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Publication Date

1974-06-01

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June 1974

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

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The Structural Nature of Amorphous Se and Te*

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Abstract

We present new photoemission measurements on amorphous and trigonal Te. These results and other recent photoemission experiments on amorphous and trigonal Se are interpreted using density of states and charge density calculations. These studies result in new insights into the possible structural nature of the amorphous phase.

Recent X-ray (XPS) and ultraviolet (UPS) photoemission measurements on Se¹ and the new experiments presented here on Te show some remarkable differences between their trigonal and amorphous phases. One of these differences corresponds to a seemingly sharper structure in the s-like states of the amorphous phase of Se which is very unusual for an amorphous spectrum. Other important differences appear as interchanging strengths in the two peaks of the p-like bonding states. To explain these differences in terms of the possible

structural nature of the amorphous phase we must first understand the origins of the structure in the crystalline spectrum.

In a recent letter² we have investigated the characteristic two peak structure of the p-like bonding states of trigonal Se and Te. Electronic charge distributions obtained from our pseudopotential calculations indicate that (1) the splitting of the two peaks in the p-like bonding states is related to the amount of mixing and hybridization of p_x , p_y , s and d states and (2) the relative strengths of these two peaks is related to the relative amount of intra-chain and inter-chain bonding. Specifically, the lower energy peak contains almost exclusively intra-chain bonding states while the higher energy peak contains states which contribute to inter-chain bonding. The s-like region of the density of states is of considerable importance since these states are very sensitive to topology. The structure in the s-like region of the density of states of trigonal Se is very similar to that of a one-dimensional chain and thus reflects the definite chain-like nature of this phase. In trigonal Te, however, the structure in the s-like region is more similar to the superposition of a one-dimensional chain density of states and a three dimensional simple cubic density of states. This is not surprising since the structure of Te can be derived from a simple cubic structure by a small trigonal distortion.

Résumé

Nous exposons de nouveaux résultats de mesures de photo-emission sur des échantillons de tellure amorphe et cristallin (trigonal). Ces résultats, et d'autres similaires sur le selenium sont interprétés à partir des calculs de densité de charge et de densité d'états. Cette étude, donne la possibilité d'aborder le problème de la nature structural de la phase amorphe sous un nouvel angle.

Let us now carefully examine the changes occurring in the amorphous phase. In Fig. 1 (top) we show the photo-emission results of Shevchik et al.¹ for trigonal and amorphous Se. In the "lone-pair" region (between -2 eV and 0 eV) we notice that relative to the crystalline spectrum the amorphous spectrum has lost some fine structure and is shifted slightly to higher energies. However in the bonding p-like region (between -6 eV and -2 eV) rather interesting changes have occurred. The lower energy peak has become weaker whereas the higher energy peak has become stronger in the amorphous phase. From our analysis of the crystalline case we suggest that this reversal corresponds to a decrease of the number of pure intra-chain bonding states. Thus there are now more electrons occupying states which are partially localized outside the chains. We should also mention that the splitting of these peaks is very sensitive to the bond angle and hence to the hybridization. This was found by performing several model calculations of trigonal phases with various bond angles. In particular for a chain with a 90° bond angle the splitting disappears completely as expected. In the amorphous phase however this splitting remains essentially unchanged suggesting that bond angle variations are relatively small.

In the s-like region (between -18 eV and -7 eV) for Se we find a very unusual effect. The dip seems to be bigger in the amorphous phase than in the trigonal phase. This suggests some very interesting structural properties. This change could not for example be caused by just a breaking of

the infinite chains. This would only tend to fill up the dip unless the chains were of order two which seems rather unlikely. A reasonable alternative is the formation of some type of rings. In particular the dip would increase if the rings were of order three, five, six or seven. Rings of order four, eight, or five and seven together, would certainly tend to fill up the dip.³ Furthermore, since the bond angles in the trigonal phase are around 104° , we would suspect that the most likely ring structures would be five-fold and six-fold^{or six-fold} and seven-fold. To demonstrate the effect of the existence of rings on the density of states we have carried out two model calculations on Se containing only six-fold and only eight-fold rings respectively. The bond angles, nearest neighbor distances and second nearest neighbor distances were taken to be the same as in the trigonal form. The results are shown in Fig. 2. We notice that the s-like region displays essentially the same behavior as that of isolated rings. The six-fold ring structure gives rise to a big dip around -13 eV while the eight-fold ring structure gives a peak. In the p-like bonding regions we essentially get the same results as in the amorphous case i.e. a shift of strength to higher energies. It is not clear here however whether this shift is due to the ring resonances or the inter-ring environment. On the basis of these results we propose that the amorphous Se sample used in the photoemission measurements contains a substantial number of atoms in ring-like configurations of order six.

This suggestion seems to be consistent with Rechten's and Averbach's⁴ interpretation of their radial distribution function data.

The photoemission results for amorphous and trigonal Te obtained by Shevchik et al.⁵ using the same sputtering technique as in the Se case give similar results. However these results differ from our photoemission data on amorphous and trigonal Te. The experimental procedure was as follows. The x-ray photoemission spectra of Te were measured with a Hewlett-Packard ESCA-spectrometer 5950A utilizing monochromatized Al K_α x-rays (1486.6 eV) with a resolution of 0.6 eV (FWHM). A single crystal of Te was cleaved just prior to insertion into the spectrometer in an atmosphere of dry nitrogen. The amorphous sample was obtained after 2 hours of Ar⁺-ion (1000 V, 10μA) bombardment. Surface contaminations of the specimens were negligible in the spectrometer vacuum of 3×10^{-9} torr even after 10 hours as judged from the in situ monitoring of the O 1s and C 1s lines. Our results are shown in Fig. 1 (bottom). In the bonding p-like region (-2 eV to -6 eV) we now find, in contrast to Se, a shift of strength to lower energies in the amorphous case. This suggests an increase in the number of the pure intra-chain bonding electrons, which would be consistent with an increase in the covalency of Te in the amorphous phase. The structural information obtained from the s-like states is somewhat more difficult to discern since there is now a filling up of the dip in the amorphous case. As we

have already mentioned a filling up of the dip could be obtained in various ways; such as regions of simple cubic structure; or four-fold, eight-fold, five and seven-fold rings; or broken chains. Regions of simple cubic structure, however, can be dismissed since these would result in a merging of the p-like bonding states with the lone-pair states. What remains therefore is to discern between a structure which could contain mostly broken chains or broken chains with a substantial amount of rings. It is however rather difficult to make a conclusive statement about the structure of this sample of Te without better experimental resolution. For instance it is not really clear that the two peaks in the p-like bonding states have not merged in the amorphous phase. One could speculate however that argon bombardment would tend to leave the system with atoms existing mostly in broken chain configurations. On the other hand, sputtering and the deposition of thin films at room temperature may favor the formation of rings.

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- * Supported in part by the National Science Foundation Grant GH 35688.
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Figure Captions

Fig. 1. X-ray and ultraviolet photoemission results (top) on trigonal (solid line) and amorphous (dashed line) Se as obtained from ref. 1. The amorphous sample was prepared by d.c. sputtering at room temperature. X-ray photoemission results (bottom) on trigonal (solid line) and amorphous (dashed line) Te as obtained in this work. Here the amorphous Te sample was obtained by Argon bombardment. The "lone-pair" states lie between -2 eV and 0 eV. The bonding p-like states lie between -6 eV and -2 eV and the s-like states are below -8 eV.

Fig. 2. The density of states of Se in model structures containing only six-fold (solid line) and only eight-fold (dashed line) rings of atoms obtained from pseudopotential calculations. The curves were broadened by about 0.7 eV to facilitate comparisons with experiment.

Fig. 1

Fig. 2

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