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Synthesis, Crystal Structure and Properties of Ag_4CuTeO_6

Wilhelm Klein, Jan Curda, and Martin Jansen*

Stuttgart, Max-Planck-Institut für Festkörperforschung

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Abstract. The new quaternary oxide Ag_4CuTeO_6 has been obtained by solid state reaction starting from stoichiometric amounts of the binary oxides at elevated temperatures and oxygen pressures. Ag_4CuTeO_6 crystallises in space group $C2/c$ with $a = 11.3021(8)$, $b = 9.6875(6)$, $c = 5.7082(5)$ Å, $\beta = 99.301(7)°$, $V = 616.77(8)$ Å^3, $Z = 4$; the structure refinement was based on 747 independent reflections and resulted in $R_1 = 3.26\,\%$, $wR_2 = 7.29\,\%$. The crystal structure consists of isolated TeO_6 octahedra which are connected by distorted CuO_4 squares, thus forming one-dimensional, infinite heteropolyanions, extending along the *c* axis. According to the approximately *fcc* packing and a distorted octahedral oxygen environment of all the cations, the structure may be regarded a derivative of the NaCl structure type.

Ag_4CuTeO_6 is paramagnetic between 300 K and 7 K, where it develops antiferromagnetic ordering. An evaluation according to the Curie-Weiss law yielded a magnetic moment of 1.86 μ_B per copper ion. The electronic conductivity shows a maximum at ~ 75 K, below a temperature characteristic of a semiconductor, above of a metal.

Keywords: Tellurium; Copper; Silver; High oxygen pressure synthesis; Magnetism

Introduction

Oxides of metals with unpaired electrons adopting crystal structures with low-dimensional building units often exhibit intriguing physical properties, in particular with respect to magnetism and electronic conductivity [1−3]. Such low-dimensional structures can cause highly anisotropic physical properties since interactions between electrons, *e.g.* magnetic coupling, preferably develop following the crystallographic orientation of the substructures. Ternary silver(I) oxides quite commonly exhibit such kind of crystal structures with anionic partial structures which are highly anisotropic [4−11]. This is caused by the characteristic tendency of monovalent silver to form extended aggregates of Ag atoms resembling sections of the element's structure, and therefore to induce a clear separation of cationic and anionic parts of the crystal structure. From ternary silver oxides anionic structures in dimensionalities from zero to three are known, thus including chains, layers and three-dimensional networks. We have started investigating ternary silver tellurates, and have noticed that this family of compounds shows an impressive chemical and crystal chemical variety, depending on the content of silver: Ag_6TeO_6 [12] contains isolated TeO_6 octahedra, Ag_2TeO_4 [13] consists of chains which represent sections of the rutile structure, which were also found in $Ag_2Hg_2(TeO_4)_3$ [14], $Ag_2Te_2O_6$ [15], occurring in two polymorphic modifications, forms layers, while three-dimensional networks are found in $Ag_2Te_4O_{11}$ [15] and in the pyrochlore-related $Ag_2Te_2O_7$ [16]. However, all these tellurates do not contain unpaired electrons and thus are diamagnetic and electrochemically insulating. We have started to use these compounds as matrices for introducing additional electronically active transition metals with the intention to produce materials with interesting properties.

Here we report on a first result obtained at inserting copper into silver tellurates, the synthesis, crystal structure and properties of Ag_4CuTeO_6.

Experimental Section

Ag_4CuTeO_6 was prepared by reacting of Ag_2O (freshly precipitated), TeO_2 (Fluka, p. a.) and CuO (Merck p.a.) in stainless steel autoclaves at elevated oxygen pressures [17]. Stoichiometric amounts of these oxides were intimately mixed and placed into gold tubes which were sealed from one side and mechanically closed (not gas-tight) from the other. Black, polycrystalline samples of Ag_4CuTeO_6 were obtained under an oxygen pressure of 380 to 420 MPa within the temperature range of 400 to 550 °C. In a typical experiment, Ag_4CuTeO_6 was synthesized from a mixture of 232 mg Ag_2O (2 mmol), 40 mg CuO (0.5 mmol) and 80 mg TeO_2 (0.5 mmol) reacted at 415 MPa oxygen pressure and 500 °C for 2 d. To prepare single crystals suitable for X-ray diffraction analysis, 1 ml H_2O was added to the starting mixture as mineraliser.

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* Prof. Dr. Martin Jansen
Max-Planck-Institut für Festkörperforschung
Heisenbergstraße 1
D-70569 Stuttgart/Germany
Tel.: +49 711 689 1500
Fax: +49 711 689 1502
E-Mail: m.jansen@fkf.mpg.de

X-ray diffraction powder data were collected with a Stoe Stadi-P diffractometer (Cu $K\alpha_1$, Ge monochromator, linear PSD) in steps of 0.1° over a 2θ range from 10 to 90° for 24 h. The observed reflections are listed in Table 1.

Table 1 Experimental X-ray powder data for Ag_4CuTeO_6 with $d > 1.48$ Å.

d_{obs} [Å]	I / I_0	h	k	l	d_{obs} [Å]	I / I_0	h	k	l	d_{obs} [Å]	I / I_0	h	k	l
7.3112	1.4	1	1	0	2.3645	55.1	2	0	2	1.7184	0.8	3	5	0
4.7095	5.9	−1	1	1	2.3409	7.6	−4	2	1	1.6832	6.1	−6	0	2
4.2484	5.6	1	1	1	2.3287	95.0	−3	3	1	1.6807	29.4	5	3	1
3.6721	8.0	0	2	1	2.2234	0.6	2	4	0	1.6390	29.6	−1	3	3
3.1765	0.8	−3	1	1	2.1733	1.5	5	1	0	1.6148	11.3	0	6	0
3.1028	1.9	1	3	0	2.1558	0.8	3	3	1	1.6030	0.7	2	2	3
2.9328	3.4	2	2	1	2.1139	2.0	−2	4	1	1.5918	0.7	6	2	1
2.7885	43.2	4	0	0	2.0401	1.2	1	3	2	1.5811	1.1	−7	1	1
2.6946	54.0	−2	0	2	1.9483	1.5	−3	3	2	1.5602	1.4	1	5	2
2.6672	100.0	1	3	1	1.9090	2.7	1	5	0	1.5522	2.0	0	6	1
2.5330	1.7	1	1	2	1.8661	3.2	−5	1	2	1.5179	2.0	−3	5	2
2.4378	1.6	3	3	0	1.7742	1.0	1	1	3	1.5127	1.0	−2	6	1
2.3701	8.4	−3	1	2	1.7470	3.7	−2	2	3	1.4833	0.6	0	4	3

Table 2 Crystallographic data and details of the structure determination of Ag_4CuTeO_6.

compound	Ag_4CuTeO_6
space group	$C2/c$ (No. 15)
a	11.3021(8) Å
b	9.6875(6) Å
c	5.7082(5) Å
β	99.301(7)°
cell volume V	616.77(8) Å^3
formula units Z	4
molar mass	718.62 g/mol
density (calculated)	7.7391 g/cm^3
absorption coefficient μ	20.478 mm^{-1}
absorption correction	semi-empirical
2θ-range	5.56−55.98°
hkl-region	$-14 \le h \le 14$ $-12 \le k \le 12$ $-7 \le l \le 7$
measured reflections	3098
$R(int)$	4.17 %
independent reflections	747
independent reflections (I $2\sigma(I)$)	545
parameters	58
$R(F)$ ($I > 2\sigma(I)$ / all data)	3.26 % / 5.32 %
$R_w(F^2)$ ($I > 2\sigma(I)$ / all data)	7.29 % / 8.08 %
goodness-of-fit (all data)	1.047
extinction coefficient	0
max. difference electron density	1.76 e$^-$Å^{-3} (0.75 Å from Ag(3))
min. difference electron density	−1.18 e$^-$Å^{-3} (1.30 Å from Ag(3))
depository no.	CSD-416931

Table 3 Atomic coordinates and isotropic displacement parameters[a] in Å^2 for Ag_4CuTeO_6.

Atom	Wyckoff position	x	y	z	U_{eq}
Ag(1)	4e	1/2	−0.07322(12)	1/4	0.0255(3)
Ag(2)	4d	1/4	1/4	1/2	0.0318(4)
Ag(3)	8f	0.23784(7)	0.41857(10)	0.02575(15)	0.0273(3)
Cu	4e	1/2	0.58246(17)	1/4	0.0133(4)
Te	4e	1/2	0.27509(9)	1/4	0.0101(2)
O(1)	8f	0.3870(5)	0.1378(7)	0.3210(11)	0.0171(14)
O(2)	8f	0.3987(6)	0.4250(6)	0.3292(11)	0.0155(14)
O(3)	8f	0.4204(6)	0.2759(7)	−0.0806(11)	0.0155(13)

[a] U_{eq} is defined as $\exp[-8\pi^2 U(\sin^2\theta/\lambda^2)]$.

Table 4 Anisotropic displacement parameters[b] in Å^2 for Ag_4CuTeO_6.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ag(1)	0.0444(8)	0.0130(5)	0.0190(5)	0	0.0044(5)	0
Ag(2)	0.0230(7)	0.0436(9)	0.0325(7)	−0.0027(5)	0.0160(6)	0.0004(5)
Ag(3)	0.0193(4)	0.0337(6)	0.0261(4)	−0.0046(3)	−0.0045(4)	−0.0002(3)
Cu	0.0166(9)	0.0110(8)	0.0130(7)	0	0.0042(7)	0
Te	0.0123(5)	0.0112(4)	0.0067(4)	0	0.0011(3)	0
O(1)	0.017(3)	0.017(3)	0.017(3)	−0.002(3)	0.002(3)	−0.013(3)
O(2)	0.017(3)	0.013(3)	0.016(3)	−0.005(2)	0.001(3)	0.001(3)
O(3)	0.015(3)	0.019(3)	0.012(3)	−0.002(3)	0.000(3)	−0.007(3)

[b] U_{ij} are defined as $\exp[-2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$.

Table 5 Selected bond lengths /Å and angles for Ag_4CuTeO_6.

Atoms	Distance	Atoms	Angle
Te−O(1)	1.932(6) [2x]	O(1)−Te−O(2)^{i}	174.7(3)° [2x]
Te−O(2)	1.948(6) [2x]	O(3)−Te−O(3)^{i}	179.6(4)°
Te−O(3)	1.955(6) [2x]	O(1)−Te−O(1)^{i}	93.0(4)°
Cu−O(3)^{ii}	1.978(6) [2x]	O(1)−Te−O(2)	91.8(3)° [2x]
Cu−O(2)	2.002(6) [2x]	O(1)−Te−O(3)	89.3(3)° [2x]
Cu−O(2)^{iii}	2.489(6) [2x]	O(1)−Te−O(3)^{i}	91.0(3)° [2x]
Ag(1)^{vi}−O(3)^{ii}	2.425(7) [2x]	O(2)−Te−O(2)^{i}	83.5(4)°
Ag(1)^{vi}−O(1)^{vi}	2.479(7) [2x]	O(2)−Te−O(3)^{i}	88.2(3)° [2x]
Ag(1)^{vi}−O(1)^{v}	2.647(6) [2x]	O(2)−Te−O(3)	91.4(3)° [2x]
Ag(2)−O(1)	2.265(6) [2x]	O(2)−Cu−O(3)^{ii}	164.0(3)° [2x]
Ag(2)−O(2)	2.679(6) [2x]	O(3)^{ii}−Cu−O(3)^{iv}	92.1(4)°
Ag(2)−O(3)^{x}	2.831(7) [2x]	O(2)−Cu−O(3)^{iv}	95.5(3)° [2x]
Ag(3)^{i}−O(2)^{i}	2.300(7)	O(2)−Cu−O(2)^{i}	80.8(4)°
Ag(3)^{i}−O(1)^{ix}	2.303(6)	O(1)^{vi}−Ag(1)^{vi}−O(3)^{ii}	165.3(2)° [2x]
Ag(3)^{i}−O(3)^{i}	2.634(7)	O(3)^{ii}−Ag(1)^{vi}−O(3)^{iv}	71.9(3)°
Ag(3)^{i}−O(3)^{ix}	2.650(6)	O(1)^{vii}−Ag(1)^{vi}−O(3)^{ii}	111.6(2)° [2x]
Ag(3)^{i}−O(2)^{iii}	2.742(6)	O(1)^{vi}−Ag(1)^{vi}−O(1)^{vii}	68.9(3)°
Ag(3)^{i}−O(1)^{ix}	2.769(6)	O(1)−Ag(2)−O(1)	180°
Cu−Cu^{ii}	3.2708(16)	O(1)^{ix}−Ag(3)^{i}−O(2)^{i}	162.4(2)°

Symmetry codes: (i) $-x+1, y, -z+1/2$; (ii) $-x+1, -y+1, -z$; (iii) $-x+1, -y+1, -z+1$; (iv) $x, -y+1, z+1/2$; (v) $x, -y+1, z-1/2$; (vi) $x, y+1, z$; (vii) $-x+1, y+1, -z+1/2$; (viii) $-x+1/2, -y+1/2, -z+1$; (ix) $x+1/2, -y+1/2, z+1/2$; (x) $x, y, z+1$; (xi) $x+1/2, y+1/2, z$.

Single crystal data of Ag_4CuTeO_6 were collected on a Bruker AXS diffractometer with SMART-CCD (APEX) (MoK_α graphite monochromator, semi-empirical absorption correction with the program SADABS [18]).

The crystal structure was solved with direct methods [19], all metal atoms were found at this stage, while the oxygen atoms were localised by Fourier analyses. Further information concerning the data collection and processing, the crystallographic parameters, as well as details on structure solution and refinement are given in Table 2. The atomic coordinates, displacement parameters and bond lengths and angles are shown in Tables 3-5. Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-416931, the name of the authors and the citation of the paper.

Thermal decomposition experiments were performed with a STA 409 (Netzsch, Selb, Germany) with a heating rate of 10 °C/min in argon atmosphere. The decomposition of Ag_4CuTeO_6 occurs with an onset at 600 °C, as solid residues elemental silver, Ag_2TeO_3 and CuO were identified by powder X-ray diffraction. The measured weight loss at 700 °C was 4.50 % (calc. 4.45 %).

Magnetic measurements were performed on a SQUID-Magnetometer (MPMS 5.5, Quantum Design) between 5 and 350 K in magnetic fields up to 5 T.

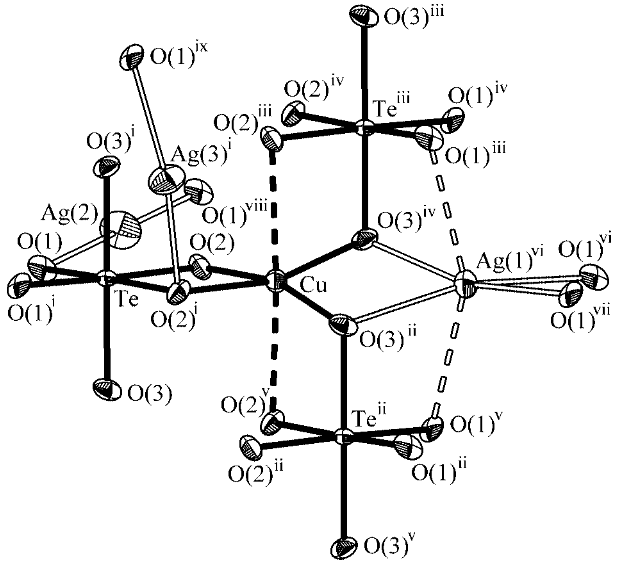

Fig. 1 Coordiations of cations in Ag_4CuTeO_6, displacement ellipsoids are drawn at the 50 % probability level, dashed lines represent distances longer than 2.48 Å for Cu-O and 2.62 Å for Ag-O separations. Symmetry codes: (i) $-x+1$, y, $-z+1/2$; (ii) $-x+1$, $-y+1$, $-z$; (iii) $-x+1$, $-y+1$, $-z+1$; (iv) x, $-y+1$, $z+1/2$; (v) x, $-y+1$, $z-1/2$; (vi) x, $y+1$, z; (vii) $-x+1$, $y+1$, $-z+1/2$; (viii) $-x+1/2$, $-y+1/2$, $-z+1$; (ix) $x+1/2$, $-y+1/2$, $z+1/2$.

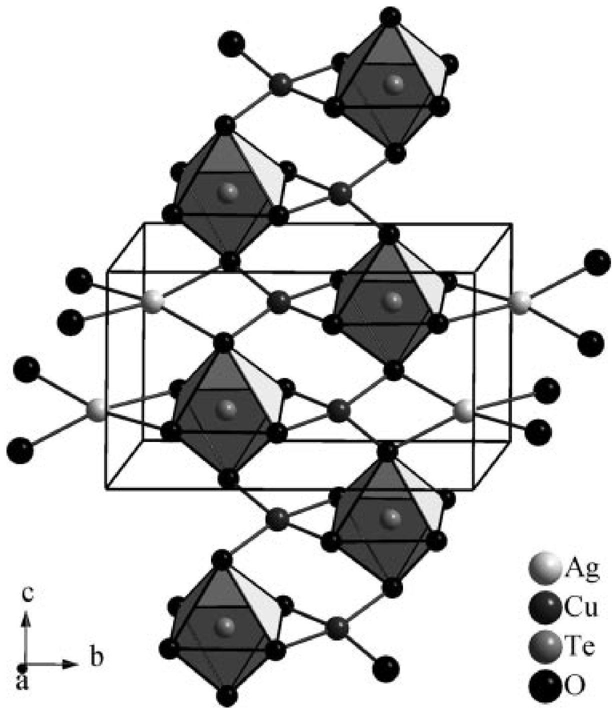

Fig. 2 $^{1}_{\infty}[CuTeO_6]^{4-}$ chains in Ag_4CuTeO_6, view approximately along [−101]. The chains are connected by Ag(1) cations in direction of the *b* axis.

Measurements of the electrical conductivity were performed by the four-point-probe method (Van-der-Pauw) on pressed pellets (diameter: 6 mm, thickness: 1 mm).

Results and Discussion

Ag_4CuTeO_6 has been obtained from solid state reactions of its binary components at elevated oxygen pressures. While the new compound forms rather easily, no further compounds have been found in this quaternary system. When using starting mixtures of compositions different from the title compound, always known ternary silver and copper tellurates were found as by-products. Obtaining copper(II) at the conditions applied here, is in accordance with our former findings [20].

The crystal structure of Ag_4CuTeO_6 exhibits well known coordination polyhedra for all cations involved. Tellurium is surrounded by a slightly distorted octahedron of oxygen atoms in an average distance of 1.945 Å. These TeO_6 octahedra are isolated from each other and are linked via copper atoms, which are situated in a twisted square coordination of oxygen atoms. The CuO_4 squares share one common edge and two vertices with the TeO_6 octahedra, as is shown in Figure 1. The dihedral angle of the four square ligands (O(2)-O(3)^{iv}-O(3)^{ii}-O(2)^{i}) is about 19°, together with two more oxygen atoms at longer distances of 2.489 Å (dotted lines in Fig. 1) a distorted octahedral 4+2 oxygen coordination results. The linkage of TeO_6 and CuO_{4+2} groups results in infinite chains extending along [001] as is illustrated in Figure 2. The chains are interconnected by Ag(1) atoms forming $^{2}_{\infty}[Ag(1)CuTeO_6]^{3-}$ slabs oriented perpendicular to [100]. These slabs are separated by layers of Ag(2) and Ag(3) atoms. While Ag(2) and Ag(3) are in an approximately linear coordination by two oxygen atoms, Ag(1) atoms are surrounded by a twisted square of oxygen atoms very similar to the copper case but with considerably longer M-O separations (Tab.1). These comply well with those of monovalent silver in a square environment as observed in the hollandite derivative $Ag_{1.8}Mn_8O_{16}$ [21, 22]. All silver atoms have additional neighbours at distances beyond 2.6 Å resulting in a 4+2 (Ag(1)) and 2+4 (Ag(2), Ag(3)) coordination, respectively. Thus for all cations a more or less distorted octahedral environment has been found. With respect to the approximately cubic close packing of the cations in the layered arrangement, the crystal structure of Ag_4CuTeO_6 can be regarded as a distorted variant of the α-$NaFeO_2$ structure type (Fig. 3), or, in an even more general view, of the rock salt structure type.

Regarding the layered nature of the crystal structure, it is not self-evident to find a relationship to the α-$NaFeO_2$ structure type here. Normally, one would expect the delafossite, $CuFeO_2$, structure type to occur [7, 8]. Here, our former observations on layered silver oxides containing Sn, Pb, Tl [9, 17] that, with increasing size of the octahedra forming the [MO_2]-slabs, the AgO_2 dumbbells prefer a tilted orientation with respect to the layer plane, is confirmed.

No short Ag-Ag separations indicative for d^{10}- d^{10} interactions are present in Ag_4CuTeO_6. Edge sharing $Te^{VI}O_6$ octahedra and $Cu^{II}O_4$ squares are also known *e.g.* from $CuTeO_4$ [23].

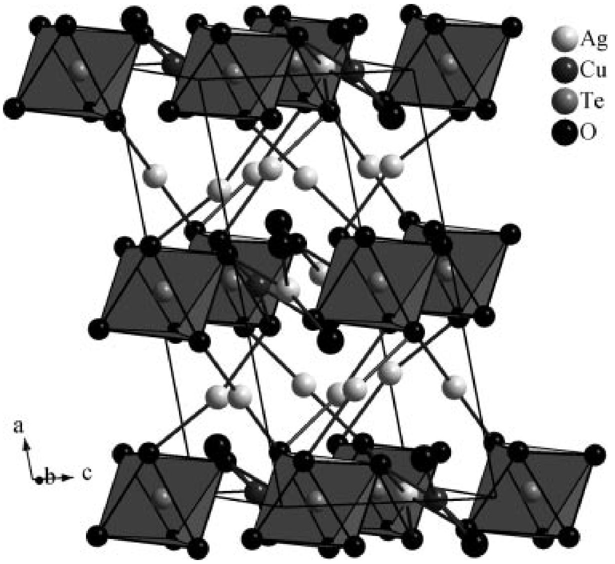

Fig. 3 Crystal structure of Ag_4CuTeO_6, view emphasizing the relationship to the α-$NaFeO_2$ structure type, with TeO_6 octahedra, Cu and Ag(1) in distorted square planar, and Ag(2)/Ag(3) in approximately linear coordination by oxygen atoms.

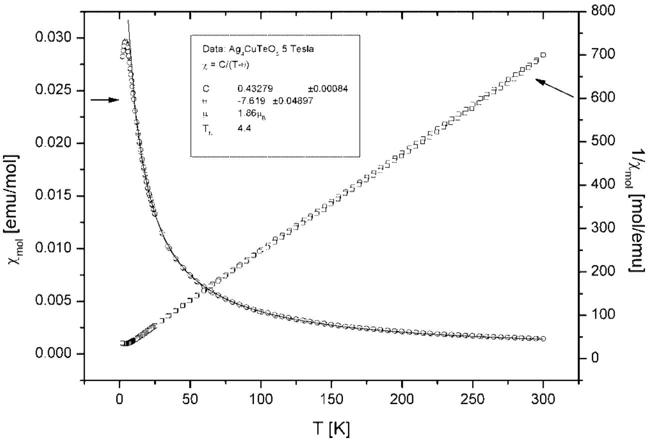

Fig. 4 Temperature dependence of the molar magnetic susceptibility and its inverse of Ag_4CuTeO_6. Parameters used for the Curie-Weiss fit are given in the insert.

Ag_4CuTeO_6 follows the Curie-Weiss law in the temperature range of 7-300 K, see Figure 4. This result is documenting that the spin $^1/_2$ sites are rather efficiently isolated. The resulting magnetic moment of 1.86 μ_B is as expected for Cu^{2+}, showing some significant orbital contribution. The electronic conductivity shows a remarkable transition from a semiconducting temperature characteristic at low temperatures and a metallic one at higher temperatures, with the maximum of conductivity at 75 K, see Figure 5.

Noteworthy this semiconductor to metal transition is not reflected in the temperature dependence of the magnetic susceptibility.

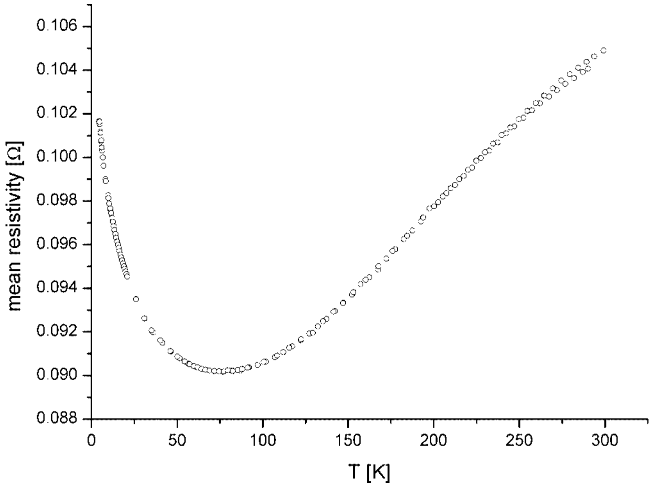

Fig. 5 Temperature dependence of mean resisitivity of Ag_4CuTeO_6.

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