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Structural models of amorphous selenium

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Neutron-diffraction experiments were performed on ball-milled amorphous selenium. The structure factor of the material was interpreted by means of reverse Monte Carlo (RMC) modeling. In addition, detailed RMC studies were carried out on numerous sets of diffraction data previously reported for amorphous Se. Based on this comparative study, it is suggested that the material, independent of the method of preparation, contains chain molecules of variable lengths and that the dominance of Se_8 rings is improbable. However, there are indications that diffraction data alone are insufficient for determining if the system contains predominantly chain- or ringlike molecules.

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I. INTRODUCTION

Amorphous selenium, *a*-Se, has been the subject of a number of diffraction studies over the past 60 years.[1–8] In addition to its technological importance, *a*-Se is a frequently used light-detecting material; the popularity of this material is due to its readiness to form the amorphous phase: casting/melt quenching,[3–6,8] vapor deposition[3] and more recently, mechanical amorphization (ball milling).[7] All are suitable methods for preparing *a*-Se. Experimental conditions are also favorable as diffraction measurements can be made at ambient temperature and pressure although in some cases[3,4] low-*T* experiments have also been performed.

Despite the fact that diffraction data abound, a fundamental question—that has been posed in virtually all of the studies—could still not be answered unambiguously. Does amorphous selenium consist of Se_8 rings or longer covalently bonded chains? It is impossible to form a coherent view from the information available in the literature. Any statement or conclusion can be found between ‘‘vitreous selenium consists mainly of Se_8 rings’’[3] and ‘‘results show that amorphous Se consists of disordered chains.’’[6] It is sometimes explicitly suggested that the structure of *a*-Se depends on the method of sample preparation,[7] whereas in the latest publication it is accepted as a matter of fact that ‘‘diffraction data can be modeled by using either rings or chains.’’[8] Although we would be inclined to accept this latter view, it should be noted that it is based on only qualitative agreement with diffraction data. Without addressing this problem in detail, the authors of Ref. 8 mention Refs. 3 and 5 as the basis for their statement. Kaplow *et al.*[3] introduced a Monte Carlo type of algorithm which was the predecessor of the one used in this study; however, since only ‘‘good’’ moves were accepted there, their calculations may have very easily run into local minima. In the study of R. Bellisent,[5] an erroneous value of the density was used (see Ref. 9) and in addition, no other models but one consisting of chains were examined.

Our main goal here is to provide large structural models that are consistent with diffraction results to within experimental errors which means that there is a quantitative agreement between measured and model structure factors. Many of the published data sets have been examined and since there seemed to be some differences between them (although particularly as far as the interpretation of the data was concerned), we felt it necessary to measure our own diffraction data for this material.

Some of the present authors have recently conducted a reverse Monte Carlo (RMC) modeling study of the disordered forms of selenium in the vicinity of the melting point.[9] The main results of that study concerned the density of *a*-Se: it was shown that during the interpretation of the experimental data,[5] that formed the basis of a recent simulation study,[10] the value for the microscopic density (of the scattering centers) had been significantly *overestimated*, by about 6%. On the other hand, in the aforementioned *ab initio* molecular-dynamics simulation study of *a*-Se,[10] the density was *underestimated* by more than 10% even though the experimental data they compared their results with were those of Ref. 5. In Ref. 9 it was also demonstrated that models based on long chains of about 1000 atoms were consistent with the data of Ref. 5; however, additional experimental results were not considered.

II. EXPERIMENT

Crystalline Se powder (3 g) was ball milled under an argon atmosphere for 6 h in a Spex mixer/mill. The vial and balls were made of chrome-steel and the ball to sample mass ratio was 5. The milling procedure consisted of milling for 15 min followed by 45 min of rest to avoid heating and then repeating the cycle until a total milling time of 6 h was reached. (This is to be compared with results of Fukunaga *et al.*[7] who found that 25 h were necessary to make all of the Bragg peaks disappear in the sample.)

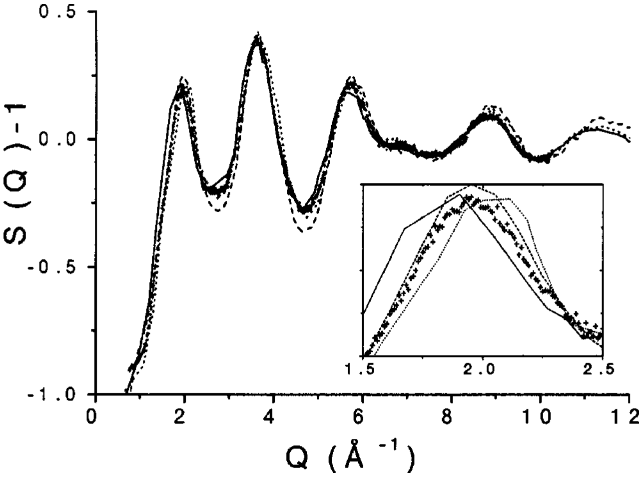

FIG. 1. Experimental structure factors of amorphous selenium. Solid line: from Ref. 3; dashed line: from Ref. 4; dots: from Ref. 5; markers: present neutron-diffraction measurement. The inset shows the environment of the first maximum, between 1.5 and 2.5 Å^{-1}. (Note that the small fluctuations on the curve corresponding to the present study are characteristic to the statistical errors of the measurement.)

Neutron-diffraction measurements have been performed on the SLAD instrument at Studsvik NFL.[11] The amorphous Se powder was contained in a thin walled vanadium container. Additional measurements were made for background, an empty container, and a solid vanadium rod for normalization purposes. Processing of raw data was carried out by using the CORRECT program package[12] which utilizes standard procedures for neutron-diffraction data correction. The resulting structure factor was then examined with the program MCGR,[13] which is an inverse method for obtaining the pair-correlation function. MCGR can refine simultaneously inelastic scattering corrections and normalize the data.

Figure 1 compares the static structure factor $S(Q)$ with some of the diffraction results published earlier. In Ref. 9, a nonstandard method, exploiting RMC modeling, was suggested for the estimation of experimental uncertainties; according to that procedure, the error levels of the current data are below 1%. (Note that the relative importance of statistical uncertainties can be neglected as compared to that of systematic errors which cannot be calculated accurately.) It has to be stressed that other data shown in Fig. 1 will not necessarily satisfy the same requirements concerning error levels.

The agreement between new and older data in general is surprisingly good. The largest discrepancies are found around the first maximum. The data of Ref. 4 show the largest deviation from the the ‘‘ribbon’’ of values formed by the various data sets, especially around the first two minima. It should be noted that although Refs. 4 and 5 both report measurements on melt-quenched samples by neutron diffraction, differences between these two are at least of the same order as the differences found in Ref. 6 between x-ray and neutron $S(Q)$'s and also to differences found in Ref. 7 between melt-quenched and ball-milled samples. Based on this observation it is suggested that until definite confirmation from new experiments is presented for investigating the subtle variations shown in the above studies, interpretation of these variations should be avoided.

III. REVERSE MONTE CARLO MODELING

In an attempt to answer the ‘‘chains or rings’’ question, we have decided to carry out detailed structural modeling studies, using reverse Monte Carlo (RMC) simulation.[14] RMC is a tool for constructing large atomic configurations for structural models that are consistent (within the experimental errors) with experimental structure factors. It is then possible to calculate the pair-correlation function $g(r)$ directly from the particle coordinates, and also, to calculate other quantities that can characterize the microscopic structure of a material (for a description of the simplest tools, see, e.g., Ref. 16). As shown by a number of examples (see, e.g., Refs. 17 and 18), it can be of great value if the pair-correlation function is calculated directly from the particle coordinates and not via the usual direct Fourier transformation. (For a recent review on RMC, see Ref. 15.)

The feature that makes RMC extremely useful in the present case is that it is possible to include *geometrical constraints* (see, e.g., Ref. 20), so that chains and rings of different lengths can be introduced into the calculations. Chain simulations were usually started from a box containing eight replicas of a 1372-atom chain generated by a random-walk procedure. Crystalline starting configurations with $20\times20\times10$ unit cells (three atoms/unit cell) were also used. No significant difference in the final calculated results could be observed which showed that there was no dependence on the starting configuration. Simulation boxes containing Se_8 rings were obtained by preliminary soft-sphere molecular-dynamics simulations using 1372 eight-membered rings. Details of this type of calculation can be found in Refs. 21 and 22.

Applying the latest form of coordination constraints,[23] it was possible to keep pre-generated flexible polymeric chains, as well as Se_8 rings, intact during the course of the entire run. Intramolecular Se-Se bond lengths were allowed to vary between 2.16 and 2.46 Å (the upper boundary was extended to 2.52 Å in some cases—without noticeable effects). ‘‘Unconstrained’’ calculations using only hard-sphere constraints have also been performed, primarily for checking if a particular set of data can be related to physically realizable structures. The number of particles in our models ranged between 8000 and 12 000, depending on the actual set of constraints. In order to investigate system size dependence, a few calculations have been carried out with 4000 and 16 000 particles; these calculations showed that system size here has no effect on the final structures formed. Another test concerned the possible effects of the different scattering vector ranges covered in the experiments considered here; calculations were carried out on ‘‘shortened’’ $S(Q)$'s (in the fashion described in Ref. 19), as well. It appears that setting the upper limit of the Q range to about 10 Å^{-1}, which is the upper limit of our experiment, does not effect the results in the particular case of a-Se. A distance of closest approach (between nonbonded Se atoms to account for excluded volume effects) has been set to be between 2.1 and 2.2 Å. In

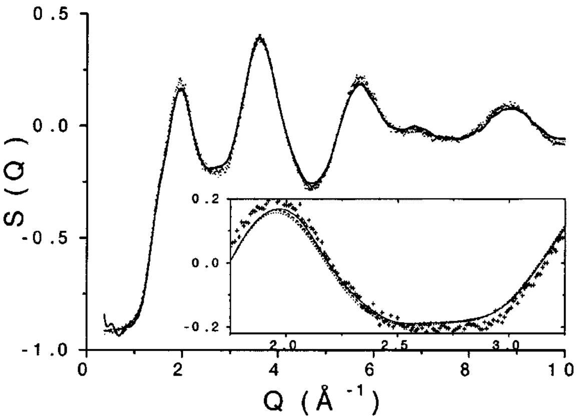

FIG. 2. Structure factors obtained from reverse Monte Carlo modeling of the experimental structure factor of a-Se determined in this study (markers). Solid line: hard-sphere constraints only; dashed line: long chains; dots: Se_8 rings. The inset shows the region where differences between experiment and models are the greatest. Note that structure factors for the RMC models run practically together.

some calculations, values up to 2.7 Å have also been tried, with no effect on the quality of the fit. (This means that for quantitative reproduction of diffraction data, the presence of threefold-coordinated covalently bonded Se atoms is not necessary.)

IV. RESULTS OF STRUCTURAL MODELING

As input for the RMC modeling, we have used the structure factors given in Refs. 3–5, as well as our own data. All of these could be modeled by unconstrained RMC calculations reasonably well, the worst case being data from Ref. 4. The RMC fit of this latter data set was closer to the other $S(Q)$'s than to the fitted data, which is a clear indication that this $S(Q)$ contains significant systematic errors, as compared to the other sets of data considered here. This structure factor was therefore not included in our further investigations.

To give an idea about the "goodness of fit," in Fig. 2, we compare the RMC simulated structure factor with only hard-sphere constraints to our experimental $S(Q)$ reported in Sec. II. Figure 2 also displays RMC structure factors for configurations of chains and rings as well. Note that RMC $S(Q)$'s are in full agreement with each other which makes it impossible to exclude any of the models at this stage of the analysis.

Figure 3 shows pair-correlation functions obtained from unconstrained reverse Monte Carlo modeling of data from Refs. 3 and 5, in comparison with the $g(r)$ obtained for our measurement. Again this comparison shows close agreement between data of Refs. 3 and 5 and the present measurement. The $g(r)$ from the present experiment follows somewhat closer the one from Ref. 5 but the difference is not significant. It appears that deviations between the $g(r)$'s are actually characteristic of present day experimental uncertainties rather than of any real differences between samples or techniques.

In Fig. 4, pair-correlation functions for the present results for a-Se are given, applying different geometrical constraints. Similar patterns were obtained for data taken from the literature. Since no strange or unphysical features appear on any of the $g(r)$'s [unlike what happened in the case of liquid Se (Ref. 9)], it is not possible to exclude any models on the basis of their respective pair-correlation functions. It can now be concluded that amorphous Se is one of the (unfortunately, not very few) cases where diffraction data alone simply do not contain the information needed for determining the difference between two or more possibilities concerning the microscopic structure. It should be stressed that up to now, as far as the authors are aware, this statement could not be made on the basis of quantitative agreement with experimental data.

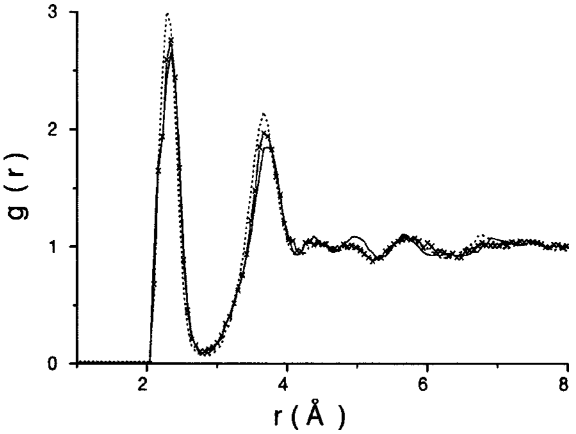

FIG. 3. Pair-correlation functions of amorphous selenium, as determined from ("unconstrained") RMC calculations. Solid line: modeling the structure factor of Ref. 3; dots: modeling the $S(Q)$ of Ref. 5; markers: modeling the present data.

Nevertheless, it still seems to be possible to go beyond such a negative statement, making use of the fact that no significant differences were found between the various sets diffraction data for a-Se. It is known that our sample was prepared from the crystalline phase that consists of long chains and that the powder was not subjected to large temperature changes (and/or phase transitions). It follows di-

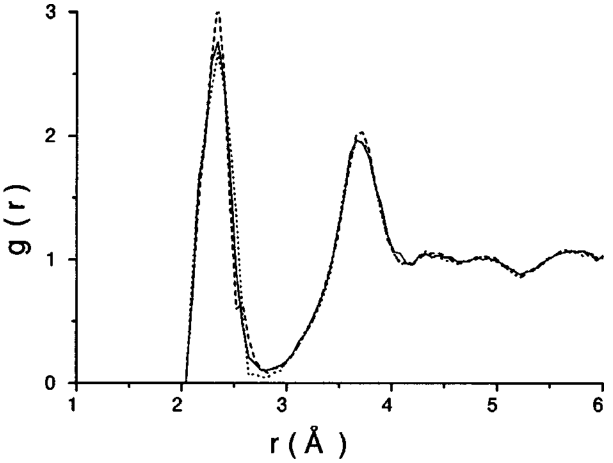

FIG. 4. Pair-correlation functions obtained from reverse Monte Carlo modeling of the experimental structure factor of a-Se determined in this study. Solid line: hard-sphere constraints only; dashed line: long chains; dots: Se_8 rings.

rectly that the dominance of long chains is sufficient for explaining all existing diffraction data measured for *a*-Se.

Detailed thermodynamic measurements are reported in Ref. 7, which—together with minute variations found in the structure factors—serve as a basis for concluding that the structure of melt-quenched *a*-Se is different from that of the mechanically alloyed sample. We would like to point out that the difference seen in the published differential scanning calorimetry signals can be interpreted simply by noting that melt quenching most probably leads to a chain structure in which chains interlock to a much higher extent then they do after ball milling. For the formation of the (chainlike) crystalline structure, therefore a more powerful relaxation process would be needed. Thus the presence of rings is not necessary for explaining the thermodynamic data.

Selenium has two monoclinic crystalline forms that are made of Se_8 rings: α- and β-Se. It would be of great interest if mechanical alloying could lead to an amorphous sample from (at least one of) these crystals—unfortunately, this investigation has not been made before. A reason for this failure may be given on the basis of structural studies on β-Se;[24,25] it was found that even at room temperature, β-Se transforms spontaneously into α-Se quite rapidly and then, although at a smaller rate, hexagonal crystalline Se is formed. It was also noted that the rate of transformation increases very rapidly with temperature. From these observations it can be conjectured that during the process of mechanical alloying of either monoclinic form of Se, first, hexagonal Se would be formed which would then undergo amorphization the same way as our sample.

From these early studies of β-Se,[24,25] another thought is worth mentioning which concerns the formation of phases containing Se_8 rings. In order to be able to avoid forming the chain structure, Se fragments have to be sufficiently isolated. For this, rather special conditions are necessary while preparing α- and β-Se (see Refs. 24 and 25). We note that such conditions cannot be maintained if *a*-Se is prepared from the hexagonal crystalline form, or from the liquid phase of Se.

V. SUMMARY

It has been shown that diffraction data measured for amorphous selenium over three decades agree to within the estimated uncertainties of the individual experiments regardless of the type of diffraction applied (neutron or x-ray) and of the method of preparation (vapor deposition, melt quenching, or mechanical milling). It is therefore suggested that, given the present standards of diffraction data, no far reaching conclusions should be drawn from differences between existing neutron- and x-ray-diffraction data or from differences between data measured for samples prepared differently, where these differences are of the order of magnitude as is shown in Fig. 1.

Based solely on diffraction data (the present investigation and taken from the literature), it is not possible to determine if amorphous selenium consists of long chains, Se_8 rings, or a mixture of both. Models of both could easily be constructed for each data set whose structure factors agreed within the experimental uncertainties (that is, all of our models agreed quantitatively with measured data). However, knowing that our sample was made from crystalline Se consisting of long chains, it is suggested that our *a*-Se sample contained primarily chain molecules. Note also that other data we considered were within experimental error levels when comparing to the present set and that there was no necessity for the presence of Se_8 rings. These results imply that, for the samples that have been investigated so far, the dominance of chainlike molecules should be considered more probable than rings in amorphous Se.

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