

The Crystal Structure of CuTe_2Cl

BY J. FENNER

Max-Planck-Institut für Festkörperforschung, 7 Stuttgart 80, Germany (BRD)

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CuTe_2Cl is monoclinic, space group $P2_1/c$, with $a=8.207$, $b=4.935$, $c=15.279$ Å, $\beta=134.92^\circ$, $Z=4$. 722 independent intensities were measured and the structure was refined to $R=5.6\%$. The basic structure unit is a pseudo-fourfold screw of Te atoms along b . The Te-Te distances in the screw are 2.737 and 2.792 Å. Cu-Cl-Cu links connect the screws to layers in the ab plane. The coordination of the Cu atom by Te and Cl is fourfold with the geometry of a slightly distorted tetrahedron.

Introduction

The preparation and some properties of six copper tellurium halides have been reported (Rabenau, Rau & Rosenstein, 1970). There exist two homologous series of isotopic compounds: CuTeX , tetragonal, and CuTe_2X , monoclinic ($X=\text{Cl}, \text{Br}, \text{I}$). They belong to the pseudo-binary systems, formed between Te and the respective Cu^{I} halide. The crystal structure of CuTe_2Cl has now been determined.

Experimental

CuTe_2Cl was synthesized by reaction of stoichiometric amounts of CuCl and Te at 350°C . The crystals are black needles. Photographs confirmed the monoclinic symmetry and the cell dimensions previously reported (Rabenau, Rau & Rosenstein, 1970). The lattice parameters, measured on a diffractometer and refined by least squares, and other data are summarized in Table 1 (standard deviations in parentheses).

Table 1. Crystallographic data

Cell dimensions*	$Z=4$
$a=8.207$ (1) Å	$V=437.94$ Å ³
$b=4.935$ (1)	$D_m=5.43$ g cm ⁻³ †
$c=15.279$ (2)	$D_x=5.37$
$\beta=134.92$ (1)°	$\mu(\text{Mo } K\alpha)=193.07$ cm ⁻¹
Symmetry: monoclinic	$F(000)=600$
Space group: $P2_1/c$	

* The matrix (100/010/101) would transform the unit cell into another one with a smaller value for β and space group symbol $P2_1/n$ (8.207, 4.935, 11.123 Å; 103.42°).

† Rabenau, Rau & Rosenstein (1970).

Intensities up to $2\theta=51^\circ$ were measured on a Syntex $P2_1$ automatic diffractometer with monochromatic Mo $K\alpha$ radiation in the ω scanning mode. The scanning range was 1.0° for each reflexion. The offset from the peak position for measuring the background inten-

sity was $\pm 0.7^\circ$. The ratio of measuring times for background to peak intensity was 0.5. Two reference reflexions remained constant during data collection. Reflexions with net negative intensities were set to zero. All reflexions with net count less than three times the standard deviation were classified as 'less-than'. Of 722 independent reflexions 304 were 'less-than'. With $\mu=193.07$ cm⁻¹ for Mo $K\alpha$ radiation and the crystal dimensions of $0.02 \times 0.07 \times 0.02$ mm along \mathbf{a} , \mathbf{b} , and \mathbf{c} respectively [\mathbf{b} parallel to rotation (φ) axis of diffractometer] an absorption correction with the interpolation method of Gauss was applied. The value of A^* with which F^2 and σ_F^2 were multiplied varied from 1.354 to 1.495.

Structure determination and refinement

The structure was solved by direct methods (162 phases, $E \geq 1.2$; program *MULTAN*). An E map showed three outstanding peaks which were interpreted as the two independent Te and the Cu atoms. The Cl atom was located from a subsequent Fourier synthesis. In the full-matrix least-squares refinement $\sum w(|F_o| - 1/k|F_c|)^2$ with $w=(1/\sigma_F)^2$ and $\sigma_F=(F^2 + \sigma_F^2)^{1/2} - F$ was

Table 2. The atomic parameters and their standard deviations

The U_{ij} as multiples of 0.01 Å² refer to $-2\pi^2(U_{11}h^2a^{*2} + 2U_{23}klb^*c^* + \dots)$ as exponent of the anisotropic temperature factor. Positional parameters are $\times 10^4$.

	Te(1)	Te(2)	Cu	Cl
x	-20 (3)	2958 (3)	3283 (6)	3296 (12)
y	4980 (5)	2795 (4)	6403 (9)	3912 (17)
z	3652 (2)	3587 (2)	2489 (4)	1185 (6)
U_{11}	1.8 (1)	1.6 (1)	2.8 (2)	2.1 (4)
U_{22}	2.7 (1)	2.9 (1)	3.6 (3)	3.0 (5)
U_{33}	1.7 (1)	1.7 (1)	3.6 (2)	2.1 (4)
U_{12}	0.2 (1)	-0.0 (1)	-0.1 (2)	-0.0 (4)
U_{13}	1.42 (9)	1.31 (9)	2.7 (2)	1.5 (4)
U_{23}	0.1 (1)	-0.1 (1)	-0.3 (2)	-0.2 (4)

minimized. The scattering factors were those of Cromer & Mann (1968). A dispersion correction was made for Cu, Te and Cl (*International Tables for X-ray Crystallography*, 1962). Refinement with isotropic temperature factors converged at $R=0.077$ and $R_w=0.073$. The computations were continued with anisotropic temperature factors and an isotropic correction for extinction (Larson, 1970). The refinement converged at $R=0.056$ and $R_w=0.048$.* The extinction coefficient con-

verged at 1.04 (18). Table 2 contains the atomic parameters. All calculations were done with programs of the systems XTL (Syntex) and X-RAY (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Discussion

CuTe_2Cl is built up of layers parallel to the ab plane (Fig. 1). The main component of a layer is a pseudo-fourfold screw of Te atoms generated by a 2_1 axis. In this screw Te-Te distances and Te-Te-Te angles alternate at 2.737 and 2.792 Å and at 99.9 and 102.7° respectively (Fig. 2), comparable to the screws of Te atoms in Te_3Cl_2 (Kniep, Mootz & Rabenau, 1976) and in elemental Te (Cherin & Unger, 1967) (Table 3). The sum of the bond radii of elemental Te is 2.74 Å (Pauling, 1960). Infinite Te-Te bonds are known only for elemental Te and its subhalides (Kniep, Mootz & Rabenau, 1976). With the formal oxidation state of zero in CuTe_2Cl the occurrence of infinite Te-Te bonds in Te compounds might be associated with the 'unsaturated' character of Te.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31899 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

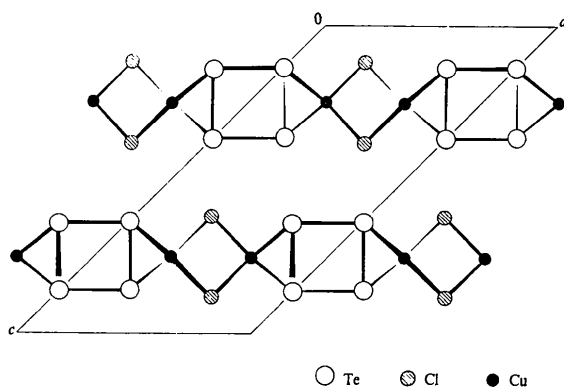


Fig. 1. CuTe_2Cl layer structure projected down b .

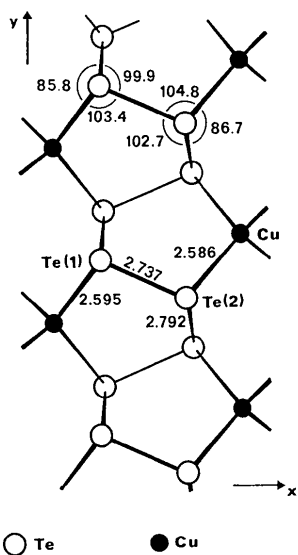


Fig. 2. The pseudo-fourfold screw of Te atoms in CuTe_2Cl . Atomic labelling is consistent with coordinates in Table 2.

Table 3. Te-Te distances (Å) and Te-Te-Te angles (°) in elemental Te and in Te compounds

CuTe_2Cl	Te	Te_3Cl_2
Te-Te distances		
2.737		2.670
2.792	2.835	2.816
Te-Te-Te angles		
99.9		92.73
102.7	103.2	101.38
		101.55

The Te screws are connected by Cu-Cl-Cu links. Each Cu atom is surrounded by two Te and two Cl atoms forming a slightly distorted tetrahedron. Table 4 shows the bond lengths, bond angles and non-bonding distances in this tetrahedron. The Cl-Cu lengths of the bridging Cl atom are 2.343 and 2.348 Å and the Cu-Cl-Cu angle is 105.3°.

Table 4. Bond lengths (Å) (underlined), bond angles (°) (upper right triangles), and non-bonding distances (Å) (lower left triangles) in the CuTe_2Cl_2 coordination tetrahedron

Symmetry codes: Te(1') and Cl' = $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

Cu	Te(1')	Te(2)	Cl'	Cl
Te(1')	<u>2.595</u> (5)	111.9 (3)	105.1 (3)	114.0 (2)
Te(2)	<u>4.294</u> (3)	<u>2.586</u> (7)	114.3 (3)	104.7 (3)
Cl'	<u>3.922</u> (8)	<u>4.144</u> (11)	<u>2.343</u> (8)	106.9 (5)
Cl	<u>4.148</u> (11)	<u>3.910</u> (13)	<u>3.767</u> (11)	<u>2.348</u> (13)

The shortest contacts between layers are non-bonding Te-Cl and Te-Te distances. The shortest Te-Cl contact (3.346 Å) is comparable to that in Te_3Cl_2 , 3.363 Å (Kniep, Mootz & Rabenau, 1976). The Te-Te contact between the layers (3.766 Å) is greater than the intermolecular Te-Te distance in elemental Te (3.495 Å) (Cherin & Unger, 1967) and in Te_3Cl_2 (3.411 Å) (Kniep, Mootz & Rabenau, 1976).*

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* *Note added in proof*:— The compound can be classified as a defect tetrahedral structure. Application of the valence electron concentration rules (Parthé, 1973) leads with $\text{VEC}=5$ and $(\text{VEC})_A=6\frac{2}{3}$ to $N_{\text{NBO}}=1$ and $\text{AA}=\frac{4}{3}$. The corresponding crystal-chemical formula $\text{Cu}^{[41]}\text{Te}_2^{[11+21]}\text{Cl}^{[21]}$ is in complete agreement with the experimental data.

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