AMORPHOUS AND CRYSTALLINE SELENIUM – A MÖSSBAUER 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 ± 0.40 mm/sec and 10.33 ± 0.08 mm/sec. Implications of these results on the chemical bonding are discussed.

THE AMORPHOUS phase of Se has been studied[1] using X-rays, electron and neutron radial distribution functions, Infrared absorption and Raman effect. It is generally held that the structural elements of this phase consists of helical chains and eight membered rings in varying proportions. In this work the Mössbauer effect on a Te^{125} impurity imbedded in Se, has been used to investigate the bulk amorphous and trigonal phases of the host. It is known[2,3] that addition of Te impurity to Se leads to the formation of copolymeric chains (*c*-chains) and mixed rings at the expense of pure Se chains and Se_8 rings in the amorphous phase of Se. The Mössbauer measurements suggest a substantially larger quadrupole splitting (QS) and isomer shift (IS) in mixed rings than in *c*-chains. This is an important result which will permit characterising the glassy state of Se using the Mössbauer effect.

Alloys of the composition $Se_{0.98}Te_{0.02}$ were prepared be 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 1hr and then slowly cooling to room temperature to precipitate
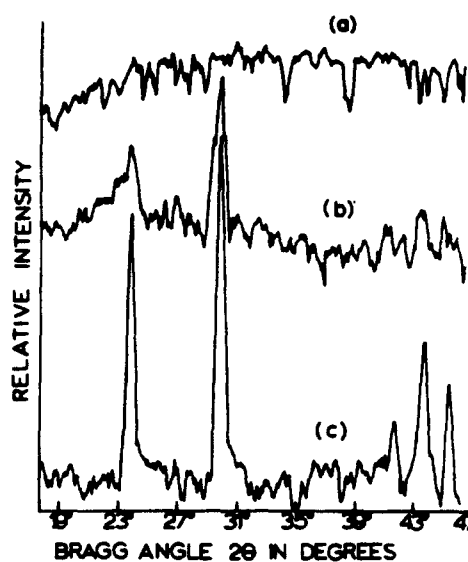

FIG. 1. X-ray diffraction patterns of $Se_{0.98}Te_{0.02}$ alloy in different phases. (a) Melt quenched in ice water to precipitate the amorphous phase-sample 'a' (b) Melt annealed at 150°C for 1hr to precipitate a partially amorphous phase-sample 'b'. (c) Melt annealed at 150°C for 50hr to precipitate the trigonal phase-sample 'c'.

a partially amorphous phase [Fig. 1 (b)]. Sample 'c' was obtained by annealing the melt at 150°C for 50hr

and then slowly cooling to room temperature to pre-
cipitate the trigonal phase of Se.X-ray patterns of
melts annealed longer than 24hr were found identical
to those of trigonal Se [Fig. 1 (c)]. Mössbauer spectra
of the different samples obtained with a source of I^{125}
in Cu at $4.2°K$ consisted of partially resolved doublets
(Fig. 2). Details of the spectrometer and calibrating
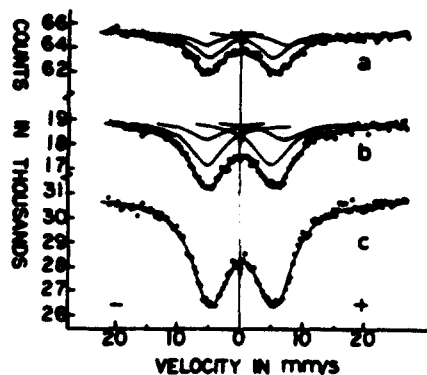procedures appear in reference 4.

FIG. 2. Mössbauer spectra of $Se_{0.98}Te_{0.02}$ alloy in
(a) amorphous, (b) partially amorphous and (c)
trigonal phase. The spectra were taken with an I^{125}
source in Cu metal at $4.2°K$. Spectra a and b were
least squares fit to two pairs of quadrupole doublets
with certain constraints (see text). Spectrum c was
least squares fit to a pair of quadrupole doublet.

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
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[5] 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
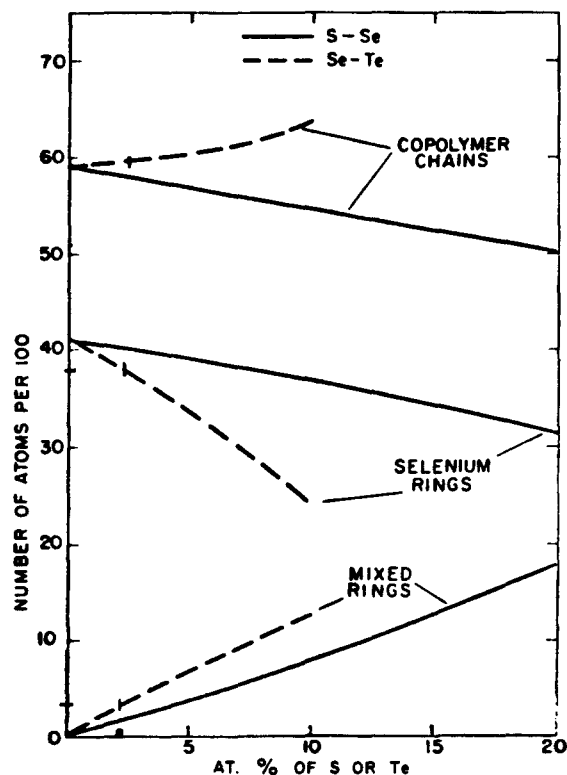

FIG. 3. Atomic distributions in Se–S and Se–Te alloys
taken from reference 3.

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 $+ 1.0 \pm 0.2$ 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.[6] 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, Se_8 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.

$$R = \frac{f_{mr}}{f_{cc}} \times \frac{N_{mr}}{N_{cc}}, \qquad (1)$$

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[3] (Fig.3). following a theoretical procedure due to Tobolsky and Owen.[2] These calculations are based on a liquid phase equilibrium copolymerisation of Se_8 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[7] the amorphous state of Se. In view of the limited resolution of the Te^{125} experiments, this result needs to be verified independently. Attempts are underway to measure the QS at Te in momoclinic Se.

REFERENCES

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Te^{125} Mössbauer Spektren der $Se_{0.98}Te_{0.02}$–Legierung in grob amorpher und in trigonaler 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 Te^{125} Positionen in gemischten Ringen wesentlich grösser ist, als in gemischten Ketten. Die Stärke des gegenseitigen Quadrupol-einflusses in gemischten Ringen und copolymeren Ketten wurde zu 12,72 ± 0,40 mm/sek, bezw. 10,33 ± 0,08 mm/sek bestimmt. Die Folgerungen aus diesen Befunden für die chemische Bindung werden besprochen.