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Relationship between Crystal Structure and Ionic Conductivity in CuTeBr

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Abstract

The high-temperature structure of CuTeBr, which exhibits fast ionic conduction, was investigated by single-crystal X-ray diffraction at 373 and 473 K. [Space group $I4_1/amd$; $T = 373$ K: $a = 16.334$ (3), $c = 4.785$ (2) Å, $R_w(F) = 1.2\%$, 303 observed reflections; $T = 473$ K: $a = 16.396$ (5), $c = 4.776$ (3) Å, $R_w(F) = 1.2\%$, 283 observed reflections.] The investigation revealed that the ionic conduction has to be highly anisotropic. A conduction path was found parallel to the c axis. From the refined anharmonic temperature factors a potential barrier of 0.1 eV (1 eV $\equiv 1.6 \times 10^{-19}$ J) was calculated for the motion of copper ions along this path. Conductivity measurements of single crystals confirmed the high anisotropy. At 473 K the conductivity parallel to the c axis is $0.15 \Omega^{-1} \text{ cm}^{-1}$ with an activation energy of 0.25 eV. This is more than ten times the conductivity perpendicular to the c axis, which has an activation energy of 0.36 eV.

Introduction

The three isotopic compounds CuTeX ($X = \text{Cl, Br, I}$) all exhibit a high copper(I) ionic conductivity (von

Alpen, Fenner, Marcoll & Rabenau, 1977) and all are fast ionic conductors at temperatures above 400 K. Among them, CuTeBr has the highest ionic conductivity and lowest activation energy. The low activation energy enables us to study the conduction mechanism with the aid of elastic X-ray diffraction at elevated temperatures. Therefore, the high-temperature structure of CuTeBr was reinvestigated using intensities collected at 373 and 473 K.

Experimental

CuTeBr was prepared by annealing stoichiometric amounts of Te (99.999% pure) and twice-distilled CuBr at a temperature of 623 K for two weeks. Single crystals were grown by the Bridgeman technique. The evacuated ampoule was heated to 753 K and lowered into a Bridgeman furnace at a rate of 10 mm d⁻¹. The crystals obtained were pin shaped, up to 2 cm long and a few mm in diameter. Large single crystals with a diameter of more than 1 cm were grown by a modified Bridgeman technique (Lamprecht & Geiger, 1982).

The crystal used for the X-ray measurement was $0.06 \times 0.06 \times 0.12$ mm. The data collection was carried out with a Philips PW 1100 four-circle

diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. The intensities of two octants in reciprocal space were measured in the ω -scan mode up to $\sin(\theta)/\lambda = 0.65 \text{ \AA}^{-1}$. 50 steps were measured over a scan width of 2° with a scan speed of $0.012^\circ \text{ s}^{-1}$. The intensities and standard deviations were calculated with the program system *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1982) which uses the Lehmann & Larsen (1974) algorithm. The standard deviation $\sigma(I)$ of the intensity I was calculated from counting statistics: $\sigma^2(I) = \sigma_{\text{stat}}^2 + (0.01I)^2$. Reflections with $I < 3\sigma(I)$ were marked as unobserved. The intensities were corrected for absorption [$\mu(\text{Mo } K\alpha) = 29.2 \text{ mm}^{-1}$] with the program *ABSORB* of the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). At 373 K, 381 unique reflections with 78 unobserved reflections were measured and the internal R value [$R(I)$] was 4.5%; at 473 K there were 372 reflections with 89 unobserved and the internal R value was 3.5%.

Crystal structure investigation

The structure of CuTeBr and the isotypic compound CuTeI has been described by Carkner & Haendler (1976), von Alpen, Fenner, Predel, Rabenau & Schluckebier (1978), Fenner & Rabenau (1976) and Fenner & Schulz (1979). Both compounds have a superstructure at room temperature which disappears when going through a first-order phase transition. Only the high-temperature structure will be described here. It consists of fourfold Te helices and chains of edge-sharing Br tetrahedra, all arranged parallel to the c axis. The copper ions are statistically distributed over four sites, all sites being only partially occupied. Three sites are found in the vicinity of the Br tetrahedra [Cu(1)–

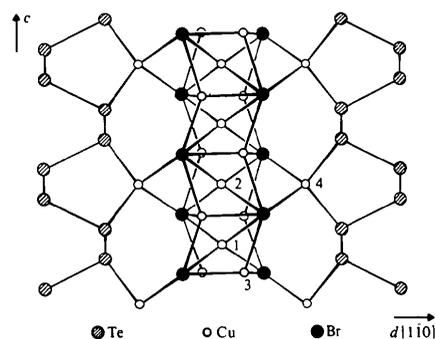


Fig. 1. Projection of part of the structure of CuTeBr parallel to $[110]$.

Cu(3)] with tetrahedral coordination. Two of these sites [Cu(1) and Cu(2)] lie within the tetrahedra. A fourth site [Cu(4)] lies between the Br chains and the Te helices, coordinated by two Br^- ions and two Te atoms (Fig. 1, Table 1).

There is a small difference between the structures reported for CuTeBr and CuTeI. In CuTeI, Cu(1) and Cu(2) are in fourfold positions with one position within each Br tetrahedron and in CuTeBr, Cu(1) and Cu(2) are in eightfold positions with two positions within each tetrahedron. The last model is a split-atom model, which is used to describe the smeared-out electron density in CuTeBr. Although this model gives a better description of the observed electron density, it does not reflect the tetrahedral symmetry of the site.

A partial Fourier synthesis of the copper ions is shown in Fig. 2. The two maxima of the electron density lie at the centers of the tetrahedra, corresponding to Cu(1) and Cu(2). There is a continuous positive electron density connecting the two sites *via* the Cu(3) site. Such a smeared-out electron density can be described in two ways – by split atoms or by large

Table 1. Atomic parameters for CuTeBr, origin at centre $2/m$

$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j.$$

	Atomic position (Wyckoff notation)	Occupation probability	x	y	z	B_{eq} (\AA^2)
$T = 373 \text{ K}$						
Te	16(<i>f</i>)	1.0	0.14215 (4)	0	0	2.2
Br	16(<i>h</i>)	1.0	0	0.11569 (4)	0.6228 (3)	2.9
Cu(1)	4(<i>b</i>)	0.274 (16)	0	0.25	0.375	7.8
Cu(2)	4(<i>a</i>)	0.708 (16)	0	0.25	0.875	7.0
Cu(3)	16(<i>h</i>)	0.125 (8)	0	0.309 (2)	0.113 (4)	13.8
Cu(4)	16(<i>g</i>)	0.604 (4)	0.1320 (2)	0.1180	0.375	4.3
$T = 473 \text{ K}$						
Te	16(<i>f</i>)	1.0	0.14253 (4)	0	0	2.8
Br	16(<i>h</i>)	1.0	0	0.1157 (1)	0.6217 (3)	3.7
Cu(1)	4(<i>b</i>)	0.246 (21)	0	0.25	0.375	8.6
Cu(2)	4(<i>a</i>)	0.641 (18)	0	0.25	0.875	8.3
Cu(3)	16(<i>h</i>)	0.168 (11)	0	0.324 (2)	0.120 (4)	17.7
Cu(4)	16(<i>g</i>)	0.581 (4)	0.1324 (1)	0.1176	0.375	5.4

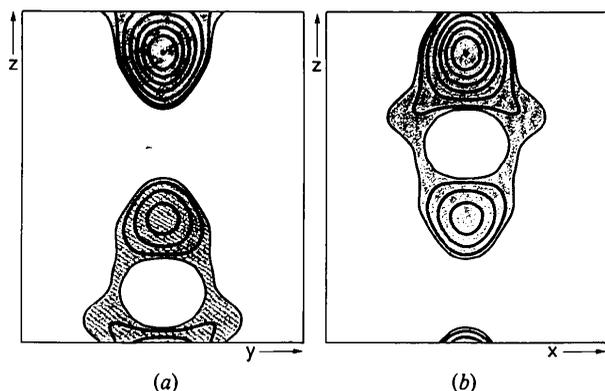


Fig. 2. Partial Fourier synthesis (a) in the yz plane, $x = 0$, and (b) in the xz plane, $y = 0.25$. The highest maximum corresponds to Cu(2), the second maximum to Cu(1). The two maxima are connected *via* Cu(3).

anharmonic thermal vibrations. In the following we shall describe three different models which were used for CuTeBr. The models are compared using the data collected at 473 K, since the differences are more pronounced at the higher temperature.

Model (1) (the split-atom model)

Because of the symmetry and the electron density shown in Fig. 2, 16-fold atomic positions were chosen for Cu(1) and Cu(2), which correspond to four positions in one Br tetrahedron. Each position is slightly displaced from the center towards the face of a tetrahedron. Only harmonic temperature factors were used in the refinement. This model leads to $R_w(F) = 1.6\%$ and a goodness of fit of 1.9; it gives large vibrational amplitudes of more than 1 Å.

The following two models are anharmonic models. Anharmonic thermal vibrations are described by the Gram-Charlier series expansion up to the fourth order (Johnson & Levy, 1974; Zucker & Schulz, 1982). From the refined data the probability density function (p.d.f.) was calculated for each atom. The p.d.f. gives the probability of finding an atom in a volume element close to its equilibrium position. Only positive values of the p.d.f. are physically meaningful and, therefore, those models which lead to large negative values have to be rejected.

Model (2)

The partial Fourier synthesis (Fig. 2) does not show a peak at the Cu(3) site. Therefore one model was refined with only three copper-ion sites [Cu(1), Cu(2) and Cu(4)]. Fourfold sites for Cu(1) and Cu(2) did not give R_w below 3%; only when we used 16-fold positions for Cu(2) did we get R_w below 2%; introducing 16-fold positions for Cu(1), however, did not improve the

result. The final R_w is 1.4% with a goodness of fit of 1.8. The p.d.f. always shows large negative values.

Model (3)

All four copper-ion sites are included; Cu(1) and Cu(2) are in the fourfold positions reported for the structure of CuTeI. Anharmonic temperature factors were refined for all sites as in model (2). The final R_w is 1.2% with a goodness of fit of 1.4. Only small negative regions of the p.d.f. remain with low absolute values and the combined p.d.f.'s of the copper ions give a density very similar to the electron density of the partial Fourier synthesis.

This model is significantly better than the other two models without leading to physically meaningless results. It was also refined with the data collected at 373 K leading to a weighted R value of 1.2% and a goodness of fit of 1.9.*

Discussion

The conduction path in CuTeBr can be derived from the partial Fourier synthesis. It connects the sites Cu(1)–Cu(3) and Cu(3)–Cu(2). The path runs entirely within the Br chains parallel to the c axis.

Using the approximation of single-atom potentials, one can calculate the potential along the conduction path from the p.d.f.'s by:

$$V(\bar{x}) = -kT \ln[\sum w_i(\text{p.d.f.})_i(\bar{x})].$$

$V(\bar{x})$ is the potential at point \bar{x} , k the Boltzmann constant, T the absolute temperature, w_i the occupancy and $(\text{p.d.f.})_i$ the probability density of the i th atom (Zucker & Schulz, 1982; Bachmann & Schulz, 1982). The resulting potential along the lines Cu(1)–Cu(3) and

* Lists of structure factors and all refined parameters for data collected at 373 and 473 K have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36878 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

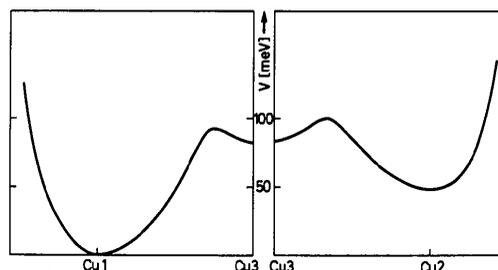


Fig. 3. Variation of the potential along Cu(1)–Cu(3) and Cu(3)–Cu(2). The conduction path from one unit cell to another is Cu(1)–Cu(3)–Cu(2)–Cu(3)–Cu(1).

Cu(3)–Cu(2) is shown in Fig. 3. The potential at Cu(1) and Cu(2) is very flat towards a neighboring copper-ion site and steep towards the Br⁻ ion in the opposite direction. The overall potential barrier for ionic motion is 0.1 ± 0.03 eV.

Unlike Cu(1), Cu(2) and Cu(3), the Cu(4) site appears to be isolated. No measurable electron density is found between Cu(4) and any other site and the p.d.f. falls rapidly to zero outside the equilibrium position of Cu(4). This means that the potential barrier between Cu(4) and another copper-ion site is very high compared to the potential barrier along the conduction path and no measurable portion of the ions is activated to this level at the temperature at which the intensities were measured. The barrier is therefore higher than 0.2 eV.

The results show that ionic conduction in CuTeBr has to be highly anisotropic with good conductivity parallel to the *c* axis.

Conductivity

The conductivity of CuTeBr has only been reported for polycrystalline samples (von Alpen *et al.*, 1977). We therefore measured the conductivity of single crystals parallel and perpendicular to *c*. AC measurements were carried out in the frequency range between 1 and 10^6 Hz at temperatures from 300 to 523 K. The conductivity was derived from impedance plots. A plot of σT versus $1/T$ is shown in Fig. 4.

The conductivity perpendicular to the *c* axis compares very well with the previously reported conductivity of powders. It is $7 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ at 473 K and has an activation energy of 0.36 eV. The conductivity parallel to the *c* axis is more than ten times higher, $0.15 \Omega^{-1} \text{cm}^{-1}$ at 473 K, with an activation energy of 0.25 eV. The error in these values is about 20%.

The conductivity thus shows the predicted anisotropy. There is, however, a large difference between

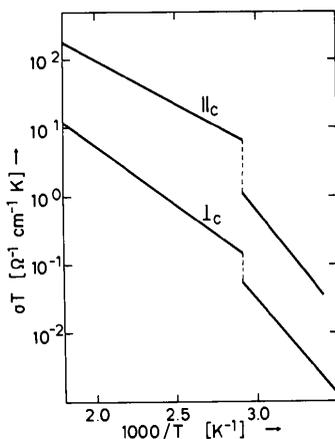


Fig. 4. A plot of σT versus $1/T$ for CuTeBr.

the potential barrier derived from X-ray diffraction studies (0.1 eV) and the activation energy of the conductivity (0.25 eV).

A small difference is expected, because the occupancy of the copper-ion sites changes with temperature; the copper ions are more evenly distributed at higher temperatures. Furthermore, ions can be activated from the Cu(4) site, which accounts for about 0.01 eV.

Richards (1977) studied a theoretical model of one-dimensional conduction. The model has two nonequivalent sites *A* and *B*, alternately arranged and at different potentials, ΔA and ΔB , from the potential maximum. For a half-filled model he predicts an activation energy of $\Delta A + \frac{1}{2}(\Delta A - \Delta B)$ which corresponds to 0.04 eV in the case of CuTeBr. Although this model is simpler than the actual arrangement of the copper ions in CuTeBr, it gives the right order of magnitude.

The large difference cannot be fully explained by these effects. It may be due to correlated motion between neighboring ions or correlation that leads to short-range order. The superstructure at room temperature, where the ions are ordered, is a hint that short-range order exists. We have, therefore started an investigation of the diffuse X-ray scattering of CuTeBr.

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