New Interpretation of the Soft-X-Ray Absorption Spectra of Several Alkali Halides*

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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 interchain and intrachain 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, bandwidths 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 Shevchik *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 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

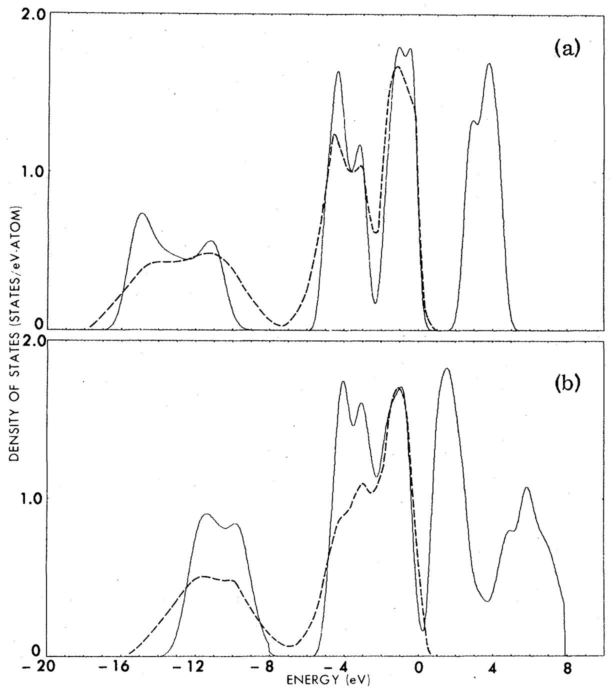

FIG. 1. Calculated densities of states (solid lines) for trigonal Se (a) and Te (b), which have been broadened by 1.2 eV for the *s*-like states and by 0.7 eV for the remaining states. Superimposed are the experimental photoemission spectra (dashed lines). The scales for the XPS and UPS curves are arbitrary.

the atomic s-like states of Se and Te. The next band contains p-like bonding states which lie between − 6.0 and − 2.2 eV for Se and for Te. Finally the topmost valence states are predominately nonbonding p-like in nature. These identifications are reconfirmed on our present calculations; moreover the widths, positions, and number of peaks in the densities of states are now in good quantitative agreement with experiment.

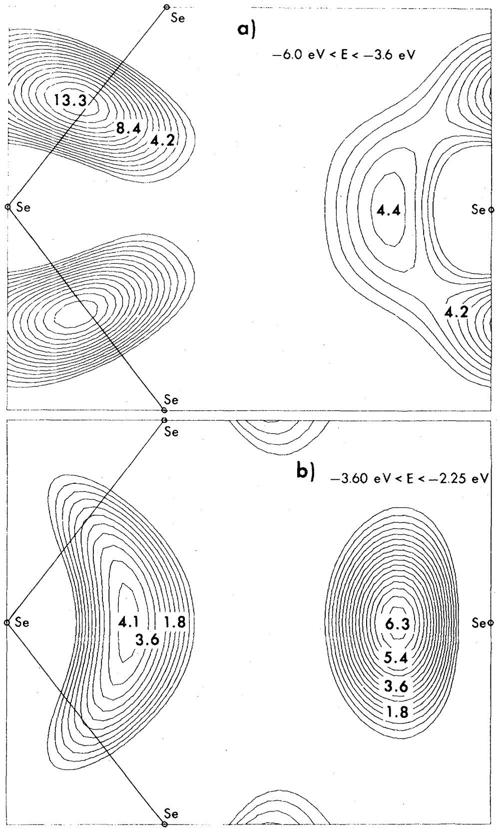

FIG. 2. Bonding charge of trigonal Se for the (a) lower and (b) upper p-like bonding states, calculated as described in the text. Only positive contours are shown, with values in units of e/Ω. The contour separation is 0.84 units in (a) and 0.36 units in (b).

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 following standard procedures.[10] 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_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 Figs. 2(a) and 2(b) for the energy intervals $[-6.0, -3.6]$ and $[-3.6, -2.25]$, respectively. This charge distribution reproduces just the localized parts of the total charge density in this energy range. 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 *intrachain 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 arise in part from hybridization and which contribute to the *interchain 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. 2(b)]. The charge found within the chains [left half of Fig. 2(b)] is a residual charge of the lower bonding p states. In fact both Figs. 2(a) and 2(b) show some residual charge, indicating that an absolute separation on the energy scale of the two types of states is impossible. The intrachain bonding states lie lower in energy than the interchain bonding states since the potential is strongest between neighboring atoms within a chain.

Some measure of intrachain versus interchain bonding strengths is given by the magnitude of the respective bonding charges. For Se we have found 0.07e for the intrachain bond and 0.04e for the interchain bond. It is instructive to compare these values with 0.05e and 0.04e for the intrachain and interchain bonds of Te, respectively. The ratio ξ of intrachain to interchain 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.

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Localized Enhancement Effects in Pd-Ag Alloys

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Low-temperature electrical resistivities of Pd-Ag alloys show a positive T^2 temperature dependence in the concentration range above 60 at.% Ag. This behavior supplements the well-known resistivity minima observed in alloys with lower concentrations of Ag, and strongly favors the model of scattering from localized exchange-enhanced Pd d states, as against $s \rightarrow d$ scattering in the rigid-, or collective-, band description of the alloys.

Two conflicting models for the electronic structure of Pd-Ag alloys are currently being advanced as possible explanations of the electrical resistivity behavior of these alloys. The resistivity minima observed by Edwards, Chen, and Legvold[1] in Pd-Ag alloys in the concentration range between 25 and 55 at.% Ag have been explained by the authors in terms of scattering of conduction electrons from exchange-enhanced pockets of holes associated with statistical clusters of Pd atoms—a distinction being made between the localized density of d states and the itinerant d band, also associated with Pd atoms. However, Rowlands and Greig[2] who observed similar minima in the Pd-Rh system found the calculated value of the coefficient A of the T^2 term in the resistivity of an alloy containing 4% Rh (obtained by using the rigid-band model[3] approximation as applied to the Pd-Ag system by Coles and Taylor[4]) to be very close to the experimental value, and therefore they argued in favor of the rigid-, or collective-, band description of the alloys. This assertion is further supported, it is now claimed, by some recent resistivity measurements on the Pd-Ag system by Ahmad and Greig,[5] who have observed two resistance minima in a $Pd_{0.60}Ag_{0.40}$ alloy, as also found in the Cu-Ni system.[6] These authors have put forward a qualitatively plausible explanation of the anomaly as due to a combination of two terms in the resistivity—a term $\rho_0(1 - AT^2)$ due to the reduction of $s \rightarrow d$ scattering cross section resulting from the broadening of the Fermi level within the d-band states,[4,7] and an ideal resistivity term $\rho_{\text{ideal}} \sim BT^2 + CT^4$ at low temperatures which changes to a term linear in T at higher temperatures, giving rise to the maximum in the resistivity which follows the first minimum at lower temperatures. The second minimum results since the low-temperature $1 - AT^2$ dependence is gradually modified and flattens off at high temperatures, as it must, leaving the linear term in the resistivity dominant. On the basis of this, the authors argue, the observed anomalies in the Pd-Ag and Cu-Ni systems may be regarded as caused by $s \rightarrow d$ scattering of conduction electrons into the d-band states.[4,7]

As suggested by Edwards, Chen, and Legvold,[1] of course, the $1 - AT^2$ term in the resistivity discussed above could equally well be obtained from the process of scattering of conduction electrons from exchange-enhanced localized pockets of