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Elastic and viscoelastic properties of amorphous selenium and identification of the phase transition between ring and chain structures

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Using a broadband mechanical spectrometer, the tensile modulus and stress relaxation of amorphous selenium were studied in the glass transformation range. Bimodal spectra were recorded under isothermal conditions in the time range $10^{-1}\ \mathrm{s} < t < 10^5$ s. It was found that the structural equilibrations of the two contributions to the stress decay proceed independent of one another. The mechanical correlation functions of stabilized supercooled liquid Se can be described using a weighted sum of two stretched exponentials. The temperature dependences of the relative relaxation strengths are compared with results from a rotational isomeric state model. Our results are consistent with the existence of a cooperative transition, near 300 K, between ringlike and chain elements in the disordered chain model of Misawa and Suzuki. This transition has been kinetically inaccessible to previous measurements.

I. INTRODUCTION

Amorphous selenium (*a*-Se) has been referred to as one of the best studied of all substances.[1] Among the reasons that have stimulated the intense interest in this material are not only its enormous technical importance, e.g., as a photoconductor,[2] but also the notion that glassy selenium may constitute one of the simplest polymers possible. For a long time it has been believed that, by analogy to liquid sulfur,[3] the *supercooled* liquid state of selenium contains polymeric chains and eight membered rings, in proportions that depend on temperature[4] as well as on thermal history.[5] These beliefs have in part been based on the thermodynamic arguments developed (in analogy to liquid sulfur[6]) by Eisenberg and Tobolsky.[7] A number of experiments were interpreted in the spirit of these arguments.[8,9] In particular results from infrared (IR) and Raman spectroscopy seemed to confirm the notion of a ring-chain equilibrium.[10,11] The analysis of these measurements was based on the comparison of the vibrational spectra of *a*-Se with those of its trigonal[12] (sometimes called hexagonal) or monoclinic[13] modifications. These crystalline structures are built from helical chains (the trigonal form) or contain eight membered rings (the monoclinic form).

Later evidence from IR, Raman,[14] and neutron[15] scattering experiments indicated that the atomic level structure of amorphous selenium is more complex than that of liquid sulfur. A refinement of the simple ring-chain picture is due to Misawa and Suzuki who developed the disordered chain model for *a*-Se.[16] This variety of the rotational isomeric state model[17] assumes that amorphous Se is not simply a mixture of cyclooctaselenium and polymeric chains but "includes a molecule having both ring and chain conformations of Se in a single molecule."[16] This model incorporates the three coordinated Se species long considered responsible for many of the interesting properties of amorphous selenium. It also provides a means of reconciling the old results of dissolution experiments by Brieglieb[4] with Lucovsky's objections[14] to the presence of free octaselenium rings in *a*-Se in significant quantities. (Illumination by visible light is sufficient to activate the electron switch at three-coordinated Se sites needed to free the rings for dissolution. The Brieglieb study thus continues to indicate reliably the fraction of ringlike atoms in the sample.) While the Misawa-Suzuki model seems to have many advantages, it left open the question of cooperative interactions between molecules and the consequent possibility of a cooperative transition analogous to that known in liquid sulfur. The authors recognized[16] that increasing molecular cooperation, expected to show up in the vicinity of the glass transition, should modify the model predictions in this temperature range. Such cooperation would provoke a sulfurlike polymerization transition in selenium, but, despite numerous efforts to identify such a transition, no unambiguous experimental evidence has so far been obtained.

Another topic of continuing interest has been the study of stabilization of selenium glass, which obviously is of great technological importance. The effects of structural state dependence, although a general feature of the glass transformation range,[18] has received special attention in the case of *a*-Se because of the proximity of its calorimetric glass temperature $T_g = 310$ K to ambient.[19] In *a*-Se the structural relaxation has been investigated by a number of means including calorimetric,[20] viscosimetric,[21] dilatometric,[22] ultrasonic,[23-25] and dielectric[26] techniques. One of the most direct ways to monitor structural equilibration may be mechanical stress relaxation as employed in the present study. We have used a broadband spectrometer also in order to check whether the stress decay is bimodal as has been suggested previously.[27,28]

II. EXPERIMENTS AND ANALYSES

The amorphous selenium used for this study was taken from the same batch, which has been characterized ear-

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lier using calorimetric and viscosimetric experiments.[29] It was prepared by Halfpap using high purity starting material (99.9999%) as described in Ref. 29.

Details of the transient viscoelastometer and of experimental procedure and checks that have been performed are given elsewhere.[30] Tensile mechanical stress autocorrelation functions of *a*-Se have been recorded in the time range 10^{-1} s $< t < 10^5$ s. In this paper the decay functions are given in normalized form thus avoiding numerical uncertainties introduced by the geometric form factor.[30] In addition stress vs strain curves have been recorded at several temperatures in and below the glass transformation range. The time used to build up the total strain (10–50 μm) was of the order of 1 s so that the linear behavior needed to yield Young's modulus at each temperature could be observed up to temperatures somewhat above the calorimetric glass point at which the average relaxation time is of the order of 200 s.

A. Elastic properties

Using ultrasonic measurements in the 1–20 MHz range, the elastic constants of *a*-Se have been determined by numerous researchers.[31] At low frequencies ($f \leq 1$ Hz) only shear moduli have been reported as a function of temperature[27,32] or frequency.[28] In Fig. 1 we compare the temperature dependence of the tensile (or Young's) modulus $Y(T)$ from the present study with the shear constants $G(T)$ obtained by Eisenberg and Tobolsky using a 5-seconds experimental time-scale.[27] In Fig. 1 the shear modulus commences its fall towards zero with increasing temperatures before the tensile modulus. Although some difference would be expected from the fact that the time-scale used for the determination of $Y(T)$ is shorter by a factor of approximately five it seems from results discussed later in Sec. II C that the differences in the temperatures where the falls start is not primarily a time scale effect. It is quite possible that the complex microstructure of amorphous selenium, leading to the bimodal stress relaxation spectra presented below, also gives rise to rather different response times to external shear strains and bulk compressions.

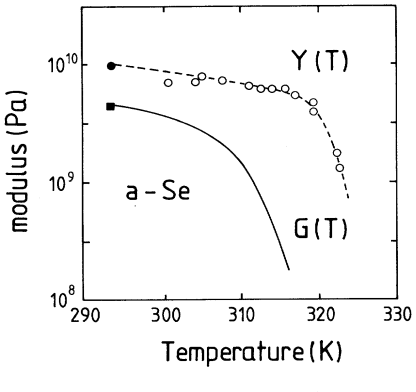

FIG. 1. Tensile moduli $Y(T)$ and shear moduli $G(T)$ of amorphous selenium. Open circles are results from the present investigation. They have been normalized to match Young's modulus of $Y = 9.8$ GPa as determined from ultrasonic measurements at ambient temperature (closed circle, Ref. 31). Elastic shear constants taken at 1–20 MHz (closed square, Ref. 31) and at a very low frequency from Ref. 27 ("five second moduli," displayed as a solid line) have been included for comparison. The dashed line is a guide to the eye only.

It is noted that the tensile moduli presented in Fig. 1 reflect equilibrium values. We observed that samples quenched from above the glass transition got stiffer on annealing below T_g. This can be viewed as a confirmation of earlier ultrasonic experiments: Here an increase in the sound velocity with time has been reported for quenched *a*-Se samples.[24] Fictive temperature effects, which are a general feature of glass formers far from structural equilibrium are discussed in more detail in the following section.

B. Structural equilibration

Amorphous selenium samples were kept at 335 K for at least 30 min in accordance with the suggestions by Chang and Bestul.[33] These authors noted that heating of *a*-Se to temperatures above its T_g of 310 K lead to a completely equilibrated state irrespective of the previous thermal history. After annealing at 335 K the samples were cooled to several temperatures between 300 and 308 K at rates of 1–2 K/min, while carefully excluding light.[34] Immediately after temperature stabilization an initial stress relaxation measurement was made followed by repeat runs after various holding (annealing) periods at the same temperature. Figure 2 shows the results obtained in successive runs at an annealing temperature of

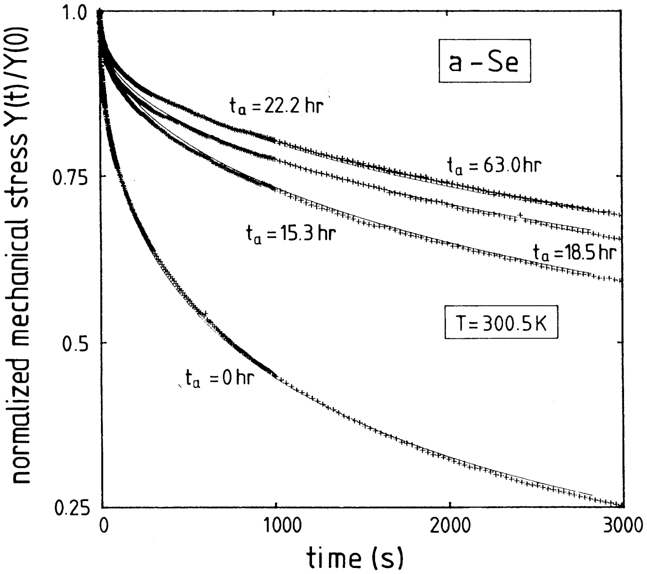

FIG. 2. Time dependence of normalized tensile stress $Y(t)/Y(t=0)$ of amorphous selenium, which has previously been quenched from an equilibrium state obtained by annealing at 335 K, well above the glass transition temperature. The labels indicate the times at which the measurements have been started relative to the time of commencement of the first run. The solid lines are calculated using Eq. (1) with $\beta = 0.47$ and $Y_2 = 0$. The variation in the relaxation times are given in Fig. 4.

$T=300.5$ K. It is clear that the time required to relax the initial stress increases rapidly with annealing time t_a. Data at 307.5 K obtained as part of this first series of stepwise T increases and equilibrations are of special importance in our discussion, and are presented below. They show that there is a slow equilibration process affecting the long-time part of the stress relaxation function. For a quantitative description of the stress relaxation, the Kohlrausch function[35]

$$Y(t)=Y_1\exp[-(t/\tau)^{\beta}]+Y_2\ , \tag{1}$$

was used. Here the relaxation of the tensile stress is characterized by a relaxation time τ and a fractional exponent $\beta \le 1$. $Y(0)=Y_1+Y_2$ and Y_2 are Young's moduli for $t \to 0$ (as presented in Sec. II A) and $t \to \infty$, respectively. In the glass transformation range of viscoelastic bodies, Y_2 usually approaches zero for long times. It may be nonzero, however, in crystalline solids[36] and polymeric substances which show a rubbery plateau.[37] The best least squares fit to the $t_a=0$ curve in Fig. 2 yielded $Y_2=0.03Y$. A good description of the data was also obtained using $Y_2=0$ (see Fig. 2).

In Fig. 3 structural equilibration data for $T>304$ K are displayed as $\log_{10}[-\ln Y(t)/Y(0)]$ vs $\log_{10}t$. This representation gives a straight line if Eq. (1) (with $Y_2=0$) is obeyed. For $T=304.6$ K (which was reached by quenching directly from 335 K) this is seemingly the case. The slope of these curves gives the fractional exponent β, and from Fig. 3 is seen to be slightly greater in the unannealed than in the annealed state, as seen before.[38]

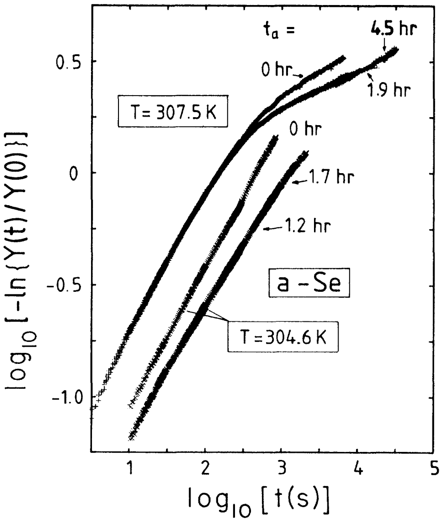

FIG. 3. Tensile autocorrelation functions $\log_{10}\{-\ln[Y(t)/Y(0)]\}$ of a-Se as a function of $\log_{10}t$. In this representation Eq. (1) yields a straight line with slope β. Temperatures T and annealing times t_a (in hours after starting the first run) are indicated near the curves. Measurements at 307.5 K followed measurements made first at lower temperatures starting at 300.5 K (Fig. 2). Note that the strength of the slow process increases with time as structural equilibrium is approached from below. Measurements at 304.6 K were made after quench from above, but only the fast process is being followed.

The changes of the time constants $\Delta\log_{10}\tau$ used to characterize the stress decay on annealing at $T=300.5$ and 304.6 K are summarized in Fig. 4. One notes that the total change $\Delta\log_{10}\tau$ (implying a change in the fictive temperature T_F, Ref. 39) is larger for the stabilization at the lower temperature. This is expected because in both runs the samples were quenched using similar cooling rates and hence must have fallen out of thermal equilibrium at about the same temperature. The difference between T_F and T was therefore greater at $T=300.5$ K, so the driving force to relaxation was greater. The relaxation of the fictive temperature has previously been described with Eq. (1).[40] The quality of the results presented in Fig. 4 does, however, not allow us to draw any conclusions about the functional form of the temporal relaxation of T_F in a-Se. In order to estimate the time constant, which governs this process, we have chosen a single exponential decay. The relaxation times for the overall structure obtained by this procedure are larger by factors of 5 and 9 than the *equilibrium* stress relaxation times for the short process $\langle\tau_s\rangle$ extrapolated from Fig. 7 below, for $T=304.6$ K and 300.5 K, respectively. A similar ratio of equilibration to stress relaxation time (~ 10) has been obtained previously for a nitrate melt.[38]

The stress relaxation curves obtained at 307.5 K do not give a straight line in the representation of Fig. 3. Apparently an additional relaxation process shows up at long times. At first glance the change in slope suggests that this relaxation is characterized by a smaller β. It is, however, noted that the linearization procedure described above is expected to work only if the decay function is properly normalized. This condition is met for neither of the two relaxation processes. A remarkable feature of these spectra is that the equilibration of the long-time decay is still progressing, while the structural relaxation associated with the faster process is already complete. This observation suggests that the relaxations have different microscopic origins.

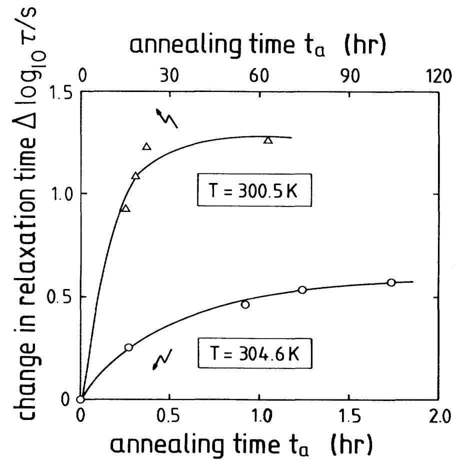

FIG. 4. Variation of the stress relaxation times with annealing time at two different temperatures, each reached by quenching to the annealing temperature from 335 K. The lines are guides to the eye only.

C. Stress relaxation at structural equilibrium

Figure 5 shows the time dependence of the normalized tensile stress of carefully equilibrated amorphous selenium. The wide spectral range of almost six decades accessible with the transient viscoelastometer used for this work allowed the detection of bimodal decays at several temperatures. Indications for such a composite relaxation have existed before from measurements of the tensile[27] and shear moduli.[28] As shown in Fig. 5 the spectral shapes of the mechanical correlation functions change with T. This casts doubts on the validity of the thermorheological simplicity assumption, used in Ref. 27. While the time-temperature superposition principle has been demonstrated to hold for the electrical relaxation,[41] it seems to be more appropriate to describe the mechanical properties of *a*-Se in terms of two independent processes, weighted by a coefficient z

$$Y(t)=Y_1[\exp\{-(t/\tau_S)^{\beta_S}\}+z\exp\{-(t/\tau_L)^{\beta_L}\}] \,. \tag{2}$$

The subscripts S and L stand for short- and long-time contributions to the Young modulus, respectively. The quality of the fits using Eq. (2) is demonstrated in Fig. 5. In the inset of this figure we plotted the derivative $-d[Y(t)/Y(0)]/d[\log_{10}t/s]$ of the theoretical curve for $T=307.5$ K. It gives a good impression of the separation of the average time scales of the two processes, and also of the relative widths.

At lower temperatures $T<305$ K the slow relaxation could not be detected. If we assume $\tau_S \ll \tau_L$ then the second exponential in Eq. (2) can be approximated by unity in our time window. Thus, Eq. (1) is recovered, and Y_2 for a seemingly unimodal decay function is identified as

$$Y_2=zY_1 \,. \tag{3}$$

The fact that Y_2 obtained in the low-temperature measurements was very small means that z is almost zero in these conditions, but at higher temperature it is found to be much larger. We will show in the discussion section that z, rather than being a mere fitting parameter may be related to a key material characteristic, viz., the fraction of Se atoms present in chain conformations. In Fig. 6 the coefficient z, as determined using Eqs. (1) and (2) is plotted against temperature, and will be discussed further below. Also the fractional exponent β_S, which characterizes the faster relaxation process strongly depends on temperature (Fig. 6). If $\beta_S(T)$ is linearly extrapolated (on a T or a $1/T$ scale) to lower T it crosses zero at $T_{\beta\to 0}=270\pm 10$ K. The shape parameter for the long time process is found to be $\beta_L=0.42\pm 0.1$ but the temperature dependence could not be detected.

From the fits to our stress relaxation curves the average relaxation times, given by[42]

$$\langle\tau\rangle=\tau\Gamma(1+1/\beta) \tag{4}$$

(where Γ is the gamma function) have been calculated for both long and short processes and are given in an Arrhenius plot (Fig. 7). This plot also contains relaxation times calculated from the maxima of the frequency-dependent internal friction measured in shear[28] and from creep data.[21] The relaxation times determined in susceptibility (or creep J) experiments can be transformed into modulus (M) relaxation (or retardation) times according to $\tau_M/\tau_J=J_{t=0}/J_{t\to\infty}$ $(=M_{\tau\to\infty}/M_{t=0})$.[43] From the longitudinal sound velocities v of the liquid[44] extrapolated to T_g and the glass,[25] it is found that $\tau_M \approx \tau_J(v_{\text{liq}}/v_{\text{glass}})^2 \approx 2.7\tau_J$. The time constants determined from internal friction peaks are also expected to be larger than τ_M (but smaller than τ_J). However, no transformation procedure similar to the one given above is known to us. From Fig. 7 one notes good agreement of the relaxation times $\langle\tau_S\rangle$ obtained in the various experiments. We parameterized our results for both long and short time processes in terms of an Arrhenius law,

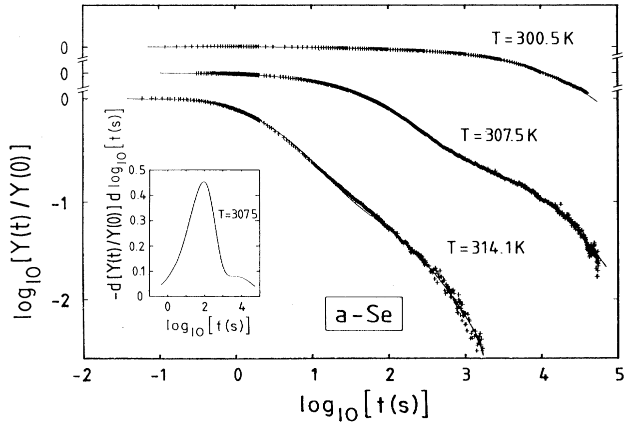

FIG. 5. Double logarithmic plot of normalized stress versus time for equilibrated Se at different temperatures. For clarity the spectra taken at $T=307.5$ and 314.1 K were *shifted downwards* by *0.25 and 0.5*, respectively. Solid lines represent fits using Eq. (1) [for $T=300.5$] and Eq. (2). The inset shows the derivative $-d[Y(t)/Y(0)]/d[\log_{10}t/s]$ of the fit to the data taken at 307.5 K. A two peak structure is clearly seen.

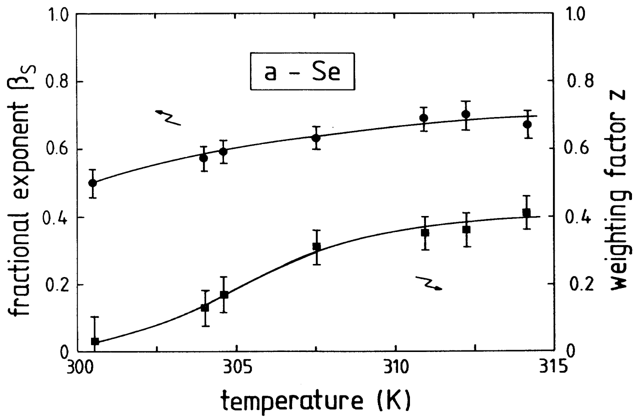

FIG. 6. Temperature dependence of the fractional exponent β_S for the fast process, and of the weighting factor z from the fits to the tensile autocorrelation functions of *a*-Se. Lines are guides to the eye only.

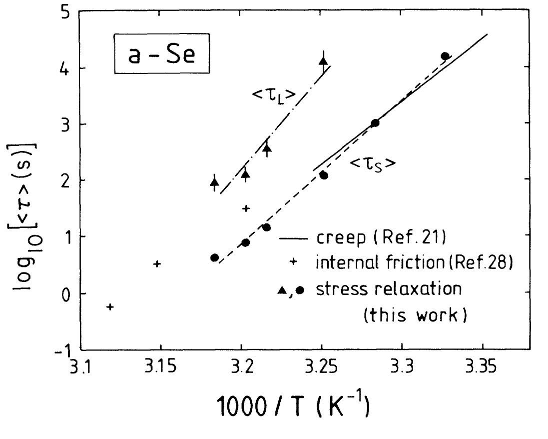

FIG. 7. Arrhenius plot of amorphous selenium relaxation times obtained using creep measurements (Ref. 21) (solid line) internal friction measurements (Ref. 28) (+) and tensile stress relaxation measurements (○ for $\langle\tau_S\rangle$, Δ for $\langle\tau_L\rangle$ from the present work). Note that the results from the creep compliance measurements (Ref. 21) have been transformed into modulus relaxation times using the procedure described in the text. The dashed line was calculated using the E_S value given in the text. The dash-dotted line is drawn to guide the eye only; its slope corresponds to an apparent activation energy E_L of 530 kJ/mol and a prefactor $\log_{10}A_L=-86$.

$$\langle\tau_S\rangle = A_S \exp(E_S/RT)\ , \tag{5a}$$

$$\langle\tau_L\rangle = A_L \exp(E_L/RT)\ , \tag{5b}$$

where A is a prefactor. The apparent activation energy E_S used to describe the tensile relaxation times $\langle\tau_S\rangle$ in the glass transformation range is $E_S=485$ kJ/mol. This value is somewhat larger than that determined by creep (see Fig. 7), enthalpy relaxation,[21] and viscosity[29] measurements, none of which distinguish long- from short-time processes. However, the large value of E_S and the unphysical value of $\log_{10}A_S=-80$ imply that the process under study is highly cooperative. Indeed, if viscosities over an extended temperature range are taken into account, deviations from the seemingly thermally activated behavior become apparent.[45]

We note that the relaxation times determined in dielectric experiments[41] when extrapolated to subaudio frequencies are significantly longer than those presented in Fig. 7. Decoupling of mechanical (and structural) from electrical degrees of freedom is a well-known phenomenon in many solids (including ionic conductors[46] as well as disordered crystals[47]). It seems to be a peculiarity of (the) amorphous (semiconductor) selenium that the electrically active modes freeze first on cooling. These modes presumably involve electron hops between chain end radicals.[41]

An accurate analysis of the longer relaxation times is hampered by a considerable experimental uncertainty. From Fig. 7 it is, however, clear that the apparent hindering barrier E_L necessary to parameterize the slower process is slightly larger than E_S and in fact may be only the average of a diverging process related to the phase transition.

III. DISCUSSION

The bimodal spectra of *a*-Se obtained in this work provide clear evidence for two independent relaxation processes. In principle, there exist several possibilities for the assignment of these processes. Since it is generally accepted that there is a large number of long chains present in *a*-Se as normally prepared,[14] one might be tempted to conclude that the step in the correlation functions as presented in Fig. 5 represents the entanglement plateau, which is a well-known feature in the mechanical spectra of high molecular weight polymers.[37] Indeed, both Eisenberg and Tobolsky[27] and more recently Etienne *et al.*[28] have referred to this feature, and other behavior related to it, as a clear indication of a rubberlike elasticity. On the other hand, Plazek[48] points out that such features can show up in stress decay curves under conditions where entanglement cannot occur and in which recoverable compliance-time plots show no signs of entanglement behavior. Therefore, we prefer an alternative interpretation—one which is suggested by the evidence seen in Fig. 3 that there are two different annealing timescales in the system near ambient temperature.

Figure 3 shows that although, at 307.5 K, the fast part of the relaxation has no history dependence within our preparation time window (as it does have at 304.6 K), the slow part of the relaxation changes with time during the first 1.9 h waiting time. After this time, the structure responsible is evidently also equilibrated, since the 1.9 h trace does not change after a further 2.6 h of annealing (Fig. 3). We see this as rather clear evidence that different molecular mechanisms are involved in the two parts of the complete process and find it natural to attribute the slow annealing mechanism to the pseudochemical bond-rearranging ring-chain-type equilibrium believed by many to be active in this system. Remembering that the system being observed at 307.5 K is produced from a structure previously equilibrated in the dark at a *lower* temperature, and that chains are thermodynamically preferred at higher temperatures, the observed change—an increased strength of the slow part of the total process—is consistent with the *slow* stress relaxation being due to the structural relaxation of the chain component. Presumably these are rather short chains in the Se case, since no recoverable compliance plateau—the signature of true entanglement, which requires chains of more than ~200 repeat units[48]—is found.[49–51] An arrangement of ringlike conformations as proposed by Misawa and Suzuki,[16] on the basis of structural data, can be deformed relatively easily under external stress. This is because the bonding between these structural elements is mediated by van der Waals interactions. After application of strain, these merely localized modes may be expected to relax before long-ranged deformations of the chains take place.

A quantitative confirmation of the above interpretation of our observations comes from the computation of the relaxation strength of the faster process. The relative strength f of this contribution to the stress decay is calculated from Eq. (2) for $t=0$ and gives $f=1/(1+z)$. It reflects the fraction of elastic modes originating from relaxations of ringlike conformations in the atomic level structure of a-Se, and it approaches unity at low temperatures.

In Fig. 8 we compare the fraction f from the present study with the predictions of the rotational isomeric state model. At temperatures above the calorimetric glass transition our experimental data are close to the theoretical results of Misawa and Suzuki.[16] Below $T \approx 307$ K strong deviations are noticed. For unequilibrated samples one would expect the fraction of ringlike conformations f to be no larger than its value at the glass transition. The relative ring relaxation strength, according to the viscoelastic experiments in which we have carefully annealed to equilibrium before taking the data on which this discussion is based, becomes systematically larger with decreasing temperatures than that predicted by the calculations for the disordered chain model, see Fig. 8. This is entirely consistent with the assumption of the model that any temperature-dependent interactions between molecules are absent. The authors noted[16] that "interactions between molecules should become more cooperative especially in the vicinity of the transition temperature." Inclusion of such effect should give a sharpened transition such as our results indicate in Fig. 8. The effect is reversed (z increased) on reequilibration at higher temperature, see Fig. 3 for the 307.5-K data, which were obtained after increase of T from 300.5 K. Our findings therefore suggest that a sulfurlike cooperative transition, which is kinetically inaccessible to most measurements, takes place in supercooled selenium at around 300 K, i.e., below the normal T_g as conjectured by Moynihan and Schnaus.[9]

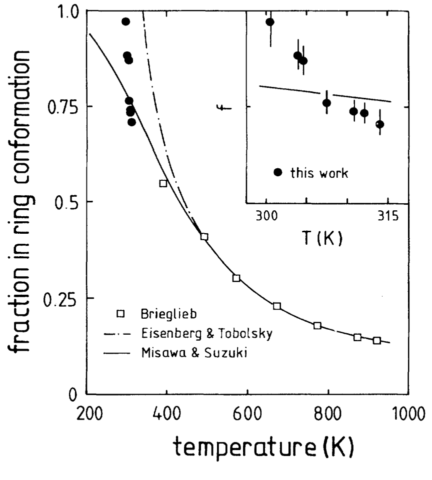

FIG. 8. Fraction f of atoms in ringlike conformations in amorphous selenium. From the weighting factors z shown in Fig. 6, the fraction was calculated as $f = 1/(1+z)$. The results from the (noncooperative) rotational isomeric state model are shown as solid line (Ref. 16). The thermodynamic model by Eisenberg and Tobolsky predicts the fraction f to vary according to the dash-dotted line (Ref. 7). Open circles represent the experimental results from the dissolution studies by Brieglieb (Ref. 4).

We now examine the relation between relaxational and thermodynamic characteristics of a-Se and in particular the relation between the relaxation time and the Kauzmann temperature T_K.[40] This is the temperature at which the extrapolated configurational entropy of the supercooled liquid equals that of the crystal. For selenium it was estimated from calorimetric data that T_K is (240 ± 10) K.[33,52] T_K may be viewed as the glass transition temperature that would be measured if the liquid were cooled infinitely slowly. Therefore this quantity has also been estimated from the temperature dependence of the relaxation time τ (or the viscosity η)

$$\tau = \tau_0 \exp[D T_0 / (T - T_0)] , \qquad (6)$$

by identifying T_0 and T_K. The Vogel-Fulcher Eq. (6) is a generalization of Eq. (5). By evaluating Eq. (6) at T_g, one finds that the liquid "strength" index, D, is given by

$$D = m_{\min}(T_g / T_K - 1) \ln(10) . \qquad (7)$$

The parameter $m_{\min} = \log_{10} \tau_g / \tau_0$ (or $\log_{10} \eta_g / \eta_0$) is found to be ≈ 16 for many glassformers. By evaluating the derivative of Eq. (6) at T_g one finds that the slope m in a scaled Arrhenius representation is given by[29]

$$m_{VF}(T_g) = [D / \ln(10)](T_K / T_g)(1 - T_K / T_g)^{-2} . \qquad (8)$$

Trivially, the slope of the Arrhenius law [Eq. (5)] when plotted vs T_g / T is given by $m_A = E_a / [R T_g \ln(10)]$. By using $m_A = m_{VF}(T_g)$ and inserting the above expression for the strength index D one arrives at

$$T_K = T_g [1 - m_{\min} \ln(10) R T_g / E_a] . \qquad (9)$$

This relation allows the calculation of T_K from the glass transition temperature $T_g = T(10^{12}$ Pa s) and the apparent activation energy E_a assuming that the process under study has remained coupled to the fundamental enthalpy relaxation. From the viscosimetric experiment of Ref. 29 one finds for a-Se $T_K = 245$ K, while the present relaxation times $\langle \tau_S \rangle$ yield $T_K = 250$ K, both in reasonably good agreement with the literature result.[33,52] We note that these correlations have been made using data in both calorimetric and transport measurements for $T > 310$ K in which cooperative ring-chain effects are minimal (see Figs. 6 and 8) and z changes smoothly with temperature. Extrapolations which include data in the range 300–310 K should give anomalous results for T_K if the ring-chain exchange gives rise to an important enthalpy contribution.

In the following we will comment on the temperature dependence of the fractional exponent β_S. Although from a theoretical viewpoint it is not clear at present whether there exists a minimum $\beta > 0$,[53] it has been observed for several supercooled liquids that $T_{\beta \to 0}$ coincides with the Kauzmann temperature T_K.[54,55] In our case the extrapolation of the data in Fig. 6 yielded[56] a $T_{\beta \to 0}$ of 270 K in reasonable agreement with T_K.

IV. SUMMARY AND CONCLUSIONS

We have studied the mechanical response of bulk quenched amorphous selenium following two types of external perturbations. First, we have used bending strains to measure Young's moduli. The subsequent relaxation of the tensile stress was monitored over a range of six decades in time. The isothermal mechanical spectra obtained in this manner are composed of two relaxation processes showing up on distinctly different time scales and having different spectral shapes. Second, by using relatively large temperature steps as perturbations we probed the nonlinear structural response. It was shown that the two relaxation processes are governed by different equilibration dynamics. We analyzed the carefully stabilized complex spectra and computed the relative strengths of the two relaxation processes. Their temperature dependences were compared to theoretical predictions. Our results together with the Misawa-Suzuki disordered chain model calculations suggest the occurrence of a sulfurlike transition between ringlike and chain elements of the disordered chain model near but below the calorimetric glass point of *a*-Se.

It appears that our broadband viscoelastic measurements are well suited to mapping out conformational changes in polymeric materials if their structural subunits possess different elastic or relaxational properties. It would be most interesting to extend our studies to supercooled liquids the average coordination of which differs from two in order to suppress or enhance one or the other of the relaxation processes observed in selenium. Possible candidates for the doping of *a*-Se are halogens,[57] which decrease the average length of the polymeric chains and should lead to a weakening of the long-time relaxations, and higher coordinated atoms, which should remove the short-time processes. For instance we recently[58] found that the degree of crosslinking introduced by replacement of 6 at. % Se by Ge and As is sufficient to lead to an almost complete suppression of the faster processes. This encourages further investigation of relaxation phenomena in alloys with even smaller doping levels.

ACKNOWLEDGMENTS

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