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Crystal structure of Cu_2Se

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The crystal structures of the low-temperature (space group *C*2/*c*, Pearson symbol *mS*144, a = 7.1379(4) Å, b = 12.3823(7) Å, c = 27.3904(9) Å, β = 94.308°, R_I = 0.0765) and high-temperature (space group *Fm*-3*m*, Pearson symbol *cF*12, a = 5.859(1) Å, $R1$ = 0.0391) modifications of Cu_2Se were determined by means of X-ray powder and single crystal diffraction. The basic features of the two modifications are similar. The Se atoms are stacked in a close-packed arrangement with the layers in the sequence *ABC*. The Cu atoms are distributed over all tetrahedral interstices. The positions of Cu are completely ordered in the low-temperature modification, whereas they are disordered in the high-temperature modification.

Cu compounds / Chalcogenides / X-ray single crystal diffraction / X-ray powder diffraction / Crystal structures

Introduction

Chalcogenides have attracted great interest over the last years due to their thermal, electrical and optical properties. Investigation of the crystal structures of chalcogenides is an important step in the search for new materials [1,2].

The existence of two modifications of the Cu_2Se compound has been known for a long time. However, suffering from the complexity of the twinning, the crystal structure of the low-temperature (LT) modification was not yet been determined. For example, a monoclinic unit cell (a = 14.087 Å, b = 20.481 Å, c = 4.145 Å, β = 90.38°) was proposed in [3]. The LT modification was also examined in [4], using X-ray single crystal and electron diffraction. On the contrary, numerous refinements have been performed of the crystal structure of the high-temperature (HT) modification (space group *Fm*-3*m*, a = 5.787 Å in [5]) because of its superionic properties.

Experimental

A sample with the nominal composition Cu_2Se was prepared by sintering the elements of purity better than 99.9 wt.% in evacuated quartz tubes. The synthesis was carried out in a tube resistance furnace. The ampoule was first heated at a rate of 30 K h^{-1} up to 1420 K, and then kept at this temperature for 3 hours. Afterwards, the sample was slowly cooled (10 K h^{-1}) to 870 K, and annealed at this temperature for 720 hours. Subsequently, the ampoule was quenched in air.

A small single crystal of Cu_2Se suitable for crystal structure investigations was selected from the sample. X-ray diffraction data were collected on a KUMA Diffraction KM-4 four-circle diffractometer equipped with a CCD detector, using graphite-monochromatized MoK_α radiation (λ = 0.71073 Å). High-temperature measurements of the Cu_2Se single crystal were performed up to 415 K using KUMA Diffraction equipment. The raw data were treated with the CrysAlis Data Reduction program [6] taking into account an absorption correction. The intensities of the reflections were corrected for Lorentz and polarization effects. The crystal structure was solved by the Patterson method and refined by the full-matrix least-squares method using SHELXL-97 [7].

The X-ray powder diffraction pattern of Cu_2Se for the crystal structure refinement was recorded using a X'Pert PRO powder diffractometer (Cu K_α radiation, 10° ≤ 2θ ≤ 100°, step scan mode with a step size of

0.02º and counting time of 3597 s per data point). The crystal structure determination was performed using the CSD [8] program.

Results and discussion

The crystal structure of the low-temperature (LT) phase of Cu_2Se was investigated in two steps. At the first step, a small single crystal of Cu_2Se was selected from the sample of the respective composition. A model of the structure was obtained from X-ray single crystal diffraction data ($R1 \approx 0.14$) at room temperature. At the second step, X-ray powder diffraction data were used for the refinement. The model of the crystal structure obtained from the single crystal investigation was used for the powder diffraction refinement. The cell parameters and experimental details of the powder diffraction refinement of LT-Cu_2Se are given in Table 1, whereas the atomic coordinates and displacement parameters are listed in Table 2. Twelve Cu positions and six Se positions were determined. All the positions are fully occupied. Since the structure of the LT phase is complex, the values of the displacement parameters were fixed. The experimental and calculated diffractograms and the corresponding difference diagram are shown in Fig. 1.

The single crystal was also investigated above room temperature. The dependence of the lattice parameters on temperature is shown in Fig. 2. The lattice parameters *a* and *b* increase, however, the parameter *c* decreases with increasing temperature; an increase of the unit cell volume is observed. The low-temperature modification of Cu_2Se transforms to the high-temperature (HT) modification above ~400 K.

A single crystal structure determination was performed on data collected at 415 K. As a result of the crystal structure solution and refinement, one Se position and three Cu positions were found. The arrangement of the Se atoms is ordered, whereas the Cu atoms are disordered. The displacement parameters of Cu were determined in isotropic approximation. The cell parameters and experimental details of the crystal structure determination for the HT phase of Cu_2Se are given in Table 3, whereas the atomic coordinates and displacement factors are listed in Table 4. One additional position of Cu was observed in the structure of HT-Cu_2Se in the present work, when compared with the results published in [5].

Table 1 Crystallographic data and experimental details for LT-Cu_2Se.

Compound	Cu_2Se
Space group	*C*2/*c* (No. 15)
a (Å)	7.1379(4)
b (Å)	12.3823(7)
c (Å)	27.3904(9)
β (°)	94.308(5)
Cell volume (Å^3)	2414.0(4)
Number of formula units per unit cell	48
Calculated density (g/cm^3)	6.803
Radiation and wavelength	Cu 1.54178 Å
Diffractometer	X'Pert PRO
Mode of refinement	Full profile
Number of atom sites	18
Structure solution and refinement	CSD
R_I	0.0765
R_p	0.1237
Texture axis and parameter	[0 0 1] 1.062(9)

Table 2 Atomic coordinates and isotropic temperature factors for LT-Cu_2Se.

Atom	Position	*x*/*a*	*y*/*b*	*z*/*c*	B_{iso} (Å^2)
Cu1	8*f*	0.364(2)	0.075(2)	0.3198(6)	2.0
Cu2	8*f*	0.890(2)	0.915(2)	0.4284(5)	2.0
Cu3	8*f*	0.881(3)	0.245(1)	0.3221(6)	2.0
Cu4	8*f*	0.405(2)	0.077(2)	0.4562(5)	2.0
Cu5	8*f*	0.226(3)	0.205(1)	0.3982(7)	2.0
Cu6	8*f*	0.903(3)	0.241(1)	0.4293(6)	2.0
Cu7	8*f*	0.623(2)	0.905(2)	0.3514(5)	2.0
Cu8	8*f*	0.865(2)	0.911(2)	0.2886(5)	2.0
Cu9	8*f*	0.526(3)	0.275(1)	0.3567(6)	2.0
Cu10	8*f*	0.654(2)	0.089(2)	0.3918(6)	2.0
Cu11	8*f*	0.991(2)	0.053(1)	0.3552(5)	2.0
Cu12	8*f*	0.263(2)	0.936(1)	0.3980(5)	2.0
Se1	8*f*	0.057(2)	0.077(1)	0.4448(4)	1.0
Se2	8*f*	0.694(2)	0.083(1)	0.3037(4)	1.0
Se3	8*f*	0.201(2)	0.237(1)	0.3104(4)	1.0
Se4	8*f*	0.082(2)	0.747(1)	0.4445(4)	1.0
Se5	8*f*	0.571(2)	0.902(1)	0.4409(4)	1.0
Se6	8*f*	0.198(2)	0.912(1)	0.3082(4)	1.0

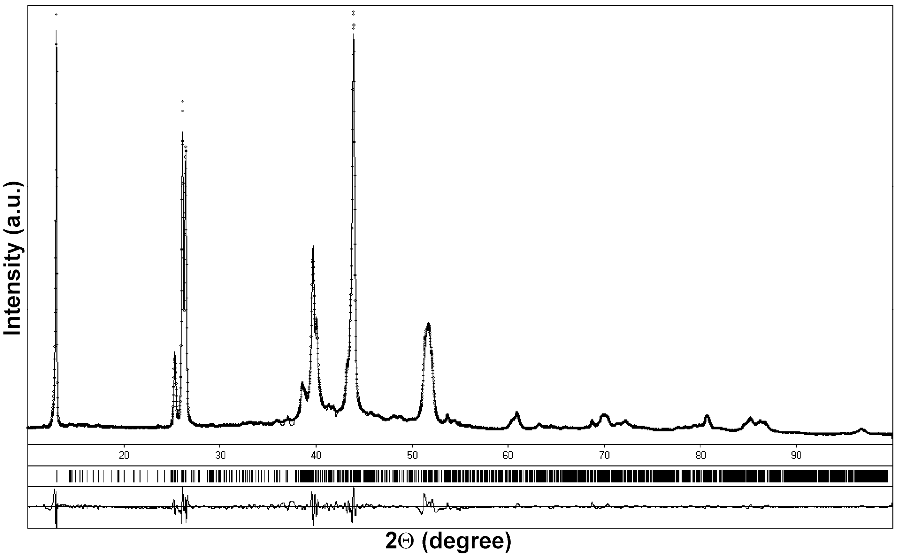

Fig. 1 Experimental and calculated diffractograms and the corresponding difference diagram for LT-Cu_2Se.

Table 3 Crystallographic data and experimental details for HT-Cu_2Se.

Compound	Cu_2Se
Formula weight	206.04
Space group	*Fm*-3*m* (No. 225)
a (Å)	5.859(1)
Volume (Å^3)	201.1(1)
Number of formula units per unit cell	4
Measurement temperature	415
Calculated density (g/cm^3)	6.803
Absorption coefficient (mm^{-1})	38.712
F(000)	368
Crystal color	black
Crystal size (mm)	0.10×0.06×0.05
θ range for data collection	6.03-29.02
Index ranges	$-7 \le h \le 7$ $-7 \le k \le 8$ $-7 \le l \le 8$
Reflections collected	535
Independent reflections	26 [$R_{int.}$ = 0.0870]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	26/0/7
Goodness-of-fit on F^2	1.295
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0391$, $wR2 = 0.1008$
R indices (all data)	$R1 = 0.0391$, $wR2 = 0.1008$
Largest difference peak and hole (e/Å^3)	0.883 and -0.708

Table 4 Atomic coordinates and displacement factors for HT Cu_2Se.

Atom	Position	x/a	y/b	z/c	Occ.	U_{eq} (Å^2)	U_{11} (Å^2)	U_{22} (Å^2)	U_{33} (Å^2)	U_{23} (Å^2)	U_{13} (Å^2)	U_{12} (Å^2)
Cu1	8*c*	1/4	1/4	1/4	0.31	0.040(2)						
Cu2	32*f*	0.309(1)	*x*	*x*	0.14	0.063(3)						
Cu3	32*f*	0.384(5)	*x*	*x*	0.03	0.05(1)						
Se	4*a*	0	0	0	1	0.037(1)	0.037(1)	0.037(1)	0.037(1)	0	0	0

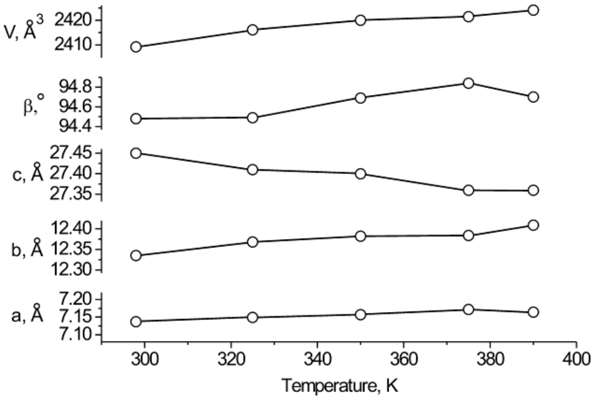

Fig. 2 Variation of the lattice parameters with temperature for LT-Cu_2Se.

Table 5 Interatomic distances (δ) and coordination numbers (CN) of the Cu atoms in the structure of LT-Cu_2Se.

Atoms		δ (Å)	CN
Cu1	-1Se3	2.32(2)	3
	-1Se6	2.35(3)	
	-1Se2	2.43(2)	
Cu2	-1Se5	2.33(2)	3
	-1Se1	2.37(3)	
	-1Se4	2.50(3)	
Cu3	-1Se3	2.33(3)	3
	-1Se2	2.45(2)	
	-1Se6	2.46(2)	
Cu4	-1Se1	2.47(2)	3
	-1Se4	2.50(2)	
	-1Se5	2.51(3)	
Cu5	-1Se1	2.42(2)	2
	-1Se3	2.43(2)	
Cu6	-1Se5	2.34(2)	3
	-1Se1	2.34(3)	
	-1Se4	2.36(3)	
Cu7	-1Se3	2.44(2)	3
	-1Se5	2.51(2)	
	-1Se2	2.63(3)	
Cu8	-1Se6	2.40(2)	4
	-1Se2	2.51(3)	
	-1Se3	2.54(2)	
	-1Se6	2.66(2)	
Cu9	-1Se4	2.43(2)	3
	-1Se6	2.53(2)	
	-1Se3	2.60(3)	
Cu10	-1Se2	2.45(2)	2
	-1Se4	2.51(2)	
Cu11	-1Se1	2.48(2)	3
	-1Se2	2.48(2)	
	-1Se6	2.67(2)	
Cu12	-1Se5	2.45(2)	3
	-1Se6	2.48(2)	
	-1Se1	2.67(2)	

Relevant interatomic distances and coordination numbers (CN) of the atoms in the low-temperature and high-temperature modifications of Cu_2Se are listed in Tables 5 and 6, respectively. The values of the Cu-Se distances correlate well with the sum of the ionic radii [9]. The Se atoms in the structure of LT-Cu_2Se are stacked in a close-packed arrangement with the layers in the sequence *ABC* (Fig. 3). The Cu atoms are distributed over all the tetrahedral interstices. For most of the tetrahedrons the Cu atoms are shifted from the center of the polyhedron to one of the triangular faces or to an edge of the tetrahedron. Two Se atoms surround each of the Cu5 and Cu10 atoms, whereas tetrahedral surrounding exists only for the Cu8 atom. The remaining symmetry-independent copper atoms are located close to the plane of a triangular face (CN = 3). The crystal structure of LT-Cu_2Se is related to the structure of the recently investigated compound Cu_2SnSe_3 [10] (Fig. 4). The Se atoms in the structure of Cu_2SnSe_3 are also stacked in a close-packed arrangement with the layers in the sequence *ABC*. However, the Cu and Sn atoms occupy only half of the tetrahedral interstices. The structure of Cu_2SnSe_3, consisting of 96 atoms per unit cell 32Cu + 16Sn + 48Se, can be obtained from the structure of LT-Cu_2Se (144 atoms per unit cell: 96Cu + 48Se) by replacement of 64 Cu atoms by 16 Sn atoms. This substitution can be realized according to the relation $4Cu^{+} \rightarrow 1Sn^{4+}$.

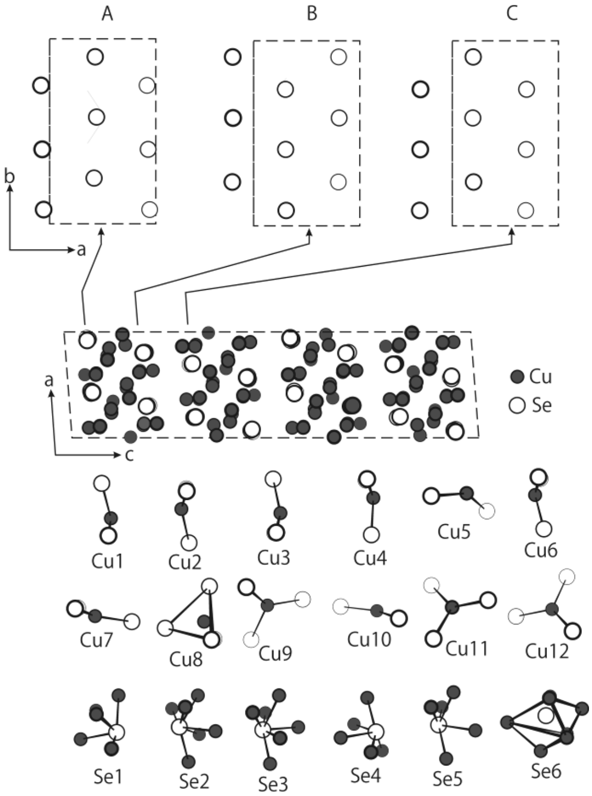

Fig. 3 Unit cell content and coordination polyhedra for LT-Cu_2Se.

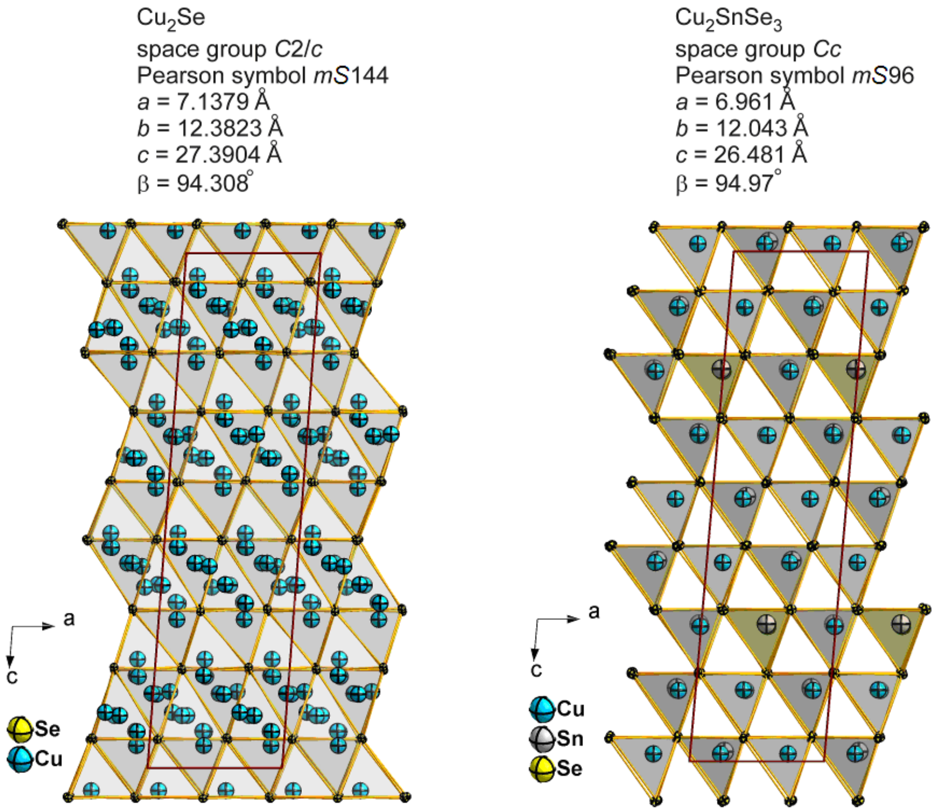

Fig. 4 Arrangement of Se tetrahedra and Cu and Sn atoms in the structures of LT-Cu_2Se and Cu_2SnSe_3.

Table 6 Interatomic distances (δ) and coordination numbers (CN) of the copper atoms in the structure of HT-Cu_2Se.

Atoms		δ (Å)	CN
Cu1	-4Se	2.5372(8)	4
Cu2	-3Se	2.404(1)	3
Cu3	-3Se	2.44(1)	3

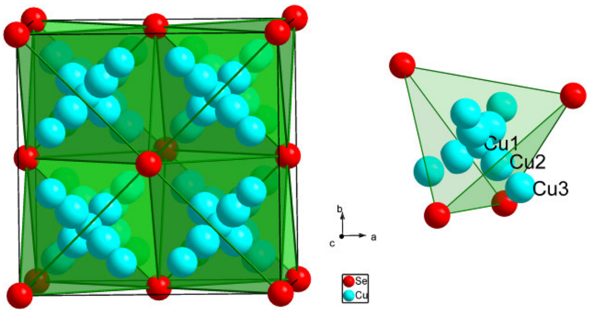

Fig. 5 Unit cell content and arrangement of Cu atoms in/near one Se_4 tetrahedron in HT-Cu_2Se.

The unit cell of the HT-phase of Cu_2Se is shown in Fig. 5. The Se atoms are stacked in a close-packed arrangement with the layers in the sequence *ABC*. The Cu1 position is located exactly at the center of the tetrahedral interstice, whereas the Cu2 and Cu3 atoms are located close to a triangular face of the tetrahedron. The total occupancy of the copper sites is $0.31\text{Cu1} + 4\cdot0.14\text{Cu2} + 4\cdot0.03\text{Cu3} = {\sim}1$. Therefore, there are no empty tetrahedrons built by four selenium atoms in the lattice. Each tetrahedron is always occupied by a copper atom, however, the copper atom can be disordered in static or dynamic manner. The latter means that Cu^+ can easily drift among the Cu1, Cu2 and Cu3 positions inside the tetrahedron.

Conclusions

The structures of the low- and high-temperature modifications of Cu_2Se have similar construction. The positions of the Se atoms in both modifications are ordered. The positions of the Cu atoms are ordered in the structure of the low-temperature modification, whereas they are disordered in the high-temperature modification.

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