15.8%, 16.0%, 16.3%, and 16.6%, the thermal expansion α decreases by 0.0%, 30.5%, 29.5%, 30.1%, and 31.5% and the Grüneisen parameter γ decreases by 9.4%, 10.2%, 10.2% ,10.1%, and 10.1 %, at temperatures of 0, 300, 600, 900, and 1200 K, respectively.

In Figs.3(a) and 3(b), we present the variations of thermal expansion α with temperature and pressure for B1 structure, respectively. It is noted that at zero pressure α increases exponentially with T at low temperatures and gradually approaches to a linear increase at high temperatures. As pressure increases,

the increase of α with temperature becomes smaller, especially at high temperatures. At a given temperature, α decreases drastically with pressure increasing. When the pressure is above 12 GPa, the thermal expansion α at 1200 K is just a little larger than that at 900 K, which means that the temperature dependence of α is very small at higher temperatures and higher pressures.

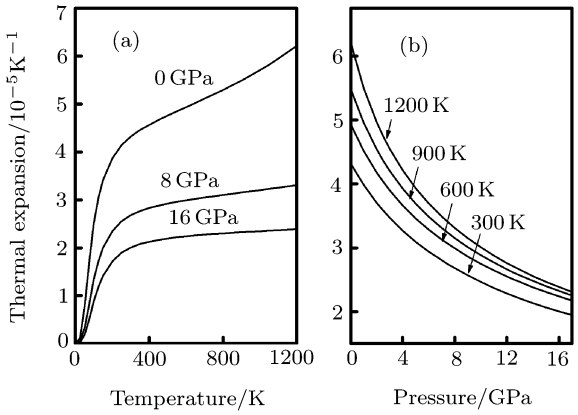


Fig.3. Thermal expansions versus temperature (a) and pressure (b) of the B1 structure for SrS.

In Fig.4, the heat capacities of SrS with the B1 and the B2 structures are plotted for four different pressures. It is shown that when $T < 800$ K, the heat capacity C_V is dependent on both temperature T and pressure P. This is due to the anharmonic approximation of the Debye model. However, at higher pressures and/or higher temperatures, the anharmonic effect on C_V is suppressed, and C_V is very close to the Dulong–Petit limit $6Nk$ ($\approx$49.90 J·mol^{-1}·K^{-1}), where N represents the Avogadro's constant.

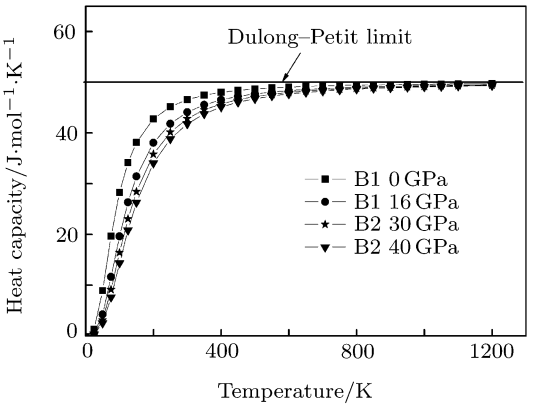


Fig.4. Heat capacities of SrS versus temperature for four different pressures.

Table 3. Heat capacity C_V , Debye temperature Θ, thermal expansion α and Grüneisen parameter γ for the B1 and the B2 structures of SrS.

T/K		P/GPa					
		B_1 structure			B_2 structure		
		0	8	16	22	30	40
0	C_V/J·mol^{-1}·K^{-1}	0.0	0.0	0.0	0.0	0.0	0.0
	Θ/K	359.4	428.7	479.6	498.5	535.2	576.4
	$\alpha/10^{-5}$K^{-1}	0.0	0.0	0.0	0.0	0.0	0.0
	γ	1.61	1.39	1.28	1.17	1.11	1.06
300	C_V/J·mol^{-1}·K^{-1}	46.58	45.22	44.11	43.67	42.80	41.80
	Θ/K	353.6	425.0	476.7	496.6	533.5	575.0
	$\alpha/10^{-5}$K^{-1}	4.35	2.69	2.01	1.87	1.57	1.30
	γ	1.64	1.41	1.29	1.18	1.11	1.06
600	C_V	49.07	48.69	48.37	48.24	47.99	47.69
	Θ/K	345.0	420.0	472.8	493.0	530.4	572.1
	$\alpha/10^{-5}$K^{-1}	4.97	3.01	2.25	2.10	1.76	1.48
	γ	1.67	1.42	1.30	1.18	1.12	1.06
900	C_V/J·mol^{-1}·K^{-1}	49.54	49.36	49.22	49.16	49.04	48.90
	Θ/K	335.3	414.7	468.6	489.3	527.0	569.1
	$\alpha/10^{-5}$K^{-1}	5.53	3.17	2.34	2.16	1.81	1.51
	γ	1.71	1.43	1.31	1.19	1.13	1.07
1200	C_V/J·mol^{-1}·K^{-1}	49.71	49.60	49.51	49.48	49.42	49.34
	Θ/K	324.3	409.1	464.4	485.4	523.6	565.97
	$\alpha/10^{-5}$K^{-1}	6.27	3.34	2.40	2.19	1.82	1.50
	γ	1.76	1.45	1.31	1.19	1.13	1.07

4. Conclusion

We have investigated the phase transition of SrS from B1 structure to B2 structure by means of the *ab initio* plane-wave pseudopotential density functional theory. It is found that the phase transformation from B1 structure to B2 structure occurs at 17.9 GPa, which is in good agreement with experimental data and other calculated results. Through the quasi-harmonic Debye model, the dependence of volume on pressure, and the dependences of thermodynamic properties, including special heat capacity, Debye temperature, thermal expansion α and Grüneisen parameter γ, on pressure and temperature have also been obtained successfully.

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