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Heat Capacity Study of the Phase Transitions in As_4S_3 and As_4S_4

By

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Heat capacity of As_4S_3 is measured in the range 100 to 500 K. The structural phase transition (β to α) and the crystalline-to-plastic phase transition (α to γ) are investigated and these phase transition temperatures are determined to be (422 ± 0.5) and (432 ± 0.5) K, respectively. The results are compared with those of P_4S_3 which are recently studied. There is a strong similarity in the thermodynamic properties between the two compounds. The plastic phase of As_4S_3 can be retained down to (391 ± 2) K with a hysteresis in the specific heat–temperature curve. Heat capacity of As_4S_4 is also measured in the range 100 to 600 K. The structural phase transition temperature (α to β) and melting temperature are determined to be (340 ± 2) and (582 ± 1) K, respectively. As_4S_4 does not transform to a plastic state, and therefore, the melting entropy (54.32 J mol^{-1} K^{-1}) is very high compared to the melting entropy (3.34 J mol^{-1} K^{-1}) of As_4S_3.

Die Wärmekapazität von As_4S_3 wird im Temperaturbereich zwischen 100 und 500 K gemessen. Dabei werden der strukturelle Phasenübergang (β zu α) und der Phasenübergang kristallin–plastisch (α zu γ) untersucht und diese Phasenübergangstemperaturen zu (422 ± 0,5) bzw. (432 ± ± 0,5) K bestimmt. Die Ergebnisse werden mit denen von P_4S_3 verglichen, die kürzlich untersucht wurden. Zwischen den beiden Verbindungen existiert eine starke Ähnlichkeit in den thermodynamischen Eigenschaften. Die plastische Phase von As_4S_3 läßt sich bis herab zu (391 ± 2) K erhalten mit einer Hysterese im Verlauf der spezifischen Wärme über der Temperatur. Die Wärmekapazität von As_4S_4 im Temperaturbereich von 100 bis 600 K wird ebenfalls bestimmt. Die strukturelle Phasenübergangstemperatur (α zu β) und die Schmelztemperatur werden zu (340 ± 2) bzw. (582 ± 1) K bestimmt. As_4S_4 geht nicht in einen plastischen Zustand über und deshalb ist die Schmelzentropie (54,32 J Mol^{-1} K^{-1}) sehr hoch verglichen zur Schmelzentropie von As_4S_3 (3,34 J Mol^{-1} K^{-1}).

1. Introduction

In a recent publication we reported on the thermal properties of P_4S_3 in the crystalline and in the plastic state [1]. The almost spherical cagelike As_4S_3 molecules are isostructural with P_4S_3 molecules having C_{3v} point group symmetry. In the crystalline phases α-P_4S_3 and β- and α-As_4S_3 belong to the same space group Pmnb (D_{2h}^{16}) and have similar molecular packings. A plastic phase is therefore also expected in As_4S_3.

As_4S_3 (dimorphite) exists in two crystalline structures, the low-temperature β-phase and the high-temperature α-modification [2, 3]. Crystal structures of both modifications have been solved and reported [2]. The β to α transformation occurs at 415 K. It is also known that α-As_4S_3 is a quenched high-temperature modification [2]. The existence of a plastic phase has been suggested by Raman scattering studies [4] and is recently found by Blachnik et al. [5] at temperatures above 424 K with X-ray and calorimetric investigations. These authors have determined the β to α phase transition temperature to be 404 K.

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The molecular As_4S_4 exists in two monoclinic forms [6]. The α-modification changes into the high-temperature β-structure at 539 K [7, 8]. The back transition could be observed near 500 K, only, if the sample was cooled extremely slowly. The existence of a plastic phase in As_4S_4 has not been reported.

We have carried out specific heat (100 to 600 K) and high-temperature X-ray diffraction studies on As_4S_3 and As_4S_4 in order to confirm the former results and to understand the absence of a plastic phase in As_4S_4.

2. Experimental

2.1 *Crystal preparation*

As_4S_3 crystals were synthesized by direct reaction of arsenic and sulphur in stoichiometric proportions. Sublimation of the reacted material in a sealed quartz tube resulted in polycrystalline lumps.

2.2 *Heat capacity measurements*

Calorimetric measurements were performed in the temperature range from 100 to 480 K using a commercial differential scanning calorimeter (Perkin Elmer, DSC-2). The samples were encapsulated in the standard "vapour-pressure" aluminium pans, which are hermetically sealed up to a pressure of about 2 bar. The typical sample weight was 40 mg for the heat capacity measurements and about 10 mg to determine the transition enthalpies. The sample chamber of the DSC was continuously flushed with a slow stream of pure and dry helium gas and the heater block was cooled by a liquid nitrogen bath. The actual heat capacity was obtained by comparison with standard samples of either benzoic acid or synthetic sapphire. The temperature and the calorimetric calibration were adjusted by using melting points, crystallographic transition temperature, and the melting enthalpy of indium. The scanning rate used was 10 K/min. Several measurements have been carried out on at least two different samples. The error in temperature is estimated to be within ± 0.3 K; the total error of the molar heat capacity is 2% below 200 K, otherwise 1.5%.

2.3 *X-ray powder diffraction*

Finely ground β-As_4S_3 powder were filled in glass capillaries of 0.1 to 0.3 mm in diameter. To avoid any reaction with oxygen the capillaries were filled with argon gas and then sealed. X-ray powder diffraction pattern (CuKα radiation) were obtained from these samples with the help of Guinier-Simon film technique [9].

3. Temperature Dependence of the Specific Heat

Our experimental data of the specific heats $c_p(T)$ of As_4S_3 and As_4S_4 as a function of temperature are shown in Fig. 1, together with data reported recently by Blachnik et al. [5]. Interpolated values of our c_p-data given in Table 1.

3.1 *As_4S_3*

The lattice specific heat increases with temperature monotonously (Fig. 1). Above 400 K three anomalies occur. At $T_{t1} = 422$ K the small peak corresponds to the first order phase transition from β-As_4S_3 to α-As_4S_3. The enthalpy of transition is rather small ($\Delta S_{t1} = 3.34$ J mol^{-1} K^{-1}). At $T_{t2} = 432$ K a large paek and a jump in the specific heat occur. This anomaly displays the first-order crystalline to plastic (α-As_4S_3 to γ-As_4S_3) phase transition, similar to that found in P_4S_3 [1] and in many other

Table 1

Interpolated values of the specific heat c_p of As_4S_3 and As_4S_4 as a function of temperature

T (K)	As_4S_3 c_p (J mol^{-1} K^{-1})	As_4S_4 c_p (J mol^{-1} K^{-1})
100	96.62	91.71
105	95.38	99.12
110	99.85	106.06
115	103.97	112.41
120	107.77	118.23
130	114.53	128.45
140	120.91	137.07
150	120.46	144.39
160	131.57	150.68
170	135.96	156.14
180	140.38	160.92
190	143.95	165.12
200	146.98	168.82
210	149.19	172.02
220	151.45	174.67
230	153.06	176.69
240	154.60	177.93
250	156.25	180.16
260	156.92	182.53
270	158.52	184.79
280	160.71	186.88
290	163.09	188.82
300	165.40	190.57
310	167.48	192.15
320	169.11	193.55
330	170.50	194.75
340	171.44	195.83
350		196.79
360	172.72	197.67
370	173.50	198.41
380	171.80	199.09
390	176.99	199.72
400	180.58	200.34
410		200.96
420		201.62
430		202.33
440		203.11
450		203.99
460		204.97
470		206.06
480		207.28
490		208.61
500		210.04

molecular crystals [10] which is characterized by an extremely high entropy of transition. The entropy of transition amounts to $\Delta S_{t2} = 30.2$ J mol^{-1} K^{-1}. Above this transition $c_p(T)$ remains nearly constant up to the melting point $T_m = 491$ K.

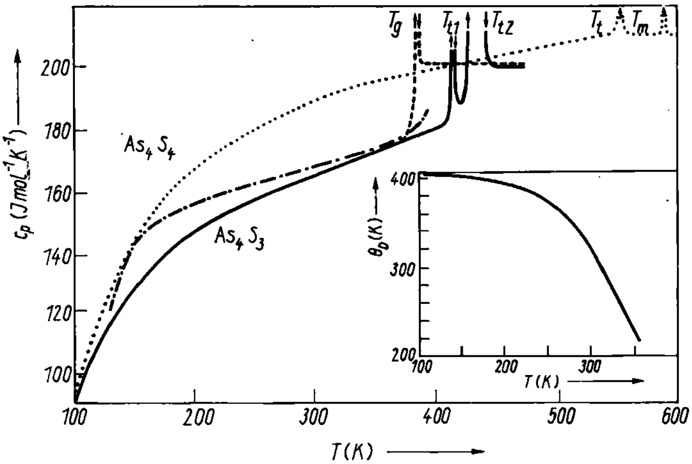

Fig. 1. Variation of the specific heat of As_4S_3 (———) and As_4S_4 (· · · · ·) with temperature. The other curve (—·—) represent data of [5] for As_4S_3. The transitions $\beta \rightarrow \alpha$ (T_{t1}) and $\alpha \rightarrow \gamma$ (T_{t2}) and the back transition $\gamma \rightarrow \beta$ (T_g) of As_4S_3 are seen to be indicated by the discontinuities of the specific heats. In the case of As_4S_4 the transition $\alpha \rightarrow \beta$ (T_t) and melting (T_m) are seen. The insert shows the temperature variation of the Debye temperature θ_D of P_4S_4, As_4S_3, and As_4S_4 after taking into account the scaling factor for different masses obtained from the specific heat data of the present work and also from that of [1]

If we cool the sample from a temperatur which is above T_{t2} (crystalline to plastic transition) we supercool the plastic phase. The very sharp back transition into the β-phase appears at $T_g = 391$ K. As in P_4S_3, T_g is rather well defined and depends only slightly on the cooling speed (1 to 80 K min^{-1}). The forward ($\beta \rightarrow \alpha$ at T_{t1}, $\alpha \rightarrow \gamma$ at T_{t2}) and back transition ($\gamma \rightarrow \beta$ at T_g) cycle can be reproducibly repeated. The specific heat during cooling remains nearly constant and shows the same temperature dependence $c_p(T)$ as the plastic phase.

The specific heats for the four phase transitions T_{t1}, T_{t2}, T_g, and T_m are shown in more suitable scale in Fig. 2a. The different transitions were analysed in terms of their transition enthalpies ΔH by graphical analysis of the continuous curves obtained by the DSC recorder. The resulting thermodynamic data are given in Table 2.

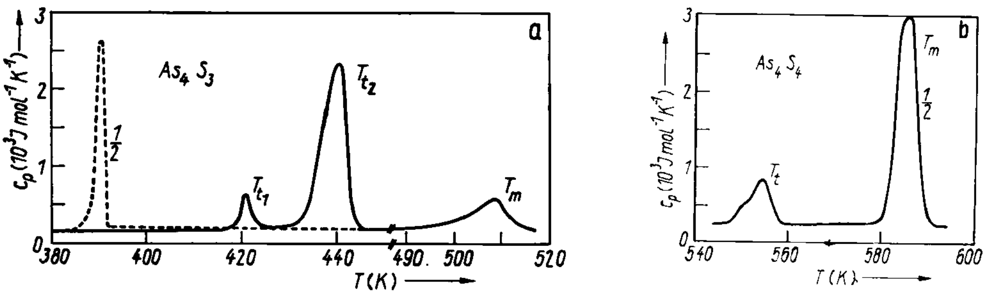

Fig. 2. Variation of the specific heat of a) As_4S_3 and b) As_4S_4 at different phase transitions. The fraction 1/2 beside the peaks indicates that the peak sizes have been reduced to one half of the actual sizes

Table 2

Thermodynamic data of As_4S_3 and As_4S_4 for the different phase transitions

	transition	temperature of transition T (K)	enthalpy ΔH (kJ/mol)	entropy ΔS (J/mol K)
As_4S_3	$\beta \to \alpha$ at T_{t1}	422 ± 0.5	1.44 ± 0.02	3.34
		415 [2, 3]		
		404 [5]	1.0 [5]	
	$\alpha \to \gamma$ (plastic) at T_{t2}	432 ± 0.5	13.04 ± 0.15	30.2
		425 [5]	13.07 [5]	30.8 [5]
	melting at T_m	484 ± 5	3.86 ± 0.04	8.0
		474 [5]	3.77 [5]	8.0 [5]
	γ (plastic) $\to \beta$ at T_g		0.61*)	
		391 ± 2	13.90 ± 0.2	
As_4S_4	$\alpha \to \beta$ at T_t	540 ± 2	3.42 ± 0.04	6.33
			3.37 [5]	
		539 [6]	3.47 [6]	
	$\beta \to \alpha$ at T_t'	395 ± 5	3.46 ± 0.1	
	melting at T_m	582 ± 1.0	31.56 ± 0.2	54.32
		591 [5]	31.68 [5]	
		580 [8]	25.10 [8]	

*) $\int_{391}^{432} \Delta c_p(T)\, dT = 0.611$.

3.2 As_4S_4

In contrast to P_4S_3 and As_4S_3 this molecular crystal does not exhibit a plastic phase. The specific heat (Fig. 1) shows only two peaks: the $\alpha \to \beta$ transformation at 540 K and the melting point near 580 K (Fig. 2b). The computed thermodynamical data are given again in Tables 1 and 2.

4. Results of the X-Ray Investigation

Fig. 3 shows a continuous Guinier-Simon photograph in the temperature region 390 to 457 K. This beautiful photograph shows the several phase changes occurring in As_4S_3 as a function of temperature. We see that at about 412 K there is a discontinuous phase transition. From the known structure of β- and α-As_4S_3 we immediately find that the discontinuity in the Guinier-Simon photograph at 412 K corresponds to a structural phase transition from β-As_4S_3 to α-As_4S_3. At about 425 K we see another discontinuity. Above this temperature we see a powder diagram which is characteristic of a plastic phase–sharp low-angle lines and disappearance of all high-angle lines. A comparison of this diagram with that of plastic β-P_4S_3 shows that plastic As_4S_3 (γ-As_4S_3) has the same structure as that of plastic β-P_4S_3. At a slightly higher temperature 438 K a further phase develops, whose composition and structure have so far not been found. When cooled back to room temperature this phase is retained. We therefore conclude that this unidentified phase is developed as a result of some chemical reaction.

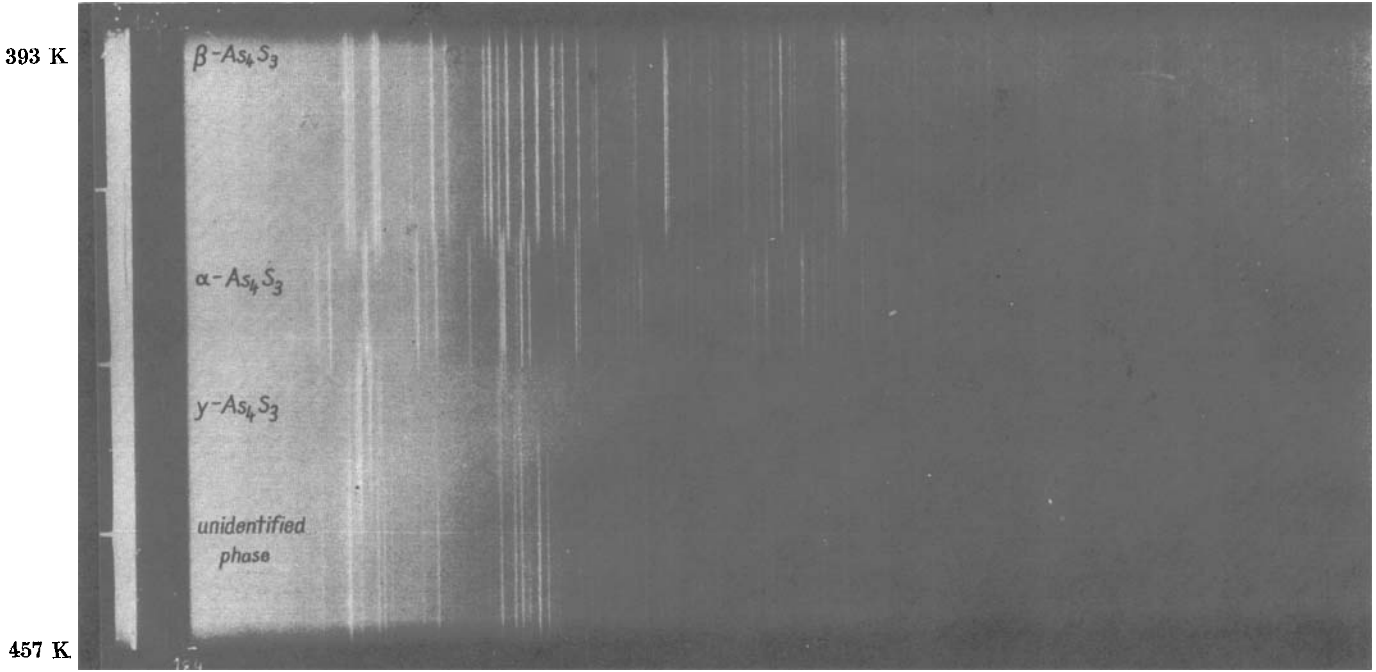

Fig. 3. Continuous Guinier-Simon film showing β → α (structural) and α → γ (crystalline to plastic) phase transitions of As_4S_3. The discontinuity in the lines at the bottom of the film is interpreted as a chemical change

5. Discussion

Comparing the specific heat measurements with the X-ray diffraction results for As_4S_3, we find a good agreement disregarding a systematic shift of about 8 K between both temperatue scales. The temperature scale of the DSC is, however, more reliable because it has been calibrated before each measurement. The X-ray diffraction confirms that the first small peak in $c_p(T)$ can be interpreted as the structural β-As_4S_3 to α-As_4S_3 phase transition. The second large peak must be interpreted as a transition from the α-As_4S_3 into a plastic orientationally disordered γ-phase. Looking at Table 2, we see that the enthalpies ΔH for the crystalline to plastic phase transition and for melting are in excellent agreement (1.5%) with the data of Blachnik et al. [5], although the transition temperatures differ. However, there are considerable differences in T_{t1}, $\Delta H(T_{t1})$, T_{t2}, and especially in $c_p(T)$ in the temperature range between 100 and 300 K, if we compare our data to those of Blachnik et al. [5] (see Table 2). It should be noted that the melting of As_4S_3 is characterized by a broad peak over nearly 20 K.

We note that the variation of the equivalent Debye temperature $\theta_D(T)$, as calculated from $c_p(T)$ between 100 and 380 K, is identical for As_4S_3 and As_4S_4. Furthermore, scaling the $\theta_D(T)$ of P_4S_3 by the corresponding masses of the molecules $M(As_4S_3)/M(P_4S_3) = 1.23$ we find quantitative agreement between the $\theta_D(T)$ curves for the three compounds which is shown in the insert of Fig. 1. This indicates the similarity of the three lattices. In addition, the scaling factor also holds for the temperature of the transition of crystalline to plastic phases and for the melting points of P_4S_3 and As_4S_3 (see Table 2). However, this is no more valid in the case of As_4S_4 which has a much higher melting point and does not transform to the plastic state. The c_p data ($T < 300$ K) of Blachnik et al. do not fit in this picture. This very different temperature dependence of c_p below 300 K may be connected to rather low $T_{t1} = 404$ K obtained by Blachnik et al. in comparison to our data and those of [2]. The difference in $\Delta H(T_{t1})$ amounts to 40%. Such large deviations cannot be explained by experimental eross. The question arises, whether the experimental conditions (vapour pressure, humidity, etc.) influence the results. We found that reproducible c_p-measurements were not possible with "open" pans above 430 K. We therefore used vapour-pressure pans which withstand an internal pressure of 2 bar.

Our $c_p(T)$ data of As_4S_3 clearly show the characteristics of "plastic" crystals: undercooling, hysteresis, and very low entropy of fusion ($\Delta S < 20$ J mol^{-1} K^{-1}). Similar results have been obtained by us in the case of the plastic P_4S_3. Above T_{t1} the almost spherical As_4S_3 molecules gain rotational freedom or alternatively they execute large librations sitting on different potential wells and continuously reorienting themselves. For a complete free rotation of the As_4S_3 molecule three additional degrees of freedom appear and these should increase the specific heat by $\Delta c_p = 25$ J mol^{-1} K^{-1}. The difference in the specific heat between the crystalline and the plastic state ammounts to Δc_p (390 K) $= 21.5$ and Δc_p (420 K) $= 17.5$ J mol^{-1} K^{-1}. Taking into account Neumann-Kopp's rule, we expect $c_p \approx 175$ J/mol K for As_4S_3 at sufficiently high temperature. This value is reached near $\theta_D \approx T \approx 400$ K, whereas in the plastic state As_4S_3 has a $c_p \approx 200$, $\Delta c_p \approx 25$ J mol^{-1} K^{-1}. However, this agreement should be taken only qualitatively. It is to be noted that in addition to the contribution due to the excitation of rotational degrees of freedom there should be further contribution due to the volume change at the phase transition and due to the difference in the centre of gravity structures of the crystalline and the plastic phases.

The phenomenon of undercooling gives rise to the hysteresis in the specific heat (Fig. 1). The forward and back transition cycle ($\beta \rightarrow \alpha \rightarrow \gamma \rightarrow \beta$) is reproducible. The following equation is satisfied (Table 2):

$$\Delta H(T_{t1}) + \Delta H(T_{t2}) = \Delta H(T_g) + \int\limits_{T_g}^{T_{t2}} \Delta c_p(T)\,\mathrm{d}T\,.$$

The ratio $T_g/T_{t2} = 0.9$ falls in the range observed for other plastic crystals [10].

The second characteristic of "plastic" crystals is the low entropy of melting. The measured value $\Delta S = 8.0$ J mol^{-1} K^{-1} is comparable to that of many other plastic crystals [11]. As in the case of P_4S_3 [1] the back transition of As_4S_3 at T_g is spontaneous and nearly independent of the cooling speed (1 to 80 K min^{-1}). Inspection of the low-temperature side of the transition at T_g did not reveal any "frozen in" states. No configurational entropy is retained below T_g. Thus, we argue that (again as in P_4S_3) the back transition is not "glass-like".

The present $c_p(T)$ data for As_4S_4 and the transition enthalpies $\Delta H(\alpha \rightarrow \beta)$ and $\Delta H(T_m)$ (Fig. 1 and Table 2) agree within 1.5% with the recently published data of Blachnik et al. [5]. The melting point $T_m = 582$ K obtained by us is in better agreement with the results of Street and Munir [8] than with $T_m = 591$ K found by Blachnik et al. [5].

We found for T_t (α-As_4S_4 to β-As_4S_4) a large reproducible hysteresis. The back transition occurs at $T_t' = 395$ K.

There are no indications of any further transition which could be attributed to a plastic phase in As_4S_4. The entropy of melting for As_4S_4 (54.32 J mol^{-1} K^{-1}) is nearly ten times more than that of materials which exist in the plastic state.

The Guinier-Simon photographs of the As_4S_3 and P_4S_3 in the plastic states are practically identical (Fig. 3) indicating that the plastic γ-As_4S_3 is isotypic with the plastic β-P_4S_3. Recently we found from the single-crystal investigation with X-ray diffractometer that β-P_4S_3 crystallizes in the space group R3 with $a = 15.85$ Å and $\alpha = 89.53°$ [12]. The centres of gravity of P_4S_3 molecules have been found to be arranged like Mn atoms in β-Mn [13] allowing for a small rhombohedral distortion. Blachnik et al. [5] on the other hand have indexed the Guinier photograph of the γ-As_4S_3 on the basis of a tetragonal cell with $a = 16.9$ and $c = 21.75$ Å. One may be able to index the Guinier diagram with this large unit cell but the single-crystal investigation on β-P_4S_3 suggests this to be wrong. Results of these structural investigations will be published elsewhere [12].

From our recent thermal expansion and compressibility measurements [1, 14] we have stablished that P_4S_3 is prone to a larger volume change with application of temperature and pressure compared to As_4S_3. This suggests that P_4S_3 should be more plastic than As_4S_3. That this is really so can be seen from the melting entropy data which are 25.2 and 30.2 J mol^{-1} K^{-1} for P_4S_3 and As_4S_3, respectively, taking into account Timmermans criterion [15] of the plastic state. As_4S_4 does not have a plastic phase. This can be understood from the fact that As_4S_4 molecules are not spherical like P_4S_3 and As_4S_3. The almost spherical shape of the P_4S_3 and As_4S_3 molecules favours the formation of the plastic states. Another reason is the strength of the intermolecular interaction which must be far too strong in As_4S_4 for the formation of the plastic phase.

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