

First-Principles Study of the Three Polymorphs of Crystalline 1,1-Diamino-2,2-dinitroethylene

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The electronic structure, optical spectra, and thermodynamic properties of the three FOX-7 polymorphs (α , β , and γ) have been studied systematically using density functional theory. The LDA (CA-PZ) and generalized gradient approximation (GGA) (PW91) functions were used to relax the three FOX-7 phases without any constraint. Their density of states and partial density of states were calculated and analyzed. The band gaps for the three phases were calculated and the sequence of their sensitivity was presented. Their absorption coefficients were computed and compared. The thermodynamic functions including enthalpy (H), entropy (S), free energy (G), and heat capacity (C_p) for the three phases were evaluated.

Key Words : FOX-7, Density functional theory, Electronic structure, Optical spectra, Thermodynamic properties

Introduction

1,1-Diamino-2,2-dinitroethylene, known as FOX-7, is a novel insensitive high power explosive.¹ FOX-7 is known to exist in three crystalline phases, denoted as α , β , and γ .²⁻⁵ The α -phase is stable on heating to 388 K, the β -phase from 388 K to ~435 K, and the γ -phase from 435 K until thermal decomposition at 504 K. The crystal structure of the α -phase determined previously using single crystal X-ray diffraction^{1,4} presents an infinite two-dimensional wave-shaped layer structure consisting of FOX-7 molecules packed "head-to-tail" within the layers. The crystal structure of β -FOX-7 at 393 K was recently determined.⁴ In the β -phase, the dipolar FOX-7 molecules are packed head-to-tail in wave-shaped layers, as observed in the α -phase. Only slight changes in both crystal axes and positional parameters are required to transform from the monoclinic α -phase. The crystal structure of the γ -phase has been determined by Crawford *et al.*⁵ γ -FOX-7 consists of four planar layers, each containing two crystallographically independent molecules, and the wave-shaped layers of FOX-7 molecules formed in head-to-tail arrangements in α - and β -FOX-7 are flattened in γ -FOX-7 forming planar layers.

Many studies have been done on FOX-7 to investigate its structural and vibrational properties both in gas and solid phases,⁶ equation of state,⁷ detonation properties,⁸ mechanical compression,⁹ chemical decomposition process under external pressure,¹⁰ and high-pressure far- and mid-infrared spectra.¹¹ However, they are mainly focused on studying the effects of pressure or temperature on the properties of α -FOX-7 and its phase transitions. The differences in the properties of the three polymorphs of FOX-7 caused by different crystal structures are still not well studied and understood. It is known that different polymorphs of explo-

sives possess different performance including sensitivity, density, chemical reactivity, detonation velocity and pressure, and thermal stability. In order to understand the behavior of the explosives well, it is very necessary to investigate the differences in the structure and properties of their different polymorphs. For instance, a famous explosive HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), which also possesses more than one phases (α , β , δ , and γ), has been investigated systematically¹²⁻¹⁵ and the results show that the properties like densities, energy transfers rate, electronic, and vibrational properties of the α -, β -, δ -, and γ -phase are different each other. These differences can provide useful information for understanding the differences in the sensitivity and decomposition mechanism for four HMX polymorphs. Therefore, the three polymorphs of FOX-7 continue to inspire more research efforts to comprehend the differences in their properties further.

Energetic materials possess a complex chemical behavior; it thus is a challenging task to investigate their microscopic properties. Theoretical calculations can play an important role in studying the physical and chemical properties of complex energetic solids at the atomic level. Previously, density functional theory (DFT) has been used successfully to study the properties of some explosives including HMX,¹³ TATB (1,3,5-triamino-2,4,6-trinitrobenzen),¹⁶ HNS (hexanitrostilbene),¹⁷ and styphnic acid.¹⁸ As the electronic, optical, and thermodynamic properties of the three FOX-7 polymorphs are not systematically investigated and compared, there is a clear need to gain an understanding of those at the atomic level.

In this study, we report a systematic study of the electronic, optical, and thermodynamic properties of the three FOX-7 polymorphs (α , β , and γ) using density functional theory. Our main purpose is to examine the differences in the

microscopic properties of the three polymorphs.

Computational Method

The calculations performed in this study were done within the framework of DFT based on CASTEP code,¹⁹ using Vanderbilt-type ultrasoft pseudopotentials²⁰ and a plane-wave expansion of the wave functions. The self-consistent ground state of the system was determined by using a band-by-band conjugate gradient technique to minimize the total energy of the system with respect to the plane wave coefficients. The electronic wave functions were obtained by using a density-mixing minimization method²¹ for the self-consistent field calculation and the structures were relaxed by using the Broyden, Fletcher, Goldfarb, and Shannon (BFGS)²² method. The LDA functional proposed by Ceperley and Alder²³ and parameterized by Perdew and Zunger,²⁴ named CA-PZ, was employed. The cutoff energy of plane waves was set to 310 eV. Brillouin zones sampling was performed by using the Monkhost-Pack scheme with a k-point grid of $2 \times 2 \times 1$, $2 \times 2 \times 1$, and $1 \times 2 \times 1$ for α -, β -, and γ -FOX-7, respectively. The values of the kinetic energy cutoff and the k-point grid were determined to ensure the convergence of total energies.

The α phase of FOX-7 crystallizes in a monoclinic lattice with $P2_1/n$ space group and contains four $C_2H_4N_4O_4$ molecules per unit cell.⁴ The β phase crystallizes in an orthorhombic lattice with $P2_12_12_1$ space group and contains four $C_2H_4N_4O_4$ molecules per unit cell.⁴ The γ phase crystallizes in a monoclinic lattice with $P2_1/n$ space group and contains eight $C_2H_4N_4O_4$ molecules per unit cell.⁵ Figure 1 displays the unit cell of the three FOX-7 poly phases, and

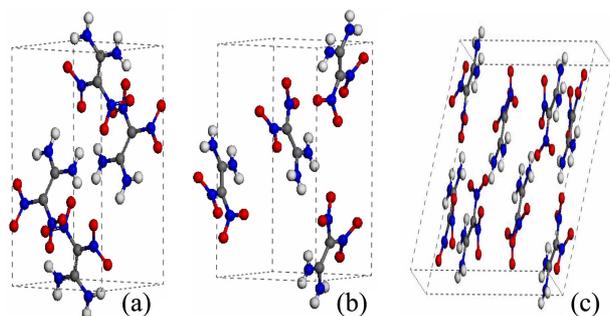


Figure 1. Unit cell of α -FOX-7 (a), β -FOX-7 (b), and γ -FOX-7 (c). Gray, blue, red, and white spheres stand for C, N, O, and H atoms, respectively.

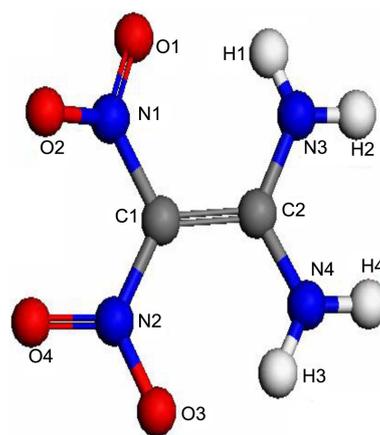


Figure 2. Atomic numbering of $C_2H_4N_4O_4$ molecule in FOX-7.

atomic numbering of $C_2H_4N_4O_4$ molecule in the FOX-7 phase is shown in Figure 2.

The experimental crystal structure of FOX-7^{4,5} was relaxed to allow the lattice configurations, cell shape, and volume to change at an ambient pressure without any symmetry constraints. In the geometry relaxation, the total energy of the system was converged less than 2.0×10^{-5} eV, the residual force less than 0.05 eV/Å, the displacement of atoms less than 0.002 Å, and the residual bulk stress less than 0.1 GPa.

Results and Discussion

Bulk Properties. As a base and a well-studied benchmark, the LDA (CA-PZ) and generalized gradient approximation (GGA) (PW91²⁵) functions were selected to relax bulk α -, β -, and γ -FOX-7 without any constraint. The calculated lattice parameters are shown in Table 1 together with their experimental values.^{4,5} It is found that the errors in the LDA (CA-PZ) results are smaller than those in the GGA (PW91) results in comparison with the experimental values for α -, β -, and γ -phase. This indicates that the accuracy of the LDA function is better than that of the GGA. Part of bond lengths and bond angles of the α -, β -, and γ -phase along with corresponding experimental data are given in Table 2. It is seen that the bond lengths and bond angles compare well with the experimental values. We also note that the errors in the calculated C-NO₂ (C1-N1 and C1-N2) bond lengths are relatively higher than those in the calculated C-C and C-NH₂ bond lengths in comparison with the experimental results. These discrepancies may be due to the

Table 1. Calculated and experimental lattice parameters for α -, β -, and γ -FOX-7

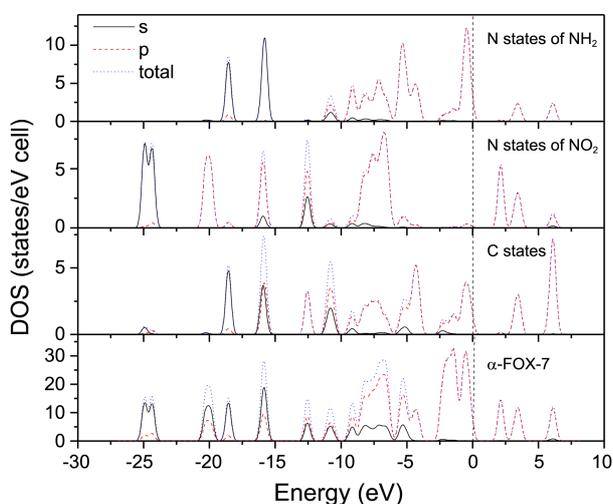
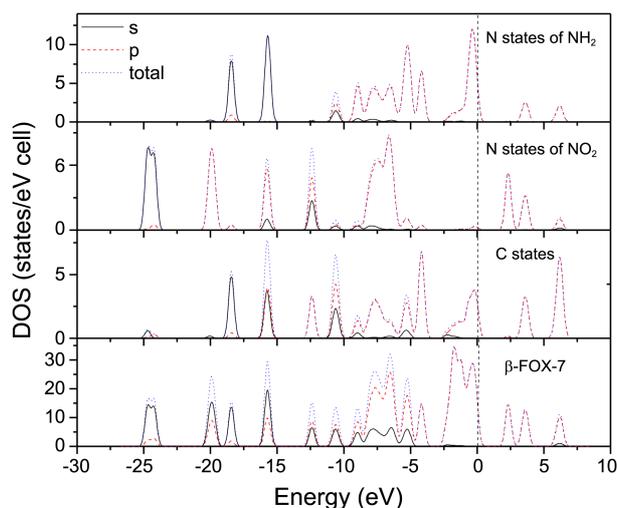
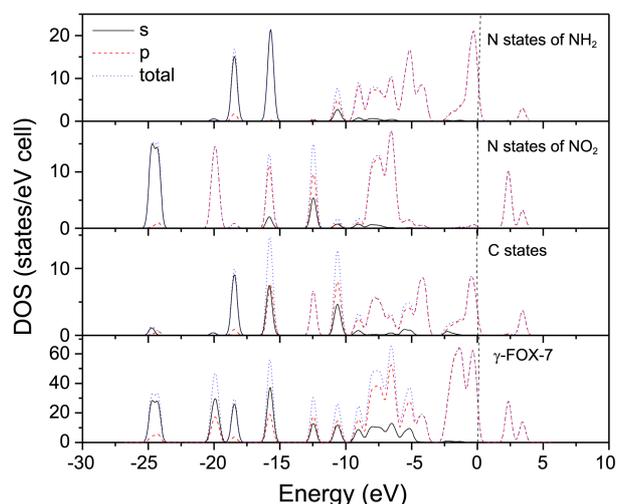
	α -phase			β -phase			γ -phase		
	Expt. ⁴	LDA	GGA	Expt. ⁴	LDA	GGA	Expt. ⁵	LDA	GGA
a (Å)	6.934	6.820	7.600	6.974	6.817	7.044	13.354	13.161	18.012
b (Å)	6.623	6.523	10.354	6.635	6.714	7.874	6.895	6.779	7.339
c (Å)	11.312	11.106	11.424	11.648	11.500	11.864	12.050	11.852	12.481
β (°)	90.06	90.66	94.02	90	90	90	111.10	110.34	106.49
Volume (Å ³)	519.5	494.1	896.9	538.9	526.4	658.0	1035.1	991.5	1581.9

Table 2. Calculated and experimental bond lengths (Å) and bond angles (deg) for α -, β -, and γ -FOX-7

	α -phase		β -phase		γ -phase	
	Expt. ⁴	This work	Expt. ⁴	This work	Expt. ⁵	This work
C1-C2	1.458	1.453	1.447	1.450	1.450	1.457
C1-N1	1.388	1.384	1.405	1.399	1.442	1.415
C1-N2	1.417	1.395	1.397	1.385	1.389	1.388
C2-N3	1.309	1.319	1.312	1.322	1.325	1.325
C2-N4	1.315	1.324	1.308	1.322	1.318	1.321
N1-C1-C2	124.4	123.3	122.2	121.4	121.8	121.6
N2-C1-C2	119.4	119.8	121.6	122.1	122.8	122.2
N3-C2-C1	120.4	120.6	121.0	120.8	120.9	121.3
N4-C2-C1	121.2	120.2	120.7	119.8	121.1	120.1
N1-C1-N2	116.2	116.8	116.2	116.4	115.2	116.3
N3-C2-N4	118.3	119.1	121.6	120.3	118.0	118.5

intermolecular hydrogen bonding interactions presented in the crystal lattice, which are not well described by DFT. In a word, the comparisons confirm that our computational parameters are reasonably satisfactory. Therefore, we used LDA in all subsequent calculations.

Electronic Structure. It is known that the density of states (DOS) is helpful for analyzing the changes in electronic structure and could interpret experimental spectra. To obtain information about the bond nature of the crystal FOX-7, Figures 3-5 display the DOS and partial DOS (PDOS) of α -, β -, and γ -FOX-7, respectively. Several main features can be summarized as follows. (i) The top of the DOS valence band shows two main peaks for the three phases, which are predominately from the p states. After that, several main peaks in the upper valence band are superimposed by the s and p states. (ii) The conduction band of each phase is dominated by the p states. This indicates that the p states for each phase play a very important role in their chemical reaction. (iii)

**Figure 3.** Total and partial density of states (DOS) of C-states, N-states of NH₂, N-states of NO₂, and α -FOX-7. The Fermi energy is shown as a dashed vertical.**Figure 4.** Total and partial density of states (DOS) of C-states, N-states of NH₂, N-states of NO₂, and β -FOX-7.**Figure 5.** Total and partial density of states (DOS) of C-states, N-states of NH₂, N-states of NO₂, and γ -FOX-7.

There is an obvious difference in the PDOS of the C atoms for the three phases. A sharp peak appears in the conduction band from 5 to 7.5 eV for the α - and β -phase, while the γ -phase does not have this peak. The same is true of the PDOS of the N atoms of NH₂ and the N atoms of NO₂. This may be caused by the wave-shaped layers of FOX-7 molecules formed in head-to-tail arrangements in the α and β phases and the planar layers formed in the β phase. (iv) Although the peaks located from -8.0 to -3.0 eV for the β and γ phases are more split and sharp than those of the α phase, the differences of the DOS between the three phases are very small. This is due to the small differences in their local molecular packing. (v) The PDOS of the C states and the N states of NH₂ are far larger than that of the N states of NO₂. This means that the former make more important contributions to the valence bands than the latter. Thus, the N atoms of NH₂ and the C atoms may act as active centers, that is, their electrons may be easy to transfer from the valence

Table 3. Calculated band gaps for α -, β -, and γ -FOX-7

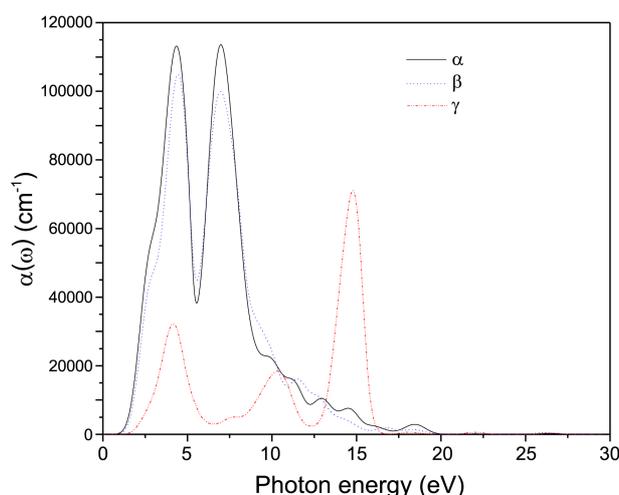
	α -phase	β -phase	γ -phase
Band gap (eV)	1.902	2.200	2.213

band to the conduction band. (vi) In the energy range from -5.0 to 0 eV, the DOS of the three phases are superimposed by the N states of NH_2 and the C states, while the N states of NO_2 make very little contribution. This shows that the C- NO_2 bonds are weaker than the C- NH_2 bonds. It may thus be inferred that the C- NO_2 fission may trigger the thermal decomposition of FOX-7. This agrees with the previous studies.^{10,26} (vii) Some strong peaks occur at the same energy in the PDOS of a particular C atom and a particular N atom of NH_2 . This shows that the two atoms are bonded strongly. Similarly, a particular N atom of NO_2 and a particular C atom in the ring are strongly bonded.

The sensitivity of energetic materials is a parameter which determines how easily a fast reaction can be initiated in a sample when subjected to an external stimulus, usually at normal temperature and pressure. Band gap is an important parameter to characterize the electronic structure of solids. Our previous theoretical studies^{13,16-18,27-29} on energetic crystals within the framework of periodic DFT have shown that a first-principles band gap criterion²⁹ is founded to measure sensitivity for a series of energetic crystals. In other words, for energetic crystals with similar structure or with similar thermal decomposition mechanism, the smaller the band gap is, the easier the electron transfers from the valence band to the conduction band, and the more they become decomposed and exploded. A possible explanation may be that the increased sensitivity is caused by the increased number of excited states due to optical band gap reduction. Table 3 presents the energy gaps between the valence and conduction band for α -, β -, and γ -FOX-7 at ambient pressure. It is seen that the band gap increases in the sequence of α -, β -, and γ -FOX-7, suggesting that the sensitivity of the three FOX-7 polymorphs decreases in the sequence of α -, β -, and γ -FOX-7 at ambient pressure.

It is reported that the hydrogen bonds can influence the sensitivity of FOX-7.^{4,5} There are 18 hydrogen bonds per a β - and γ -FOX-7 molecule but only 14 for a α -FOX-7, indicating that β - and γ -FOX-7 have stronger hydrogen bonding interactions than α -FOX-7. In addition, the overall average O \cdots H distances for β - and γ -FOX-7 are 248 and 243 pm, respectively, indicating that γ -FOX-7 has slightly stronger hydrogen bonding interactions than β -FOX-7. Thus, the total hydrogen bonding interactions increase in the sequence of α -, β -, and γ -FOX-7, which is the same as the order of their band gaps.

Optical Properties. In this section, we turn to investigate the optical absorption coefficients of α -, β -, and γ -FOX-7. The interaction of a photon with the electrons in the system can result in transitions between occupied and unoccupied states. The spectra resulting from these excitations can be described as a joint density of states between the valence and conduction bands. The imaginary part $\varepsilon_2(\omega)$ of the dielectric

**Figure 6.** Absorption spectra of the α -, β -, and γ -FOX-7.

function can be obtained from the momentum matrix elements between the occupied and unoccupied wave functions within the selection rules, and the real part $\varepsilon_1(\omega)$ of dielectric function can be calculated from imaginary part $\varepsilon_2(\omega)$ by Kramer-Kronig relationship. Absorption coefficient $\alpha(\omega)$ can be evaluated from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$.³⁰

$$\alpha(\omega) = \sqrt{2} \omega (\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega))^{1/2} \quad (1)$$

The absorption coefficients $\alpha(\omega)$ of α -, β -, and γ -FOX-7 are shown in Figure 6. The absorption spectra are active over various regions corresponding to the molecular or lattice structures of the individual material. The evolution pattern of absorption spectra for the α - and β -phase is qualitatively similar but different from that of the γ -phase. The peaks at 4.3 eV and 7.5 eV correspond to N-O vibration, while the peak at 14.7 eV does to C=C vibration. It is seen that the absorption coefficients of the N-O vibration of the α - and β -FOX-7 are much higher than that of the γ -FOX-7, while the α - and β -FOX-7 possess much lower absorption coefficients of the C=C vibration than the γ -FOX-7. This is because the α - and β -FOX-7 phases have similar crystal structure and their molecules are packed head-to-tail in wave-shaped layers, while the wave-shaped layers of FOX-7 molecules formed in head-to-tail arrangements in α - and β -FOX-7 are flattened in γ -FOX-7 forming planar layers. The differences in crystal packing lead to great differences in the chemical environments of the N-O and C=C bonds among different phases. In addition, the total absorption coefficient in the absorption region of 0-20 eV for the three FOX-7 phases increases in the order of α -, β -, and γ -phase. This indicates that the optical activity of the three polymorphs decreases in the sequence of α -, β -, and γ -phase.

Thermodynamic Properties. In this section, the thermodynamic functions including enthalpy (H), entropy (S), free energy (G), and heat capacity (C_p) for the three phases are evaluated and displayed in Figure 7. Since α -, β -, and γ -FOX-7 exist in the temperature range of 0-388 K, 388-435 K, and 435-504 K, respectively, their thermodynamic func-

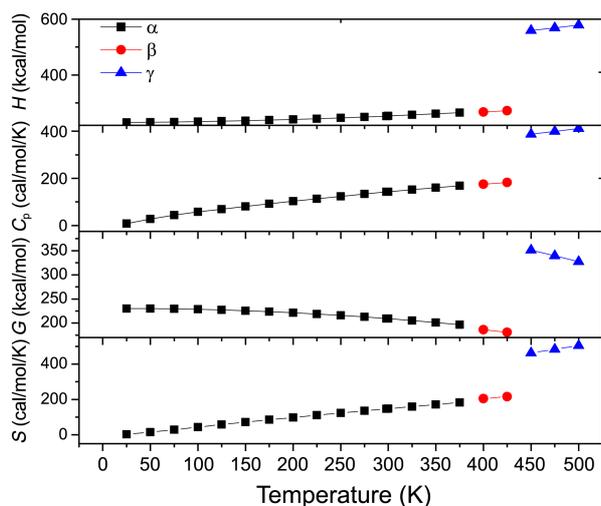


Figure 7. Thermodynamic properties of the α -, β -, and γ -FOX-7.

tions are calculated in their corresponding temperature ranges. It is seen that for all of the three phases, the calculated S values increases with the increasing temperature. This is because the main contributions to the S are from the translations and rotations of the molecules at lower temperature, while the vibrational motion is intensified and makes more contributions to S at higher temperature. The same is true for H and C_p . However, G decreases gradually with the increasing temperature. The β -phase at 400 K has higher S value than the α -phase at 375 K about 21.8 cal/mol/K, which is much higher than the increase value (11.4 cal/mol/K) of S for α -phase from 350 K to 375 K. This shows that the S value increases when the phase transition occurs during 375–400 K, in agreement with the experimental results.⁴ The S of the γ -phase at 450 K (462.3 cal/mol/K) is much higher than that of the β -phase at 425 K (215.2 cal/mol/K), indicating that S also increases when the β -phase transforms to the γ -phase. The H , G , and C_p of the γ -phase are significantly higher than those of the β -phase, showing that the phase transition occurred at 435 K is quite endothermic and not spontaneous. While the differences of H and G between the α - and β -phase in the temperature range of 375–400 K are small, indicating that the phase transition at 388 K is relatively easier when compared with the β - γ phase transition occurred at 435 K.

Conclusions

In this study, we have systematically studied the electronic, optical, and thermodynamic properties of the three FOX-7 polymorphs (α , β , and γ) using density functional theory. The results show that the N atoms of NH_2 and the C atoms act as active centers. The C- NO_2 fission may trigger the thermal decomposition of FOX-7. From the band gaps for the three FOX-7 phases, it could be concluded that their sensitivity decreases in the sequence of α -, β -, and γ -FOX-7.

The α and β phases have higher absorption coefficients of the N-O vibration than the γ phase, while the former possess much lower absorption coefficients of the C=C vibration

than the latter. The optical activity of the three polymorphs decreases in the sequence of α -, β -, and γ -phase. Both the two phase transitions occurred at 388 and 435 K makes S increase, especially the latter one. The β - γ phase transition occurred at 435 K is quite endothermic and not spontaneous. The α - β phase transition is much easier to happen than the β - γ phase transition.

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