80 *J. Am. Chem. Soc.* **2000,** *122,* 80−86

Syntheses, Structures, Physical Properties, and Theoretical Study of $LaCu_{0.40}Te_2$, $NdCu_{0.37}Te_2$, $SmCu_{0.34}Te_2$, $GdCu_{0.33}Te_2$, and $DyCu_{0.32}Te_2$

Fu Qiang Huang,[†] Paul Brazis,[‡] Carl R. Kannewurf,[‡] and James A. Ibers*,[†]

Contribution from the Department of Chemistry and Department of Electrical and Computer Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208

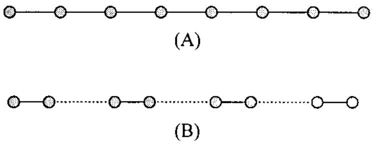
Received June 11, 1999

Abstract: Five rare-earth copper tellurides have been synthesized by the reactions of the elements at 1073 K. The isostructural compounds $LaCu_{0.40}Te_2$ ($a = 7.7063(13)$ Å, $b = 8.5882(14)$ Å, $c = 6.3115(10)$ Å, $T = 153$ K), $NdCu_{0.37}Te_2$ ($a = 7.6349(7)$ Å, $b = 8.3980(8)$ Å, $c = 6.18388(6)$ Å, $T = 153$ K), $SmCu_{0.34}Te_2$ ($a = 7.6003(10)$ Å, $b = 8.3085(11)$ Å, $c = 6.1412(8)$ Å, $T = 153$ K), $GdCu_{0.33}Te_2$ ($a = 7.5670(15)$ Å, $b = 8.2110(16)$ Å, $c = 6.0893(12)$ Å, $T = 107$ K), and $DyCu_{0.32}Te_2$ ($a = 7.5278(13)$ Å, $b = 8.1269(14)$ Å, $c = 6.0546(11)$ Å, $T = 107$ K) crystallize with four formula units in space group D_{2h}^{11}-*Pbcm* of the orthorhombic system. In each, the rare-earth (*Ln*) atom is coordinated by a bicapped trigonal prism of Te atoms and the Cu atom is coordinated by a tetrahedron of Te atoms. Infinite linear $Te^{(1+x)-}$ chains run parallel to *c*, with Te−Te distances decreasing from 3.1558(5) Å in $LaCu_{0.40}Te_2$ to 3.0273(3) Å in $DyCu_{0.32}Te_2$. Both the thermopower and conductivity data in the *c* direction show $LaCu_{0.40}Te_2$ to be a semiconductor at all temperatures, and $NdCu_{0.37}Te_2$, $SmCu_{0.34}Te_2$, and $GdCu_{0.33}Te_2$ to be semiconductors above 150−200 K. The thermopower data for these three compounds exhibit very high peaks of approximately 900 μV/K in the vicinity of 150 K, followed by a rapid decrease at lower temperatures. This behavior deviates from the trend expected for semiconductors. Hückel calculations predict that the $Te^{(1+x)-}$ chains in $LnCu_xTe_2$ should show metallic properties. Possible reasons for this discrepancy between theory and experiment involve distortions of the Te chains or disorder of the Cu atoms. $GdCu_{0.33}Te_2$ is paramagnetic with $\mu_{eff} = 7.74(3)\ \mu_B$, typical for Gd^{3+}.

Introduction

The study of low-dimensionsal solids is a central one in solid-state chemistry.[1,2] Such solids exhibit interesting physical properties, including superconductivity and charge density waves.[3−5] Coupled electronic lattice instabilities, such as charge density waves, are an important facet of structural stability in solids. A subgroup of low-dimensional solids is one in which there are one-dimensional chains of closely spaced atoms. Such systems display a variety of specific physical phenomena. These very simple systems are especially attractive because chemical correlations between structure and properties are more easily arrived at than in more complex topologies.[6]

Scheme 1



Two types of one-dimensional chains are illustrated in Scheme 1.[7] In part A the atoms are equally spaced and if they are from the main group then there is only a single σ and a single π band. As a result there is no band gap and the chain is metallic. Part B of Scheme 1 illustrates a common distortion that occurs in such systems wherein dimers are formed.[8−15] More complicated distortions of part A occur; these take the form of charge density waves. All such distortions open up a band gap at the Fermi level and the resultant chain is now insulating. Such distortions are favored and thus chains of equally spaced main group atoms are found infrequently in solid-state chemistry. The few known examples include $CsTiUTe_5$,[16] $Dy_3Cu_2Te_7$,[7] and $LaCu_{0.28}Te_2$.[17,18] Conductivity measurements

---

[†] Department of Chemistry.

[‡] Department of Electrical and Computer Engineering.

(1) Rouxel, J., Ed. *Crystal Chemistry and Properties of Materials with Quasi-one-dimensional Structures*; Physics and Chemistry of Materials with Low-Dimensional Structures. Series B, Quasi-One-Dimensional Materials; D. Reidel: Dordrecht, The Netherlands, 1986.

(2) Monceau, P., Ed. *Electronic Properties of Inorganic Quasi-one-dimensional Compounds*; Physics and Chemistry of Materials with Low-dimensional Structures. Series B, Quasi-One-Dimensional Materials; D. Reidel: Dordrecht, The Netherlands, 1985; Parts I and II.

(3) Withers, R. L.; Wilson, J. A. *J. Phys. C: Solid State Phys.* **1986**, *19*, 4809−4845.

(4) Chaussy, J.; Haen, P.; Lasjaunias, J. C.; Monceau, P.; Waysand, G.; Waintal, A.; Meerschaut, A.; Molinié, P.; Rouxel, J. *Solid State Commun.* **1976**, *20*, 759−763.

(5) Monçeau, P.; Ong, N. P.; Portis, A. M.; Meerschaut, A.; Rouxel, J. *Phys. Rev. Lett.* **1976**, *37*, 602−606.

(6) Day, P. In *Solid State Chemistry Compounds*; Cheetham, A. K., Day, P., Eds.; Clarendon Press: Oxford, 1992; pp 31−59.

(7) Huang, F. Q.; Lee, S.; Choe, W.; Auriel, C. *Inorg. Chem.* Submitted for publication.

(8) Schewe-Miller, I.; Böttcher, P. *Z. Kristallogr.* **1991**, *196*, 137−151.

(9) Furuseth, S.; Fjellvåg, H. *Acta Chem. Scand.* **1991**, *45*, 694−697.

(10) Haneveld, A. J. K.; Jellinek, F. *J. Less-Common Met.* **1970**, *21*, 45−49.

(11) Stöwe, K. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1419−1422.

(12) Wu, E. J.; Pell, M. A.; Ibers, J. A. *J. Alloys Compd.* **1997**, *255*, 106−109.

(13) Krönert, W.; Plieth, K. *Z. Anorg. Allg. Chem.* **1965**, *336*, 207−218.

(14) Ben Salem, A.; Meerschaut, A.; Rouxel, J. *C. R. Acad. Sci., Ser. 2* **1984**, *299*, 617−619.

(15) Choi, K.-S.; Patschke, R.; Billinge, S. J. L.; Waner, M. J.; Dantus, M.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1998**, *120*, 10706−10714.

(16) Cody, J. A.; Ibers, J. A. *Inorg. Chem.* **1995**, *34*, 3165−3172.

(17) Dung, N.-H.; Pardo, M.-P.; Boy, P. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *39*, 668−670.

10.1021/ja9919635 CCC: $19.00

Table 1. Crystal Data and Structure Refinement for $LaCu_{0.40}Te_2$, $NdCu_{0.37}Te_2$, $SmCu_{0.34}Te_2$, $GdCu_{0.33}Te_2$, and $DyCu_{0.32}Te_2$[64]

compound	$LaCu_{0.40}Te_2$	$NdCu_{0.37}Te_2$	$SmCu_{0.34}Te_2$	$GdCu_{0.33}Te_2$	$DyCu_{0.32}Te_2$
formula weight	419.65	423.03	426.99	433.42	437.78
space group	*Pbcm*	*Pbcm*	*Pbcm*	*Pbcm*	*Pbcm*
a (Å)	7.7063(13)	7.6349(7)	7.6003(10)	7.5670(15)	7.5278(13)
b (Å)	8.5882(14)	8.3980(8)	8.3085(11)	8.2110(16)	8.1269(14)
c (Å)	6.3115(10)	6.18388(6)	6.1412(8)	6.0893(12)	6.0546(11)
V (Å^3)	417.72(12)	396.49(7)	387.80(9)	378.34(13)	370.41(11)
Z	4	4	4	4	4
T (K)	153(2)	153(2)	153(2)	107(2)	107(2)
λ(Mo Kα_1)	0.71073	0.71073	0.71073	0.71073	0.71073
d_{calcd} (g/cm^{-3})	6.676	7.087	7.314	7.609	7.850
cryst dim. (mm)	0.014 × 0.086 × 0.276	0.042 × 0.030 × 0.200	0.076 × 0.060 × 0.440	0.030 × 0.026 × 0.277	0.028 × 0.020 × 0.250
lin. abs coeff (cm^{-1})	256.81	291.99	314.27	341.80	371.02
transm factors	0.132−0.870	0.122−0.437	0.121−0.549	0.378−0.408	0.325−0.494
$R(F)^a$ ($F_o^2 > 2\sigma(F_o^2)$)	0.0288	0.0199	0.0253	0.0230	0.0229
R_w $(F_o^2)^b$ (all data)	0.0750	0.0488	0.0687	0.0487	0.0574

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$ for $F_o^2 \geq 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 \leq 0$.

have only been made on $CsTiUTe_5$; surprisingly, these show that the compound is semiconductive along the Te chain direction.[16]

To investigate the properties of compounds containing linear infinite chains of chalcogen atoms we chose a series based on the very simple $LaCu_{0.28}Te_2$[17] structure type. We report here the syntheses, structures, physical properties, and band structures of a series of compounds of formula $LnCu_xTe_2$ (Ln = rare earth), namely $LaCu_{0.40}Te_2$, $NdCu_{0.37}Te_2$, $SmCu_{0.34}Te_2$, $GdCu_{0.33}Te_2$, and $DyCu_{0.32}Te_2$. The crystallographic results indicate that these compounds do indeed contain infinite linear chains of equally spaced Te atoms. Consistent with type A of Scheme 1, Hückel calculations predict that the $Te^{(1+x)-}$ chains in $LnCu_xTe_2$ should show metallic properties. On the other hand, conductivity measurements along the chain direction indicate semiconducting behavior. In this paper we discuss some possible reasons for this discrepancy in terms of small distortions consistent with the crystallographic results.

In addition to conductivity measurements, thermopower measurements on four members of the $LnCu_xTe_2$ series are discussed. Three of these exhibit exceedingly high thermopower of about 900 μV/K in the vicinity of 150 K. To put this value in context, Bi_2Te_3 alloys typically have thermopower of around 200 μV/K at 293 K. Such materials are commercially favored for Peltier cooling applications, having a thermoelectric figure of merit $ZT = S^2T\sigma/\kappa$ of about 1,[19] where S is the thermopower, σ is the conductivity, and κ is the thermal conductivity. The present $LnCu_xTe_2$ compounds are not candidates for such applications, as they are semiconductors. Nevertheless, they, as well as other so-called Kondo insulators,[20] are of particular interest because of their thermoelectric properties which may extend to other systems containing linear chains of main-group atoms.

Experimental Details

Syntheses. The compounds $LaCu_{0.40}Te_2$, $NdCu_{0.37}Te_2$, $SmCu_{0.34}Te_2$, $GdCu_{0.33}Te_2$, and $DyCu_{0.32}Te_2$ were prepared by the reactions of the rare-earth elements La (Reacton, 99.9%), Nd (Alfa, 99.9%), Sm (Alfa, 99.9%), Gd (Alfa, 99.9%), and Dy (Aldrich, 99.9%) with Cu (Alfa, 99.999%) and Te (Aldrich 99.8%) in the corresponding flux of $LnCl_3$. The mixtures of 1.0 mmol Ln, 0.5 mmol Cu, 2.0 mmol Te, and 5.0 mmol $LnCl_3$ were loaded into fused silica tubes under an argon atmosphere in a glovebox. These tubes were sealed under a 10^{-4} Torr atmosphere and then placed in a computer-controlled furnace. The samples were heated to 1073 K at 1 deg K/min, kept at 1073 K for 3 days, cooled at 0.05 deg K/min to 573 K, and then cooled to room temperature. The reaction mixtures were washed free of chloride salts with water and then dried with acetone. In each reaction the major component consisted of black needles. Analysis of these crystals with an EDX-equipped Hitachi S-4500 SEM showed only the presence of Ln, Cu, and Te approximately in the ratio of 3:1:6. These compounds are stable in air for several months. They can also be synthesized with the use of a KI flux.

Structure Determinations. Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at 107 K on a computer-controlled[21] Picker diffractometer (Ln = Gd, Dy) or at 153 K on a Bruker Smart-1000 CCD diffractometer.[22] Intensity data on the Picker diffractometer were collected by the θ-2θ scan technique. Six standard reflections measured every 100 reflections throughout data collection showed no significant variations in intensity. The data were processed[23] and corrected for absorption effects.[24] Intensity data on the Bruker diffractometer were performed with the program SMART.[22] Cell refinement and data reduction were carried out with the use of the program SAINT[22] and face-indexed absorption corrections were carried out numerically with the use of XPREP.[25] Only for Ln = Sm was there an indication of a larger cell: an $a \times b \times 3c$ supercell could be found when very weak reflections were included in the cell refinement.[26] No attempt was made to solve the structure in this supercell.

All the structures were solved with the direct methods program SHELXS of the SHELXTL PC suite of programs,[25] and they were refined with the use of the full-matrix least-squares program SHELXL.[25] Each final refinement included anisotropic displacement parameters, a secondary extinction correction, and variable occupancy of the Cu atom. Additional experimental details are shown in Table 1 and in Supporting Information. Table 2 gives positional parameters and equivalent isotropic displacement parameters and Table 3 presents selected bond distances and angles.

Electrical Conductivity. For each of the compounds $LaCu_{0.40}Te_2$, $NdCu_{0.37}Te_2$, $SmCu_{0.34}Te_2$, $GdCu_{0.33}Te_2$, and $DyCu_{0.32}Te_2$ the composition of two single crystals was confirmed with EDX measurements. The electrical conductivity of each of the single crystals was measured with the use of a computer-controlled, four-probe technique.[27] Electrical

---

(18) Beck, J.; Bock, G. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1971−1975.

(19) Yim, W. M.; Rosi, F. D. *Solid-State Electron.* **1972**, *15*, 1121−1140.

(20) Jones, C. D. W.; Regan, K. A.; DiSalvo, F. J. *Phys. Rev. B* **1998**, *58*, 16057−16063.

(21) Huffman, J. C.; Streib, W. E. Unpublished work, 1990.

(22) SMART Version 5.054 and SAINT-Plus Version 6.0 Data Collection and Processing Software for the SMART System; Bruker Analytical X-ray Instruments, Inc., Madison, WI, 1997, 1999.

(23) Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273−3277.

(24) de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014−1018.

(25) Sheldrick, G. M. SHELXTL PC Version 5.0 An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data; Siemens Analytical X-ray Instruments, Inc. Madison, WI, 1994.

(26) The possible supercell for $SmCu_{0.34}Te_2$ is a = 7.6020(17) Å, b = 8.2940(18) Å, c = 18.449(4) Å.

(27) Lyding, J. W.; Marcy, H. O.; Marks, T. J.; Kannewurf, C. R. *IEEE Trans. 1nstrum. Meas.* **1988**, *37*, 76−80.

Table 2. Atomic Coordinates, Equivalent Isotropic Displacement Parameters, and Site Occupancies for $LaCu_{0.40}Te_2$, $NdCu_{0.37}Te_2$, $SmCu_{0.34}Te_2$, $GdCu_{0.33}Te_2$, and $DyCu_{0.32}Te_2$

atom	*x*	*y*	*z*	U_{eq}[a]	occup.
$LaCu_{0.40}Te_2$					
La	0.23763(6)	0.55956(5)	0.2500	0.0147(2)	1
Cu	0.4120(4)	0.2023(4)	0.0686(6)	0.0182(12)	0.202(4)
Te1	0.61756(6)	0.40840(6)	0.2500	0.0116(2)	1
Te2	0.08211(6)	0.2500	0.0000	0.0145(2)	1
$NdCu_{0.37}Te_2$					
Nd	0.24076(4)	0.56039(4)	0.2500	0.01187(15)	1
Cu	0.4083(4)	0.2025(4)	0.0709(6)	0.0162(10)	0.186(3)
Te1	0.61688(5)	0.40923(4)	0.2500	0.01002(15)	1
Te2	0.07876(5)	0.2500	0.0000	0.01135(15)	1
$SmCu_{0.34}Te_2$					
Sm	0.24175(5)	0.56051(5)	0.2500	0.0113(2)	1
Cu	0.4075(5)	0.2020(5)	0.0729(8)	0.0142(14)	0.169(4)
Te1	0.61662(7)	0.40944(6)	0.2500	0.0100(2)	1
Te2	0.07694(7)	0.2500	0.0000	0.0109(2)	1
$GdCu_{0.33}Te_2$					
Gd	0.24352(5)	0.56011(5)	0.2500	0.00692(11)	1
Cu	0.4053(6)	0.2012(6)	0.0759(8)	0.0123(14)	0.164(4)
Te1	0.61576(7)	0.40935(6)	0.2500	0.00605(12)	1
Te2	0.07511(7)	0.2500	0.0000	0.00652(12)	1
$DyCu_{0.32}Te_2$					
Dy	0.24445(5)	0.55954(4)	0.2500	0.00695(13)	1
Cu	0.4053(6)	0.2013(6)	0.0754(8)	0.0104(14)	0.158(4)
Te1	0.61566(7)	0.40909(6)	0.2500	0.00648(14)	1
Te2	0.07326(7)	0.2500	0.0000	0.00658(14)	1

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

contacts consisted of fine gold wire (25 and 60 μm diameter) attached to the crystals with gold paste. Samples were placed under vacuum for at least 24 h to allow the gold paste to dry completely, which improved contact performance. Excitation currents were kept as low as possible, typically below 1 mA, to minimize any nonohmic voltage response and thermoelectric effects at the contact−sample interface. Measurements of the sample cross-sectional area and voltage probe separation were made with a calibrated binocular microscope.

Thermopower Measurements. Variable-temperature thermopower data were taken with the use of a slow-ac measurement technique.[28] The measurement apparatus featured Au(0.07% Fe)/Chromel differential thermocouples for monitoring the applied temperature gradients. Samples were mounted on 60 μm gold wire by means of gold paste. Fine gold wire (10 μm in diameter) was used for sample voltage contacts, which were made as long as possible to minimize thermal conduction through the leads. The sample and thermocouple voltages were measured with the use of Keithley Model 181 and Keithley Model 182 nanovoltmeters, respectively. The applied temperature gradient was in the range of 0.1 to 0.4 K. Measurements were taken under a turbopumped vacuum maintained below 10^{-5} Torr. The sample chamber was evacuated for 1−3 h prior to cooling to remove any residual water vapor or solvents in the gold paste.

Magnetic Susceptibility. A 18.4 mg sample of $GdCu_{0.33}Te_2$ containing single crystals was used for magnetic susceptibility measurements. Composition of the sample was verified by EDX measurements. The magnetization was measured at 100 G between 5 and 300 K with the use of a Quantum Design SQUID magnetometer. All measurements were corrected for core diamagnetism.

Extended Hückel Calculations. All calculations were performed on the hypothetical compounds $LaCuTe_2$, $LaCu_{1/2}Te_2$, and $LaCu_{1/3}Te_2$ with the use of the YAeHMOP package.[29−31] The parameters used for Cu and Te orbitals are listed in Table 4. Band structure calculations were all carried out on the $a \times b \times 3c$ cell.

Results and Discussion

Crystal Structures. The compounds $LnCu_xTe_2$ (Ln = La, Nd, Sm, Gd, Dy) are isostructural. Figure 1 presents two views of the structure; for clarity the Ln−Te bonds are not shown and Cu atoms are displayed in accordance with the discussion below concerning their disorder. The Ln atoms, which have crystallographically imposed m symmetry, are coordinated by eight Te atoms at the vertexes of a bicapped trigonal prism, as shown in Figure 2. The Ln−Te distances are close to those observed in the $LnTe_2$ structures. To take $LaCu_{0.40}Te_2$ as an example, the La−Te distances range from 3.1970(8) to 3.3585(5) Å compared with those in $LaTe_2$ of 3.260(7) to 3.381(5) Å.[32] The Cu atoms occupy from 16% ($DyCu_{0.32}Te_2$) to 20% ($LaCu_{0.40}Te_2$) of a general position in space group *Pbcm*. These Cu atoms form chains parallel to *c* (Figure 1). Each Cu atom is in a distorted tetrahedron of Te atoms. Tetrahedral coordination of Cu is common in chalcogenide systems, such as $LaCu_{0.28}Te_2$, $K_{1.5}Dy_2Cu_{2.5}Te_5$, $KCu_{7-x}S_4$, and $Mo_3Cu_{2-x}S_4$.[17,33−36] If the Cu site were 100% occupied, the composition would be $LnCu_2Te_2$, and impossible Cu−Cu distances of about 1.2 Å would result. At 50% occupancy the composition would be $LnCuTe_2$ and a zigzag chain of Cu atoms with Cu−Cu distances of about 3.2 Å could result. At 25% occupancy the composition would be $LnCu_{0.5}Te_2$ and no Cu−Cu distances shorter than the *c* lattice constant need occur. The refinement model employed assumes random occupation of the site.

An interesting feature of this structure type is the infinite linear Te2−Te2 chain parallel to *c*, with Te2−Te2 distances decreasing from 3.1558(5) Å in $LaCu_{0.40}Te_2$ to 3.0273(3) Å in $DyCu_{0.32}Te_2$. (The Te2−Te2 distance is $c/2$.) These distances are longer than the Te−Te distance of 2.84 Å in elemental Te,[37] but much shorter than the 4.4 Å van der Waals separation.[37] For $LnCu_xTe_2$, the formal oxidation states of Ln and Cu are 3+ and 1+, respectively. The oxidation state of the isolated Te1 atoms is presumably 2−, so each Te2 atom has charge $-(1 + x)$. If x were equal to 1, then the Te2···Te2 interaction would be too long for bonding. As we go from Ln of La to Dy, x decreases from 0.40 to 0.32. As a consequence, each Te2 atom has a lower formal charge and the Te2−Te2 bond becomes stronger and shorter. As a further illustration of this effect and as an indication that the change in Te2−Te2 distance arises from a change in x rather than from a change in Ln (i.e., from the lanthanide contraction) note that $LaCu_{0.28}Te_2$[17,38] at room temperature crystallizes in space group *Pbcm* in the cell a = 7.726(4) Å, b = 8.603(5) Å, c = 6.246(2) Å, and V = 415.2(3) Å^3 whereas the present $LaCu_{0.40}Te_2$ at 153(2) K crystallizes in *Pbcm* in the cell a = 7.7063(13) Å, b = 8.5882(14) Å, c = 6.3115(10) Å, and V = 417.72(12) Å^3. The differences between the a and b cell constants of 0.0197(53) and 0.0148(64) Å are expected owing to the different temperatures involved. Thus the difference in the c cell constants of −0.0655(30) Å is clearly

---

(28) Marcy, H. O.; Marks, T. J.; Kannewurf, C. R. *IEEE Trans. Instrum. Meas.* **1990**, *39*, 756−760.

(29) Landrum, G. Yet Another Extended Hückel Molecular Orbital Package (YAeHMOP), Version 2.0, 1997.

(30) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397−1412.

(31) Whangbo, M.-H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 6093−6098.

(32) Wang, R.; Steinfink, H.; Bradley, W. F. *Inorg. Chem.* **1966**, *5*, 142−145.

(33) Huang, F. Q.; Choe, W.; Lee, S.; Chu, J. S. *Chem. Mater.* **1998**, *10*, 1320−1326.

(34) Yvon, K.; Paoli, A.; Flükiger, R.; Chevrel, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *33*, 3066−3072.

(35) Li, H.; Mackay, R.; Hwu, S.-J.; Kuo, Y.-K.; Skove, M. J.; Yokota, Y.; Ohtani, T. *Chem. Mater.* **1998**, *10*, 3172−3183.

(36) Hwu, S.-J.; Li, H.; Mackay, R.; Kuo, Y.-K.; Skove, M. J.; Mahapatro, M.; Bucher, C. K.; Halladay, J. P.; Hayes, M. W. *Chem. Mater.* **1998**, *10*, 6−9.

(37) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, 1984.

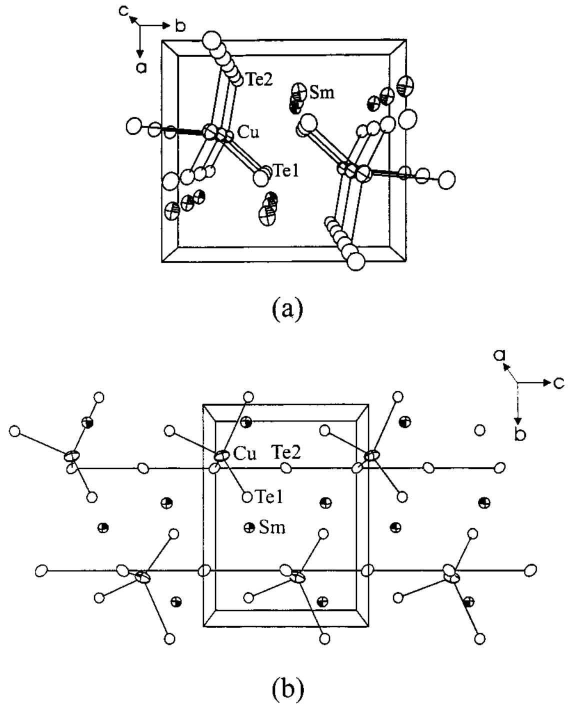
(38) The literature preparation (ref 17) of $LaCu_{0.28}Te_2$ is different from the preparation of $LaCu_{0.40}Te_2$ described here and involves the use of I_2 vapor transport at 1275 K.

Table 3. Selected Bond Lengths (Å) for $LaCu_{0.40}Te_2$, $NdCu_{0.37}Te_2$, $SmCu_{0.34}Te_2$, $GdCu_{0.33}Te_2$, and $DyCu_{0.32}Te_2$

	$LaCu_{0.40}Te_2$	$NdCu_{0.37}Te_2$	$SmCu_{0.34}Te_2$	$GdCu_{0.33}Te_2$	$DyCu_{0.32}Te_2$
Ln−Te1	3.1970(8)	3.1247(5)	3.0924(7)	3.0590(8)	3.0296(7)
Ln−Te1	3.2027(8)	3.1397(6)	3.1133(7)	3.0767(8)	3.0501(8)
Ln−Te1 × 2	3.3585(5)	3.2873(3)	3.2634(4)	3.2352(6)	3.2153(6)
Ln−Te2 × 2	3.3157(6)	3.2732(4)	3.2530(5)	3.2288(6)	3.2063(5)
Ln−Te2 × 2	3.3520(7)	3.2980(5)	3.2715(6)	3.2499(7)	3.2260(6)
Cu−Te1	2.637(3)	2.603(3)	2.584(4)	2.566(5)	2.545(5)
Cu−Te1	2.731(4)	2.707(3)	2.669(4)	2.625(5)	2.604(5)
Cu−Te1	2.781(4)	2.712(3)	2.705(4)	2.701(5)	2.682(5)
Cu−Te2	2.611(3)	2.585(3)	2.583(4)	2.572(4)	2.572(4)
Te2−Te2 × 2	3.1558(5)	3.0919(3)	3.0706(4)	3.0446(6)	3.0273(5)

Table 4. Atomic Parameters Used for the Extended Hückel Calculations

element	orbital	H_{ii} (eV)	ζ_1	ζ_2	C_1	C_2
Cu	4s	−11.40	2.20			
	4p	−6.06	2.20			
	4d	−14.00	5.95	2.30	0.5933	0.5744
Te	5s	−20.80	2.51			
	5p	−14.80	2.16			



(a)

(b)

Figure 1. Unit cell of $SmCu_{0.34}Te_2$, idealized as $SmCu_{0.50}Te_2$, viewed down (a) *c* and (b) *a*. The 90% displacement ellipsoids are displayed here and in Figure 2. For the sake of clarity, no Sm−Te interactions are shown.

significant. That $LaCu_{0.40}Te_2$ has a significant longer *c* axis repeat is once again the result of the higher Cu content.

Physical Properties. Conductivity measurements were made along the *c* axis (the direction of the Te2 infinite chain) as a function of temperature for $LaCu_{0.40}Te_2$, $NdCu_{0.37}Te_2$, $SmCu_{0.34}Te_2$, and $GdCu_{0.33}Te_2$, and at room temperature for $DyCu_{0.32}Te_2$. Results for *Ln* = La, Nd, Sm, and Gd are shown in Figure 3 and the room temperature conductivities are given in Table 5. The electrical conductivity for all samples exhibits semiconducting behavior in this direction. The conductivities of $NdCu_{0.37}Te_2$, $SmCu_{0.34}Te_2$, and $GdCu_{0.33}Te_2$ show fairly similar behavior over the entire temperature range. The conductivity for these compounds declines by more than 11 orders of magnitude as the temperature decreases from 340 to 4.2 K. The conductivity at the higher temperatures (above ∼150−200 K) agrees well with an Arrhenius fit. Below approximately 200 K the data for these three compounds show a shallow minimum near or slightly below 150 K, and a rapid decrease below 50 K. The conductivity of $LaCu_{0.40}Te_2$ shows much less dependence on temperature, exhibiting a drop of about 1 order of magnitude from 340 to 4.2 K.

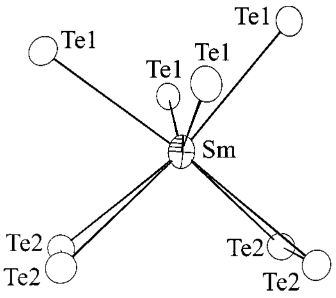


Figure 2. The coordination about Sm in $SmCu_{0.34}Te_2$.

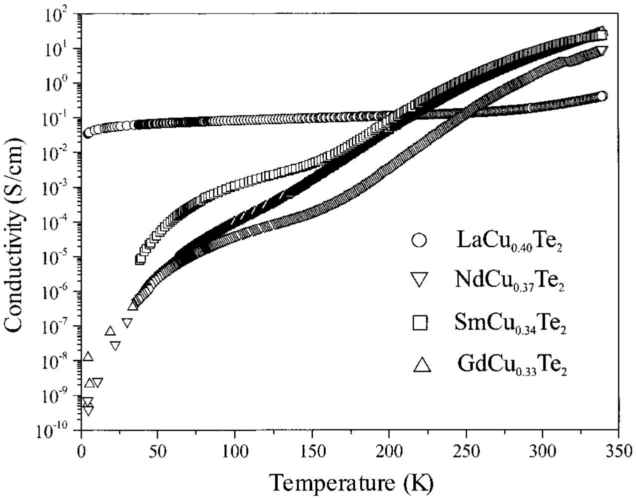


Figure 3. Single-crystal electrical conductivity σ along *c* (the Te2−Te2 direction) vs *T* for $LaCu_{0.40}Te_2$, $NdCu_{0.37}Te_2$, $SmCu_{0.34}Te_2$, and $GdCu_{0.33}Te_2$.

Table 5. Te2−Te2 Bond Length, Cu Content, and Room Temperature Conductivity σ (S/cm) for $LnCu_xTe_2$

compd	Te2−Te2[a]	*x*	σ
$LaCu_{0.40}Te_2$	3.1558(5)	0.404	0.205
$NdCu_{0.37}Te_2$	3.0919(3)	0.372	2.07
$SmCu_{0.34}Te_2$	3.0706(4)	0.338	6.25
$GdCu_{0.33}Te_2$	3.0446(6)	0.328	6.68
$DyCu_{0.32}Te_2$	3.0273(5)	0.316	6.90

[a] This distance is *c*/2.

The thermopower data exhibit p-type behavior for all materials (Figure 4). $NdCu_{0.37}Te_2$, $SmCu_{0.34}Te_2$, and $GdCu_{0.33}Te_2$ show similar behavior as the temperature decreases from 300 K where the values are on the order of 200 to 400 μV/K. The magnitude

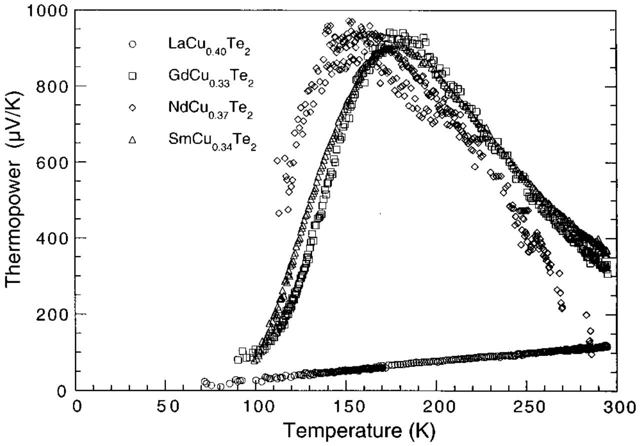


Figure 4. Thermopower versus *T* for the series of *Ln*Cu$_x$Te$_2$ compounds.

of the thermopower increases as the temperature decreases, which is characteristic of a semiconductor material. However, the thermopower data for the three compounds exhibit a very high peak of approximately 900 μV/K in the vicinity of 150 K, followed by a rapid decrease at lower temperatures. LaCu$_{0.40}$Te$_2$ shows considerably lower thermopower values, with a linear decrease with temperature. Although this behavior is more typical of metallic materials, the magnitude of the thermopower is usually associated with semiconductor behavior.

Both the thermopower and conductivity data above 150−200 K for NdCu$_{0.37}$Te$_2$, SmCu$_{0.34}$Te$_2$, and GdCu$_{0.33}$Te$_2$ are typical of semiconductors. Below about 150 K, where the peak in the thermopower data occurs, the behavior deviates from the trend expected for semiconductors. The behavior observed here has been previously reported for CePd$_3$B$_x$ alloys,[39] Nd$_x$Ce$_{3-x}$Pt$_3$Sb$_4$,[20] CePd$_3$,[40] and CeIn$_3$.[40] Such behavior has been attributed to the Kondo effect.[41,42] For metallic CePd$_3$ and CeIn$_3$, the Kondo effect is associated with the scattering of conduction electrons by the partially localized Ce 4f electrons. However, the Kondo effect also has been used to describe this behavior in semiconducting materials[20,39] including SmB$_6$,[43] which have been referred to as Kondo insulators. Since La^{3+} has no 4f electrons, we find that the behavior of LaCu$_{0.40}$Te$_2$ is different and is typical of a semiconductor throughout the entire temperature range.

A plot of 1/χ vs *T* is shown in Figure 5 for GdCu$_{0.33}$Te$_2$ This material is paramagnetic above 7 K. The susceptibility data were fit by a least-squares method to the Curie−Weiss equation $\chi = C/(T - \theta)$, where *C* is the Curie constant and θ is the Weiss constant. The resulting values for *C* and θ are 7.48(4) emu·K/mol and −17.94(3) K, respectively. The calculated effective magnetic moment of 7.74(3) μ_B agrees reasonably well with the theoretical value of 7.94 μ_B for Gd^{3+}.[44]

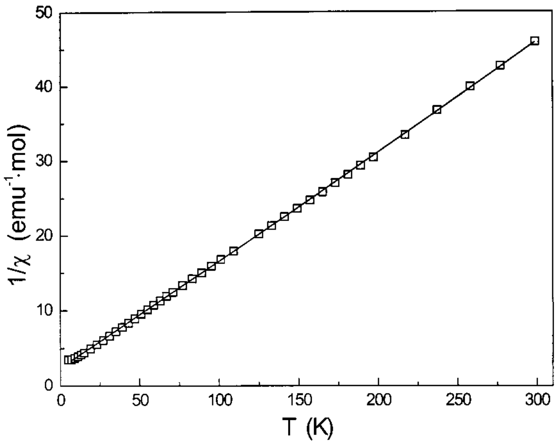


Figure 5. Plot of the molar susceptibility 1/χ vs *T* for GdCu$_{0.33}$Te$_2$. The solid line is the least-squares fit.

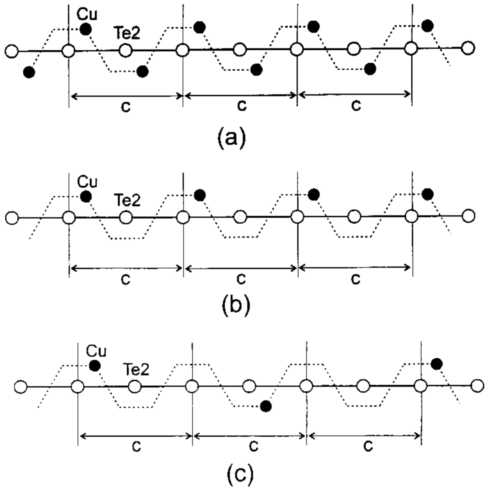


Figure 6. The positions of Cu atoms for (a) LaCuTe$_2$, (b) LaCu$_{1/2}$Te$_2$, and (c) LaCu$_{1/3}$Te$_2$ in an $a \times b \times 3c$ cell used in the theoretical calculations.

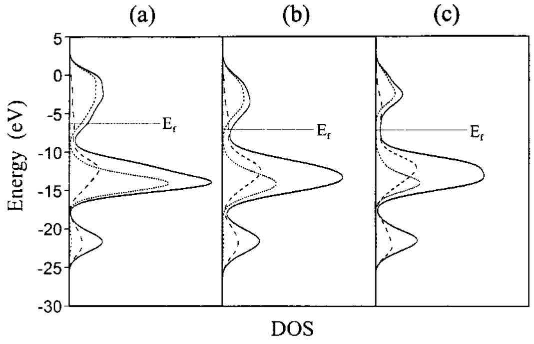


Figure 7. The density of states (DOS) of (a) LaCuTe$_2$, (b) LaCu$_{1/2}$Te$_2$, and (c) LaCu$_{1/3}$Te2. The total DOS is the solid line, the DOS of Te2 atoms is the dashed line, and the DOS of Cu atoms is the dotted line.

Theoretical Calculations. One might expect the present compounds to show metallic conductivity in the direction of the infinite linear Te2−Te2 chains (*c*); however, the compounds are semiconducting in this direction. To examine this in more detail an extended Hückel tight binding calculation was made on the two-dimensional copper telluride layer of the hypothetical compounds LaCuTe$_2$, LaCu$_{1/2}$Te$_2$, and LaCu$_{1/3}$Te$_2$. The placement of Cu atoms in these compounds is shown in Figure 6. The density of states (DOS) for each compound is shown in Figure 7. Note that the DOS around the Fermi surface is not equal to zero and hence these compounds should be metallic. The DOS of the Cu atoms in LaCu$_x$Te$_2$ is sensitive to *x*. When $x = 1/2$, most of the contribution comes from the Te2 atoms. When $x = 1/3$, all the contribution comes from Te2 atoms and none from Te1 or Cu atoms. These results may explain why

---

(39) Houshiar, M.; Adroja, D. T.; Rainford, B. D. *Physica B* **1996**, *223 & 224*, 268−270.

(40) Gambino, R. J.; Grobman, W. D.; Toxen, A. M. *Appl. Phys. Lett.* **1973**, *22*, 506−507.

(41) Kondo, J. *Prog. Theor. Phys.* **1964**, *32*, 37−49.

(42) Kondo, J. *Prog. Theor. Phys.* **1968**, *40*, 695−705.

(43) Nefedova, E. V.; Alekseev, P. A.; Klement'ev, E. S.; Lazukov, V. N.; Sadikov, I. P.; Khlopkin, M. N.; Tsetlin, M. B.; Konovalova, E. S.; Paderno, Y. B. *J. Exp. Theor. Phys.* **1999**, *88*, 565−573.

(44) Hatfield, W. E. In *Solid State Chemistry: Techniques*; Cheetham, A. K., Day, P., Eds.; Clarendon Press: New York, 1987; pp 122−162.

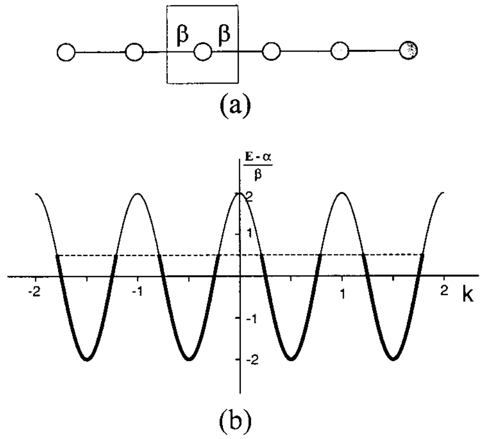


Figure 8. (a) An linear chain of equally spaced Te atoms, where the length of the box is the translational unit and α and β are Hückel Coulomb and resonance parameters; (b) the band structure with a band filling of f, where the thick part is the occupied band, the dashed line is the Fermi surface, and k is the reciprocal space index corresponding to one translational unit chosen to be of length 1.

LaCu$_{0.40}$Te$_2$ with the highest content of Cu has the flattest dependence of σ vs T (Figure 3).

The band structure at the Hückel approximation for a linear array of equally spaced Te2 atoms is shown in Figure 8a. The thick and thin lines in Figure 8b represent filled and unfilled orbitals, respectively. Their intersection is the one-dimensional Fermi surface. If f ($0 \le f \le 1$) denotes band filling, then $f = 0$ means the band is empty, $f = 1$ means it is full, and $f = 1/2$ means all the bonding orbitals are occupied and all the antibonding orbitals are empty. For a Te$^{(1+x)-}$ chain, $f = (1 + x)/2 > 1/2$, and some antibonding orbitals must be occupied. As f (or x) increases, the Te2−Te2 bond becomes weaker and longer, consistent with the experimental results in Table 5.

Why do the theoretical calculations predict metallic behavior in the c direction whereas this is not found experimentally? One conjecture is that the model of equally spaced linear Te2 atoms (Figure 1) is incorrect and that the Te2 chain is distorted. Most of the linear Q chains in chalcogenides have been found to distort into alternating $Q-Q$ separations, as shown in part B of Scheme 1. This kind of distortion occurs commonly in low-dimensional structures as a result of charge density waves[1,13,16,45−50] and has been used, within the tight-binding model, to explain metal-to-insulator transitions.[1,49,51−55]

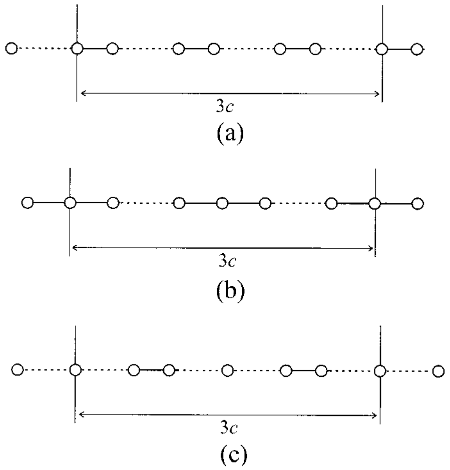


Figure 9. Three distortion models of the linear Te chain. The solid lines connect the shorter bonds with stronger bonding and the dashed lines connect the longer bonds with weaker bonding.

Now consider three distortion models of the Te chain in a $a \times b \times 3c$ cell in Figure 9, as could be found when very weak reflections were included in the cell refinement of SmCu$_{0.34}$Te$_2$. In each model, the unique Te2−Te2 distance in the $a \times b \times c$ cell is separated into two different distances. In each the Te atoms in the chain may have interactions with their neighbors. In model a of Te$_2^{2-}$ dimers, each Te atom has charge −1. Linear Te^{1-} chains in Cs$_3$Te$_5$ and ZrTe$_3$ have this distortion.[8,9] In model b of Te$_3^{2-}$ trimers, each Te atom has average charge −2/3. In model c of two monomers and two dimers, each Te atom has average charge −4/3.

Since this average charge is close to that on the Te atoms in the present compounds, model c has been investigated by means of extended Hückel calculations. The z' coordinates for the six Te2 atoms in Figure 9c are 0, $1/6 + \Delta z'$, $1/3 - \Delta z'$, 1/2, $2/3 + \Delta z'$, $5/6 - \Delta z'$, and the translational unit is $3c$ where c is the c axis length in SmCu$_{0.34}$Te$_2$. Given the crystallographic results, what limit can we place on $\Delta z'$? Since the Te2−Te2 chains are well separated in the crystal structure we assume that there is no communication from one chain to the next. Consequently, model c manifests itself in the $a \times b \times c$ cell as Te2 atoms slightly displaced from the $z = 0$ position. Any distortions in the present structures are very small, for as seen in Figures 1 and 2 the displacement ellipsoids of the Te2 atoms are nearly spherical in SmCu$_{0.34}$Te$_2$, a typical member of this series. We can estimate an upper limit to $\Delta z'$ in the following way. The principal mean-square atomic displacements of the Te2 atoms in SmCu$_{0.34}$Te$_2$ are 0.0138, 0.0108, and 0.0080 Å^2. If we take 0.0080 Å^2 as the mean-square displacement for a "spherical" Te2 atom in this structure, then how far can we move a half "spherical" atom on either side of $z = 0$ to give when superimposed an "ellipsoidal" atom centered at $z = 0$ whose mean-square-displacement in the c direction is 0.014 Å^2? A simple graphical solution to this problem leads to a separation of the half "spherical" atoms of ~0.02 Å. A difference of 0.02 Å corresponds to $\Delta z' = 0.0004$. To be generous we take $\Delta z' = 0.001$, corresponding to a difference between long and short Te−Te separations of 0.055 Å. The band structure for $\Delta z' = 0.001$ in Figure 10 shows the Te2 chain is now an insulator, whereas it is a metallic conductor at $z = 0$. The energy level of the HOMO is 0.233 eV lower and the energy level of the LUMO is 0.255 eV higher than that for $\Delta z' = 0$. The resultant energy gap is 0.489 eV. The energy gap for $\Delta z' = 0.0004$ is 0.192 eV, well above kT, and the chains should be semiconducting.

This calculation indicates that a distortion in the Te2−Te2 chain sufficiently small to be compatible with the crystallographic results would still lead to an insulating system. But, of course, from the present data there is no proof that such a

---

(45) Furuseth, S.; Brattås, L.; Kjekshus, A. *Acta Chem. Scand. Ser. A* **1975**, *29*, 623−631.

(46) Beck, H. P.; Dausch, W. *Z. Naturforsch., B: Chem. Sci.* **1988**, *43*, 1547−1550.

(47) Noël, H. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1715−1717.

(48) Tremel, W.; Hoffmann, R. *J. Am. Chem. Soc.* **1987**, *109*, 124−140.

(49) Lee, S.; Foran, B. J. *J. Am. Chem. Soc.* **1996**, *118*, 9139−9147.

(50) Park, S.-M.; Park, S.-J.; Kim, S.-J. *J. Solid State Chem.* **1998**, *140*, 300−306.

(51) Monceau, P. In *Electronic Properties of Inorganic Quasi-One-Dimensional Materials*; Monceau, P., Ed.; D. Reidel Publishing Company: Boston, 1985; Vol. II, pp 139−268.

(52) Zhang, X.; Li, J.; Foran, B.; Lee, S.; Guo, H.-Y.; Hogan, T.; Kannewurf, C. R.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1995**, *117*, 10513−10520.

(53) Canadell, E.; Whangbo, M.-H. *Chem. Rev.* **1991**, *91*, 965−1034.

(54) Whangbo, M.-H.; Canadell, E.; Foury, P.; Pouget, J.-P. *Science* **1991**, *252*, 96−98.

(55) Lee, S.; Foran, B. *J. Am. Chem. Soc.* **1994**, *116*, 154−161.

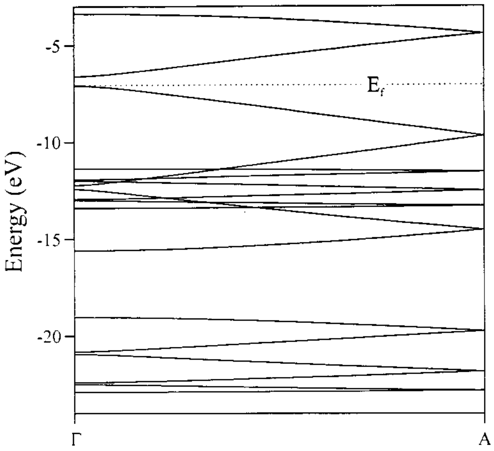


Figure 10. The band structure for the $Te^{-4/3}$ chain with $\Delta z' = 0.001$, where the dashed line is the Fermi surface, and Γ and *A* are the *k*-points of (0, 0, 0) and (0, 0, 1/2), respectively.

distortion is actually present. Nevertheless, other effects can result in the present compounds being nonmetallic in the direction of the Te2−Te2 chains. For any finite amount of disorder there are no extended states in one dimension.[56] The transition from metallic to insulating induced by disorder has been discussed extensively.[57−63] In the present compounds it is very likely that the Cu atoms are disordered, since the random model discussed above for their occupancy proves to be satisfactory. If the Cu atoms are randomly disordered, then the Te2 atoms to which they are bonded must also be affected.

Acknowledgment. This research was supported by NSF Grant DMR97-09351. Use was made of the MRL Central Facilities supported by the National Science Foundation at the Materials Research Center of Northwestern University under Grant No. DMR96-32472. We thank Charlotte Stern, Christopher G. Pernin, and Yuting Yang for assistance.

Supporting Information Available: Further crystallographic details, anisotropic displacement parameters, and complete metrical details for $LaCu_{0.40}Te_2$, $NdCu_{0.37}Te_2$, $SmCu_{0.34}Te_2$, $GdCu_{0.33}Te_2$, and $DyCu_{0.32}Te_2$ (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA9919635

---

(56) Mott, N. F.; Twose, W. D. *Adv. Phys.* **1961**, *10*, 107−163.

(57) Anderson, P. W. *Phys. Rev.* **1958**, *109*, 1492−1505.

(58) Nagaoka, Y. *Prog. Theor. Phys. Suppl.* **1985**, *84*, 1−15.

(59) Oleksyn, O.; Schobinger-Papamantellos, P.; Ritter, C.; de Groot, C. H.; Buschow, K. H. J. *J. Alloys Compd.* **1997**, *252*, 53−58.

(60) Yamada, H.; Ikeda, K. S. *Phys. Rev. E* **1999**, *59*, 5214−5229.

(61) Skinner, J. L. *J. Phys. Chem.* **1994**, *98*, 2503−2507.

(62) Kramer, B.; MacKinnon, A. *Rep. Prog. Phys.* **1993**, *56*, 1469−1564.

(63) Henkie, Z.; Cichorek, T.; Pietraszko, A.; Fabrowski, R.; Wojakowski, A.; Kuzhel, B. S.; Kepinski, L.; Krajczyk, L.; Gukasov, A.; Wisniewski, P. *J. Phys. Chem. Solids* **1997**, *59*, 385−393.

(64) The isostructural compounds $CeCu_xTe_2$ and $PrCu_xTe_2$ were also prepared in the same manner with the use of Ce (Alfa, 99.9%) and Pr (Alfa, 99.9%). Their lattice constants are as follows: Ce (Picker, 107 K), a = 7.6534(15) Å, b = 8.4969(16) Å, c = 6.1979(12) Å; Pr (Bruker, 153 K) a = 7.6520(26) Å, b = 8.4415(47) Å, c = 6.1954(18) Å.