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Augmented-Plane-Wave Calculation of Energy Bands in Simple Cubic Tellurium[†]

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Augmented-plane-wave energy-band calculations have been performed for Te having a hypothetical simple cubic crystal structure whose lattice spacing is based on extrapolation of experimental results in the metastable Te-Au and Te-Ag systems. The eigenvalues, calculated along five axes of high symmetry, indicate that simple cubic Te is expected to be metallic, and to have a relatively high density of states at the Fermi surface. The properties deduced from the band structure are compared with those of the high-pressure phases of Te and are found to be similar to those of the phase which exists between 40 and 70 kbar at room temperature.

I. INTRODUCTION

The simple cubic crystal structure, although discussed extensively in many textbooks, occurs quite rarely in nature. With the exception of one allotropic form of Po, this structure does not exist in any known equilibrium elements or alloys. However, since the advent of rapid quenching from the liquid state, metastable simple cubic phases have been observed in several alloy systems, the most interesting of which are based on Te.[1,2] It is possible in the binary alloys Te-Au and Te-Ag to produce a single-phase simple cubic alloy over a wide range of compositions extending as high as 85-at.% Te. The proximity of the high end of this range to pure Te suggests that the band structure of hypothetical simple cubic Te should be of some interest. The only unknown parameter required to perform augmented-plane-wave (APW) calculations of this type is an appropriate lattice spacing, and a reasonable value for this may be obtained by extrapolation of the Te-Au and Te-Ag experimental data.

Additional interest in these particular calculations is provided by the existence of several high-pressure phases of Te with properties quite different from those of hexagonal Te. Several investigations[3-7] have shown that Te undergoes phase transitions at room temperature around 40 and 70 kbar, proceeding from the *A*8 selenium structure to an unidentified structure and finally to a simple rhombohedral arrangement isomorphic with β-polonium. The unidentified phase existing between 40 and 70 kbar has been found by Bridgman[8] and others[9] to be metallic, and Matthias[10] has discovered that it is also superconducting with a transition temperature of 3.3 °K. Jamieson and McWhan[7] have shown that if a simple cubic phase of Te exists it should occur in this pressure range and in a region below room temperature. Although their x-ray diffraction data and that of Kabalkina *et al.*[11] definitely cannot be indexed to a simple cubic pattern, Mössbauer studies[12] show the absence of a quadrupole moment above 40 kbar, indicating that this phase could be related to a distorted simple cubic structure. With this possibility in mind, it is of additional interest to compare properties deduced from the simple cubic band structure with those observed in the high-pressure phases.

II. APW TECHNIQUE

The method used to perform the APW calculations is basically that of Loucks,[13] with minor modifications to allow compatibility with the computing system and the particular form of the input data. The muffin-tin potential was constructed starting from the atomic wave functions for neutral Te calculated by Herman and Skillman.[14] The appropriate Coulombic and exchange contributions were then determined using Poisson's equation, Slater's free-electron exchange approximation, and considering spherically symmetric contributions from the closest 14 shells of atoms as described in

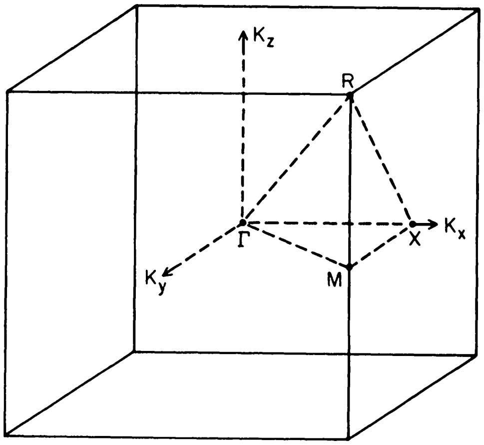

FIG. 1. First Brillouin zone for the simple cubic structure.

Chap. 3 of Ref. 13. The value of the potential to be used between APW spheres was determined by averaging the potential described above over the region between the APW sphere, and a sphere whose volume was that of the Wigner-Seitz unit cell. The entire energy scale was then shifted in the usual manner to cause this average potential to be zero.

The choice of an APW sphere radius and the actual numerical construction of the potential are dependent on finding an appropriate value of lattice spacing for simple cubic Te. Extrapolation of the Te-Au and Te-Ag experimental data[1,2] predicts values of 3.17 and 3.08 Å, respectively. Another type of prediction may be obtained based on the assumption that the structure above 40 kbar has approximately the same atomic volume as the simple cubic structure would have. If the 5.5% volume reduction which Bridgeman has found at 40 kbar[3] is applied to the volume per atom of normal Te, the resulting volume is 32.11 Å^3/atom. The equivalent simple cubic lattice spacing for this atomic volume is 3.18 Å, which is in close agreement with the value obtained by extrapolating the Te-Au data. Considering the above, the value of 3.17 Å was chosen to determine the complete band structure, and calculations using 3.08 Å were performed only at the symmetry points for comparison with the other values. The same size APW sphere radius was used for calculations with both lattice parameters, and was chosen to be 1.38 Å, a value slightly less than one-half of the smaller lattice spacing.

The set of reciprocal lattice vectors to be used in expanding the APW wave functions was selected by requiring convergence of the energy eigenvalues at each of the symmetry points to 0.005 Ry. To

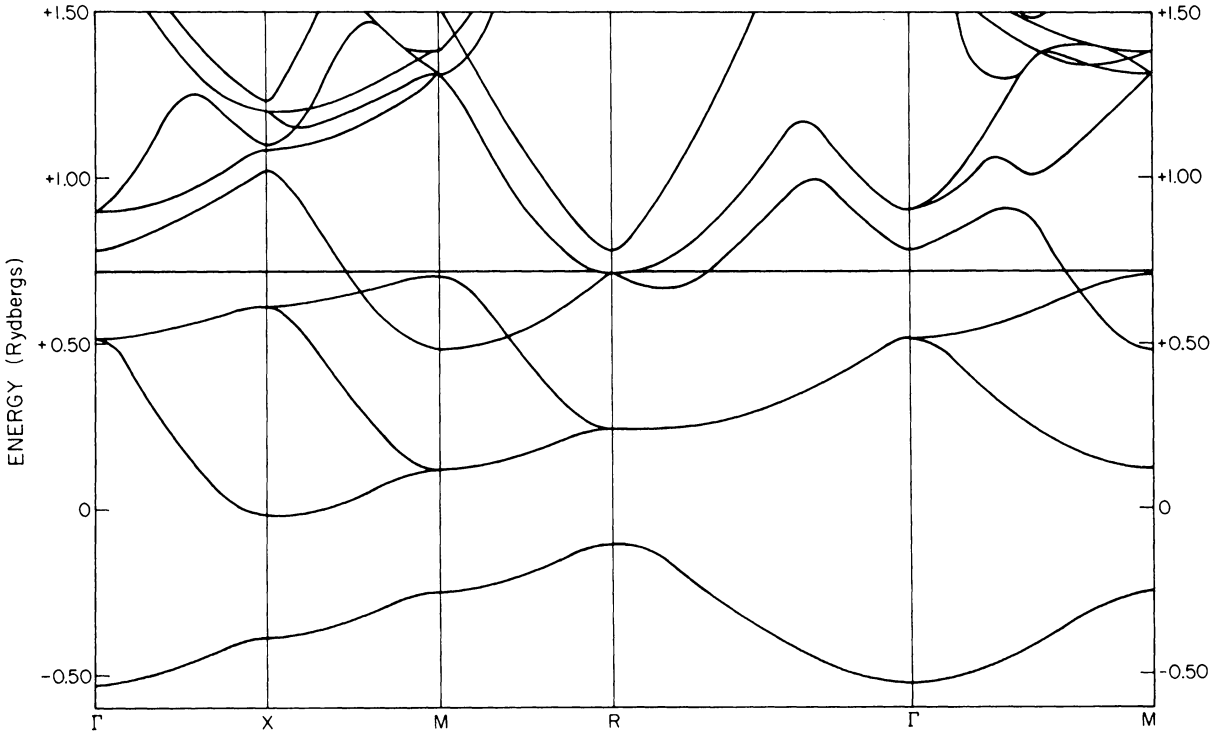

FIG. 2. Energy bands along the five segments joining the symmetry points for a = 3.18 Å (all energies are shifted up by 0.821 Ry).

TABLE I. Energy eigenvalues are shown below at the four symmetry points for both values of lattice spacing. Those values associated with $a = 3.17$ Å are shifted up by 0.821 Ry and those for 3.08 Å by 0.870 Ry.

Symmetry points	Energy (3.17 Å)	Energy (3.08 Å)
Γ	−0.53	−0.52
	+0.51 (3)	+0.59 (3)
	+0.72	+0.77
	+0.78	+0.88
	+0.90 (2)	+0.96 (2)
X	−0.39	−0.35
	−0.02	−0.01
	+0.61 (2)	+0.71 (2)
	+0.72	+0.77
	+1.02	+1.10
	+1.08	+1.15
	+1.10	+1.22
	+1.20 (2)	+1.27 (2)
	+1.23	+1.30
M	−0.25	−0.18
	+0.12 (2)	+0.15 (2)
	+0.48	+0.51
	+0.70	+0.82
	+0.72	+0.77
	+1.31 (3)	+1.40 (2)
		+1.43
	+1.38 (2)	+1.47 (2)
R	−0.11	−0.01
	+0.24 (3)	+0.29 (3)
	+0.71 (3)	+0.77 (3)
	+0.78	+0.75

achieve this degree of convergence required the use of 32 reciprocal-lattice vectors, and it was decided that the effort required to realize the usual degree of convergence (0.001 − 0.002 Ry) was not feasible in this case. The calculation of individual eigenvalues was carried to a final accuracy of 0.01 Ry.

III. RESULTS AND DISCUSSION

Although the construction of the first Brillouin zone for the simple cubic lattice is probably familiar to anyone interested in solid-state physics, this zone is illustrated in Fig. 1 in order that there be no confusion concerning identification of the symmetry points. The energy-band structure for the five segments joining the symmetry points is shown in Fig. 2, and the comparison of energy eigenvalues at the symmetry points for the two values of lattice spacing is shown in Table I. The information in this table shows that as the lattice spacing becomes smaller, all the eigenvalues are shifted up by amounts ≤ 0.1 Ry. Although the shifting is not uniform, it is small enough so that the statements to be made concerning the band structure at 3.17 Å are probably also true for 3.07 Å. It is clear after examination of Fig. 2 that the lower bands can be identified as having had their origin from 5*s* or 5*p* atomic orbitals. Band 1 may be considered to have 5*s* origin, and the particular degeneracies of bands 2, 3, and 4 along various symmetry axes are quite suggestive of the directional characteristics of atomic *p* states. Following this same pattern, bands 5–8 may be loosely regarded as associated with the atomic 5*d* orbitals, although any correlation becomes less distinctive as energy increases.

Probably the most obvious conclusion to be drawn from these calculations is in regard to electrical properties. Even without determining the density of states it is possible to predict that the material associated with this band structure would be a metallic conductor. Since Te has six electrons which must be considered in bands shown, semiconducting properties would result only if the highest eigenvalue associated with band 3 were lower than the lowest eigenvalue associated with band 4, as occurs in normal hexagonal Te. The degeneracies along the $\Gamma \rightarrow X$, $\Gamma \rightarrow M$, and $\Gamma \rightarrow R$ directions clearly prohibit this possibility, and, in fact, it can be seen that the three *p* bands (2, 3, and 4) almost completely overlap each other. In addition, nonwithstanding the degeneracies in bands 2, 3, and 4, the large dip in band 6 in the $\Gamma \rightarrow M$ direction would be sufficient to ensure that the density of states was nonzero between bands 3 and 4.

Without calculating the eigenvalues over the entire first Brillouin zone and determining the electronic density of states as a function of energy, it is impossible in a metallic conductor to determine the theoretical Fermi energy. It is, however, possible to approximate a region within which the Fermi energy falls, and to consider the mean density of states averaged over a region including several energy bands. In this case it is known that the Fermi energy must fall below the highest point in band 3 and above the lowest point in band 4. This implies that E_F must fall in the region $0.25 < E_F < 0.60$ Ry. (All energies are shifted up by 0.821 Ry.) A more detailed examination of the variation of $E(\vec{k})$ indicates that the lower limit of this region can probably be raised to ~0.40 Ry. Assuming that the extreme values of energy for bands 2, 3, and 4 lie at the symmetry points, the mean density of states for these bands can be calculated from the energy range in which they are confined. The extreme values of energy of interest here are found for bands 2 and 4 at the symmetry point *X*. Bands 2, 3, and 4, representing six electron states per atom, are confined to ~0.7 Ry, resulting in a mean density of states of ~9 electron states/atom/Ry. Again, examination of the variation of $E(\vec{k})$ indicates that the largest number of eigenstates are probably contained between 0.3 and

0.6 Ry, implying that the density of states in this region, hence also in the region of the Fermi surface, may be of the order of ~12–15 electron states/atom/Ry. Although in no way certain, these figures should provide a very crude idea of the density of states around the Fermi surface.

The central reason for obtaining this rough value of density of states at the Fermi surface is to attempt to decide if this particular material might reasonably be expected to be superconducting. Comparison with calculations by Burdick[15] and Mattheiss[16] show that $N(E_F)$ for simple cubic Te is about three or four times larger than $N(E_F)$ for a metal like Cu, and about 50 to 60% as large as $N(E_F)$ for most of the β-tungsten ($A15$) superconductors. According to the theory of Bardeen, Cooper, and Schrieffer,[17] the transition temperature of a superconductor depends primarily on the product of $N(E_F)$ and V, where V is the phonon mediated attractive electron pair potential. Several investigators have proposed that the orthogonal chain structure found in the β-tungsten arrangement is at least partially responsible for the phonon coupling which causes V to be positive,[18] and Weger[19] has attempted to show that these chains are also responsible for the high $N(E_F)$ found in β-tungsten compounds. The simple cubic structure also has three orthogonal chains of atoms, although they are not packed as close together as the atoms in a β-tungsten chain. Considering these factors [the relatively high $N(E_F)$ and the chain structure], the Te simple cubic structure might be regarded as being favorable to superconductivity in the same manner as the β-tungsten structure, although not to the same degree. It is not unreasonable then to expect that simple cubic Te might be superconducting although certainly not in as high a temperature range as the $A15$ superconductors.

IV. CONCLUSIONS

The band structure of hypothetical simple cubic Te predicts electrical properties quite different from those of normal Te. Comparison of the metallic conductivity and the possibility of a superconducting transition with the observed properties of the phase of Te which forms at 40 kbar suggests that the structure of this phase may be more closely related to the simple cubic lattice than a cursory examination of the x-ray data indicates. Whether a true simple cubic phase exists in this pressure range at lower temperatures, or the $A8$ structure goes directly to the simple rhombohedral configuration remains an interesting but unsolved problem.

The probability of a relatively high density of states in the region of the Fermi surface has in itself some interesting implications. If this could be shown to be a property of the simple cubic structure itself, and not just simple cubic Te, then this, combined with the orthogonal chains mentioned previously, could make the simple cubic structure in general rather favorable to superconductivity. Indeed, this possibility would be very consistent with the growing number of metastable simple cubic phases which are found to be superconducting in the range of 1–7 °K.

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