AMORPHOUS AND CRYSTALLINE SELENIUM – A MOSSBAUER EFFECT STUDY

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Te$^{125}$ Mössbauer spectra of Se$_{0.98}$Te$_{0.02}$ alloy in bulk amorphous and trigonal phases reveal partially resolved quadrupole doublets. The average quadrupole splitting in the amorphous phase is found to be 10 per cent larger. This observation, in the framework of the ring-chain model of amorphous Se suggests a substantially larger quadrupole interaction at Te$^{125}$ sites in mixed rings than in copolymeric chains. The strength of the quadrupole interaction in mixed rings and copolymeric chains is found to be $12.72 \pm 0.40$ mm/sec and $10.33 \pm 0.08$ mm/sec. Implications of these results on the chemical bonding are discussed.

Alloys of the composition Se$_{0.98}$Te$_{0.02}$ were prepared by melting in vacuo 99.9999% pure Se with isotopically enriched Te$^{125}$. Three identical melts were subjected to different heat treatments to precipitate the different phases as follows. Sample 'a' was obtained by quenching the melt in ice water to precipitate the amorphous phase. The absence of long range order was confirmed by X-rays (Fig. 1 (a)). Sample 'b' was obtained by annealing the melt at 150°C for 1 hr and then slowly cooling to room temperature to precipitate a partially amorphous phase [Fig. 1 (b)]. Sample 'c' was obtained by annealing the melt at 150°C for 50 hr...
and then slowly cooling to room temperature to precipitate the trigonal phase of Se. X-ray patterns of melts annealed longer than 24 hr were found identical to those of trigonal Se [Fig. 1 (c)]. Mössbauer spectra of the different samples obtained with a source of $^{125}$I in Cu at 4.2°K consisted of partially resolved doublets (Fig. 2). Details of the spectrometer and calibrating procedures appear in reference 4.

The analysis of the Mössbauer spectra was carried out first, to obtain the average QS in the different samples. A least squares fit of the spectra to a pair of Lorentzian lines of equal width and intensity gave the average QS in samples 'a', 'b' and 'c' of 11.24 ± 0.16, 10.95 ± 0.11 and 10.33 ± 0.08 mm/sec respectively. One observes an increase in the average QS on vitrifying doublets, in each case constraining the QS and IS of the Se host. This result, in the light of the ring-chain model of amorphous Se can be understood as follows. We postulate the existence of two inequivalent Te sites in the amorphous phase of Se, one located in mixed rings and the other in c-chains. We suggest that the QS in mixed rings is larger than that in c-chains, and that the increase in the average QS observed for the amorphous samples results from an increase in the population ratio of mixed rings to c-chains.

Our recent experiments with Te-Se alloys show that the QS observed in the trigonal phase of the Se$_{0.98}$Te$_{0.02}$ alloy must be attributed to a Te site covalently bonded to two Se near neighbours in the trigonal symmetry of c-chains. It follows that the QS observed for sample 'c' is the one for c-chains.

The QS in mixed rings was obtained from the Mössbauer spectra of the amorphous samples 'a' and 'b' as follows. Analysis of these spectra was carried out by least squares fitting to two pairs of quadrupole doublets, in each case constraining the QS and IS of one of the pairs to the values of these parameters obtained from sample 'c'. The result of this analysis gave the QS and IS of the other pair as 12.72 ± 0.40 and + 1.0 ± 0.2 mm/sec respectively. These parameters are attributed to a Te site in mixed rings. The analysis also gave $R$, the intensity ratio of mixed rings to c-chains for the samples 'a' and 'b' of 0.48 ± 0.06 and 0.39 ± 0.06 respectively.

The larger QS in mixed rings over that in c-chains is particularly intriguing since for pure Se, the Se-Se-Se covalent bond length and angle in the monoclinic and trigonal phases are just about the same. The
dominant contribution to the electric field gradient at Te comes from the unbalanced '5p' electron density which is determined by the symmetry and bond lengths. Te forms with its two near neighbour Se in the ring and chain geometry. For pure Se, Se₈ rings are considerably smaller in length than helical chains. Therefore one may expect the rings to be stiffer in accommodating a larger Te atom for Se to form a mixed ring. It is conceivable that the Se–Te–Se bond is more distorted in mixed rings than in c-chains, and in particular the length of the Te–Se bond is smaller in the mixed-ring geometry than in the c-chain geometry. The larger QS and IS in mixed rings could then be understood as resulting from a larger time average of both the unbalanced '5p' electron density and the 's' electron density respectively. The conjecture of a shorter Te–Se bond in mixed rings is also supported by the measured intensity ratio R for the amorphous samples which suggests that the recoil-free-fraction at Te in mixed rings is higher than that in c-chains. The ratio R is given by the product of the recoil-free-fraction ratio and the population ratio of mixed rings to c-chains, i.e.,

\[ R = \frac{f_{mr}}{f_{cc}} \times \frac{N_{mr}}{N_{cc}}, \]

where f and N designate the recoil-free-fraction and population respectively. The subscripts mr and cc stand for mixed rings and c-chains respectively. Clearly, if \( f_{mr} > f_{cc} \), then it follows from (1) that \( R > N_{mr}/N_{cc} \).

That this appears to be the case here, is borne out by the fact that the measured ratio R is substantially larger than the population ratio of 0.07 for mixed rings to copolymeric chains calculated for a 2 at.% Te impurity in Se by Schottmiller et al.² (Fig. 3), following a theoretical procedure due to Tobolsky and Owen.³ These calculations are based on a liquid phase equilibrium copolymerisation of Se₈ rings, mixed rings and copolymeric chains; and parameters appropriate to the initiation and propagation reactions involved are utilised for obtaining the statistical distribution of the different structural elements in the melt.

In the framework of the chain-ring model of amorphous Se, the present Mössbauer measurements show the existence of a substantially larger quadrupole interaction at Te in mixed rings than in c-chains. This is an important result and needs careful investigation. The significance of this result is that it will permit characterising the amorphous state of Se. In view of the limited resolution of the Te¹²⁵ experiments, this result needs to be verified independently. Attempts are underway to measure the QS at Te in monoclinic Se.

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REFERENCES


Te¹²⁵ Mössbauer Spektren der Se₈,₉₂Te₉₈,₉₂—Legierung in grob amorpher und in trigonalen Phase zeigen teilweise aufgelöste Quadrupol-Dubletts. Die durchschnittliche Quadrupolaufspaltung in der amorphen Phase ist 10% größer. Diese Beobachtung deutet im Zusammenhang mit dem Ring-Ketten-Modell des amorphen Selens darauf hin, dass die gegenseitige Beeinflussung der Quadrupole in den Te¹²⁵ Positionen in gemischten Ringen wesentlich größer ist, als in gemischten Ketten. Die Starke des gegenseitigen Quadrupoleinflusses in gemischten Ringen und copolymeren Ketten wurde zu 12,72 ± 0,40 mm/sek, bzw. 10,33 ± 0,08 mm/sek bestimmt. Die Folgerungen aus diesen Befunden für die chemische Bindung werden besprochen.