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New Interpretation of Photoemission Measurements on Trigonal Se and Te*

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Abstract

New pseudopotential calculations of the densities of states of trigonal Se and Te, (in excellent agreement with recent photoemission measurements) are used to show that two easily resolved peaks in the photoemission data are directly related to inter- and intra-chain bonding. This identification is accomplished by calculating electronic charge densities as a function of energy for different energy regions. Finally we introduce a new method for determining bonding charges by extracting short wavelength components of the electronic charge density.

The electronic structure of trigonal Se and Te has been the subject of many experimental and theoretical studies.[1] Recently the advent of new ultraviolet (UPS)[2] and X-ray (XPS)[2,3] photoemission measurements has provided important information about all the valence bands and has revealed some inadequacies of present theoretical calculations.[4-6] In one of these calculations[4] a complete merging of s- and p-like bands was proposed which disagrees qualitatively with the recent photoemission data. Other calculations[5,6] show a separation of s- and p-like bands which is in qualitative agreement with these experiments, however band widths and important structure in the p-like bonding states are not obtained correctly. The experimentally observed characteristic two-peak structure in the p-like bonding states is, as we shall show, intimately related to two distinct types of bonding states so that precise calculations are necessary before a detailed understanding of the electronic structure and bonding nature of Se and Te can be obtained. Finally the information gained by a careful examination of the crystalline forms of Se and Te is a considerable aid in understanding the amorphous phases[3,7] of Se and Te as well.

In this letter we thus present new calculations of the electronic densities of states of trigonal Se and Te using the empirical pseudopotential method (EPM)[8] which for the first time agree quantitatively with all the observed structure in the experimental photoemission spectra. A detailed discussion of the calculations and the parameters

used will be given elsewhere.[3] In Fig. 1 we show the results of our EPM calculations for the density of states along with the recent photoemission results of Schevchik et al.[2] for Se and Joannopoulos et al.[3] for Te. The calculated spectra were convoluted with an energy dependent broadening function in order to facilitate comparisons with experiment. The experiments on Se were obtained by using UPS and XPS measurements on a sputtered and subsequently annealed films, while those on Te were obtained using XPS on a single crystal. All observed structures in the experimental spectra are reproduced to within 0.3 eV. As in earlier EPM calculations[5,6,9] the lowest band represents essentially the atomic s-like states of Se and Te. 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. These identifications are reconfirmed in our present calculations, moreover the widths, positions, and number of peaks in the densities of states are now in good quantitative agreement with experiment.

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. This entails summing over states whose energies (in eV) fall within [-6.0,-3.6] and [-3.6,-2.25] for Se and [-6.0,-3.5] and [-3.5,-2.2] for Te. Once we have calculated the total charge density of each energy interval, we can 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 λ_o between short and long wavelength components was found to lie naturally at $\lambda_o = d$ where d is the nearest neighbor separation in Se and Te. The results obtained for Se by retaining only Fourier components with $\lambda \leq \lambda_o$ are shown in Fig. 2 (a) and (b) for the energy intervals [-6.0,-3.6] and [-3.6,-2.25] respectively. The results for Te are similar and will not be presented here.[3] We notice immediately that the lower energy peak in the p-like bonding states represents states involved in intra-chain bonding. The charge is well localized in the bonds between atoms belonging to the same chain. In the upper or higher energy peak of the p-like bonding states we find states which contribute to the inter-chain bonding in the crystal. Now the charge is displaced out of the bonds and is concentrated in the region between neighboring chains (right half of Fig. 1B). The charge found within the chains (left half of Fig. 1b) is a residual charge of the lower bonding p-states. In fact both figures (1a and 1b) show some residual charge, indicating that an absolute separation on the energy scale of the two types of states is impossible. The intra-chain bonding states lie lower in energy than the inter-chain bonding states since the potential is strongest between neighboring atoms within a chain.

Some measure of intra-chain vs. inter-chain bonding strengths is given by the magnitude of the respective bonding charges. For Se we have found 0.07 e^- for the intra-chain bond and 0.04 e^- for the inter-chain bond. It is instructive to compare these values with 0.05 e^- and 0.04 e^- for the intra- and inter-chain bonds of Te respectively. The ratio of intra-chain to inter-chain bonding charge decreases from 1.75 for Se to 1.25 for Te and thus reflects the more three-dimensional or more isotropic character of Te. Furthermore we believe that the smaller amount of total bonding charge in Te is indicative of its more metallic character.

Finally we should emphasize that the accuracy of the bonding charges we have obtained should be considered mostly in a relative sense rather than individually.

Acknowledgment

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Figure Captions

Fig. 1. Calculated densities of states (solid lines) for trigonal Se (a) and Te (b), which have been broadened by 1.2 eV for the s-like states and by 0.7 eV for the remaining states. Superimposed are the experimental photoemission spectra (dashed lines). The scales for the XPS and UPS curves are arbitrary.

Fig. 2. Bonding charge of trigonal Se for the a) lower and b) upper p-like bonding states, calculated as described in the text. Only positive contours are shown, with values in units of e/Ω.

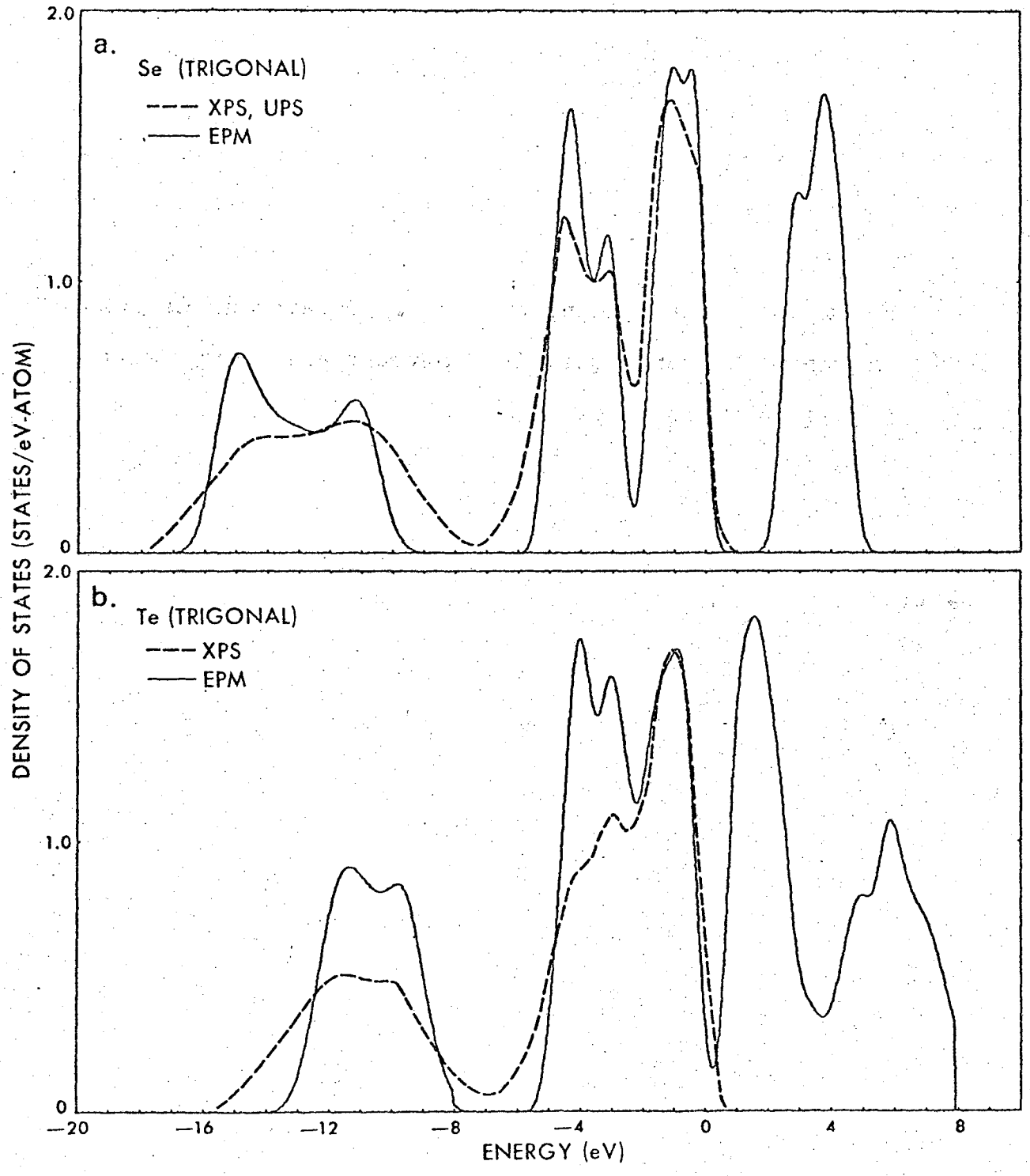
a.
Se (TRIGONAL)
XPS, UPS
EPM
b.
Te (TRIGONAL)
XPS
EPM
DENSITY OF STATES (STATES/eV-ATOM)
2.0
1.0
0
−20
−16
−12
−8
−4
0
4
8
ENERGY (eV)

Figure 1

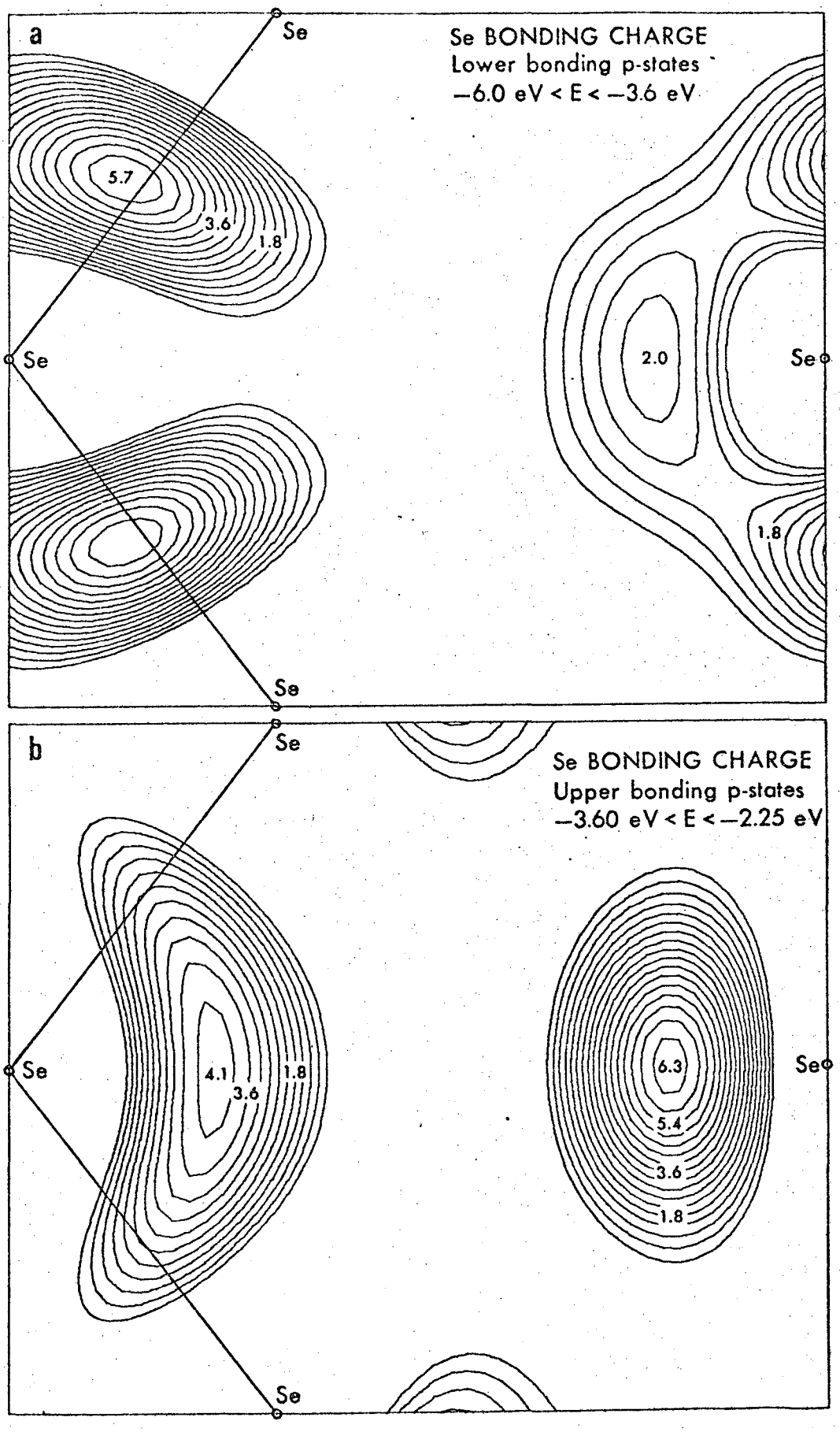
a
Se
Se BONDING CHARGE
Lower bonding p-states
−6.0 eV < E < −3.6 eV
5.7
3.6
1.8
Se
2.0
Se
1.8
Se
b
Se
Se BONDING CHARGE
Upper bonding p-states
−3.60 eV < E < −2.25 eV
Se
4.1
3.6
1.8
6.3
Se
5.4
3.6
1.8
Se

Figure 2

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