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Electronic States of Te above the High-Pressure Phase Transition

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A self-consistent pseudopotential band-structure calculation for the recently determined high-pressure (above 38 kbar) monoclinic tellurium structure is presented. The density of states and charge densities for representative regions within the unit cell are calculated. Our results show that high-pressure monoclinic tellurium is metallic, and that a crystal bond-length asymmetry is caused by an electronically driven distortion. The results also predict a highly anisotropic conductivity.

It has been known for many years that selenium and tellurium undergo structural phase transitions at about 140 and 48 kbar, respectively. Nevertheless, there has been much controversy[1-8] as to the mechanism and exact pressure of the transitions, and the stability and structures of the phases above the transitions. Recently, the structure of the high-pressure phase of Te seems to have been determined.[9] Above 38 kbar, the structure is slightly monoclinic ($\beta = 92.7°$), space group C_2^2, and characterized by a puckered layer structure with four atoms per unit cell, as shown in Fig. 1. To study the electronic structure and the nature of the bonding in this material, we have performed self-consistent pseudopotential calculations[10] with an orthorhombic ($\beta = 90°$) approximation to the unit cell. The band structure, density of states, and energy-specific charge densities are presented. Our results show that the material is metallic, and predict the conductivity will be highly anisotropic. Moreover, a bond-length asymmetry of the crystal is explained as an electronically driven distortion.

The results of our self-consistent pseudopotential calculations for the band structure and density of states are shown in Fig. 2, and energy-specific charge densities for the shaded planar regions of Fig. 1 are shown in Fig. 3. The density of states is large at the Fermi level, so that high-pressure Te is metallic, and there is a gap of about 1 electron volt between the lowest four bands, and the upper bands. Four bands cross the Fermi level from Γ to X, and no bands cross along Γ to Y or Γ to Z, indicating a highly anisotropic conductivity, with major conduction occur-

ring along the $\hat{x}$ axis.

Since the bonds formed by each Te atom and its four nearest neighbors lie along nearly mutually perpendicular axes, the electronic states are expected to separate into s-like states at each atomic site, and p-like states oriented along the bond axes. If so, many of the features of the band structure should be characteristic of bands
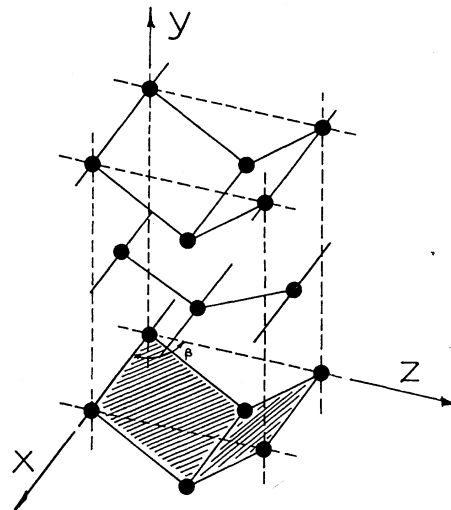

FIG. 1. Primitive cell for Te at 45 kbar, with $\beta = 90°$. The lattice constants are 3.104, 7.513, and 4.766 Å, along the x, y, and z directions, respectively. First– (2.80 Å) and third– (3.11 Å) nearest-neighbor bonds occur within the zigzag chains parallel to the y-z plane. Second– (3.10 Å) nearest-neighbor bonds occur within the linear chains parallel to the x axis. The shaded regions represent the regions for which the charge densities have been plotted.
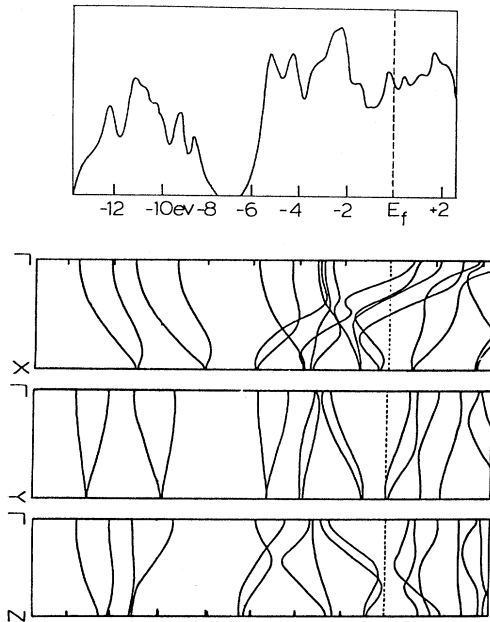
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FIG. 2. Density of states, and the band structure from Γ to X, Γ to Y, and Γ to Z.
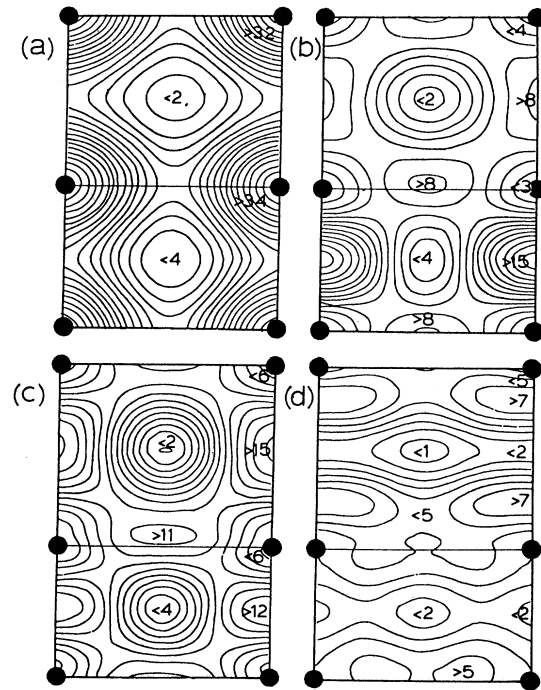

FIG. 3. Charge densities for different energy intervals, with $E_F = 0$ eV, for the shaded regions in Fig. 1. Measured in number of electrons per primitive cell. Charge density (a) between -16 and -7 eV, (b) between -7 and -4 eV, (c) between -4 and -1.5 eV, and (d) between -1.5 eV and E_F.

comprised of such states. For instance, four s-like bands would be expected, one for each atom in the unit cell, and these bands should be lowest in energy. Figure 3(a) shows the charge density for the lowest four bands. As expected, the charge is clustered about each atomic site, showing pronounced s-like behavior. Likewise, the states forming colinear bonds along the $\hat{x}$ axis should comprise four one-dimensional-like p bands. These bands should be almost flat from Γ to Y or Z, since the overlap between adjacent orbitals should be small in those directions. From Γ to X, these bands should decrease rapidly in energy, as the state configurations change from antibonding to bonding. Though mixing precludes bands comprised solely of these states, examination of the band structure from Γ to X (Fig. 2) shows this behavior for segments of several different bands. Four bands cross the Fermi level along this direction, decreasing rapidly in energy toward X. As these bands mix with lower bands, the lower bands assume their character, and, in turn, drop rapidly in energy toward X. The charge densities in Figs. 3(b), 3(c), and 3(d) show that the charge configuration in the orbitals along the $\hat{x}$ direction remains nearly constant over a wide range of energies, which would be expected for a linear chain of p-like states. Moreover, the slight antibonding

character seen in Fig. 3(d) along this direction indicates these orbitals are slightly more than half occupied.

The states comprising *each* of the other two orbitals should also form four p-like bands. These two orbitals join zigzag chains of atoms parallel to the y-z plane. Thus the states of *each* orbital should separate into two bonding and two antibonding bands. Since the two orbitals are associated with bonds of different lengths, the bonding-antibonding splitting will be greater for the shorter bond. From Γ to Y and Γ to Z in Fig. 2, the fifth through tenth lowest bands occur in three pairs, and can be identified as the short-bonding, long-bonding, and long-antibonding pair, respectively. Figure 3(b) shows the charge density for an energy interval encompassing primarily the lowest pair of bands, and the charge density between short bonds along the zigzag chain is twice that between other neighbors. Figure 3(c) contains mostly the charge density of the next lowest pair of bands, and the maximum density now occurs in the longer bond of the zigzag chain. Fin-

ally, Fig. 3(d) representing primarily the charge density for the highest occupied pair of bands, shows an abrupt change in the charge density of both orbitals in the zigzag chain, from bonding to antibonding character. We note, however, that the longer orbital is more fully occupied than the shorter one. This indicates clearly that the position of the Fermi level lies between the antibonding bands of these two orbitals.

All band identifications have been qualitative, because of the amount of band mixing and overlap present. However, the correspondence between the simple model of independent s-like and p-like states and the actual band structure is quite evident.

Just below the phase transition, the indications are that trigonal tellurium is very slightly semi-metallic with a very small pocket of holes at the H point.[11] Although such a Fermi surface might suggest mode softening for small phonon wave-vectors, no appreciable softening is observed.[9] To understand what structural rearrangements may be responsible for the phase transition, one must consider first that the transition can be accomplished without breaking any bonds! Under pressure, the helical chains of the tri-gonal phase can undergo a simple structural dis-tortion to alternate their helicity from one cell to the next along the $\vec{c}$ axis. This is easily accom-plished by rotating two atoms in alternating unit cells along the $\vec{c}$ axis by $\pi/3$. The resulting struc-ture is rather similar to the β-Po structure. Similar modifications to the helicity along the chains can be obtained if torsional phonon modes in the vicinity of the A–H–M plane of the Brillouin zone were getting soft. These modifications al-low the chains to flatten out in a zigzag pattern (as in the y–z plane of Fig. 1) under pressure. These chains can then bond together with neigh-boring chains and easily form the puckered layer structure shown in Fig. 1.

To understand why the zigzag bonds are of un-equal lengths in the actual crystal, we consider the following argument. If they were of equal length, and the peak in the density of states re-sulting from their antibonding bands lay within the broad energy range spanned by the states which comprise the orbitals of the linear chains along the $\hat{x}$ axis, the Fermi level would be con-strained to fall within the antibonding peak. In that case, the crystal would be subject to a Pei-erls-like distortion which breaks the symmetry of the bonds in the zigzag chains, and allows the bands of the (now) weaker bond to become more fully occupied than those of the stronger bond. Apparently, the bond-length asymmetry in high-pressure tellurium is precisely such a distortion. We also note that the different occupancies of the antibonding bands predict a difference in the force constants of the two bonds that is significantly larger than that expected solely from the length disparity, and a resulting large frequency gap be-tween the branches of the phonon spectrum from Γ to Z.

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