Title
NEW INTERPRETATION OF PHOTOEMISSION MEASUREMENTS ON TRIGONAL Se AND Te

Permalink
https://escholarship.org/uc/item/5qz0j9hf

Authors
Schluter, M.
Joannopoulos, J.D.
Cohen, Marvin L.

Publication Date
1974-06-01
NEW INTERPRETATION OF PHOTOEMISSION MEASUREMENTS ON TRIGONAL Se AND Te

M. Schlüter, J. D. Joannopoulos and Marvin L. Cohen

June 1974

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

TWO-WEEK LOAN COPY
This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
New Interpretation of Photoemission Measurements on Trigonal Se and Te

M. Schlüter, † J. D. Joannopoulos and Marvin L. Cohen
Department of Physics, University of California, Berkeley, CA 94720
and
Inorganic Materials Research Division,
Lawrence Berkeley Laboratory, Berkeley, CA 94720

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.\textsuperscript{1} Recently the advent of new ultraviolet (UPS)\textsuperscript{2} and X-ray (XPS)\textsuperscript{2,3} photoemission measurements has provided important information about all the valence bands and has revealed some inadequacies of present theoretical calculations.\textsuperscript{4-6} In one of these calculations\textsuperscript{4} a complete merging of s- and p-like bands was proposed which disagrees qualitatively with the recent photoemission data. Other calculations\textsuperscript{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, \textit{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 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)\textsuperscript{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 Schervnchik 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 \( \lambda_o \) 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 \textit{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 \textit{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 $0.07 \, \text{e}^-$ for the intra-chain bond and $0.04 \, \text{e}^-$ for the inter-chain bond. It is instructive to compare these values with $0.05 \, \text{e}^-$ and $0.04 \, \text{e}^-$ 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

Part of this work was done under the auspices of the U.S. Atomic Energy Commission.
References

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

† Swiss National Science Foundation postdoctoral fellow.

1. J. Stuke, in The Physics of Se and Te, ed. by W. C.
2. N. J. Shevchik, J. Tejeda, M. Cardona and D. W. Langer,
3. J. D. Joannopoulos, M. Schlüter, M. L. Cohen, L. Ley,
   S. Kowalczyk, R. McFeeley and D. A. Shirley, to be
   published.
4. S. Tutihasi and I. Chen, Phys. Rev. 158, 623 (1967);
   B8, 5781 (1973).
7. M. Schlüter, J. D. Joannopoulos and M. L. Cohen, to
   be published.
   by H. Ehrenreich, F. Seitz and D. Turnbull (Academic,
   1973 Sanibel Symposium, to be published.
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.
Figure 1
Se BONDING CHARGE
Lower bonding p-states
$-6.0 \text{ eV} < E < -3.6 \text{ eV}$

Se BONDING CHARGE
Upper bonding p-states
$-3.6 \text{ eV} < E < -2.25 \text{ eV}$

Figure 2
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.