A Theoretical and Experimental Study of the Electronic Transport Properties of the Compounds Cu_2MTe_3 (M = Ti, Zr, Hf)

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A theoretical model that involves metal nonstoichiometry is proposed to explain the unexpected electronic conductivities in the close-packed ternary tellurides Cu_2MTe_3 (M = Ti, Zr, Hf). Conductivity, thermoelectric power, and Hall effect measurements indicate that these compounds are hole carriers with a concentration of the order of 5×10^{19} cm^{-3} for M = Zr at 300 K. Such a concentration corresponds to roughly 0.4% Cu vacancies or 0.2% Zr vacancies, levels below the detection limit by X-ray diffraction methods of the corresponding elements in the M = Hf compound. © 1992 Academic Press, Inc.

Introduction

Recently the synthesis of the new close-packed ternary tellurides Cu_2MTe_3 (M = Ti, Zr, Hf) was described, along with the structure for M = Hf (*1*). The coordination polyhedra about the metals in Cu_2HfTe_3 as well as the long $Te \cdots Te$ separations ($Te \cdots Te \geq 3.711(1)$ Å) suggest that this compound may be formulated as $Cu_2^I Hf^{IV} Te_3^{II-}$, a closed-shell system that one would expect to exhibit insulating or semi-

conducting properties. From unit cell dimensions the three compounds Cu_2MTe_3, M = Ti, Zr, Hf, appear to be isostructural. Surprisingly, all three compounds are metallic, exhibiting room temperature resistivities of 9.0×10^{-4} Ω cm, 7.0×10^{-3} Ω cm (vide infra), and 3.8×10^{-4} Ω cm (*1*), respectively, and positive slopes in their resistivity versus temperature curves. Additionally, from magnetic susceptibility measurements Cu_2ZrTe_3 is a Pauli paramagnet, with $\chi = 3.5 \times 10^{-4}$ emu mol^{-1} (*1*), a signa-

ture of metallic behavior that we would expect to find in the Ti and Hf analogues as well.

In this paper we describe the results of extended Hückel (2, 3) band-structure calculations on Cu_2ZrTe_3; these calculations suggest that nonstoichiometry could play an important role in determining the unexpected transport properties. We also describe the measurements of additional transport properties and the additional refinements of the X-ray diffraction data for Cu_2HfTe_3 that were engendered by these calculations. The physical measurements confirm metallic behavior in these compounds and indicate p-type conduction, consistent with nonstoichiometry in the form of metal deficiencies, as suggested by the theoretical calculations, but such deficiencies cannot be detected from the X-ray diffraction data.

Experimental

Transport properties. Thermoelectric power data were obtained for the three compounds Cu_2MTe_3, M = Ti, Zr, Hf, over the temperature range 80 to 320 K, four-probe dc resistivity measurements for M = Ti and Zr were made from 5 to 300 K, and the Hall coefficient was determined at room temperature for M = Zr. A computer automated measurement system (4, 5) was employed to obtain thermopower and resistivity data with both the current and thermal gradient applied along the crystallographic b-axis (the needle axis). For all measurements and all materials, electrode connections to the small single crystals (typical dimensions 0.18 mm by 0.18 mm by 1.0 mm) were made with the use of 25- and 60-μm gold wires and gold bonding paste. A five-probe configuration was used for the Hall measurement to avoid geometrical alignment errors (6). The usual signal averaging technique for sensing current and magnetic field directions was

employed; the magnetic field strength was 0.8 T.

Crystallographic calculations. The crystal-structure determination of Cu_2HfTe_3 (1) was carried out on 1509 unique diffraction data collected at 111 K. The original refinement (20 variables) of a stoichiometric model involving isotropic thermal motion of the atoms converged to a value of $R(F^2)$ of 0.048 and to a value of $R(F)$ of 0.034 for the 1426 reflections having $F_0^2 \geq 3\sigma(F_0^2)$. Because the material is highly absorbing the original refinement was terminated at the isotropic stage. A more extensive refinement of the X-ray diffraction data for Cu_2HfTe_3 was performed with the aim of detecting possible nonstoichiometry suggested by the theoretical calculations. First, the six independent atoms in the stoichiometric model were allowed to vibrate anisotropically. The anisotropically refined model resulted in nearly spherical ellipsoids for all six atoms (Table I) and no significant improvement in $R(F^2)$. Next, a series of refinements was carried out for both the isotropic and anisotropic models in which site occupancies were included as additional variables. Since it is mathematically impossible to vary all site occupancies simultaneously, several different models were refined. In refinement A, the Hf site occupancy was fixed at 1.00 and the site occupancies of atoms Cu(1), Cu(2), Te(1), Te(2), and Te(3) were varied (Table IIA). In refinement B (Table IIB) the site occupancies of the three Te atoms were fixed at 1.00 and those of Cu and Hf were varied. In refinement C (Table IIC), the site occupancies of the two Cu atoms were fixed at 1.00, and those of Hf and Te were varied.

Results and Discussion

Our band-structure calculations on Cu_2Zr Te_3 are summarized in Fig. 1, which shows the density of states (DOS) and its Cu and Zr projections. Details of the band-structure

TABLE I

ANISOTROPIC THERMAL PARAMETERS FOR Cu_2HfTe_3

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hf(1)	0.00596(11)	0.00662(12)	0.00602(11)	0	0.001211(67)	0
Te(1)	0.00499(14)	0.00538(16)	0.00485(14)	0	0.00106(10)	0
Te(2)	0.00588(14)	0.00654(16)	0.00531(14)	0	0.00135(10)	0
Te(3)	0.00562(14)	0.00602(16)	0.00539(14)	0	0.000652(98)	0
Cu(1)	0.00821(27)	0.00896(33)	0.00667(27)	0	−0.00020(21)	0
Cu(2)	0.00752(26)	0.00842(33)	0.00685(27)	0	0.00106(21)	0

calculations are given in the Appendix. As anticipated, an energy gap of approximately 1.2 eV lies between the top of the largely Te $5p$ valence band and the bottom of the conduction band, which is almost entirely of Zr d character. Admittedly, our method of calculation may overestimate this band gap, and the possibility of a semimetal cannot be discounted out of hand. As expected from the long Te$\cdots$Te contacts, there is no

TABLE II

REFINEMENTS

Atom	Multiplicity old	Multiplicity isotropic	Multiplicity anisotropic
Refinement A: Te and Cu occupancies			
Te(1)	1.00	1.038(3)	1.041(3)
Te(2)	1.00	1.035(3)	1.038(3)
Te(3)	1.00	1.038(3)	1.040(3)
Cu(1)	1.00	1.013(5)	1.016(4)
Cu(2)	1.00	1.024(4)	1.027(4)
$R(F^2)$		0.048	0.045
Refinement B: Hf and Cu occupancies			
Hf	1.00	0.963(2)	0.962(2)
Cu(1)	1.00	0.977(5)	0.978(4)
Cu(2)	1.00	0.989(4)	0.988(4)
$R(F^2)$		0.048	0.045
Refinement C: Hf and Te occupancies			
Hf	1.00	0.981(3)	0.980(3)
Te(1)	1.00	1.019(4)	1.018(4)
Te(2)	1.00	1.016(4)	1.015(3)
Te(3)	1.00	1.019(4)	1.018(4)
$R(F^2)$		0.048	0.045

evidence of significant Te$\cdots$Te interactions, which would destabilize the top of the valence band. Indeed, sufficient interactions could conceivably push a Te–Te antibonding band above the bottom of the Zr d band, partially occupying this Zr band with electrons to yield a metal. In the present case, the Te atoms are too weakly interacting for this to occur. With the Fermi level in this gap, Cu formally has 10 electrons and Zr none, justifying the assignment Cu^I, Zr^{IV} and Te^{II-}. There is ample evidence (7–12) from structural and XPS results that copper chalcogenides almost invariably contain exclusively Cu^I, regardless of what their stoichiometries might suggest. As the DOS in Fig. 1 demonstrates, our band-structure calculation supports this view, the top of the valence band being almost entirely Te based. Thus, any small concentration of holes in this band would be predominantly Te based; Cu remains formally Cu^I.

We now consider two possible schemes for nonstoichiometry and their effects on the calculated band structure: Te vacancies or Cu vacancies. In each case, we find that a rigid-band model describes the behavior of the system remarkably well. Such a rigid-band picture would place two electrons into the conduction band for each Te vacancy formed in the lattice, producing an n-type conductor. To mimic this type of vacancy, we have calculated the band structure of a supercell doubled along the b-axis of Cu_2Zr Te_3, removing one Te atom from the center
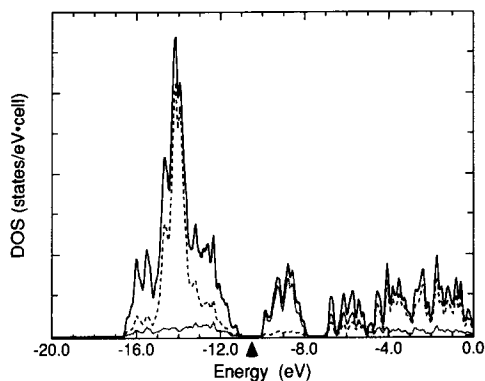
FIG. 1. Calculated density of states (DOS) for stoichiometric Cu_2ZrTe_3. Solid line, total DOS; dashed line, Cu projection; dotted line, Zr projection. The Fermi level is indicated by an arrow.

of the supercell (Te vacancy concentration ~4%). The choice of this vacancy concentration is dictated by computational economy rather than the experimental results. Indeed, as indicated below, the transport data indicate carrier concentrations attributable to roughly 0.4% Cu vacancies (or 0.2% Zr vacancies), requiring for Cu vacancies a supercell ten times the size of our model calculation. Nonetheless, the qualitative results of our model would certainly remain unchanged were we to do a calculation on such a large cell or were we to consider Zr vacancies rather than Cu vacancies. The top panel of Fig. 2 shows the DOS for our model system. Comparison with Fig. 1 shows that the Te vacancy has disturbed the electronic structure only slightly, while a Fermi level of -10.1 eV, slightly above the bottom of the conduction band, corroborates the rigid-band model. Again within the rigid-band picture, each copper vacancy removes one electron from the top of the valence band, producing a p-type conductor. When we remove one Cu atom from the same supercell as above (Cu vacancy concentration ~6%), we obtain the band-structure picture in the bottom panel of Fig. 2. As expected from rigid-band considerations, the DOS matches

well with that of the stoichiometric compound, the Fermi level dropping slightly into the valence band ($E_f = -11.3$ eV) to produce a p-type metal. Clearly, the nature of the carriers distinguishes between these two vacancy mechanisms—Te vacancies yield electron carriers, while metal vacancies produce hole carriers. We now discuss the results of physical measurements that were engendered by these calculations.

Electrical resistivity (ρ) and thermoelectric power (S) data for typical samples of Cu_2ZrTe_3 are shown in Fig. 3. These transport data are fairly typical of metallic behavior. The resistivity is less than 8 mΩ cm for temperatures below 320 K, and $d\rho/dT$ is positive down to 10 K. The thermopower values are positive, increasing from 4 $\mu V/K$ at 80 K to 15 $\mu V/K$ at 320 K. In general, the electronic transport properties of the other compounds ($M =$ Ti, Hf) follow the same pattern and are within an order of magnitude of those for $M =$ Zr, as summa-
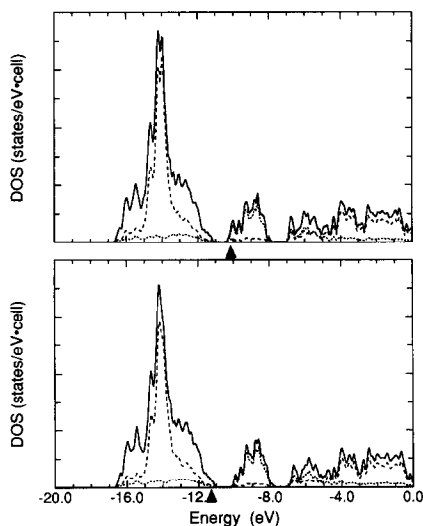

FIG. 2. Calculated density of states (DOS) for model vacancy structures. Top, Te vacancy; Bottom, Cu vacancy. Solid line, total DOS; dashed line, Cu projection; dotted line, Zr projection. The Fermi level is indicated by an arrow.
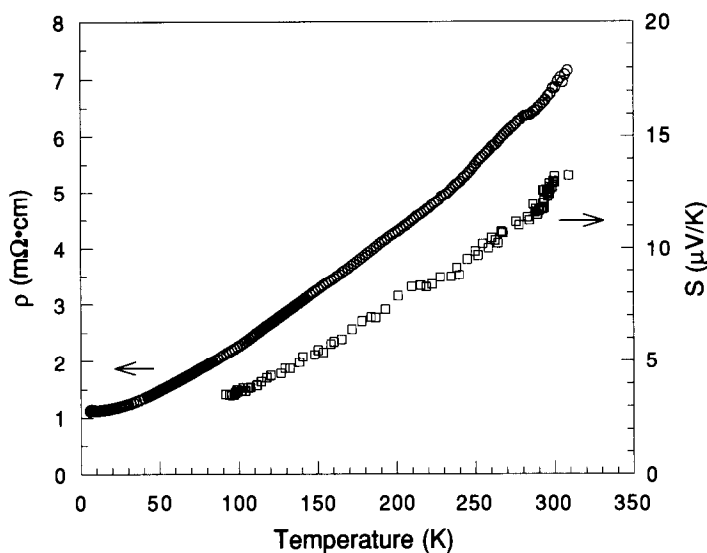
FIG. 3. Variable temperature resistivity and thermopower data for a single crystal of Cu$_2$ZrTe$_3$.

rized in Table III. The sign of the Hall coefficient (R_H) for Cu$_2$ZrTe$_3$ is positive, in agreement with the thermoelectric power. A single-band, single-carrier model was used to determine the carrier concentration (p) and Hall mobility (μ_H). The value of μ_H falls within the range exhibited by many metallic conductors. The positive Seebeck coefficient clearly indicates hole conductivity for these compounds, and the Hall coefficient corroborates this for Cu$_2$ZrTe$_3$. These results definitely rule out a Te-vacancy model but are consistent with a metal-vacancy model. The carrier concentration corresponds to roughly 0.4% Cu vacancies or 0.2% Zr vacancies. Some copper chalcogenides exhibit copper deficiencies and are fast-ion conductors, e.g., Cu$_{2-x}$S,Cu$_{2-x}$Se (13). However, the positive slope of the resistivity versus temperature curve for the present compounds argues for electronic conduction rather than activated ionic conduction. Finally, we note that excess Te in the lattice would also lead to p-type conduction, and such a possibility cannot be ruled out on the basis of our calculations alone. Because of the close-packed nature of the structures, excess Te seems unlikely, for there are no obvious sites to be occupied.

We now turn to the question of whether

TABLE III

ELECTRONIC TRANSPORT DATA FOR Cu$_2M$Te$_3$, M = Ti, Zr, Hf

Compound	ρ(100 K) (mΩ cm)	ρ(300 K) (mΩ cm)	S (100 K) (μV/K)	S (300 K) (μV/K)	R_H (300 K) (cm^3/C)	μ_H (300 K) (cm^2/V sec)	p (300 K) (cm^{-3})
Cu$_2$TiTe$_3$	0.4	0.9	12	30	—	—	—
Cu$_2$ZrTe$_3$	2.2	7	3.5	13	0.2	30	5 × 10^{19}
Cu$_2$HfTe$_3$	0.25^a	0.38^a	20	50	—	—	—

^{a} These values were obtained from ac resistivity measurements (1).

possible metal vacancies can be detected from the X-ray diffraction data on $Cu_2Hf Te_3$. As the results summarized in Table II indicate the resultant site occupancies do not differ significantly between the isotropic and anisotropic models. Refinements A, B, and C of the anisotropically refined structure result in the formulations $Cu_{2.043(4)} Hf_{1.00}Te_{3.119(3)}$, $Cu_{1.966(4)}Hf_{0.962(2)}Te_{3.00}$, and $Cu_{2.00}Hf_{0.980(3)}Te_{3.051(4)}$, respectively. All three formulations are consistent with p-type conduction. But it is evident that the three different refinements are inconsistent. For example, Refinement A affords an average Cu occupancy of ≈ 1.022 while in Refinement B this value is ≈ 0.983. However, the atomic ratios are reasonably consistent among the three models, with Cu/Hf being about 2.040, Cu/Te being 0.655, and Hf/Te being 0.322. If one takes these results at face value then there is the suggestion of Cu and especially of Hf deficiency in Cu_2HfTe_3. However, the inconsistencies among the three refinements noted above and the fact that $R(F^2)$ is insignificantly changed as we refine occupancies indicate that these X-ray data are not adequately sensitive for the detection of possible nonstoichiometry. At possible vacancies of roughly 0.4% Cu or 0.2% Hf, as deduced from the carrier concentration in Cu_2ZrTe_3, this is not a surprising result.

But note that the X-ray data do not preclude the presence of nonstoichiometry at the levels deduced from the transport data for Cu_2ZrTe_3, and nonstoichiometry at these small levels in a number of high-temperature superconducting cuprates (14) dramatically affects their transport properties. Thus, the theoretical prediction that nonstoichiometry is responsible for the transport properties in Cu_2MTe_3 is an appealing one, much more so than postulating the presence of the same, undetected impurity at roughly the same concentration in all three compounds. Moreover, the presence of Cu deficiencies in $Cu_{1.85}Zr_2Te_6$ (15), a sec-ond phase in the synthesis of Cu_2ZrTe_3, lends further credence to our argument.

Appendix

Band-structure calculations. The one-electron band structure of Cu_2ZrTe_3 was calculated from the tight-binding method with an extended Hückel-type Hamiltonian (2, 3). As the structure of the Zr analogue has not been determined, the coordinates of the Hf analogue (1) were used. The similar atomic radii and stereochemical behavior of Hf and Zr suggest that this is a reasonable approximation. The parameters used are as follows: Cu, $4s$: $H_{ii} = -11.4$ eV, $\zeta = 2.20$; $4p$: $H_{ii} = -6.06$ eV, $\zeta = 2.20$; $3d$: $H_{ii} = -14.0$ eV, $\zeta_1 = 5.95$, $c_1 = 0.59332$, $\zeta_2 = 2.30$, $c_2 = 0.57442$. Zr, $5s$: $H_{ii} = -8.0$ eV, $\zeta = 1.817$; $5p$: $H_{ii} = -5.4$ eV, $\zeta = 1.776$; $5d$: $H_{ii} = -10.2$ eV, $\zeta_1 = 3.835$, $c_1 = 0.62242$, $\zeta_2 = 1.505$, $c_2 = 0.57822$. Te, $5s$: $H_{ii} = -20.8$ eV, $\zeta = 2.51$; $5p$: $H_{ii} = -13.2$ eV, $\zeta = 2.16$.

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