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THERMOCHEMICAL DATA AND PHASE TRANSITION OF ARGYRODITE-TYPE IONIC CONDUCTORS ME_6PS_5HAL AND ME_7PS_6 (ME = Cu, Ag; HAL = Cl, Br, I)

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ABSTRACT

The molar heat capacities of five argyrodite compounds have been measured in the temperature range, 2–500 K by adiabatic and differential scanning calorimetry. The heat capacity of two other chalcogenides, Cu_3PS_4 and Ag_3PS_4, has been determined between 100 and 500 K. The Cu_6PS_5HAL (HAL = Cl, Br, I) compounds show structural phase transitions at 241, 257 and 270 K, respectively. In Cu_6PS_5Cl a second new phase transition has been detected at 165 K. These phase transformations have been characterized thermodynamically. The thermodynamic standard values of entropy, enthalpy and Gibbs free energy at 298.15 K were calculated from the specific heat data and the heat of formation was computed from the results of vapour pressure measurements and specific heat data.

INTRODUCTION

Compounds of the general formula ME_6PS_5HAL (ME = Ag, Cu; HAL = Cl, Br, I) and ME_7PS_6 are members of a new family of acentric structures [1], denoted argyodites. These materials have recently attracted much interest because of some unique physical and chemical properties which have been reviewed in ref. 2. The argyrodites can built up with a vast range of different chemical substitutions. Their incomplete occupancy of certain cation sites leads to ionic conductivity in various compounds and to the occurrence of order–disorder phenomena and crystallographic phase transitions [3].

The general formula of argyrodites is written as: $A^{m+}_{(12-n-y)/m}B^{n+}X^{2-}_{6-y}Y^{-}_{y}$ where m = oxidation number of A atoms, being Cu^+, Ag^+, Cd^{2+}, Hg^{2+}, n = oxidation number of B atoms, being Ga^{3+}, Si^{4+}, Ge^{4+}, P^{5+}, As^{5+}, $x = 6 - y$ = number of X atoms per B atom with $X^{2-} = S^{2-}$, Se^{2-}, Te^{2-} and

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y = number of Y atoms per B atom with $Y^- = Cl^-, Br^-, I^-$, for $0 \leqslant y \leqslant 1$. The compounds have a common, cubic, high temperature phase of overall symmetry $F\bar{4}3m$ generally with 4 formula units per unit cell. Characteristic of the architecture of all argyrodites is the building unit of interpenetrating, centered and distorted anion icosahedra which form a tetrahedrally close-packed sublattice. The icosahedron is constructed from 20 triangular surfaces in such a manner that the resulting geometry has three fivefold rotational axes neglecting the icosahedral deformation. The anion sublattice is similar to that formed by the metal ions in the Laves phase of $MgCu_2$. The metal cations only occupy one half of their cubic lattice sites and reside in various coordinates as described in ref. 1. Twenty four metal cations (e.g., Cu_6PS_5Br, $Z = 4$) are distributed randomly among the 48 equivalent lattice sites [1]. The B ions are coordinated almost tetrahedrally by four anions. The free lattice sites in conjunction with the icosahedral structure of the anions are common features of the argyrodite structure which favours ionic conductivity.

At low temperatures the high temperature (α-phase) transforms into various ordered low temperature modifications (β-phase) which is mostly of monoclinic symmetry. It is not yet clear whether these transitions are of first or second order type. The arrangement of the A cations in the low temperature structure is ordered in various ways, depending on composition. The ordering is a direct result of the splitting of the cubic lattice sites into non equivalent positions due to the distortion of the cell at the phase transition.

The initial aim of this paper was to establish the basic thermodynamic functions of the ME_6PS_5HAL compounds. These data were required to calculate the thermal equilibrium equations in the gas-phase in order to optimize the conditions of crystal growth by chemical vapour transport (CVT) [4].

This paper reports on the first measurements of the specific heat of six copper and silver argyrodites. From these measurements the thermodynamic standard values as function of temperature have been calculated over a wide temperature range ($2 < T < 500$ K) and the heat of formation at 298.15 K derived. New crystallographic phase transitions were found. The former detected structural transformations in the three Cu-argyrodites are characterized quantitatively for the first time by their thermal parameters. Finally the anomalous temperature behaviour of the heat capacity at very low temperatures is discussed with regard to the tunnelling processes of Cu anions by analogy with the tunnelling in amorphous materials.

EXPERIMENTAL

All samples were synthesized by reacting stoichiometric amounts of high purity elements in evacuated and sealed quartz ampoules for 6 days at 600°C. The resulting products were identical to those investigated previously

[1,2]. Single crystals with a size from 10 to 500 mm^3 and polycrystalline pressed samples were used for the experiments.

The specific heat capacity at low temperatures (1.5–100 K) has been measured with an adiabatic calorimeter [5]. The values above 100 K were determined with a differential scanning calorimeter (Perkin-Elmer, DSC–2). The adiabatic measurements, were carried out using the well known Nernst method, by means of an automatic process-control and data acquisition system [5] in conjunction with a highly reproducible, low heat capacity sample holder [6]. The investigated samples typically had a weight of 0.6 to 1.5 g. Thus the sample holder heat capacity amounted to 10–40%, depending on temperature and sample weight. The overall calorimetric error of the heat capacity determinations is estimated to be less than 1.2%. Systematic errors have been ruled out by measuring standard samples of copper and sapphire [5].

In the DSC–2 calorimeter, a twin cell, heat-flow instrument the samples have been encapsulated into the standard pans of aluminium and continuously flushed with a stream of pure and dried helium gas (or argon above 350 K). The heater block is thermalized in the low temperature range (100–350 K) by a temperature-controlled liquid-nitrogen continuous flow cryostat permitting temperature to be controlled to within ± 0.05 K [7]. The data on the specific heat were computed by comparison with standard samples of sapphire. The temperature error does not exceed ± 0.15°C. The absolute calorimetric error of the specific heat curve is estimated to be 1.5%.

RESULTS

The experimental molar heat capacities C_p of the Cu_6PS_5Hal-compounds (Hal = Cl, Br, I) are represented as function of temperature in Fig. 1, in a double logarithmic plot. These data refer to molar weights of 607.99, 652.44 and 699.43 respectively. In the same plot the results for Ag_6PS_5Cl and Ag_7PS_6 are shown. For the sake of clarity only smoothed curves obtained from the best fit to the about 300 individual experimental points below 100 K are plotted. At temperatures above 100 K the data, taken by the DSC–2, were digitized every degree, but are also shown as a smoothed line in Fig. 1. The low temperature results (1–10 K) are depicted in more detail in Fig. 2 in terms of C_p/T vs. T^2. The specific heat $C_p(T)$ above 100 K of three further argyrodites are plotted in Fig. 3. This representation includes three samples Cu_3PS_4, Ag_3PS_4 and Cu_7PS_6 for which the specific heat has been determined only at temperatures $T \geqslant 100$ K. Anomalous heat capacities or phase transitions have been observed only for the three Copper argyrodites, Cu_6PS_5Hal (Hal = Cl, Br, I) and will be analyzed below.

In order to represent our specific heat capacity results quantitatively, we

TABLE 1

Thermodynamic data for Cu_6PS_5Hal (Hal = Cl, Br, I), Ag_6PS_5Cl and Ag_7PS_6 and the specific heats of Cu_7PS_6, Cu_3PS_4 and Ag_3PS_4

T (K)	C_p(J K^{-1} mol^{-1})	$H_T^0 - H_0$ (kJ mol^{-1})	S_T^0(J mol^{-1} K^{-1})	T (K)	C_p(J K^{-1} mol^{-1})	$H_T^0 - H_0$ (kJ mol^{-1})	S_T^0 (J mol^{-1} K^{-1})
Cu_6PS_5I				Ag_7PS_6			
4.000	2.66695E−01	1.68053E−01	5.10756E−02	6.000	3.28880E 00	4.94926E−01	2.52970E 00
5.000	6.99394E−01	6.23795E−01	1.50971E−01	7.000	5.54084E 00	1.16369E 00	6.89739E 00
6.000	1.52730E 00	1.70035E 00	3.44933E−01	8.000	8.31546E 00	2.07935E 00	1.37859E 01
7.000	2.80278E 00	3.82993E 00	6.70649E−01	9.000	1.15466E 01	3.24104E 00	2.36810E 01
8.000	4.44874E 00	7.43072E 00	1.14899E 00	10.000	1.51787E 01	4.64249E 00	3.70148E 01
9.000	6.32748E 00	1.28048E 01	1.77976E 00	12.000	2.31352E 01	8.10406E 00	7.52302E 01
10.000	8.34611E 00	2.01313E 01	2.54979E 00	14.000	3.15684E 01	1.22961E 01	1.29837E 02
12.000	1.30138E 01	4.12819E 01	4.46504E 00	16.000	4.05791E 01	1.70938E 01	2.01896E 02
14.000	1.86870E 01	7.28320E 01	6.88555E 00	18.000	4.99873E 01	2.24141E 01	2.92422E 02
16.000	2.52603E 01	1.16649E 02	9.80125E 00	20.000	5.94380E 01	2.81713E 01	4.01874E 02
18.000	3.24033E 01	1.74256E 02	1.31855E 01	25.000	8.08244E 01	4.38171E 01	7.5447E 02
20.000	3.96672E 01	2.46341E 02	1.69762E 01	30.000	9.69848E 01	6.00577E 01	1.20106E 03
25.000	5.63212E 01	4.87539E 02	2.76714E 01	35.000	1.13043E 02	7.62027E 01	1.72581E 03
30.000	7.03268E 01	8.04926E 02	3.92060E 01	40.000	1.24911E 02	9.21200E 01	2.32248E 03
35.000	8.38288E 01	1.18999E 03	5.10509E 01	45.000	1.33923E 02	1.07368E 02	2.97023E 03
40.000	9.88857E 01	1.64592E 03	6.32047E 01	50.000	1.42138E 02	1.21905E 02	3.66044E 03
45.000	1.15594E 02	2.18176E 03	7.58080E 01	60.000	1.59137E 02	1.49306E 02	5.16589E 03
50.000	1.31214E 02	2.80023E 03	8.88258E 01	70.000	1.75332E 02	1.75098E 02	6.84118E 03
55.000	1.40037E 02	3.48265E 03	1.01827E 02	80.000	1.87003E 02	1.99399E 02	8.66223E 03
60.000	1.43670E 02	4.18628E 03	1.14070E 02	90.000	1.95899E 02	2.21926E 02	1.05757E 04
65.000	1.52268E 02	4.92554E 03	1.25900E 02	100.000	2.07384E 02	2.43131E 02	1.25893E 04
70.000	1.61671E 02	5.71028E 03	1.37526E 02	110.000	2.22152E 02	2.63567E 02	1.47346E 04
80.000	1.79560E 02	7.41868E 03	1.60312E 02	120.000	2.38755E 02	2.83603E 02	1.70385E 04
90.000	1.93952E 02	9.28942E 03	1.82330E 02	130.000	2.54969E 02	3.03363E 02	1.95084E 04
100.000	2.05171E 02	1.12870E 04	2.03366E 02	140.000	2.68881E 02	3.22786E 02	2.21301E 04
110.000	2.15155E 02	1.33887E 04	2.23390E 02	150.000	2.79608E 02	3.41721E 02	2.48752E 04
120.000	2.25707E 02	1.55921E 04	2.42555E 02	160.000	2.87561E 02	3.60033E 02	2.77129E 04
130.000	2.37331E 02	1.79067E 04	2.61075E 02	180.000	3.00975E 02	3.94670E 02	3.35971E 04

140.000	2.48911E 02	2.03387E 04	2.79093E 02
160.000	2.65420E 02	2.54992E 04	3.13523E 02
180.000	2.79592E 02	3.09534E 04	3.45627E 02
200.000	2.91821E 02	3.66719E 04	3.75741E 02
220.000	3.01069E 02	4.26056E 04	4.04011E 02
240.000	3.08756E 02	4.87036E 04	4.30536E 02
260.000	3.19055E 02	5.49729E 04	4.55622E 02
270.00	3.28500E 02	5.82027E 04	4.67817E 02
271.00	3.26000E 02	5.85287E 04	4.69020E 02
272.00	3.23000E 02	5.88517E 04	4.70207E 02
273.00	3.21500E 02	5.91732E 04	4.71385E 02
274.00	3.20500E 02	5.94937E 04	4.72554E 02
275.00	3.19000E 02	5.98127E 04	4.73714E 02
276.00	3.18500E 02	6.01312E 04	4.74868E 02
277.00	3.17000E 02	6.04482E 04	4.76013E 02
278.00	3.16500E 02	6.07647E 04	4.77151E 02
279.00	3.15500E 02	6.10802E 04	4.78282E 02
280.00	3.15000E 02	6.13952E 04	4.79407E 02
281.00	3.14500E 02	6.17097E 04	4.80526E 02
282.00	3.14000E 02	6.20237E 04	4.81640E 02
283.00	3.13500E 02	6.23372E 04	4.82748E 02
284.00	3.13100E 02	6.26503E 04	4.83850E 02
285.00	3.12700E 02	6.29630E 04	4.84947E 02
300.00	3.10580E 02	6.50740E 04	5.00791E 02
Cu_6PS_5Cl			
5.000	2.67883E−01	4.09258E−01	1.35358E−01
6.000	5.23378E−01	7.91267E−01	2.04295E−01
7.000	9.77069E−01	1.52246E 00	3.16101E−01
8.000	1.68882E 00	2.83210E 00	4.89909E−01
9.000	2.69780E 00	4.99998E 00	7.44067E−01
10.000	4.01545E 00	8.33138E 00	1.09383E 00
12.000	7.50604E 00	1.96767E 01	2.11838E 00

200.000	3.11511E 02	4.27055E 02	3.97466E 04
220.000	3.23582E 02	4.57427E 02	4.61213E 04
240.000	3.32900E 02	4.85985E 02	5.26869E 04
260.000	3.41782E 02	5.12985E 02	5.94344E 04
280.000	3.50227E 02	5.38625E 02	6.63553E 04
300.000	3.58235E 02	5.63064E 02	7.34406E 04
Ag_6Ps_5Cl			
6.000	6.40426E 00	2.20144E 00	9.86149E 00
7.000	9.77733E 00	3.43534E 00	1.79099E 01
8.000	1.35865E 01	4.98532E 00	2.95603E 01
9.000	1.77509E 01	6.82281E 00	4.52023E 01
10.000	2.21517E 01	8.91979E 00	6.51442E 01
12.000	2.97614E 01	1.36862E 01	1.17666E 02
14.000	3.84028E 01	1.89392E 01	1.86033E 02
16.000	4.76839E 01	2.46628E 01	2.71967E 02
18.000	5.75103E 01	3.08453E 01	3.77142E 02
20.000	6.69739E 01	3.74016E 01	5.01763E 02
25.000	8.52245E 01	5.44613E 01	8.85718E 02
30.000	9.98612E 01	7.12890E 01	1.34833E 03
35.000	1.15823E 02	8.79300E 01	1.88912E 03
40.000	1.27908E 02	1.04227E 02	2.50003E 03
45.000	1.36631E 02	1.19824E 02	3.16257E 03
50.000	1.43129E 02	1.34570E 02	3.86262E 03
60.000	1.54534E 02	1.61657E 02	5.34999E 03
70.000	1.71072E 02	1.86700E 02	6.97689E 03
80.000	1.82911E 02	2.10348E 02	8.74914E 03
90.000	1.94036E 02	2.32523E 02	1.06330E 04
100.000	2.07251E 02	2.53626E 02	1.26371E 04
110.000	2.23252E 02	2.74110E 02	1.47875E 04
120.000	2.41017E 02	2.94291E 02	1.71081E 04
130.000	2.58512E 02	3.14282E 02	1.96069E 04

TABLE 1 (continued)

T (K)	C_p(J K^{-1} mol^{-1})	$H_T^0 - H_0$ (kJ mol^{-1})	S_T^0(J mol^{-1} K^{-1})	T (K)	C_p(J K^{-1} mol^{-1})	$H_T^0 - H_0$ (kJ mol^{-1})	S_T^0 (J mol^{-1} K^{-1})
14.000	1.19090E 01	3.89643E 01	3.59624E 00	140.000	2.73575E 02	3.34012E 02	2.22701E 04
16.000	1.69615E 01	6.77436E 01	5.51018E 00	150.000	2.84808E 02	3.53294E 02	2.50655E 04
18.000	2.25045E 01	1.07135E 02	7.82359E 00	160.000	2.92346E 02	3.71931E 02	2.79538E 04
20.000	2.84780E 01	1.58048E 02	1.05001E 01	180.000	3.07028E 02	4.07107E 02	3.39294E 04
25.000	4.49644E 01	3.41143E 02	1.86025E 01	200.000	3.17906E 02	4.39987E 02	4.01729E 04
30.000	6.06862E 01	6.05684E 02	2.82053E 01	220.000	3.27221E 02	4.70744E 02	4.66285E 04
35.000	7.56801E 01	9.46809E 02	3.86925E 01	240.000	3.34091E 02	4.99527E 02	5.32454E 04
40.000	9.02593E 01	1.36181E 03	4.97541E 01	260.000	3.39023E 02	5.26473E 02	5.99791E 04
45.000	1.04397E 02	1.84868E 03	6.12066E 01	280.000	3.42911E 02	5.51743E 02	6.67992E 04
50.000	1.17861E 02	2.40466E 03	7.29099E 01	300.000	3.47038E 02	5.75536E 02	7.36970E 04
60.000	1.41622E 02	3.70616E 03	9.65731E 01	Cu_6PS_5Br			
70.000	1.59926E 02	5.21870E 03	1.19853E 02	5.000	3.23871E−01	4.68644E−01	1.44843E−01
80.000	1.72506E 02	6.88511E 03	1.42086E 02	6.000	6.35377E−01	9.32348E−01	2.28516E−01
90.000	1.88971E 02	8.69148E 03	1.63343E 02	7.000	1.15902E 00	1.81041E 00	3.62822E−01
100.000	2.04557E 02	1.06611E 04	1.84081E 02	8.000	1.93794E 00	3.33577E 00	5.65334E−01
110.000	2.17696E 02	1.27742E 04	2.04210E 02	9.000	3.02445E 00	5.78939E 00	8.53057E−01
120.000	2.29677E 02	1.50110E 04	2.23666E 02	10.000	4.46170E 00	9.50277E 00	1.24295E 00
130.000	2.42743E 02	1.73714E 04	2.42552E 02	12.000	8.20928E 00	2.20429E 01	2.37564E 00
140.000	2.58042E 02	1.98737E 04	2.61089E 02	14.000	1.26884E 01	4.27152E 01	3.96000E 00
150.000	2.73355E 02	2.25330E 04	2.79430E 02	16.000	1.81441E 01	7.34212E 01	6.00198E 00
155.000	2.78793E 02	2.39144E 04	2.88489E 02	18.000	2.41957E 01	1.15688E 02	8.48413E 00
160.000	2.80595E 02	2.53149E 04	2.97382E 02	20.000	3.05514E 01	1.70405E 02	1.13607E 01
160.50	2.875E 02			25.000	4.65885E 01	3.63373E 02	1.99060E 01
161.50	2.910E 02			30.000	6.23156E 01	6.35668E 02	2.97916E 01
162.50	2.975E 02			35.000	7.83431E 01	9.87087E 02	4.05941E 01
163.50	3.350E 02			40.000	9.44365E 01	1.41934E 03	5.21141E 01
164.50	4.970E 02			45.000	1.08459E 02	1.92797E 03	6.40793E 01
165.50	5.400E 02			50.000	1.20510E 02	2.50297E 03	7.61848E 01
166.50	3.660E 02			60.000	1.40645E 02	3.80652E 03	9.98959E 01

167.50	3.080E 02		
168.50	3.025E 02		
169.50	3.000E 02		
170.50	3.000E 02		
180.000	3.00476E 02	3.18261E 04	3.35809E 02
200.000	3.10068E 02	3.79371E 04	3.67993E 02
220.000	3.18591E 02	4.42183E 04	3.97920E 02
225.000	3.21920E 02	4.58192E 04	4.05115E 02
230.000	3.26437E 02	4.74395E 04	4.12237E 02
235.000	3.32631E 02	4.90863E 04	4.19321E 02
238.50	3.540E 02		
239.50	3.660E 02		
240.50	3.700E 02		
241.50	3.400E 02		
242.50	3.300E 02		
245.000	3.15856E 02	5.38513E 04	4.37826E 02
250.000	3.15725E 02	5.54303E 04	4.44206E 02
260.000	3.15373E 02	5.85858E 04	4.56581E 02
270.000	3.15334E 02	6.17389E 04	4.68481E 02
280.000	3.15861E 02	6.48944E 04	4.79957E 02
300.000	3.17968E 02	7.12323E 04	5.01820E 02

T (K)	Cu_7PS_6	Cu_3PS_5	Ag_3PS_4
100.000	1.89729E 02	9.86903E 01	1.07677E 02
110.000	2.09433E 02	1.07892E 02	1.19505E 02
120.000	2.26882E 02	1.17175E 02	1.29479E 02
130.000	2.41939E 02	1.25537E 02	1.37902E 02
140.000	2.54701E 02	1.33056E 02	1.45048E 02
150.000	2.65438E 02	1.39808E 02	1.51159E 02
160.000	2.74529E 02	1.45867E 02	1.56449E 02
180.000	2.89476E 02	1.56180E 02	1.65263E 02
200.000	3.02433E 02	1.64510E 02	1.72586E 02

70.000	1.64177E 02	5.32887E 03	1.23316E 02
80.000	1.86324E 02	7.08535E 03	1.46738E 02
90.000	2.01852E 02	9.03259E 03	1.69655E 02
100.000	2.10917E 02	1.11003E 04	1.91432E 02
110.000	2.18047E 02	1.32445E 04	2.11863E 02
120.000	2.27758E 02	1.54704E 04	2.31225E 02
130.000	2.40267E 02	1.78096E 04	2.49942E 02
140.000	2.50812E 02	2.02692E 04	2.68164E 02
150.000	2.56050E 02	2.28063E 04	2.85667E 02
160.000	2.66127E 02	2.54287E 04	3.02589E 02
180.000	2.80012E 02	3.08964E 04	3.34773E 02
200.000	2.89136E 02	3.65963E 04	3.64791E 02
220.000	2.94817E 02	4.24378E 04	3.92625E 02
240.000	3.03485E 02	4.84077E 04	4.18592E 02
250.000	3.12347E 02	5.14832E 04	4.31145E 02
253.00	3.15000E 02	5.24150E 04	4.35245E 02
254.00	3.16000E 02	5.27310E 04	4.36489E 02
255.00	3.19000E 02	5.30500E 04	4.37740E 02
256.00	3.21000E 02	5.33710E 04	4.38994E 02
257.00	3.22500E 02	5.36935E 04	4.40249E 02
258.00	3.22400E 02	5.40159E 04	4.41499E 02
259.00	3.19000E 02	5.43349E 04	4.42730E 02
260.00	3.11500E 02	5.46464E 04	4.43928E 02
261.00	3.09500E 02	5.49559E 04	4.45114E 02
262.00	3.08500E 02	5.52644E 04	4.46292E 02
263.00	3.09500E 02	5.55739E 04	4.47468E 02
264.00	3.06500E 02	5.58804E 04	4.48629E 02
265.00	3.05500E 02	5.61859E 04	4.49782E 02
266.00	3.05400E 02	5.64913E 04	4.50930E 02
267.00	3.05100E 02	5.67964E 04	4.52073E 02
268.00	3.04450E 02	5.71009E 04	4.53209E 02
269.00	3.04200E 02	5.74051E 04	4.54340E 02
270.00	3.04000E 02	5.77091E 04	4.55466E 02

TABLE 1 (continued)

T (K)	C_p(J K^{-1} mol^{-1})	$H_T^0 - H_0$ (kJ mol^{-1})	S_T^0(J mol^{-1} K^{-1})	T (K)	C_p(J K^{-1} mol^{-1})	$H_T^0 - H_0$ (kJ mol^{-1})	S_T^0 (J mol^{-1} K^{-1})
220.000	3.14090E 02	1.71322E 02	1.79029E 02	271.00	3.03500E 02	5.80126E 04	4.56586E 02
240.000	3.20956E 02	1.77026E 02	1.84722E 02	272.00	3.03100E 02	5.83157E 04	4.57700E 02
260.000	3.29336E 02	1.81981E 02	1.88524E 02	273.00	3.03000E 02	5.86187E 04	4.58810E 02
280.000	3.36642E 02	1.86490E 02	1.93092E 02	274.00	3.03000E 02	5.89217E 04	4.59916E 02
300.000	3.43947E 02	1.90806E 01	1.97660E 02	275.00	3.03200E 02	5.92249E 04	4.61018E 02
350.000		1.95111E 02	2.09079E 02	276.00	3.03500E 02	5.95284E 04	4.62118E 02
400.000		1.99959E 02		277.00	3.03800E 02	5.98322E 04	4.63215E 02
450.000		2.04806E 02		278.00	3.04000E 02	6.01362E 04	4.64308E 02
500.000		2.09654E 02		279.00	3.04000E 02	6.04402E 04	4.65398E 02
550.000		2.14501E 02		280.00	3.04200E 02	6.07444E 04	4.66484E 02
				300.00	3.10440E 02	6.68911E 04	4.97278E 02

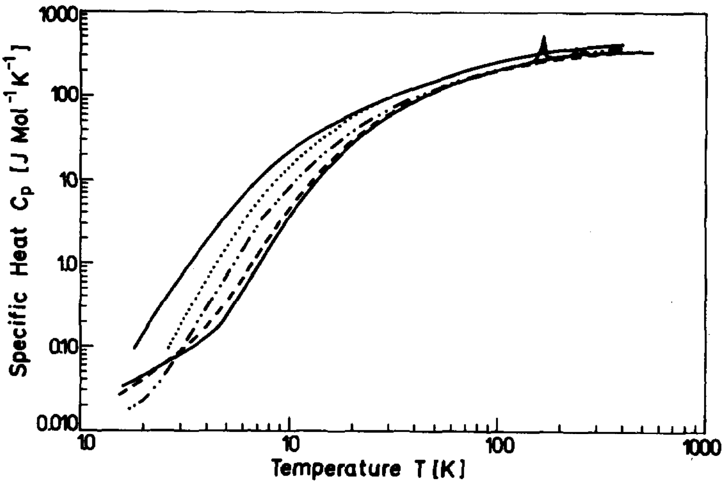

Fig. 1. Specific heat as function of temperature in double-logarithmic plot: (———) Cu_6PS_5Cl (lower curve); (- - - - - -) Cu_6PS_5Br; (– · · –) Cu_6PS_5I; (· · · · · ·) Ag_7PS_6; (———) Ag_6PS_5Cl (upper curve).

carried out fits of the measured data points using the general formulae

$$C_p = \sum_{i=1}^{n} a_i \cdot T^i \text{ or } C_p = \sum_{i=1}^{n} b_i (\ln T)^i \tag{1}$$

The standard deviation from the polynomial fit was generally less than 0.7%. Selected values of the resulting smoothed C_p data are listed in Table 1.

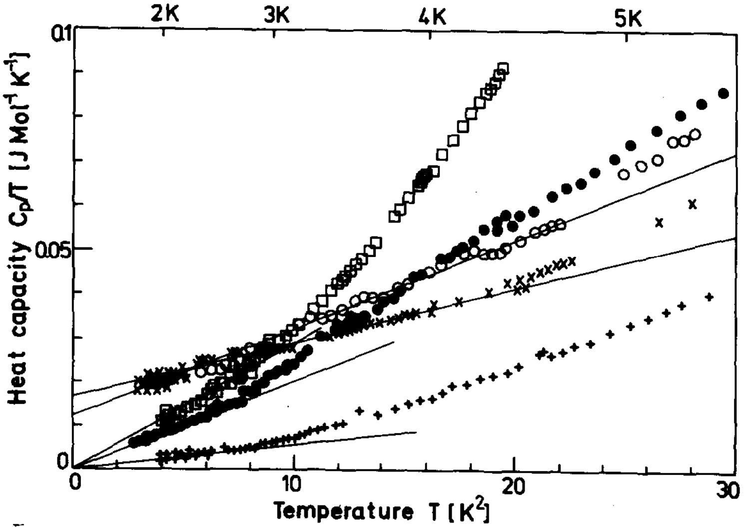

Fig. 2. Heat capacity C_p/T vs. T^2 at temperatures below 6 K for: (×) Cu_6PS_5Cl; (○) Cu_6PS_5Br; (□) Cu_6PS_5I; (+) Ag_7PS_6; (●) Ag_6PS_5Cl.

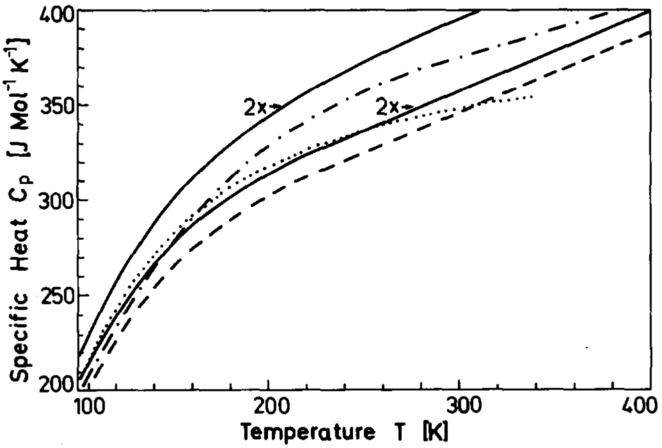

Fig. 3. Specific heats at $T \geqslant 100$ K for: (–·–) Ag_7PS_6; (······) Ag_6PS_5Cl; (------) Cu_7PS_6. (———) Ag_3PS_4 (upper curve); (———) Cu_3PS_4 (lower curve). The two curves for Ag_3PS_4 and Cu_3PS_4 have been multiplied by a factror of two for representation on the same diagram.

Above 300 K the temperature dependences of the specific heats are linear and therefore are described by

$$C_p = A + B \cdot T \qquad (2)$$

The values of A and B are tabulated in Table 2.

The low temperature limiting Debye temperatures θ_0 are calculated from the formula $C_p = (12\pi^4/5)\ Nkn\ (T/\theta_0)^3$, for $T \leqslant 7$ K, where N is Avogadro's number, k denotes the Boltzmann constant and n is the number of atoms per molecular unit (see insert Fig. 2). Table 2 contains the values which we computed for θ_0.

DISCUSSION

Heat capacity of the lattices

The lattice heat capacities of the investigated samples (Figs. 1 and 3) behave rather normally. This becomes evident on inspection of the tempera-

TABLE 2

Debye temperatures θ_0 ($T \rightarrow 0$) for some argyrodites and the coefficients A and B representing the high temperature specific heat ($T > 280$ K) by eqn. (2)

	Cu_6PS_5Cl	Cu_6PS_5Br	Cu_6PS_5I	Ag_6PS_5Cl	Ag_7PS_6	Cu_7PS_6	Cu_3PS_4	Ag_3PS_4
θ_0	269	232	204	93	161	–	–	–
A	305.24	290.23	298.08	278.57	238.0	234.36	161.18	129.14
B	0.04762	0.0670	0.04167	0.1704	0.4010	0.3653	0.09695	0.2284

ture dependence of the Debye temperature $\theta(T)$, as deduced from our C_p data. The continuous increase of the heat capacities at high temperatures ($T \geqslant 200$ K) indicates the occurrence of anharmonic lattice vibrations.

At high temperatures ($T \geqslant \theta$) the specific heats reach the high temperature limiting values expected by the Dulong–Petit law and the heat capacities of the ME_6PS_5Hal-compounds have identical values, being approximately 325 J mol^{-1} K^{-1}, as can be seen in Figs. 1–4. Similarly, the expected values of $C_p \simeq 200$ J mol^{-1} K^{-1} for Cu_3PS_4 and Ag_3PS_4 agree with our experiments. The specific heat C_p of the two ME_7PS_6 (ME = Ag, Cu) compounds, however, exceeds the expected high temperature limiting C_p value of 350 J mol^{-1} K^{-1} strongly (Fig. 3). The strong linear increase of $C_p(T)$ is usually an indication of strong anharmonicity. At the present time, the origin of this unusual behaviour of $C_p(T)$ in Ag_7PS_6 and Cu_7PS_6 is not clear.

At temperatures below 100 K, as expected, the molar heat capacities differ considerably. This difference is explained qualitatively by the different molecular masses of the components. It is evident that the heavier Ag atoms in the Ag compounds, Ag_7PS_6 and Ag_6PS_5Cl lead to a lower Debye temperature, θ, than that found for the Cu compounds (see Fig. 2). Similarly, in the Cu_6PS_5Hal the increase of mass of the halogen atom (going from Cl to I) gives rise to a systematic increase of the $C_p(T)$ curve as function of temperature and a corresponding decrease of θ, respectively (see Fig. 2). The influence of molecular mass in these isotropic structures is best expressed by θ_0 as can be seen in Table 1.

Both, Figs. 1 and 2, reveal an anomalous specific heat at low temperatures, clearly visible below 10 K. In this temperature region a T^3-dependence (Debye's law) for insulating materials is expected.

However, there is evidence of a clear linear contribution to the specific heat of the Cl- and Br-compounds, which cannot be explained in terms of an electronic contribution. Similar "quasi-linear" temperature behaviour of the specific heat at low temperatures has been reported for some ionic conductors recently [8–10]. It was proposed that the excess heat capacity originates from a broad spectrum of localized low energy excitations. The phenomenological model is based on the assumption that certain atoms or groups of atoms reside in a double well potential giving rise to two-level systems [11,12]. It has now been established that the low temperature properties of disordered materials, especially amorphous solids are dominated by the presence of such low-energy excitations [13]. The occurrence of tunnelling systems in ionic conductors is favoured because of the existence of free lattice sites. Therefore we attribute the excess specific heat in the present Me_6PS_5Hal-compounds to the structural disorder of the Cu-ions which can move by tunnelling from one lattice site to another, because in these materials in a simple model 24 Cu atoms of the unit cell are distributed, more or less randomly, among 48 distorted tetrahedra [14]. At room temperature the Cu atoms make strongly anharmonic vibrations and are able to overcome the rather flat potential barrier to the neighboured lattice site [2,15]. It has been shown from the structural analysis by X-rays that in Cu_6PS_5Br and Cu_6PS_5Cl the structural disorder of the A-cation sublattice partially still exists below the phase transition (see also next section) [3]. Consequently only one half of the lattice sites are occupied. Evidently, the fact that the ratio of the number of ions diffusing (or tunnelling at low temperatures) to the number of free lattice positions is unity creates the best conditions for tunnelling of ions. Therefore it is not astonishing that Cu_6PS_5Cl exhibits the highest excess heat capacity in disordered solids found up to now. The Cu density is essentially concentrated around two symmetrically equivalent positions. Furthermore, the structure analysis indicates a high mobility of the Cu ions only within the tetrahedra. The double well potential of the Cu-argyrodites is largely anharmonic [14]. Thus all essential prerequisites are given. We assume that the spectrum of low frequency tunnelling motion will be cumulated at certain frequencies rather than being distributed smoothly in energy like in the amorphous because the structural neighbourhoods of the Cu cations are identical. Preliminary results of investigation of the specific heat at very low temperatures ($0.05 < T < 4$ K) confirm this suggestion.

The heat capacity of Cu_6PS_5Cl can be represented by a superposition of a few Schottky-type anomalies below 1 K which represents characteristic tunnelling frequencies. The tunnelling model implies that, in addition to a distribution of attempt frequencies, there must also be a distribution of barrier heights or activation energies. Such distributions are produced by ion–ion interaction [8]. These results will be discussed quantitatively elsewhere.

The probability of tunnel motion of the Cl ion is greater than that for Br and I, because of its smaller mass. Our experiments confirm this interpretation: the excess heat is greatest for the Cl compound, smaller for Cu_6PS_5Br and not observable for Cu_6PS_5I. This explanation agrees with electrical measurements of the ionic conductance. The electronic conductivity constitutes only 10^{-5} of the total conductivity at room temperature in Cu_6PS_5Cl, whereas in Cu_6PS_5Br the ionic conductivity exceeds the electronic counterpart by a factor of 1000. Finally, electronic and ionic conductivity are of comparable magnitude in Cu_6PS_5I [16].

Due to their larger mass the Ag ions are not as able to diffuse (or to tunnel) as the Cu ions. There is no indication of any excess heat capacity at low temperatures in our experiment in the case of Ag_6PS_5Cl. It should be noted, however, that no precise structure determination has yet been made for Ag_6PS_5Cl.

Phase transition

The heat capacity of Cu_6PS_5Cl clearly shows two phase transitions at 165 and 241 K. In the corresponding bromine and iodine compound only one transition at 257 and 270 K, respectively, was observed. These transitions are shown in Fig. 4. The heat capacity anomalies in the three compounds near 250 K have already been reported [1,2] in connection with structure investigations. Our present data, however, are the first quantitative investigations of the thermodynamic parameters of these materials. Since the temperature scale in calorimetric measurements is much more precise than in crystallographic structure measurements, this may partially explain the considerable differences of the transition temperatures between the present data and those reported previously [1,2].

The three heat capacity anomalies near 250 K could be attributed, by X-ray analysis, to the transition from the cubic high temperature $F\bar{4}3m$ phase into the monoclinic low temperature phase Cc which has been described shortly in the introduction. The transitions are rather broad and therefore the determination of the net contribution of C_p to the transition is not straightforward. In order to evaluate $C_p^{\mathrm{trans}}(T)$ we had to construct the lattice heat capacity in the vicinity of the transition by interpolation of the $\theta(T)$ curve below and above the transition. This interpolation has been done smoothly as can be seen in the thin line in Fig. 4 for Cu_6PS_5Cl. Then the lattice specific heat C_p^L is calculated from the interpolated $\theta(T)$ curve. Finally subtraction of $C_p^L(T)$ from the totally measured $C_p(T)$ provides the specific heat C_p^{trans} which is associated with the transition itself. The $C_p^{\mathrm{trans}}(T)$ curve is rather broad and the increase with temperature at the low temperature side is much broader and nearly exponential, whereas the decrease is quite sharp on the high temperature side of the transition. No hysteresis between heating and cooling of the samples has been detected.

Structural investigations [3] confirm that the transition is associated with a

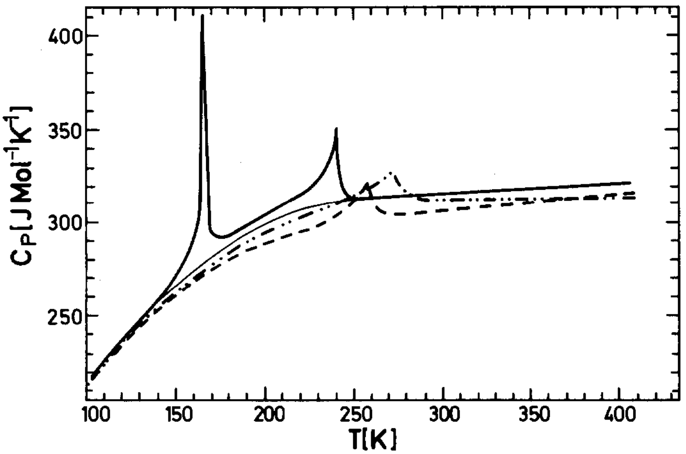

Fig. 4. Specific heat as function of temperature near the phase transition for: (———) Cu_6PS_5Cl; (–· · –) Cu_6PS_5Br; (- - - - - -) Cu_6PS_5I.

continuous distortion of the anion sublattice and an ordering of the Cu ions. Therefore the transition from disorder to order is smeared out over a rather large temperature range. At least, at 40 K, the Cu atoms are still partially disordered. These features lead us to the conclusion that three transitions in Cu_6PS_5Hal are second order. The enthalpies ΔH_{tr} and entropies ΔS_{tr} of the transitions computed from C_p^{trans} are listed in Table 3. We note that the ΔS values are identical to within 5%, being 1.9 J mol^{-1} K^{-1}, which provides clear evidence that an isotypic crystallographic change occurs in the three compounds from the cubic space group $F\bar{4}3m$ to the monoclinic space group Cc [1,2]. The second anomaly at low temperature, $T_c = 165$ K, in Cu_6PS_5Cl has been observed for the first time and not yet been identified by structure analysis. Therefore the interpretation is difficult, but there are indications that the transition is also a crystallographic one into a further low temperature phase of type Pc [4]. Our thermodynamic data suggest again a second order transition.

Thermodynamic data

Integration of the $C_p(T)$ curves including the phase transition region yields the standard enthalpy increment $H_T^0 - H_0^0$, the standard entropy S_T^0 and the function $-[G_T^0 - G_0^0]/T$, respectively. The values are calculated from the coefficients, as received by eqn. (1). Some standard values obtained by integration of $C_p(T)$ are given in Table 1, especially the values at 298.15 K. The thermodynamic functions were required in order to optimize the CVT growth conditions [4]. The heats of formation were evaluated from the following relations

$$H_{298}^0 \text{ (Argyrodite)} = \Delta_f H_T - \int_{298}^{T} C_p(T)\, dT$$

in which the heat of formation itself is given by

$$\Delta_f H_T(Cu_6PS_5Hal) = \Sigma r_i (\Delta_f H_T)_i - \Delta_D H_T$$

($\Sigma r_i(\Delta_f H_T)_i$ = sum of the heats of formation of the dissociation products, $\Delta_D H^T$ = heat of dissociation.) The first term of the right hand side can be taken from tabulated data and the second term the dissociation enthalpy is

TABLE 3

Temperatures, enthalpies ΔH_{tr} and entropies ΔS_{tr} of phase transitions in Cu_6PS_5Hal

Compound	T_{tr} (K)	ΔH_{tr} (J mol^{-1})	ΔS_{tr} (J mol^{-1} K^{-1})
Cu_6PS_5Cl (I)	165 ± 0.5	625 ± 10	3.62
Cu_6PS_5Cl (II)	241 ± 0.5	478 ± 10	1.98
Cu_6PS_5Br	257 ± 0.5	505 ± 10	1.96
Cu_6PS_5I	270 ± 0.5	507 ± 10	1.57

given by the temperature dependence of the dissociation pressure [4] by the second law method

$$\ln(P_2/P_1) = -\frac{\Delta_D H_T}{RN}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where R is the gas constant; P_2, P_1 the dissociation pressures at T_2 and T_1 deduced from vapour pressure measurements [4]; $\Delta_D H^T$ denotes the heat of dissociation and N represents the sum of moles of gaseous dissociation products associated with one mole of dissociated Cu_6PS_5Hal.

The heats of formation H^0_{298} of the argyrodites Cu_6PS_5Hal calculated in this way are 9% larger than the sum ΣH^0_{298} of the heats of formation of the binary constituents (Cu_2S, CuHal) and ternary (Cu_3PS_4) components. The entropies S^0_{298} were calculated using the relationship $S^0_{298} = \int_0^{298} C_p(T) \mathrm{d}\ln T$. The thermodynamic data, thus derived are tabulated in Table 4. Values for S^0_{298} calculated according to the Neumann–Kopp rule (S^0_{298} (compound) $= \Sigma S^0_{298}$ (multiple constituents)) appear in Table 4 in brackets. The deviation between these estimated data and the values as acquired by integration of the $C_p(T)$ curves is less than 5%.

Our results also agree with preliminary calorimetric investigations, in which the standard reaction heat of $Cu_3PS_4 + Cu_2S + CuHal \rightarrow Cu_6PS_5Hal$ was measured.

TABLE 4

Heats of formation of Me_7PS_6 and Me_6PS_5Hal ($Me = Cu$, Ag; $Hal = Cl$, Br, I)

Compound	H^0_{298} (kJ mol^{-1})	S^0_{298} (J mol^{-1} K^{-1})
Cu_6PS_5Cl	510 ± 20	500 ± 10 (485.0)
Cu_6PS_5Br	477 ± 20	495.2 ± 6 (494.0)
Cu_6PS_5I	439 ± 20	498.1 ± 6 (494.6)
Cu_7PS_6	414 ± 20	– (519.0)
Cu_3PS_4	255 ± 20	– (277.1)
Ag_6PS_5Cl	–	573.4 (587.3)
Ag_7PS_6	–	560.8 (596.3)
Ag_3PS_4	–	– (310.2)

CONCLUSION

In conclusion, we have measured the specific heat capacity of six argyrodites of the type Me_6PS_5Hal (Me = Ag, Cu; Hal = Cl, Br, J) and Me_7PS_6 (Me = Ag, Cu) between 2 and 500 K. The $C_p(T)$ data have been used to establish and to tabulate the thermodynamic functions of these compounds; two further compounds (Cu_3PS_4, Ag_3PS_4) were measured only above 100 K. The heats of formation are calculated and are of comparable magnitude. Apparently, the observed crystallographic phase transitions in Cu_6PS_5Hal are second order with $\Delta H \approx 500$ J mol^{-1} and $\Delta S \approx 1.9$ J mol^{-1} K^{-1}.

The data presented in this paper aided significantly in the optimization of the conditions for the growth of argyrodites by chemical vapour transport (CVT).

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REFERENCES

1 W.F. Kuhs, R. Nitsche and K. Scheunemann, Acta Crystallogr., Sect. B, 34, (1978) 64.
2 W.F. Kuhs, R. Nitsche and K. Scheunemann, Mater. Res. Bull., 14 (1979) 1115.
3 W.F. Kuhs and W. Konz, Acta Crystallogr., accepted.
4 S. Fiechter, J. Eckstein and R. Nitsche, J. Cryst. Growth, 61 (1983) 275.
5 E. Gmelin and P. Rödhammer, J. Phys. E, 14 (1981) 223.
6 E. Gmelin and K. Ripka, Cryogenics, 21 (1981) 117.
7 M. Ohl and E. Gmelin, private communication.
8 P.J. Anthony and A.C. Anderson, Phys. Rev. B, 16 (1977) 3827.
9 E. Gmelin and K. Guckelsberger, J. Phys. C, 14 (1981) L21.
10 H.U. Beyeler, L. Pietronero and S. Strässler, Phys. Rev. B, 22 (1980) 2988.
11 P.W. Anderson, B.J. Halperin and C. Varma, Philos. Mag., 25 (1972) 1.
12 W.A. Philips, J. Low Temp. Phys., 7 (1972) 357.
13 W.A. Philips (Ed.), Amorphous Solids, Springer Verlag, Berlin, 1981.
14 W.F. Kuhs and G. Heeger, Exp. Bericht No. 5-11-094, Kernforschungsanlage, 7500 Karlsruhe, F.R.G.
15 W. Konz, Doctoral Thesis, University of Freiburg, 1983.
16 E. Frenzel, Thesis, University of Freiburg, 1984.