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ELECTRONIC DENSITIES OF STATES OF AMORPHOUS  
AND TRIGONAL SE AND TE\*

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We have used the Empirical Pseudopotential Method to obtain electronic densities of states and charge distributions for the valence electrons in trigonal Se and Te. We have explored the relation between density of states structure and charge density. Specifically, structures in recent photoemission spectra are identified with particular interchain and intrachain bonding states. These results are then used to interpret the changes observed in the experimental photoemission spectra of amorphous Se and Te.

We present here new calculations of the electronic densities of states of trigonal Se and Te (using the empirical pseudopotential method (EPM) which for the first time agree quantitatively with all the observed structure in recent experimental photoemission spectra. In Fig. 1 we show the results of our EPM calculations for the density of states along with the recent photoemission results of Shevchik et al. [1] for Se, and Schlüter et al. [2] for Te. The calculated spectra were convoluted with an energy dependent broadening function in order to facilitate comparisons with experiment. The lowest band represents essentially the atomic s-like states of Se and Te. In Se the density of states of this band strongly resembles that of a one dimensional chain whereas in Te, there is, in addition, structure resembling the density of states of a simple cubic lattice. The next band contains p-like bonding states which lie between -6.0 eV and -2.2 eV for Se and for Te. Finally the top most valence states are predominantly non-bonding p-like in nature.

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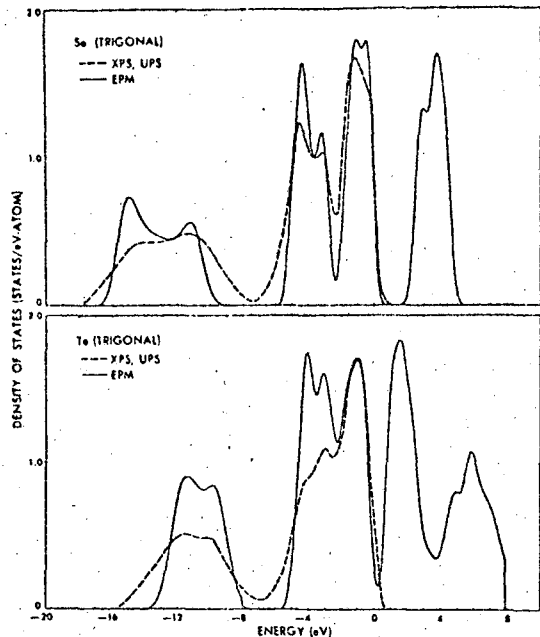
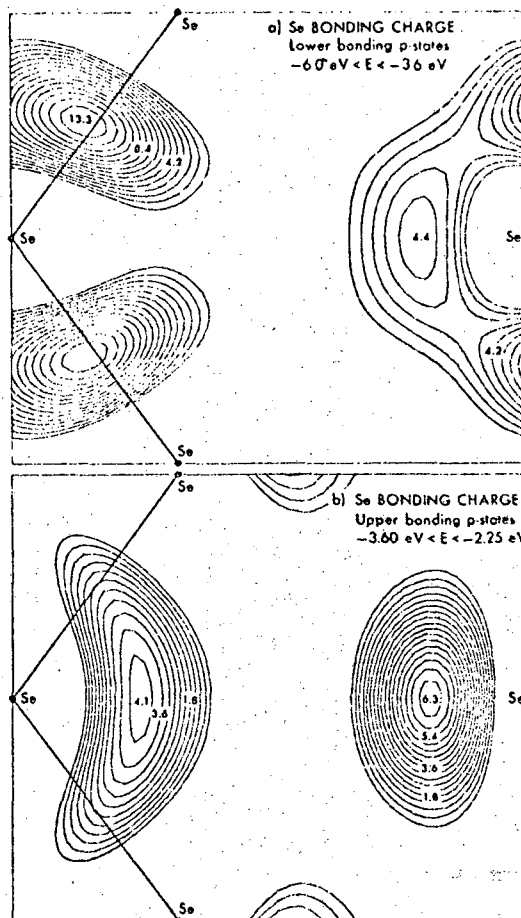


FIG. 1: Calculated broadened density of states and photo-emission spectra for trigonal Se (top) and Te (bottom).

FIG. 2: Bonding charge of trigonal Se for the (a) lower and (b) upper p-like bonding states.



In order to understand the origin of the characteristic two-peak structure found in the p-like bonding states of both Se and Te we have calculated the electronic charge distributions of states in each peak. We then go one step further and isolate the short wavelength Fourier components from the long wavelength Fourier components. This introduces a new method of defining bonding charges and a way to separate out the effects of metallicity. The cutoff or boundary wavelength  $\lambda_0$  between short and long wavelength components was found to lie naturally at  $\lambda_0 = d$  where  $d$  is the nearest neighbor separation in Se and Te. The results obtained for Se by retaining only Fourier components with  $\lambda \leq \lambda_0$  are shown in Fig. 2 (a) and (b). The results for Te are similar and will not be presented here [2]. The charge in the lower energy peak of the p-like bonding states is well localized between atoms belonging to the same chain and thus corresponds to states representing intra-chain bonding. In the upper or higher energy peak of the p-like bonding states the charge is

displaced out of the bonds and is concentrated in the region between neighboring chains. This charge arises in part because of the mixing and hybridization of  $p_x$ ,  $p_y$ , s and d states. Moreover we find that the amount of charge concentrated in the right half of Fig. 2b depends strongly on the interchain separation and can thus be identified as an inter-chain bonding charge.

If we compare the photoemission spectra of trigonal Se [1] and Te [2] with those of amorphous Se [1] and Te [2] (see Fig. 3) we find two very interesting differences occurring in the s-like

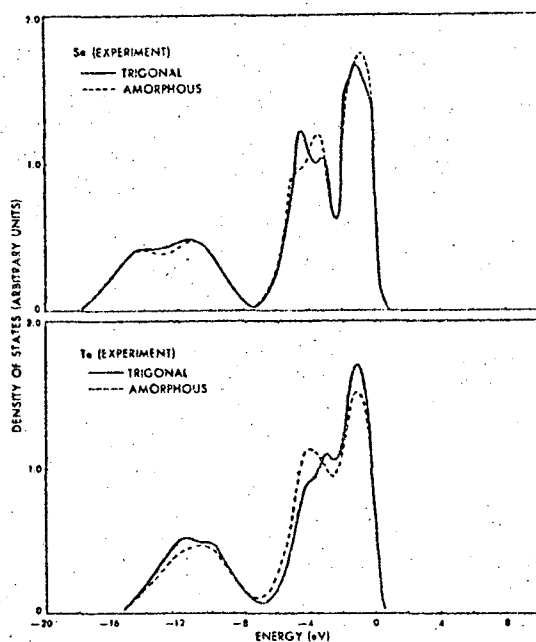


FIG. 3: Photoemission spectra on trigonal and amorphous Se (top) and Te (bottom) as obtained from refs. [1] and [2] respectively.

and bonding p-like states respectively. In Se the lower energy peak of the p-like bonding states 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 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. In the s-like region 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. For example it could not 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 possible 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. Furthermore, since the bond angles in the trigonal phase are

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about  $104^\circ$  we would suspect that the most likely ring structures would be of type five-fold and six-fold, or six-fold and seven-fold. We therefore propose that amorphous Se contains a substantial number of atoms in ring-like configurations with the rest of the atoms being members of chains.

The photoemission results for amorphous and trigonal Te obtained by Shevchik et al. [3] using the same sputtering technique as in the Se case give similar results. However these results differ considerably from photoemission data on amorphous Te prepared by argon bombardment [2]. The latter results are shown in Fig. 3 (bottom). In the bonding p-like region we now find, in contrast to Se, a shift of strength to lower energies. 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. It is difficult to make a conclusive statement about the structure of this sample of Te without better experimental resolution. 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 at room temperature with the deposition of thin films may favor the formation of rings.

#### REFERENCES

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- [2] Schlüter, M.; Joannopoulos, J. D.; Cohen, M. L.; Ley, L.; Kowalczyk, S.; Pollak, R.; Shirley, D. A.: to be published
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