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Raman Spectroscopy Study of the Reaction between Sodium Sulfide or Disulfide and Sulfur: Identity of the Species Formed in Solid and Liquid Phases

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The reactions of sodium sulfide or disulfide with sulfur, when heated, are examined through Raman spectroscopy. It is shown that whatever the composition of the mixtures, the solid sodium sulfide or disulfide transforms into the crystalline α-Na_2S_4 phase in a first step, with α- or β-Na_2S_2 as an intermediate. The reaction, which proceeds when the sulfur melts, is assumed to be related to the polymerization−depolymerization mechanism responsible for the formation of smaller rings and sulfur chains in molten S_8. This confirms the strong reactivity of the radical sulfur chain molecules. This solid α-Na_2S_4 formed may further react around 200 °C with Na_2S in excess. This solid-state reaction leads to the formation of β-Na_2S_2. It is shown that, after the liquid of composition Na_2S_4 is heated above 400 °C, a glass is formed upon cooling. Annealing this glass around 124 °C yields a new γ-Na_2S_4 crystalline phase where the S_4^{2-} anions have a smaller torsion angle. This new phase is metastable and transforms into the α phase upon prolonged heating at 200 °C. The solids, formed from heating the mixtures $Na_2S + (n/8)S_8$ or $Na_2S_2 + (n'/8)S_8$ with $n' = n - 1$, for $n \leq 3$ are only crystalline β-Na_2S_2 or α,γ-Na_2S_4 and glassy Na_2S_4, and for $3 < n < 4$ α and γ-Na_2S_4 and α, β, γ, and δ-Na_2S_5 depending on the heating treatment. For $n > 4$, higher polysulfides decompose under crystallization into Na_2S_5 and sulfur. The liquids formed from these mixtures show the formation of all the S_{n+1}^{2-} anions although Na_2S_3 and Na_2S_6 do not crystallize from these liquids.

Introduction

The discovery of the sodium−sulfur battery as a potentially high-energy density power source[1−3] renewed the interest in the study of the various reduced species occurring in liquid and solid phases of the sodium−sulfur system. The sodium−sulfur phase diagram is rather well documented.[2,5−7] It is deduced mainly from the differential thermal analysis[3,5] (DTA) or from hot-stage microscopy studies[4,6,8] and measurements of battery open circuit voltage.[2] The DTA of liquids of appropriate composition, during their cooling, was made under stirring to prevent the strong tendency of polysulfides for supercooling. Structures of the most stable crystalline phases were determined by X-ray: α- and β-Na_2S_2,[9] α-Na_2S_4,[10] and α-Na_2S_5.[11] A Raman spectroscopy study of the solid and liquid phases by Janz et al.[12] gives some insight into some metastable phases of these polysulfides but their formation conditions and their structure remain almost unknown and require more information.

A general study of the Raman spectra of the polysulfide anions in relation to their structure[13,14] led us to investigate reactions of sodium sulfide or disulfide with sulfur upon heating. This reaction is one of the most general ways to prepare the polysulfides.[15,16] Oei[5] analyzed these reactions for two mixtures $Na_2S + (n/8)S_8$ with $n = 1$ and 2 and suggested the intermediate formation of Na_2S_5 from its differential thermal analysis. Janz et al.[3] partly failed to observe this early reaction stage of Na_2S with sulfur. Furthermore, they thought to observe an inverse-crystallization phenomenon as the sulfur content increased. We shall see that the interpretation of the observations of Oei et al.[5] and Janz et al.[3] are both erroneous and are related to the peculiar properties of the Na_2S_2 and Na_2S_4 compounds.

We shall also try to specify the conditions of formation of some metastable species and to discuss the liquid structure along to their Na_2S_n composition.

Experimental Section

Na_2S, Na_2S_2, and Na_2S_4 were synthesized by the reaction of adequate amounts of Na (Fluka, >99%) and sulfur (Fluka, >99.999%) in liquid ammonia, as previously described.[13] Each mixture of Na_2S or Na_2S_2 with adequate amounts of sulfur, after being finely ground together, was poured in a 3-mm diameter quartz tube. The tube was sealed under vacuum. This tube was then placed in a small cylindrical furnace. Three holes in the furnace allowed us to record Raman spectra.

An XY multichannel Dilor spectrometer equipped with a double monochromator as filter and with a liquid nitrogen cooled Wright CCD

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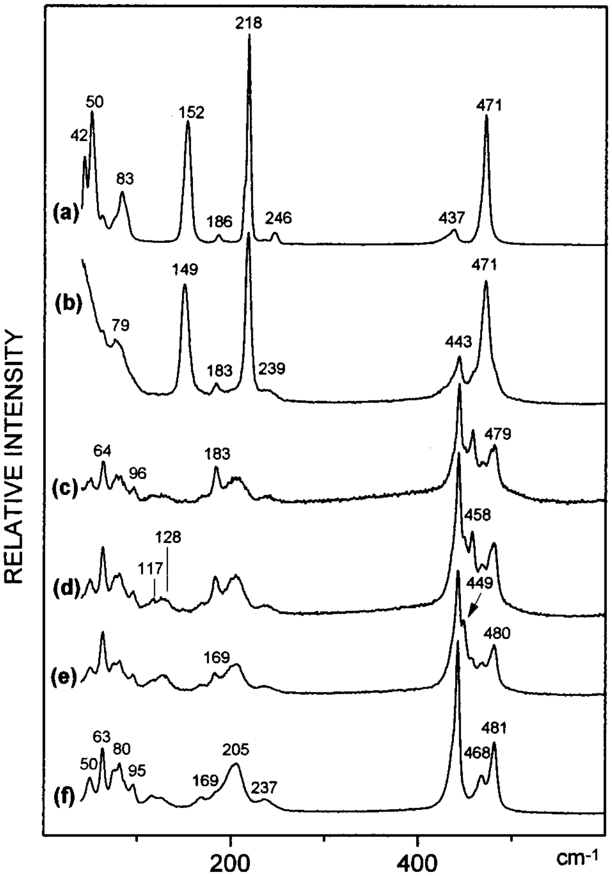

Figure 1. Raman spectra of the $Na_2S + (6/8)S_8$ mixture at various temperatures: (a) 25 °C; (b) 120 °C; (c) 120 °C (1 h later); (d) 140 °C; (e) 160 °C; (f) 160 °C (17 mn later). $\lambda_0 = 514.5$ nm; laser power (lp) = 3 mW; slit width (sw) = 100 μm; spectral slit width (ssw) = 3.1 cm^{-1}; integration time = 12 s (a), 60 s (b), 120 s (c−f).

mosaic detector (1200 × 300) was used. An Olympus microscope was coupled with the XY spectrometer to record at room-temperature Raman spectra of the various phases of the products. In these conditions, the laser power was kept below 1 mW. Raman spectra were excited by the 514.5 nm line of an argon-ionized Spectra Physics laser.

Results

1. Reaction between Na_2S or Na_2S_2 and Sulfur. We carefully examined the reactions between Na_2S or Na_2S_2 and sulfur, namely $Na_2S + (n/8)S_8$ with $n = 1, 2, 3, 3.6, 4, 5, 6,$ and $Na_2S_2 + (n'/8)S_8$ with $n' = 2, 4, 6$, by slowly heating the mixtures from room temperature to about 500 °C for 2−4 h, and by subsequently cooling slowly the mixture to room temperature for 2−3 h. The reactions were monitored step by step by Raman spectroscopy according to temperature. In this section we report only the Raman spectra recorded at temperatures lower than ca. 200 °C, i.e., well below the melting temperature of Na_2S_4. As we shall illustrate for some characteristic mixtures, α-Na_2S_4 was directly formed from Na_2S or β-Na_2S_2 in the crystalline state at the melting temperature of sulfur. It can be seen in Figure 1 that with a large excess of sulfur ($n = 6$), at around 120 °C the melting of sulfur is indicated by the disappearance of the sulfur lattice lines at 42 and 50 cm^{-1} and the broadening of the other sulfur lines. Simultaneously, a new band is observed at 443 cm^{-1} with a shoulder near 479 cm^{-1} on the high-wavenumber side of the sulfur stretching vibration band at 471 cm^{-1}. Likewise, another shoulder is observed on the low-wavenumber side of the 471 cm^{-1} band. When the mixture was maintained at this temperature for 1 h, the main bands of sulfur at 152, 218, and 471 cm^{-1} disappeared (Figure 1c). The stretching vibration bands at 479, 468, and 443 cm^{-1} and bending vibration bands at 205 and 237 cm^{-1}, which clearly identify the α-Na_2S_4 crystalline compound,[12] increased, and new bands appeared mainly at 458 and 183 cm^{-1}. These bands must be ascribed to the formation of crystalline α-Na_2S_2. The band at 458 cm^{-1} corresponds to the stretching mode of the S_2^{2-} anion, and the 183 cm^{-1} one, to a lattice mode. These modes were observed by Eysel et al.[17] at 454 and 182 cm^{-1}, respectively. They are different from those of the β-Na_2S_2 form observed by Janz et al.[12] at 451 and 134.5 cm^{-1}. As the temperature was progressively raised to 140 and 160 °C, the intensity of the α-Na_2S_2 bands at 458 and 183 cm^{-1} decreased strongly and a new band appeared at 449 cm^{-1} and a broader one at 130 cm^{-1}, belonging to β-Na_2S_2. These new bands characterize the conversion of α-Na_2S_2[17] to β-Na_2S_2. This transformation was observed by Janz et al.[3] between 117 and 194 °C and by Oei[5] above 150 °C. Finally, this β-Na_2S_2 species still reacts with sulfur to give α-Na_2S_4 as a crystal in equilibrium with molten sulfur not seen in the observation field (Figure 1f). In the mixture with $n = 2$, the results are similar; the reaction also begins above 100 °C. The α-Na_2S_2 and β-Na_2S_2 intermediate species were also observed and disappeared between 160 and 180 °C.

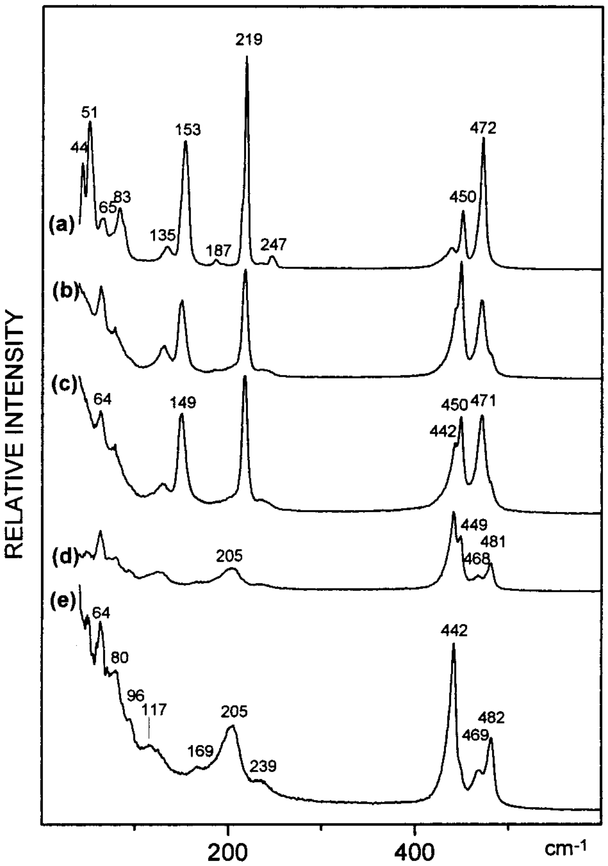

Figure 2. Raman spectra of the $Na_2S_2 + (4/8)S_8$ mixture at various temperatures: (a) 25 °C; (b) 90 °C; (c) 120 °C; (d) 140 °C; (e) 160 °C. $\lambda_0 = 514.5$ nm; lp = 3 mW; sw = 100 μm; ssw = 3.1 cm^{-1}; integration time = 30 s (a−d), 60 s (e).

Let us now consider the mixtures of β-Na_2S_2 with a large excess of sulfur, $n' = 4$ (Figure 2). The spectrum of the initial mixture exhibited the lines of β-Na_2S_2 at 65, 135, and 449 cm^{-1} with those of sulfur. The sulfur melting was characterized by

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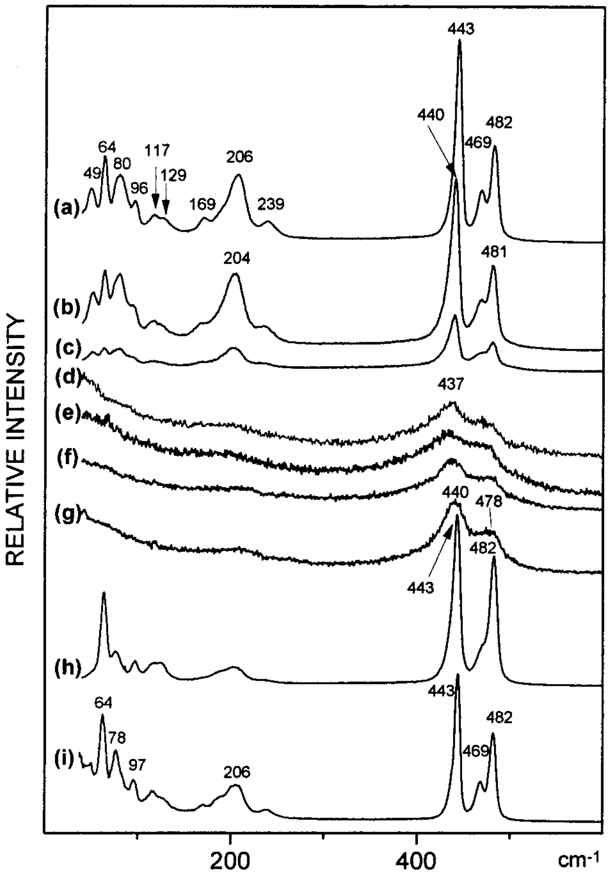

Figure 3. Raman spectra of pure Na_2S_4 at various temperatures. Heating steps: (a) 25 °C; (b) 225 °C; (c) 250 °C; (d) 350 °C; (e) 400 °C. Cooling steps: (f) 275 °C; (g) 200 °C; (h) 160 °C; (i) 60 °C. $\lambda_0 = 514.5$ nm; lp = 3 mW; sw = 200 μm; ssw = 6.2 cm^{-1}; integration time = 30 s (a–c), 90 s (d–g), 60 s (h, i).

the disappearance of lattice modes at 44 and 51 cm^{-1} at 90 °C, a temperature lower than the melting temperature of pure sulfur. Likewise, the α-Na_2S_4 formation was characterized by shoulders on the low-wavenumber side of the 449 cm^{-1} band and on the high-wavenumber side of the 471 cm^{-1} sulfur band. The conversion of β-Na_2S_2 into α-Na_2S_4 proceeded as the temperature was raised and was completed at 160 °C, as previously observed (Figure 2e).

As we have seen, the mixtures of sodium sulfide or disulfide with sulfur lead to the formation of α-Na_2S_4 in the solid state with the intermediate formation of Na_2S_2 at temperatures lower than 160 °C.

2. Reactivity of Na_2S_4 and Stability of the Species Formed during Cooling. The heating of the various investigated mixtures, at temperatures around 200 °C, involves α-Na_2S_4 and either Na_2S or sulfur, depending on the value of n or n'. The Raman spectra recorded for these mixtures heated above 200 °C will display the species resulting from the reactivity of Na_2S_4 with Na_2S or with sulfur.

2.1. System with $n = 3$. To clarify the behavior of α-Na_2S_4 upon heating, we prepared a sample of α-Na_2S_4 from reaction of Na_2S with S_8 dissolved in a stoichiometric amount in liquid ammonia (Figure 3a). On heating, this compound melts above 250 °C in good agreement with its congruent melting point at 290 ± 5 °C.[7] At 350 °C, the spectrum of this liquid of homogeneous composition Na_2S_4 displays a main broad band at 437 cm^{-1}, which looks like the envelope of the broadened bands of the solid. After heating to 400 °C, the cooled liquid crystallized around 160 °C to display again the spectrum of the α-Na_2S_4 crystalline form characterized by its bending vibration modes at 206 and 239 cm^{-1}. This α-form was heated at 500 °C for 2 h, and after slow cooling (22 h), we obtained the spectrum of an homogeneous glass shown in Figure 4a, and previously obtained by Janz et al.[12] An annealing at 120 °C of this glass led to a new crystalline form γ-Na_2S_4 with the bending vibration modes located at 227 and 269 cm^{-1}, much higher wavenumbers than for α-Na_2S_4 (Figure 4b,c). This new form is named γ by analogy with the γ-Na_2S_5 form that also has a glassy state, as already observed.[12] The broad bands observed at 220 and 265 cm^{-1} for the glass indicate that its structure is close to that of γ-Na_2S_4. When slowly heated, this new form melted at ca. 230 °C, a temperature lower than that of the pure α-form (Figure 4d). This liquid, heated either at 300 or 600 °C, led again to the glass or to the γ-form depending on cooling conditions. To check the stability of this new form, we heated the γ-Na_2S_4 polysulfide sample for 24 h at 124 °C without any change in its spectrum, but after a subsequent heating at 200 °C for 17 h the product was fully transformed into the α-form, indicating that the γ-form is a metastable form of Na_2S_4 produced at a high temperature.

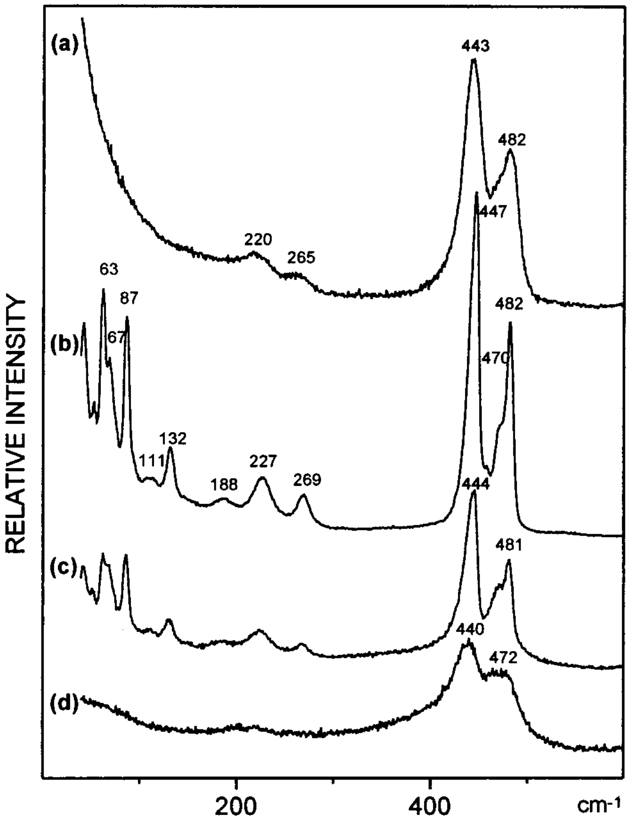

Figure 4. Raman spectra of γ-Na_2S_4 at various temperatures: (a) 25 °C; (b) 120 °C (after 1 h); (c) 200 °C; (d) 230 °C. $\lambda_0 = 514.5$ nm; lp = 3 mW; sw = 200 μm; ssw = 6.2 cm^{-1}; integration time = 300 s (b), 600 s (a, c, d).

Both mixtures of $Na_2S + (n/8)S_8$ and $Na_2S_2 + (n'/8)S_8$, heated at about 100 °C, led to the formation of α-Na_2S_4 that melts by heating and has the same behavior as that of the previously examined pure α-Na_2S_4 shown in Figures 3 and 4.

2.2. Systems with $n = 1$ and $n = 2$. In these mixtures, the observation of α-Na_2S_4 at temperatures close to 150 °C is a consequence of the reaction $Na_2S + (n/8)S_8 \rightarrow (n/3)Na_2S_2 + (1 - n/3)Na_2S$. The observation of Na_2S_2 suggests that this species could be an intermediate product of the formation of α-Na_2S_4. The excess of Na_2S, with regard to the stoichiometry

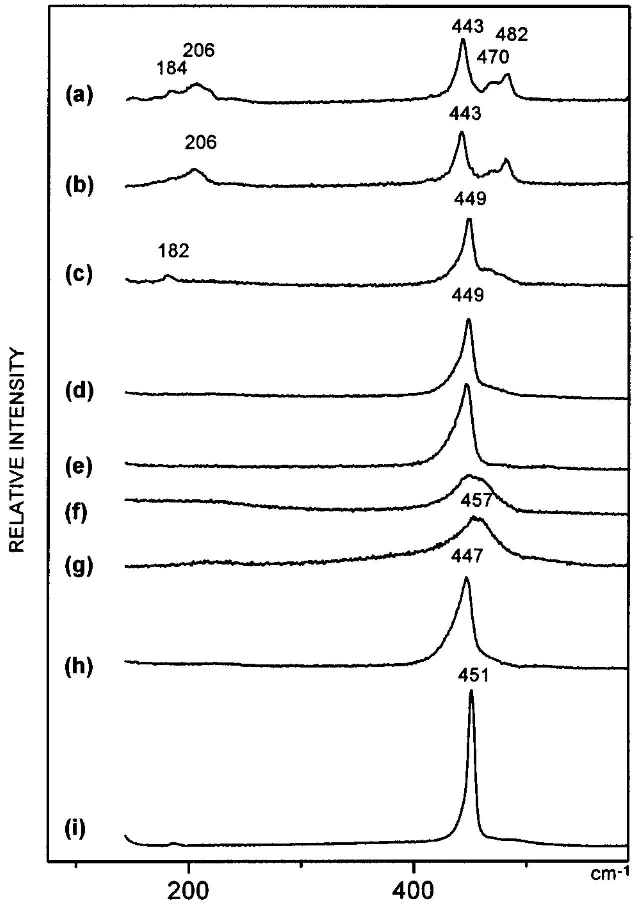

Figure 5. Raman spectra of the $Na_2S + (1/8)S_8$ mixture at various temperatures: (a) 150 °C; (b) 175 °C; (c) 200 °C; (d) 250 °C; (e) 350 °C; (f) 400 °C; (g) 450 °C; (h) 350 °C (cooling); (i) 75 °C (cooling). $\lambda_0 = 514.5$ nm; lp = 3 mW; sw = 200 μm; ssw = 6.2 cm^{-1}; integration time = 300 s (c, d, e, h, i), 600 s (a, b, f, g).

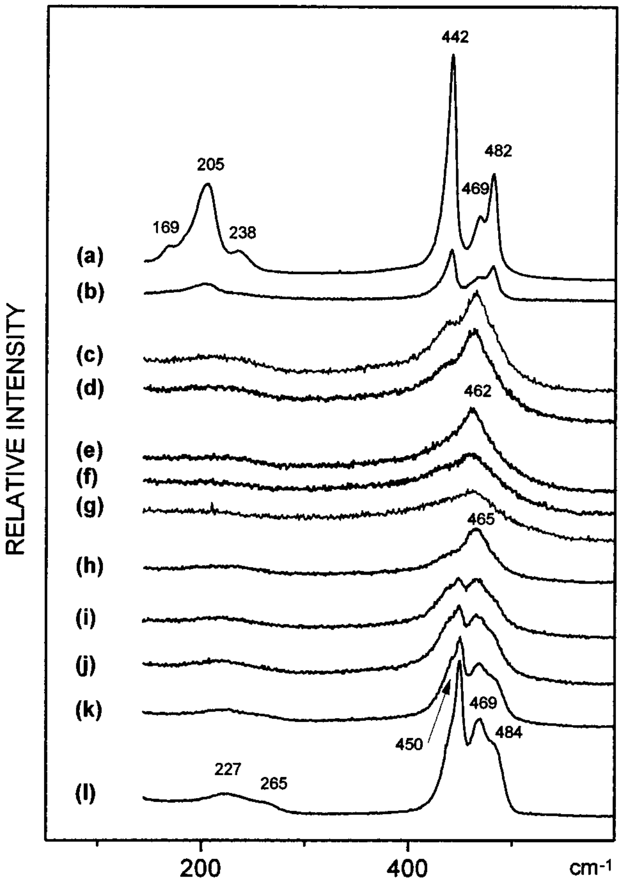

Figure 6. Raman spectra of the $Na_2S + (2/8)S_8$ mixture at various temperatures. Heating steps: (a) 200 °C; (b) 225 °C; (c) 250 °C; (d) 300 °C; (e) 350 °C; (f) 400 °C; (g) 450 °C. Cooling steps: (h) 225 °C; (i) 200 °C; (j) 180 °C; (k) 100 °C; (l) 25 °C. $\lambda_0 = 514.5$ nm; lp = 3 mW; sw = 200 μm; ssw = 6.2 cm^{-1}; integration time = 180 s (a, b), 300 s (c–l).

of the Na_2S_4 formed, decreases with the increase of sulfur in the initial mixture.

For $n = 1$, the excess of Na_2S is 2 times larger than the amount of formed α-Na_2S_4 (Figure 5a). Then we observed, upon heating around 200 °C, a solid-state reaction between α-Na_2S_4 and Na_2S, giving β-Na_2S_2 (Figure 5c). This is the only example, among the investigated samples, of a reaction between two species in the solid state. This solid phase was characterized by the ν(SS) stretching band at 449 cm^{-1}, but a small amount of the α-Na_2S_2 phase still coexists, as indicated by the small intensity lattice mode at 182 cm^{-1} and the shoulder above 450 cm^{-1}. The broadening of the 449 cm^{-1} band on its low-wavenumber side may be due to the presence of hot band (transitions $v = n \rightarrow v = n + 1$). This broadening on the low-wavenumber side (Figure 5d) increased with temperature up to 350 °C (Figure 5e). Between 350 and 450 °C the product melted and yield a broad symmetric line at 457 cm^{-1}. This low melting temperature for β-Na_2S_2, compared to the known one (470 ± 10 °C),[7] probably reflects an inhomogeneity of the mixture with Na_2S. This liquid crystallized upon cooling around 350 °C, leading to an almost pure β-Na_2S_2, characterized by a thin line at 451 cm^{-1} at 75 °C (Figure 5i). The behavior of the mixture with $n = 2$ is different (Figure 6). In this case, the Na_2S left in excess is half the amount of α-Na_2S_4. The melting of Na_2S_4 is observed around 250 °C. After the melting, Na_2S_4 reacts with the excess of Na_2S (Figure 6). The spectrum of this liquid displays a broad band at 462 cm^{-1} and a shoulder around 443 cm^{-1} (Figure 6c) and is quite different from that of pure α-Na_2S_4 liquid at a similar temperature, where the main band is located at 440 cm^{-1} (Figure 3). Further heating of the liquid to 350 °C led to the disappearance of the shoulder and left a broad band unchanged at 462 cm^{-1} for this liquid of stoichiometric composition Na_2S_3. After heating to 450 °C the spectrum of the liquid upon cooling shows, as expected, the superposition of the spectrum of Na_2S_2, characterized by a thin band at 450 cm^{-1}, and that of a glassy form of Na_2S_4, as we have seen before. It is indeed known that Na_2S_3 is not stable in the solid state, and the cooling of the liquid with the overall Na_2S_3 composition leads to the eutectic $Na_2S_2 + Na_2S_4$.[2,5,12]

2.3. Systems with $n > 3$. As we have seen before, these systems lead to the formation of α-Na_2S_4 with an excess of sulfur, in a first step, along with the following reactions:

$$Na_2S + (n/8)S_8 \rightarrow Na_2S_4 + [(n-3)/8]S_8$$

$$Na_2S_2 + (n'/8)S_8 \rightarrow Na_2S_4 + [(n'-2)/8]S_8$$

For the mixture with $n = 3.6$, which corresponds to the composition of the eutectic $1Na_2S_4 + 2Na_2S_5$,[5] after the formation of crystallized α-Na_2S_4, the mixture of $Na_2S_4 + (0.6/8)S_8$ melts around 240 °C (Raman spectra not shown). After the liquid was heated to 500 °C, and after cooling, the formed Na_2S_4 phase is γ-Na_2S_4 and the Na_2S_5 phases are α-Na_2S_5 and γ-Na_2S_5 (Figure 7), whose Raman spectra were identified by Janz et al.[12]

For the mixture with $n = 4$, we have examined more carefully the behavior of the liquid obtained by melting of the primary

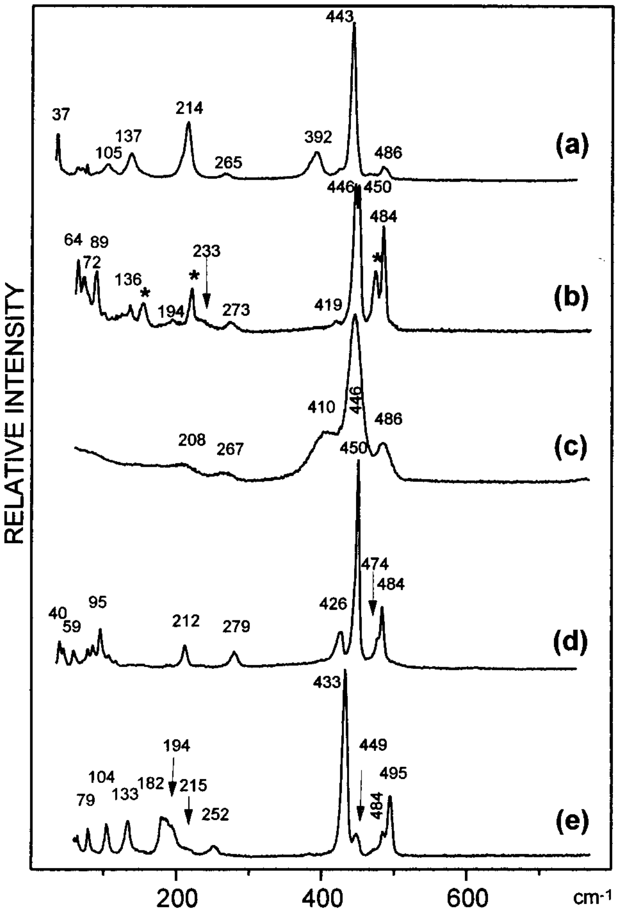

Figure 7. Raman spectra of various forms of Na_2S_5. $\lambda_0 = 514.5$ nm; macro sample (c) and micro sample with magnification ×50 (a, b, d, e). $*$ indicate sulfur lines. (a) α-Na_2S_5: lp = 0.140 mW; sw = 120 μm; ssw = 3.7 cm^{-1}; integration time = 300 s. (b) β-Na_2S_5: lp = 0.075 mW; sw = 200 μm; ssw = 6.2 cm^{-1}; integration time = 240 s. (c) glass: lp = 0.075 mW; sw = 200 μm; ssw = 6.2 cm^{-1}; integration time = 300 s. (d) γ-Na_2S_5: lp = 3 mW; sw = 100 μm; ssw = 3.1 cm^{-1}; integration time = 120 s. (e) δ-Na_2S_5: lp = 0.075 mW; sw = 200 μm; ssw = 6.2 cm^{-1}; integration time = 600 s.

formed α-Na_2S_4 phase (Figure 8a). The spectrum of the liquid, between 230 and 240 °C, showed a low-wavenumber broad band around 400 cm^{-1}, which did not appear in the liquid formed from pure α-Na_2S_4. This liquid, after being heated to 300 °C for 1 h and then cooled, began to crystallize around 200 °C and led to the α-Na_2S_4 form with traces of sulfur (Figure 8e). This sample, heated again at 300 °C, led to the same result. The sample was heated once more to 400 °C and, after cooling, led to a mixture of γ-Na_2S_5, δ-Na_2S_5, α-Na_2S_5, and α-Na_2S_4. Their respective Raman spectra were identified separately by Raman microscopy in the cooled sample tube (Figure 7). The same sample heated again at 550 °C for 2 h and then slowly cooled (22 h) led essentially to polycrystalline γ-Na_2S_5 and α-Na_2S_5.

The other mixtures with $n = 5$, 6 or $n' = 4$, 6, after melting of the primary formed α-Na_2S_4 phase, and heating of the liquid to 500 °C, led to the various forms of Na_2S_5, upon cooling, in the crystalline form α, β, γ, and δ-Na_2S_5 or in the glass γ-form type (Figure 7). There is, nevertheless, a predominance of the γ-form after heating the liquid above 500 °C. We observed that the γ-form is transformed into the α-form, after heating at 200 °C over 21 h, as for Na_2S_4. Both β- and δ-forms, observed after cooling, disappeared with time, indicating their metastable character.

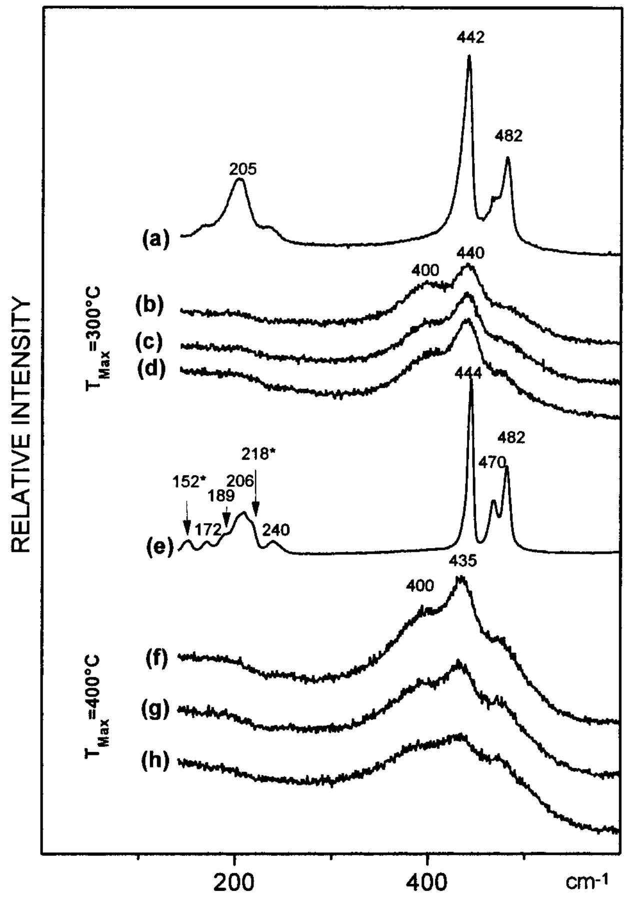

Figure 8. Raman spectra of the $Na_2S + (4/8)S_8$ mixture at various temperatures, up to 300 °C [(a) 230 °C; (b) 240 °C; (c) 250 °C; (d) 250 °C (cooling); (e) 25 °C (cooling)] and annealing up to 400 °C [(f) 300 °C; (g) 350 °C; (h) 400 °C]. $\lambda_0 = 514.5$ nm; lp = 3 mW; sw = 200 μm; ssw = 6.2 cm^{-1}; integration time = 60 s (e), 300 s (a, b), 360 s (c, d, f−h).

Discussion

1. Reactivity of Sulfur with Na_2S and Na_2S_2. The reaction of Na_2S or Na_2S_2 with sulfur was missed by Janz et al.[3] In their experiments, the weighing of the components of the mixture was made directly in the microscopic DSC pan, used as the reaction chamber, which prevented therefore a good mixing of the reactants. In our experiments, as in those of Oei,[5] the appropriate amounts of each compound were thoroughly mixed before filling the reaction tube, as recommended in the Rosen and Tegman method.[15] These authors noticed that for a reaction temperature of 200−230 °C a solid-state reaction was achieved with 80−90% conversion.[15] In agreement with the exothermic peak observed by Oei around 110 °C,[5] we observed that the reaction begins between 90 and 120 °C when the sample is submitted to a slow heating. This onset of reaction seems to correspond to the melting of the rhombic-sulfur; its most intense lattice lines at 42 and 50 cm^{-1} disappeared,[18] as shown in Figures 1 and 2. The sulfur melting point (119.6 °C)[19] seems slightly lowered in these mixtures with sodium sulfide or disulfide. The molecular composition of liquid sulfur near its melting point is very complex and is still in discussion.[20,21] An

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equilibrium between S_8 rings and chains was proposed,[22−25] as well as the formation of smaller rings such as S_6 and S_7. The presence of sulfur chains was supposed to be responsible for the presence of free spins detected around 150 °C in liquid sulfur.[26] It is thus not surprising that such reactive chain molecules react at the surface of Na_2S crystals forming α-Na_2S_2 in the crystalline state, as confirmed by the observation of its lattice mode at 183 cm^{-1}:

$$-S-S-S-S- + S^{2-} \rightarrow -S-S-S-S-S^{2-} \rightarrow S_2^{2-} + -S-S-S-$$

This surface reaction is analogous to that proposed to explain the formation mechanism of S_6 and S_7 rings from S_8 through a polymerization−depolymerization mechanism,[27] or for the formation[28] of SCN^- from S_8 and CN^-. The S_2^{2-} anion formed at the Na_2S/sulfur interface needs to diffuse into the Na_2S solid to form the α-Na_2S_2 crystal. This explains that this intermediate species is slowly formed and shows the known phase transition α-Na_2S_2 → β-Na_2S_2 around 170 °C.[7]

A similar mechanism may be assumed to explain the formation of the S_4^{2-} anions from the more reactive sulfur chain molecules. Nevertheless, it is possible that trace amounts of small chain molecules such as S_2 might be the diffusing entity in the Na_2S_2 lattice to form α-Na_2S_4. Such a species is indeed known to exist in the vapor in equilibrium with sulfur[19,29] or sulfides.[30] The much higher temperature range of the reaction observed by Janz et al.[3] above 200 °C is due to the high viscosity of sulfur at temperatures above its λ-point (159.4 °C).[31,32] The decrease in viscosity at 200 °C allows the wetting of the Na_2S crystals to produce the reaction.

2. Reactivity and Thermal Behavior of Na_2S_4. The α-Na_2S_4 crystalline phase, formed in the primary step of the reactions between Na_2S and S_8 for $n < 3$ coexists with an excess of Na_2S. We have seen that, when this excess of Na_2S is large, Na_2S_4 decomposes to form Na_2S_2 around 200 °C (Figure 5c). At this temperature, the vapor pressure of α-Na_2S_4 (mp = 290 ± 5 °C) is much larger than that of β-Na_2S_2 (mp = 470 ± 10 °C) or Na_2S (mp = 1168 ± 15 °C).[7] Either the decomposition of Na_2S_4 to form S atoms or S_2 molecules that react with Na_2S or the diffusion of S atoms between neighboring crystals is responsible for the transformation. The formed pure crystalline β-Na_2S_2 melts above 350 °C (Figure 5e−f). Its mixtures melt at a much lower temperature (between 225 and 250 °C) as, for example, the eutectic mixture (Na_2S_2 + Na_2S_4) that melts at 235 °C.[7] This indicates that such a eutectic mixture was not formed even locally during the reaction.

The Raman spectrum of the liquid (Figure 6c) is quite different from that of pure Na_2S_4 at a similar temperature (Figure 4c), as will be discussed later on. This lowering of the melting temperature of Na_2S_4 in the presence of Na_2S or Na_2S_2 is responsible for the wrong identification by Oei[5] of the primary product formed as α-Na_2S_5 (mp = 253 ± 3 °C). This author observed a similar reaction upon heating the mixture 3Na_2S + 1Na_2S_5 since after a reaction step around 250 °C, the fusion of Na_2S_2 is clearly observed.

As we have seen, all the mixtures of initial composition leading to the stoichiometry Na_2S_4, when heated to 400 °C, give the α-Na_2S_4 crystallized form, as confirmed by the heating at 350 °C for 1 h of the mixture[5] 1Na_2S_2 + 2Na_2S_5, which leads to a product melting at 290 °C. When the corresponding liquid phase is heated above 400 °C, a glass is usually obtained after cooling to room temperature. The spectrum of this glass is very close to that of the γ-Na_2S_4 form, which crystallizes after annealing at 120 °C. This crystallization of the glass to the γ-Na_2S_4 form, which further melts at 241 °C, that is to say about 50 °C under the melting point of α-Na_2S_4, was interpreted erroneously by Janz et al. as an “inverse crystallization phenomenon” from their DSC results.[3] The comparison of the α-Na_2S_4 and γ-Na_2S_4 spectra with that of the BaS_4,H_2O compound[14] allowed us to show that the γ-Na_2S_4 form corresponds to a structure in which the S_4^{2-} anion has a torsion angle τ smaller than in the α-Na_2S_4 form ($\tau = 97.81°$)[10] as in BaS_4,H_2O ($\tau = 76.2$ or $76.5°$).[33] The comparison of the spectra of both α-Na_2S_4 and BaS_4,H_2O, based on the known geometry of the two anions, shows that the decrease of the torsion angle is mainly responsible for the increase of the bending vibration wavenumbers, as observed in the γ-Na_2S_4 spectrum. This high-temperature conformation of the S_4^{2-} anion is a metastable form, since we have shown that, by heating to 200 °C, the crystalline γ-Na_2S_4 phase was reversed to the α-Na_2S_4 phase.

3. Structure of the Liquid Phases Formed from the Na_2S_{n+1} Melts. For the mixtures with a stoichiometric composition $n < 3$, the spectra of the liquid phase change upon heating. For the Na_2S + (1/8)S_8 mixture (Figure 5f), the Raman spectrum of the liquid at 400 °C showed a band at 450 cm^{-1} with a shoulder on its high-wavenumber side. When this liquid was heated to 450 °C, this shoulder broadened and shifted to give one band only at a higher wavenumber, 457 cm^{-1} (Figure 5g). For the Na_2S + (2/8)S_8 mixture (Figure 6), the Raman spectrum just after melting at 250 °C showed one main band at 462 cm^{-1} with a shoulder on its low-frequency side around 440 cm^{-1}(Figure 6c). As the mixture was heated to 350 °C the shoulder disappeared, leaving only one broad band at 462 cm^{-1}. We believe that this last spectrum corresponds to the existence of mainly S_3^{2-} anions in this mixture. As we have seen in one type of M_2S_3 crystalline form,[13] with an S−S−S angle close to 106.5°, the S_3^{2-} anion shows an accidental degeneracy between ν_a(SS) and ν_s(SS) modes. They are both located around 466 cm^{-1}. We thus assume that the shift to higher wavenumber of the band characterizing the liquid composition Na_2S_3 is a consequence of the shift of the underlying disproportionation equilibria to the right:

$$S_2^{2-} \rightleftharpoons S^{2-} + S$$

$$S_2^{2-} + S \rightleftharpoons S_3^{2-}$$

$$\text{i.e.} \quad 2S_2^{2-} \rightleftharpoons S_3^{2-} + S^{2-}$$

Upon heating, the 462 cm^{-1} band broadened and shoulders appeared on both its high- and low-wavenumber sides, probably owing to the formation of S_4^{2-} along with the disproportionation equilibrium $S_3^{2-} + S \rightleftharpoons S_4^{2-}$. When the melt previously heated

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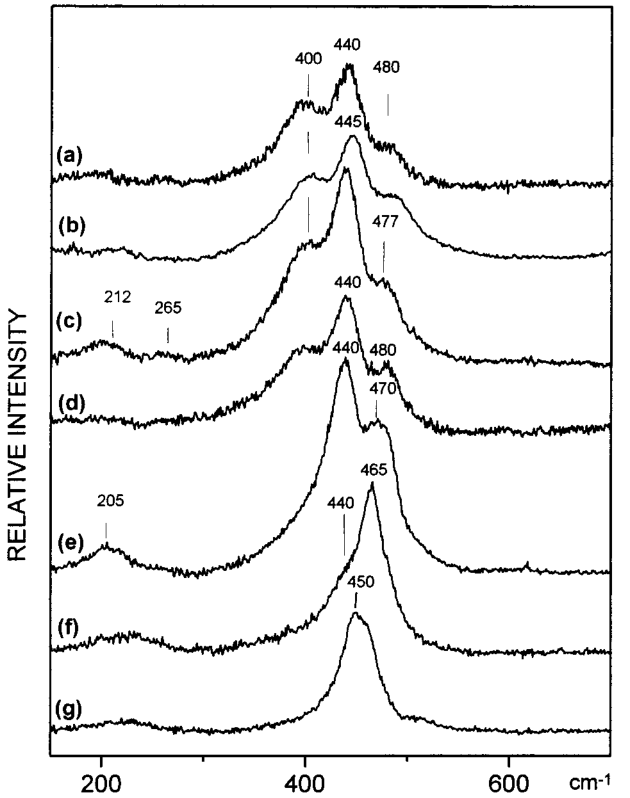

Figure 9. Raman spectra of various $Na_2S + (n/8)S_8$ mixtures in the liquid state during their cooling step: (a) $n = 6$, 250 °C; (b) $n = 5$, 225 °C; (c) $n = 4$, 250 °C; (d) $n = 3.6$, 300 °C; (e) $n = 3$, 250 °C; (f) $n = 2$, 250 °C; (g) $n = 1$, 400 °C. $\lambda_0 = 514.5$ nm; lp 2 mW (b), 3 mW (a, c−g); sw = 100 μm, ssw = 3.1 cm^{-1} (a, d) or sw = 200 μm, $\Delta\nu_{1/2} = 6.2$ cm^{-1} (b, c, e−g); integration time 240 s (b), 300 s (a, e, f), 360 s (c), 600 s (d, g).

above 400 °C was cooled, the crystallization of the eutectic mixture Na_2S_4 glass + β-Na_2S_2 occurred (Figure 6).

For the mixtures with $n > 3$, the spectra of the liquid did not change with heating (Figure 3 and 8). For instance in Figure 3 for the mixture Na_2S_4, the liquid spectrum showed a main band at 443 cm^{-1} and a shoulder at 480 cm^{-1} corresponding to the envelope of the stretching wavenumbers of the S_4^{2-} anion. Although we showed that the torsion angle of the S_4^{2-} anion in the melt decreases through heating over 400 °C, this change is almost not seen in the stretching vibration wavenumbers that remain very close in the α-Na_2S_4 and γ-form. These changes are mainly distinguished by their bending vibrations (Figures 3g and 4). This region, because of the broadening of the bands for the liquids, is overlapped by the wing of the Rayleigh line. A similar behavior of the liquid with temperature seems also valid for the Na_2S_5 mixture (Figure 8). The melting of Na_2S_4 in the presence of an excess of sulfur led to the appearance of a broad component around 400 cm^{-1} on the low-wavenumber side of the main 440 cm^{-1} band. This spectrum is also close to that of the Na_2S_5 glass (Figure 7) and probably corresponds to the presence of S_5^{2-} anions as the main species. The behavior of this liquid with temperature may be explained by a conformational change of the S_5^{2-} anion upon heating above 400 °C as for the transformation of α-Na_2S_4 into γ-Na_2S_4. This could be the consequence of a change from a stretched helical S_5^{2-} *gg*-form, as in K_2S_5,[34] to a folded S_5^{2-} *gg′*-form, as in α-Na_2S_5.[11] Steudel et al.[35] have indeed shown that this conformation change is mainly observed through the wavenumber of bending vibrations. Unfortunately, as shown for S_4^{2-}, these modes are not easily observed in the liquid state. This S_5^{2-} *gg*-form could be less stable in the solid phase than the *gg′* one and dissociates into α-Na_2S_4 + $(n/8)S_8$ upon crystallization.

We have summarized in Figure 9 the Raman spectra of the liquids obtained during the cooling step at temperatures between 225 and 300 °C for $n = 2-6$ and at 400 °C for $n = 1$. The strong changes observed between the compositions with $n = 1-3$ are in agreement with the presence of the S_{n+1}^{2-} anion as the predominant species, in each of these compositions, as indicated from the various thermodynamic models used to interpret the open circuit voltage measurements[36,37] and vapor pressure measurement[38] in the sodium−sulfur battery.

For the mixtures with $n > 3.6$, the Raman spectra of the mixtures are predominantly influenced by the bands of the S_5^{2-} anion with a small shift of the central component. Furthermore, the intensity of the high-wavenumber shoulder does not increase significantly when n increases from 4 to 6, as would be expected at 470 cm^{-1} for S_8 and at 458 cm^{-1} for the polymer sulfur.[39] The observed spectra are better related to the formation of higher polysulfide anions S_n^{2-} with $n > 5$ that have features very similar to those of the S_5^{2-} anion. This is in agreement with the emf measurements, which showed that no free sulfur is present in the melt.[40]

Conclusion

Although, after the sodium−sulfur battery program in the eighties, the interest for the sodium−sulfur system had decreased, much still remains unknown about these complicated systems. This lack of knowledge is of importance since, for instance, corrosion of metals by sulfur vapor prevented the use of a binary water−sulfur cycle to improve the output of power plants.[41] Revisiting this system allowed us to show that sulfur, as soon as it melts, reacts with sulfides Na_2S or Na_2S_2 to form α-Na_2S_4. A mechanism for such a transformation has been proposed that may also explain the fast growth of the sulfide layer from metal when it is in contact with sulfur vapor. The chemical species formed in the liquid state were identified through Raman spectroscopy. These results may be of help for the monitoring of polysulfide production during the electrochemical process.[42,43] The glassy or crystalline metastable forms appearing upon cooling of these liquids were related to the torsion angle changes of S_n^{2-} chains produced at high temperature and during their slow cooling.

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