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Thermodynamic properties of $[Ag_6M_4P_{12}]Ge_6$ (M = Ge, Sn)

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The heat capacities of the *cluster* compounds $[Ag_6M_4P_{12}]Ge_6$ (M = Ge, Sn) have been measured in the temperature range from 2 K to 310 K. Thermal decomposition into the elements was carried out under Knudsen conditions on a thermobalance combined with a mass spectrometer. The thermodynamic functions standard entropy, enthalpy, and the Debye temperatures were calculated from the heat capacity data. The vapour pressure functions derived from the Knudsen effusion data, served to calculate the third law heat of formation.

The rather complicated temperature dependence of the specific heat is qualitatively discussed by considering structural details and different contributions: electronic term ($T \leqslant 3$ K), a threefold Schottky anomaly ($\Delta E_0/k = 46(2)$ K) in the Ge-compounds (2 K $\leqslant T \leqslant 20$ K), lattice contributions influenced by the distances Ag–Ag and atomic masses (Ge and Sn) in both compounds.

1 Introduction

The compounds $[Ag_6M_4P_{12}]Ge_6$ (M = Ge, Sn) belong to a novel class of ternary cluster compounds [1, 2] with the general formula $[Ag_6M_4^{II}P_{12}]M_6^{IV}$, wherein M^{II} = Sn, Ge and M^{IV} = Si, Ge can be substituted. A detailed description of the crystal structure of these materials has been given by von Schnering and Häusler [1]. The interesting structural details of these compounds should also be reflected in their physical properties. X-ray diffraction studies [1, 2, 8] and investigations of the pressure dependence of the elastic constants [3, 4] have been performed for both compounds. Optical absorption and electrical measurements on $[Ag_6Ge_4P_{12}]Ge_6$

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have shown this compound to be a semiconductor (E_g (295 K) = 0.76 eV) [5, 10], whereas $[Ag_6Sn_4P_{12}]Ge_6$ seems to be semimetallic [6]. Recently, band structure calculations [7] were reported for these cluster compounds. According to these calculations, all materials should be found semiconductors. The occurrence of unusually large anisotropy of the thermal vibrational ellipsoids [1] at the silver atom sites is noteworthy. Elastic neutron scattering experiments [9] on single crystals result in two equally occupied atomic split positions with the silver atom. Up to now, no thermodynamic data have been reported for these compounds. Therefore, a study of the thermodynamic properties, especially the specific heats at low temperatures and the high temperature decomposition behaviour, was desirable.

2 Experimental

2.1 Sample preparation

Both compounds are prepared from high purity elements in sealed quartz ampoules as reaction vessel as well as growth container according to the method already described [1, 5]; more details will be published elsewhere [6]. The purity of Bridgman grown single crystals of $[Ag_6Ge_4P_{12}]Ge_6$ and tin flux grown $[Ag_6Sn_4P_{12}]Ge_6$ crystals was deduced from X-ray powder photographs as well as from chemical analysis.

2.2 Specific heat

In the temperature range $2\ \text{K} \leqslant T \leqslant 100\ \text{K}$ the specific heat was determined with an automated adiabatic calorimeter [11] equipped with a high reproducibility sample holder of the sapphire platform type [12]. For thermometry a commercially available germanium resistor was taken; the calorimetric accuracy is currently checked by measuring a standard copper sample. The total error of the smoothed C_p-data is estimated to be less than 0.8%.

Above 100 K a Perkin–Elmer DSC–2 scanning calorimeter was used. Experimental data were fed on-line into a HP 9825 computer via a 5-digit voltmeter which increases the resolution of the DSC–2 by about a factor of 5 with respect to the signal observed on a strip-chart recorder. The temperature scale was calibrated by observing melting and transition points of indium and various organic standard materials below room temperature. A sapphire sample served as the calorimetric reference standard. The error in temperature did not exceed 0.15 deg and the absolute calorimetric error of the computed molar specific heat is less than 1.5%.

For the heat capacity determination of $[Ag_6Ge_4P_{12}]Ge_6$ at low temperatures, a single crystal of 3.3 g was used; in case of the Sn-compound a polycrystalline sample

which was pressed to a pellet of 8 mm diameter and 9 mm thickness (4.1 g) was prepared. Smaller sample masses, typically 40 mg, were taken to perform the scanning calorimeter experiments ($100 \text{ K} \leqslant T \leqslant 300 \text{ K}$). The molar mass for $[Ag_6Ge_4P_{12}]Ge_6$ and $[Ag_6Sn_4P_{12}]Ge_6$ are taken as 1744.81 amu and 1929.21 amu, respectively.

2.3 Thermobalance—mass spectrometer system

A Netzsch-thermobalance (type STA 429) in connection with a Balzers quadrupole mass spectrometer (type QMG 511) was used to identify the vapour species evolved during the decomposition of the two compounds. The computer controlled arrangement which was already described in detail [13] enables simultaneously thermogravimetric, differential gravimetric, differential thermal and mass spectroscopic investigations. The Knudsen cell employed was fabricated from a high purity graphite rod and has an orifice area of $2.21 \cdot 10^{-4} \text{ cm}^2$. The effective orifice area of the cell was calibrated with an estimated accuracy of 95% by vaporizing elemental silver. PtRh–Pt thermocouples were used as sample holders and for thermometry. For each run, finely ground samples with a weight of about 900 mg were loaded into the cell. The temperature stability was controlled by a computer and depending on the effusion rates, the measuring time was 30 to 120 min for each step of temperature. Simultaneous registration of the relevant ion currents by the coupled mass spectrometer allowed for measuring even at low temperature ranges. In order to diminish the background the crossbeam ion source was cooled with liquid nitrogen. The pressure was held below 1 mPa at the sample and in the analyzer chamber. The mass spectra were taken in the temperature range from 570 K to 790 K with an ionizing electron energy of 70 eV and 1 mA emission current. A secondary electron multiplier was used to amplify the ion current.

2.4 DTA/TG measurements

A Netzsch DTA 404 S was used for the DTA measurements with crystalline samples in sealed quartz ampoules with a volume of about 0.5 cm^3. The heating rate was 10 deg/min. The thermogravimetric analysis (Netzsch STA 429) was performed under high vacuum (< 1 mPa) and a heating rate of 5 deg/min. Sample weights were approximately 50 mg to 100 mg of finely ground crystalline material.

3 Crystal structure

The cluster compounds crystallize cubically in the space group $I\bar{4}3\,m$ (no. 217) with lattice parameters $a = 10.322$ Å for $[Ag_6Ge_4P_{12}]Ge_6$ and $a = 10.473$ Å for $[Ag_6Sn_4P_{12}]Ge_6$. Details of the structure have been reported [1, 5]. Briefly,

the structure is characterized as an arrangement of $[Ag_6M_4P_{12}]$-clusters, being isosteric with the $Rh_6(CO)_4(CO)_{12}$ type of cluster and are interconnected by the remaining M(IV) atoms. The structural unit is shown in Fig. 1.

The 56 atoms of the unit cell occupy four different sites: 12 Ag at position 12e, 8 type-1 Ge (named hereafter Ge(1)) at position 8c, 12 type-2 Ge (named hereafter
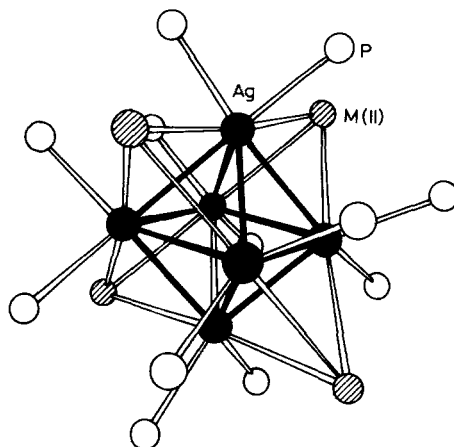

Fig. 1 Structural building unit of $[Ag_6M_4P_{12}]Ge_6$ (M = Ge, Sn)

Ge(2)) at position 12d and 24 P at position 24g. As already discussed [1, 2] the characteristic building unit is an empty Ag_6 octahedron, capped on four of its triangular faces by four Ge(1) or Sn atoms, and thus forming Ag_3M-tetrahedra. In addition, each silver atom is bonded to two P-atoms, thus completing the $Ag_6Ge_4P_{12}$-cluster. Neighbouring clusters are interconnected in such a way, that each Ge(1) or Sn atom bonds to three P atoms of the adjacent cluster forming a trigonal-pyramidal MP_3 arrangement, while the remaining Ge(2) atoms complete the structure by each forming a tetrahedral arrangement with four phosphorus atoms. Therefore the P-atoms are tetrahedrally bonded to one Ge(1) or Sn, two Ge(2) and one Ag atom. The different interatomic distances are ($[Ag_6Sn_4P_{12}]Ge_6$ in brackets): $d(Ag-Ag) = 2.852$ (2.886) Å; $d(M-Ag) = 3.029$ (3.070) Å; $d(Ag-P) = 2.532$ (2.570) Å; $d(M-P) = 2.454$ (2.566) Å; $d(Ge(2)-P) = 2.325$ (2.346) Å.

It has already been pointed out [1, 5] how the electron counting is done: From the total number of 106 valence electrons per formula unit of the cluster compounds, 96 electrons are used for all bonds between the P atoms to Ge(1), Sn, Ge(2) and Ag atoms. The bonds between P and Ge/Sn as well as between P and Ag can be considered as classical two center-two electron (2c–2e)-bonds. From the topology of the MP_3 pyramid the M(II) state follows with the lone pair directed towards the Ag_3 triangle. Thus the octahedral Ag_6-cluster and the capping atoms

form altogether four four center-two electron bonds (4c–2e) as it has been shown in Fig. 1 of Ref. 5. The remaining two electrons belong to the central Ag_6 octahedron and form an Ag_6^{4+} unit [1, 2, 8].

We like to emphasize the different bond lengths $d(Ag\text{-}Ag)$ and $d(Ag\text{-}M)$: the bond distance of silver atoms in the Ag_6 octahedra is larger in the Sn-compound, $d(Ag\text{-}Ag) = 2.886$ Å, than in the Ge-compound, being 2.852 Å. It has to be noted that in both compounds $d(Ag\text{-}Ag)$ is very close to that in elementary silver ($d = 2.889$ Å). On the other hand, the distance $d(Ag\text{-}Sn) = 3.070$ Å in the Sn-compound is much shorter as that in the Ge compound, $d(Ag\text{-}Ge) = 3.092$ Å, which is surprising and in contrast to what would be expected ($r(Sn) > r(Ge)$). Thus, going from $[Ag_6Ge_4P_{12}]Ge_6$ to $[Ag_6Sn_4P_{12}]Ge_6$ the bonding within the silver cluster is "weakened" and the Ag-Sn bonding gets more dominant.

4 Experimental results

4.1 Specific heat

The specific heats $C_p(T)$ of the two samples are tabulated as smoothed values in Table 1 for the entire temperature ranges investigated. These values have been obtained from a least square fit of more than 550 experimental data points for each compound. The standard deviation from the polynomial fit is less than 1.2% below 12 K, less than 0.7% from 12 K to 100 K and 1.2% for $T > 100$ K. Table 1 also contains interpolated values of the enthalpies $H_T^\circ - H_0^\circ$, entropies S° and the Gibbs free energy $G_T^\circ - G_0^\circ$ at selected temperatures.

The measured heat capacities are plotted as function of temperature in Fig. 2 in a double logarithmic scale in order to better visualize the low temperature range. The specific heats at very low temperature are depicted in the insert of Fig. 2 in terms of C_p/T vs. T^2 plotted in the range 0–5 K from which the low temperature limiting values of the Debye temperature, Θ_0, and the electronic contribution to the heat capacity, γ, are deduced according to the formula:

$$C_p = \gamma \cdot T + \alpha \cdot T^3 \tag{1}$$

with

$$\gamma = (\pi^2 \cdot N \cdot k^2 / 2E_F); \quad \alpha = (n \cdot 1943.8 / \Theta_0^3) \tag{2}$$

where N is Avogadro's number, k is Boltzmann's constant, E_F the Fermi energy and n denotes the number of atoms per formula unit.

Figure 3 represents the temperature dependence of the equivalent Debye temperatures Θ_D which have been calculated from the $C_p(T)$ curve after subtraction of the electronic term and dividing by the number of atoms ($n = 28$) per formula unit.

Table 1a Calorimetric values for [Ag$_6$Ge$_4$P$_{12}$]Ge$_6$

T, K	C_p, J/mol K	$H-H_O$, J/mol	S, J/mol K	$G-G_O$, J/mol
3.5	—	.12278	.06151	−.09250
4	.27367	.22209	.08784	−.12927
4.5	.51627	.41444	.13288	−.18352
5	.88811	.75976	.20531	−.26682
6	2.0486	2.1817	.46140	−.58661
7	3.9323	5.1545	.91596	−1.2571
8	6.0335	10.119	1.5758	−2.4872
9	8.3404	17.289	2.4177	−4.4697
10	10.839	26.864	3.4242	−7.3778
12	16.370	53.961	5.8790	−16.588
14	22.547	92.777	8.8586	−31.243
16	29.314	144.54	12.304	−52.333
18	36.634	210.40	16.174	−80.746
20	44.496	291.44	20.436	−117.29
25	66.623	567.69	32.674	−249.15
30	92.960	964.63	47.075	−447.62
35	118.47	1489.0	63.192	−722.68
40	145.25	2149.1	80.782	−1082.1
45	170.11	2938.3	99.343	−1532.1
50	193.25	3847.4	118.47	−2076.5
55	214.86	4868.3	137.92	−2717.4
60	235.12	5993.8	157.49	−3455.9
65	254.24	7217.7	177.07	−4292.3
70	272.39	8534.6	196.58	−5226.6
75	289.78	9940.4	215.98	−6258.0
80	306.58	11431.	235.22	−7386.1
85	322.99	13005.	254.30	−8610.0
90	339.21	14661.	273.22	−9928.9
95	355.41	16397.	291.99	−11342.
100	370.38	18211.	310.60	−12848.
110	399.44	22062.	347.28	−16138.
120	426.35	26193.	383.20	−19791.
130	451.22	30582.	418.32	−23800.
140	474.15	35211.	452.61	−28155.
150	495.25	40059.	486.06	−32849.
160	514.60	45110.	518.65	−37873.
170	532.32	50346.	550.38	−43219.
180	548.50	55751.	581.28	−48878.
190	563.24	61311.	611.33	−54842.
200	576.65	67012.	640.57	−61102.
220	599.86	78784.	696.66	−74480.
240	618.93	90978.	749.69	−88949.
260	634.67	103519	799.88	−104449
280	647.88	116348	847.41	−120926
298.15	658.35	128204	888.43	−136682
300	659.37	129423	892.51	−138330
320	669.93	142717	935.40	−156612

Table 1b Calorimetric values for $[Ag_6Sn_4P_{12}]Ge_6$

T, K	C_p, J/mol K	$H-H_O$, J/mol	S, J/mol K	$G-G_O$, J/mol K
3.5	—	.2204	.1038	− .1429
4	.27898	.33845	.13521	− .20239
4.5	.39749	.50566	.17446	− .27944
5	.56773	.74448	.22464	− .37871
6	1.1179	1.5608	.37198	− .67101
7	2.0389	3.1036	.60800	− 1.1523
8	3.3981	5.7811	.96351	− 1.9269
9	5.2013	10.044	1.4636	− 3.1279
10	7.4257	16.323	2.1231	− 4.9077
12	13.072	36.563	3.9526	− 10.868
14	20.198	69.600	6.4849	− 21.188
16	28.645	118.23	9.7197	− 37.277
18	38.238	184.94	13.637	− 60.523
20	48.784	271.82	18.204	− 92.259
25	77.908	587.36	32.165	− 216.77
30	107.90	1052.3	49.039	− 418.78
35	134.34	1660.5	67.734	− 710.21
40	167.80	2427.6	88.178	− 1099.4
45	193.80	3332.9	109.47	− 1593.3
50	216.89	4360.8	131.11	− 2194.8
55	237.54	5497.8	152.77	− 2904.5
60	256.23	6733.0	174.25	− 3722.2
65	273.41	8057.6	195.44	− 4646.6
70	289.55	9465.3	216 .30	− 5676.1
75	305.11	10952.	236.81	− 6809.0
80	320.57	12516.	257.00	− 8043.7
85	336.40	14158.	276.90	− 9378.6
90	353.04	15881.	296.60	− 10812.
95	370.99	17691.	316.16	− 12344.
100	389.44	19607.	335.81	− 13974.
110	413.13	23621.	374.06	− 17525.
120	435.06	27864.	410.96	− 21451.
130	455.32	32317.	446.59	− 25740.
140	474.01	36965.	481.03	− 30379.
150	491.20	41792.	514.33	− 35357.
160	506.98	46784.	546.54	− 40662.
170	521.45	51928.	577.72	− 46284.
180	534.69	57209.	607.90	− 52213.
190	546.79	62618.	637.14	− 58439.
200	557.83	68142.	665.47	− 64953.
220	577.12	79496.	719.57	− 78809.
240	593.25	91205.	770.50	− 93714.
260	606.92	103210	818.54	− 109609
280	618.84	115470	863.96	− 126439
298.15	628.73	126792	903.13	− 142478
300	629.71	127957	907.03	− 144152
320	640.24	140656	948.01	− 162706
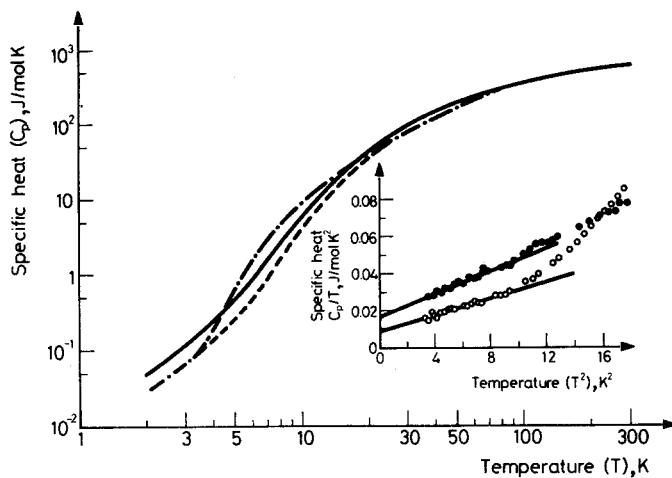
Fig. 2 Specific heat C_p of $[Ag_6M_4P_{12}]Ge_6$ (M = Ge, Sn) as a function of temperature. The insert shows the low temperature range, $T < 5$ K. ——— $[Ag_6Sn_4P_{12}]Ge_6$ and insert: ......; —·—·— $[Ag_6Ge_4P_{12}]Ge_6$ and insert: ∘∘∘∘∘; – – – indicates the calculated lattice heat capacity of $(Ag_6Ge_4P_{12}]Ge_6$ without the Schottky-anomaly
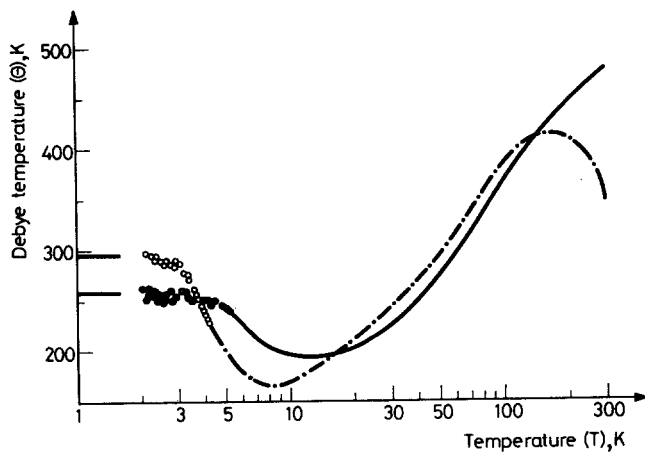
Fig. 3 Equivalent Debye temperature Θ_D as a function of temperature for ...... and ——— $[Ag_6Sn_4P_{12}]Ge_6$, + + + and – – – $[Ag_6Ge_4P_{12}]Ge_6$

4.2 DTA in closed ampoules

The DTA measurements indicate congruent melting for $[Ag_6Ge_4P_{12}]Ge_6$, but decomposition for $[Ag_6Sn_4P_{12}]Ge_6$. The melting point for $[Ag_6Ge_4P_{12}]Ge_6$ was found to be at 1026(10) K together with a small not yet identified precursor peak at 1011(10) K. A strong hysteresis was observed; the solidification occurs at 961 K. The decomposition temperature for $[Ag_6Sn_4P_{12}]Ge_6$ under its own vapour pressure is ~ 823 K. From the X-ray powder pattern the decomposition runs into a mixed cluster $[Ag_6(Sn_2Ge_2)P_{12}]Ge_6$, Ag_3Sn and into the elements (Sn, Ge and P_4), but no elemental silver is formed.

4.3 TG in dynamical vacuum

In dynamical vacuum also $[Ag_6Ge_4P_{12}]Ge_6$ does not melt congruently, but starts to decompose at 723 K (Fig. 4) according to the equation:

$$[Ag_6Ge_4P_{12}]Ge_6,s = 6\ Ag,s + 10\ Ge,s + 3\ P_4,g \qquad (3)$$
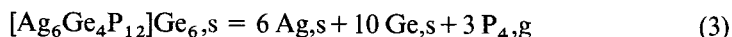
The nature of the solid products was confirmed by an X-ray powder diagram. After about 2/3 of the reaction was completed, an additional endothermic effect at about 844 K was observed which interfered the kinetics of decomposition and simulated an intermediate phase. A comparative run with 172 mg of sample showed the effect at 886 K. However, under argon atmosphere the reaction started at 873 K and the previous thermal effect could not be detected but a liquidus at 1023 K was formed. The residue had a nominal composition of $Ag:Ge:P = 6:10:3.5$.

Also the decomposition of $[Ag_6Sn_4P_{12}]Ge_6$ (Fig. 4) at identical conditions in dynamical vacuum behaves similar (no mixed cluster formation) and takes place at a slightly lower temperature. In addition to the elements, Ag_3Sn could be identified
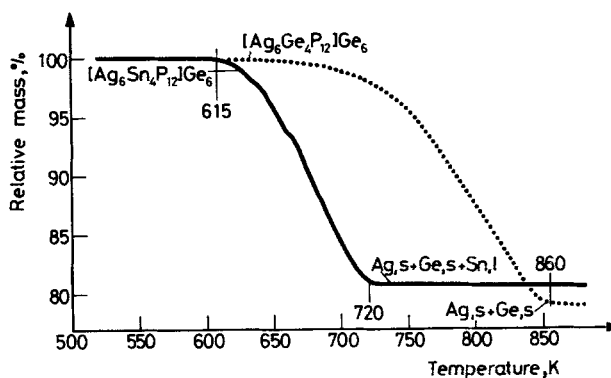

Fig. 4 Thermal decomposition of $[Ag_6Ge_4P_{12}]Ge_6$ and $[Ag_6Sn_4P_{12}]Ge_6$ as measured in dynamical vacuum

in the residue of the reaction. The latter was attributed to be a byproduct, being formed on cooling, since silver and tin are main products. No other thermal effects were observed during decomposition in vacuum. From this result the equation follows:

$$[Ag_6Sn_4P_{12}]Ge_6,s = 6Ag,s + 6Ge,s + 4Sn,l + 3P_4,g \qquad (4)$$
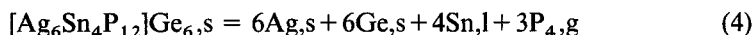
Under those conditions only traces of Ag_3Sn,s are formed as byproduct.

The phosphorus equilibrium pressure and the resulting thermodynamic data were calculated from weight loss measurements at Knudsen conditions upon occurrence of reactions Eqs (4) and (5), respectively. Although almost P_4,g appears in the gas phase, the presence and formation of P_2,g has been taken into account for the calculation of K_p. For this, the total measured effusion rate was previously converted into partial effusion rates using the well known equilibrium between P_4 and P_2 in order to calculate the partial pressures of phosphorus. The results of the vapour pressure investigation and the thermodynamic values computed from the heat capacity measurements are given in Table 2.

Table 2 Results of the vapour pressure measurements for $[Ag_6M_4P_{12}]Ge_6$ (M = Ge, Sn)
The respective standard deviations are given in parentheses

$$\ln(p_{total}/Pa) = -A \cdot 10^3 \cdot T^{-1} + B$$

$$p_{total} = p(P_4,g) + p(P_2,g)$$

		$[Ag_6Ge_4P_{12}]Ge_6$	$[Ag_0Sn_4P_{12}]Ge_6$
Cell orifice	[cm²]	$2.21 \cdot 10^{-4}$	$2.21 \cdot 10^{-4}$
Temperature range	[K]	573–789	631–758
$\Delta H^\circ_{r,T}$	[kJ mol⁻¹]	510(10)	553(6)
$\Delta S^\circ_{r,T}$	[J K⁻¹ mol⁻¹]	465(13)	556(10)
$\Delta H^\circ_{r,298}$	[kJ mol⁻¹]	562(10)	582(7)
$\Delta S^\circ_{r,298}$	[J K⁻¹ mol⁻¹]	573(13)	618(10)
A		20.6(4)	22.2(3)
B		30.4(5)	33.9(4)
2ⁿᵈ law			
$\Delta H^\circ_{f,298}$	[kJ mol⁻¹]	−173(10)	−169(7)
S°_{298}	[J K⁻¹ mol⁻¹]	836(13)	870(10)
3ʳᵈ law			
$\Delta H^\circ_{f,298}$	[kJ mol⁻¹]	−135(10)	−147(7)
with S°_{298}	[J K⁻¹ mol⁻¹]	888(13)	903.3(13)
(from C_0 data)			
$(H_{298} - H_0)$	[kJ mol⁻¹]	12.82	12.68
$(G_{298} - G_0)$	[kJ mol⁻¹]	−13.67	−14.52

Table 2 (continuation)

Thermodynamic values used for the calculation of heat of formation

$$C_p, \text{J K}^{-1} \text{mol}^{-1} = A + B \cdot T \cdot 10^{-3} + C \cdot T^{-2} \cdot 10^{5}$$

Compound	$\Delta H^0_{f,298}$, kJ mol^{-1}	S^0_{298}, J K^{-1} mol^{-1}	A, J K^{-1} mol^{-1}	B, J K^{-2} mol^{-1}	C, J K mol^{-1}
Ag (s)	0	42.70	21.31	8.54	1.52
Ge (s)	0	31.10	25.78	0.08	− 2.16
Sn (l)	6.26	51.22	21.55	6.15	12.88
P$_4$ (g)	128.80	280.00	81.89	0.68	− 13.45
P$_2$ (g)	178.66	218.13	36.31	0.80	− 4.16
Ag$_6$Sn$_4$P$_{12}$Ge$_6$ (s)		903.3	719.27	144.31	− 117.2
Ag$_6$Ge$_4$P$_{12}$Ge$_6$ (s)		888.0	765.4	88.87	− 117.2

The values of the elements are taken from Kubaschewski [14].

Firstly, the results of the vapour pressure measurements are listed: the vapour pressure equation valid for the indicated temperature range, the reaction enthalpies $\Delta H^\circ_{r,T}$ and entropies $\Delta S^\circ_{r,T}$ of the decomposition equations of reaction (Eqs (3), (4)). The latter values are obtained by a least-square refinement of the data of the temperature dependence of the equilibrium constant K_p, as represented graphically in terms of ln K_p vs. $1/T$ in Fig. 5.

Second law enthalpies $\Delta H^\circ_{r,298}$ and entropies $\Delta S^\circ_{r,298}$ of reaction, according to equations (4), (5) at 298 K were determined from the measured P$_4$ pressure and from appropriate estimation of the heat capacities of the elements as given in Table 2 (lower part) and by extrapolation of our heat capacity data to higher temperatures.
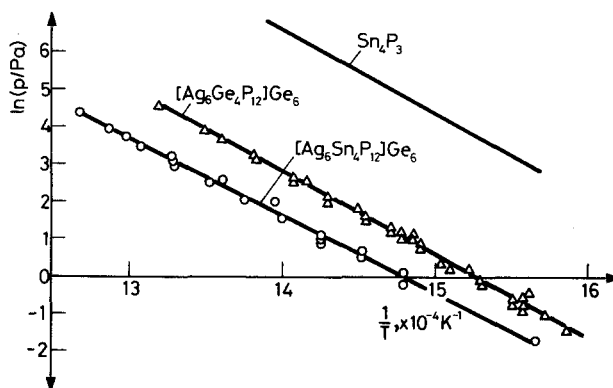

Fig. 5 ln K_p vs. $1/T$ for [Ag$_6$Ge$_4$P$_{12}$]Ge$_6$ and [Ag$_6$Sn$_4$P$_{12}$]Ge$_6$. The data for Sn$_4$P$_3$ have been included for the purpose of comparison

Secondly, for both compounds the heat of reactions were used to determine enthalpies of formation which can be expressed in terms of the enthalpy of reaction and the heats of formation of the products and reactants according to the general equation:

$$\Delta H^{\circ}_{f,T}[Ag_6Ge_4P_{12}]Ge_6, s =$$

$$= 3\Delta H^{\circ}_{r,T} + 3\Delta H^{\circ}_{f,T}(P_4, g) + 6\Delta H^{\circ}_{f,T}(Ag, s) + 10\Delta H^{\circ}_{f,T}(Ge, s) \tag{5}$$

Table 2 gives this 2ⁿᵈ and 3ʳᵈ law values of $\Delta H^{\circ}_{f,298}$, S°_{298} for $[Ag_6Ge_4P_{12}]Ge_6$, s and $[Ag_6Sn_4P_{12}]Ge_6$, s. Finally, in Table 2 the independently determined thermodynamic standard value of the entropy S°_{298} computed from the integration of the C_p-data over the entire temperature range is tabulated as well as the standard values of $(H_{298} - H_0)$ and $(G_{298} - G_0)$. The latter enthalpy value was used to calculate the 3ʳᵈ law enthalpy of formation from the free enthalpy of formation.

5 Discussion

5.1 Vapour pressure measurements

From the decomposition in dynamical vacuum (Fig. 4) it follows, that under the given conditions no further phases in the ternary or quaternary system are formed. However, these results do not necessarily exclude the existence of further phases in these systems.

The calculated 3ʳᵈ law heat of formations ($\Delta H^{\circ}_{f,298} \sim -5$ kJ atom^{-1}) agree nicely with respect to the values, observed in some simple binary phosphides [14] (based on P_{red} as reference state), e.g. $\Delta H^{\circ}_{f,298}(GeP) \sim -4.9(5)$ kJ atom^{-1}; $\Delta H^{\circ}_{f,298}(AgP_2) \sim -3.3(3)$ kJ atom^{-1}; $\Delta H^{\circ}_{f,298}(SnP) \sim -6.6(5)$ kJ atom^{-1} [19]. A simple estimation from the weighted values of 10 GeP, AgP$_2$ and 5 Ag leads to a value, being in the same order of magnitude (-1.9 kJ atom^{-1}). Taking the value of SnP, one ends up with -2.5 kJ atom^{-1}. We have included in Fig. 4 the vapour pressure of P(P_4; Sn_4P_3) in order to illustrate the phosphorus vapour pressure relations between $[Ag_6Sn_4P_{12}]Ge_6$ and Sn_4P_3, which is formed as a kineticelly favoured byproduct during the synthesis in a tin flux. This relationship demonstrates clearly, why the preparation of $[Ag_6Sn_4P_{12}]Ge_6$ is possible from a tin flux.

5.2 Specific heat

The overall temperature dependence of the specific heat as presented in Fig. 2, apparently shows no peculiar features. There is no indication of any anomaly or

phase transition in the temperature range investigated. Yet, it is immediately obvious by comparing the two investigated compounds that below 150 K the C_p-curves show a rather surprising behaviour: clearly they cross three times. In fact, this feature cannot be explained in terms of a simple vibronic model for isostructural crystals. Later, we will show that the unexpected temperature dependence presumably originates from a Schottky anomaly.

Firstly, we discuss the lattice vibrations at higher temperatures. The Neumann–Kopp rule is obeyed at high temperatures where a heat capacity of about 700 JK mol^{-1} is expected. The smaller $\Theta_D(T)$ for $[Ag_6Sn_4P_{12}]Ge_6$ in comparison to that of $[Ag_6Ge_4P_{12}]Ge_6$ in the temperature range from 40 K to 120 K (see Fig. 3) is consistent with the somewhat lower overall stiffness in the tin compound as found also in the elastic properties [3, 4]. In addition, qualitatively a decrease of the Debye temperature Θ_D at constant temperature is expected for isostructural crystals if the molecular mass of the material is increased; e.g. Sn is replaced by Ge. Above 150 K, $\Theta_D(T)$ of the Sn-compound still increases continuously with temperature, whereas $\Theta_D(T)$ of $[Ag_6Ge_4P_{12}]Ge_6$ starts to lower. This decrease of $\Theta_D(T)$ is usually connected to anharmonicity. Therefore, we conclude that in the Sn-compound the lattice vibrations are less anharmonic than in the Ge-compound. This result is supported by conclusions drawn from high pressure and elastic experiments: thereby the long wavelength acoustic modes of the Sn cluster compound was found less anharmonic than that of the Ge one [3, 4].

Secondly, we focus on the range of very low temperatures ($T < 10$ K), which is shown in the insert of Fig. 2. From our data we determine the electronic contributions to the heat capacities: γ(M = Sn) = 17(1) mJ mol$^{-1} \cdot$K^2 and γ(M = Ge) = 9(1) mJ mol$^{-1} \cdot$K^2. Qualitatively, these results are in agreement with the results of the electronic transport investigations [5] and rough band structure calculations [7]. Since $[Ag_6Ge_4P_{12}]Ge_6$ is a highly doped semiconductor with a carrier concentration of $n = 1.3 \cdot 10^{20}$ cm^{-3} at 300 K [5] and an effective mass of $m_{eff} = 1.2\ m_0$ [5], or $m_{eff} = 1.3\ m_0$ as reported in [7] (we disregard the higher value indicated in Ref. 10 and assume a spherical Fermi surface) we calculate γ(M = Ge) = 8.4 mJ mol^{-1} K^2. For the Sn compound, m_{eff} is not yet known. However, a similar effective mass as for the Ge compound was suggested [6, 7]. In consequence, we estimate from the specific heat data a carrier concentration nearly twice as high as found for the Ge-compound, if an effective mass of $m_{eff} = 1.0\ m_0$ [7] is assumed: n(M = Sn) $\approx 2 \cdot 10^{21}$ cm^{-3}. We notice that the tin compound was tentatively considered to be a semimetal [6]. A simple comparison with the values of elemental copper indicates reasonable values. In copper the γ-value is γ(Cu) = 0.7 mJ mol^{-1} K^2. Hence, for the two electrons—as encountered in the silver cluster (see above)—and taking into account the before indicated effective masses we would expect our experimentally found γ-values. Unfortunately, so far,

no precise band structure calculation has been performed and the evaluated electronic measurements gave no indications of the carrier concentrations at low temperatures. Therefore, a stringent quantitative comparison of our data with other results cannot be performed.

The Debye temperatures, according to the T^3-law are:

$\Theta_0(M = Ge) = 296(4)$ K and $\Theta_0(M = Sn) = 260(3)$ K. The ratio of both Debye temperatures for the low temperature region equals:

$$R_{exp} = \Theta_0(M = Ge)/\Theta_0(M = Sn) = 1.14 \qquad (6)$$

In the case of cubic mono- or diatomic compounds the relationship is valid at low temperatures $(T < \Theta_D/20)$:

$$\Theta_0(2)/\Theta_0(1) = R_{mass} = [a(2)/a(1)] \cdot [M(1)/M(2)]^{1/2} \qquad (7)$$

where $M(1)$ and $M(2)$ are the atomic weights of atoms (1) and (2), and $a(1), a(2)$ are their respective (cubic) lattice parameters. Empirically, we have found this equation being correct for many complex multi-atomic substances [15]. In such compounds all atoms contribute to the low temperature lattice vibrations. This contribution may be in form of an individual atom, or as part of a strongly bonded cluster of atoms acting as a single heavy unit. Taking into account the total molecular masses of the Ge- and the Sn-compound we expect a value of $R_{mass} = 1.05$ and, the foregoing equality seems not fulfilled. However, the result $R_{exp} > R_{mass}$ indicates, that not all atomic vibrations which participate in the soft vibrational modes at low temperatures are modified by replacing Ge(1) atoms by Sn atoms.

At very low temperatures, the lattice vibrations are dominated by the excitation of the heavy atoms, that means Ag and Sn or Ge(1), respectively. The four center-two electron bonds results in three weak bonds between Ag and M. With respect to an ordered split model this means that each Ge(1) is predominantly bond to only one Ag (see below). For a reasonable evaluation of the mass ratio therefore only the Ag–M bonds with their respective masses should be relevant. This yields (disregarding the neglible changes in bond length):

$$R_{mass} = 1.12$$

in good agreement with the experimental result, $R_{exp} = 1.14$.

Finally, we discuss the morefold crossing of the specific heat curves. It is remarkable and not common at all that Debye's T^3-law is valid only in an extremely limited temperature range, namely at $T \leqslant 2.5$ K, in the case of $[Ag_6Ge_4P_{12}]Ge_6$ which corresponds to $T < \Theta_D/150$. Noticeable deviation from the usual T^3-behaviour of solids are commonly observed only above temperatures of $T \geqslant \Theta_D/50$; that means above 6 K in the present compounds. In contrast to other solids we observe an unusually rapid increase of $C_p(M = Ge)$ between 2.5 and 7 K,

which is well visualized in the insert of Fig. 2. Near 8 K C_p(M = Ge) exceeds that of the Sn compound by nearly a factor of two. However, above 18 K $C_p(T)$ increases slower and again the heat capacity of the Sn-compound becomes larger. The following temperature region up to 150 K displays the expected difference in C_p between both compounds due to the above discussed differences in the molecular masses and the further crossing near 150 K which we rely—as yet explained—to the stronger anharmonicity of the Ge-compound.

After more detailed inspection of the heat capacity data and with regard to the structure of the materials we have been led to attribute the observed peculiar behaviour of $C_p(T)$ in $[Ag_6Ge_4P_{12}]Ge_6$ to a Schottky-anomaly [16]. Split positions have been encountered by elastic neutron scattering experiments [9] for the silver atoms in $[Ag_6Ge_4P_{12}]Ge_6$. In each moment every silver atom can occupy only one of the two possible positions. Following this picture, certain silver atoms (or the entire Ag_6-cluster) may be treated in the framework of a *two level* model. A single atom or a group of atoms occupy fixed lattice sites, being one place of the split positions. Transitions into the neighboured positions will take place either by thermal activation (with increasing temperature) or by tunneling. Such systems are characterized by an energy splitting ΔE_0 which either represents the thermal activation energy of the potential wall separating the positions or which, in the case of a tunneling process, is related to the distance between the two atomic positions. Due to the rather high value of ΔE_0 we believe that we are dealing here with a thermally activated system and not with a tunneling process which, in addition, has been detected predominantly in amorphous or disordered materials. The existence of such moving atoms in crystalline structures has been observed in different cases: OH^- ions or CN^- ions in alkali halides [17], some ionic conductors, e.g. Na^+ in hollandith, Cu^{2+} in Cu_6PS_5Cl [18] a.o. The occurrence of thermally activated, lattice sites changing atoms or molecules is governed by their entropy and is reflected by a characteristic temperature dependence of its specific heat which is described by the Schottky-function for a two level system:

$$\Delta C_{Sch} = m \cdot N \cdot \left(\frac{\Delta E_0}{kT}\right)^2 \cdot \frac{\exp\left(\dfrac{\Delta E_0}{kT}\right)}{\left[1 + \exp\dfrac{\Delta E_0}{kT}\right]^2} \tag{8}$$

where k is Boltzmann's constant, N is Avogadro's constant and m is the number of involved atoms per formula unit. The related change of molar entropy for such a two-level system is $\Delta S = m \cdot R \cdot \ln 2$. In order to isolate the Schottky contribution we had to determine the pure lattice term of the Ge compound. This is done by normalizing (with respect to the molar masses) the C_p(T,M = Sn)-curve by the

experimentally determined ratio of Debye temperatures, $R_{exp} = 1.14$, between 2 K and 60 K. Of course, first we deduce the electronic contribution $C_p(T, M = Sn) - \gamma T$, subsequently. we calculate $\Theta_D(T)$ as shown in Fig. 3. Then $\Theta_D(T)$ of the Sn-compound is multiplied with $R_{exp} = 1.14$. From the thus constructed $\Theta_D(T)$ curve the lattice heat capacity, of the Ge-compound $C_p^L(T)$ is calculated via the Debye-function. The remaining specific heat represents ΔC_{Sch}:

$$\Delta C_{Sch} = C_p^{exp}(T, M = Ge) - C_p^L(T) - \gamma_{Ge}(T) \qquad (9)$$

Our result, the experimental ΔC_{Sch}-contribution, is plotted in linear scale ΔC_{Sch} vs. T in Fig. 6. The parameters ΔE_0 and m were determined by the least-square method,

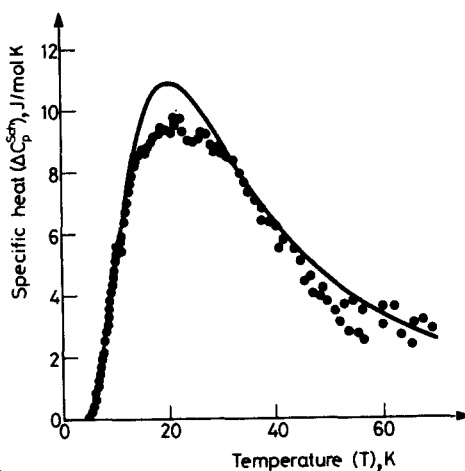**Fig. 6** Specific heat contribution ΔC_{Sch} of the Schottky-anomaly in $[Ag_6Ge_4P_{12}]Ge_6$ as a function of temperature · · · · Experimental data, derived after normalizing the lattice heat of $[Ag_6Ge_4P_{12}]Ge_6$ to that of $[Ag_6Sn_4P_{12}]Ge_6$ according to eqn. 9. ———— ΔC_{Sch}, calculated with eqn. 8 and $m = 3$, $N = 6 \cdot 10^{23}$ atom · mol^{-1}

using Eq. (9) to be: $\Delta E_0/k = 46(2)$ K and $m = 3$. The result of the fit is also shown in Fig. 6 and is in good agreement with the experimental data. The entropy amounts to $\Delta S = 16.92(30)$ J/mol·K which has to be compared with the expected value of $\Delta S = 3R \ln 2 = 17.28$ J/mol·K. As a consequence, we conclude that in $[Ag_6Ge_4P_{12}]Ge_6$ a threefold two-level Schottky type anomaly exists.

A remarkable feature is the existence of a system with $m = 3$, this means an entity with three moles of individuals. In this context we emphasize that the form of the Schottky anomaly is quite sensitive to both, the number of levels and their energetic distances whereas the maximum of the heat capacity displays predominantly the number of participating individuals (see error bars in Fig. 6). In the present case, no other choice for ΔE_0 and m will yield an approximately good agreement. An
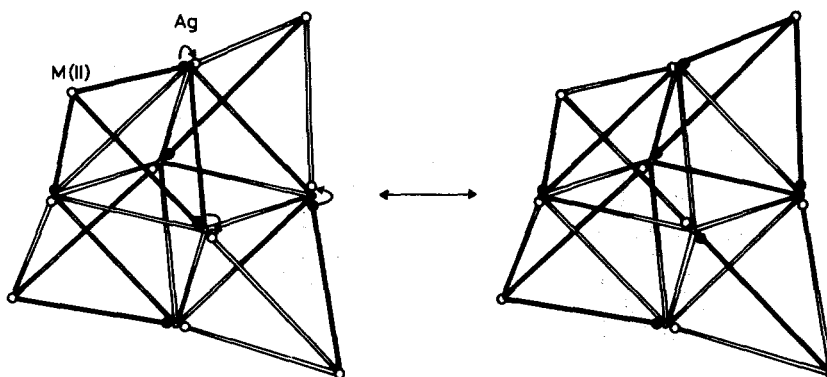
Fig. 7 Structural possibilities for two ordered models of $[Ag_6M_4P_{12}]Ge_6$. (M = Ge, Sn) (left and right). The simultaneous hopping of *three* silver atoms is indicated by arrows

explanation for the anomaly is found in the crystal structure itself: The split positions for the Ag atoms allow for a large manifold of different microstructures. Among those only one configuration exists, which preserves at least one short Ge–Ag bond for all equivalent Ge atoms and threefold (C_3) symmetry. Thus a GeAg$_3$ tetrahedrane unit is formed oriented along one of the [111] directions. This configuration is shown in Fig. 7. The transitions from one ordered state into another one requires the simultaneous hopping of exactly three silver atoms from one side of the split position into the other side. As the 4 Ge(1) atoms occupy equivalent positions, the rearrangement process moves the silver atoms at least in all possible split positions. Above the thermal energy of $\Delta E_0/k = 46$ K an increasing number of Ag$_6$Ge$_4$ units is involved. The elastic neutron scattering experiments [9] therefore show in the range 77 K $< T <$ 220 K equally occupied split positions of the silver atoms.

Another feature is the structurally determined difference between the $[Ag_6Ge_4P_{12}]Ge_6$- and $[Ag_6Sn_4P_{12}]Ge_6$-compound. In the Sn-compound the bonding between Sn and the three Ag atoms is much stronger compared to that in the Ge-compound. Therefore the activation of the Ag atom to jump into the empty part of the split position requires a higher thermal excitation energy compared to that in the Ge-compound. Consequently a similar Schottky anomaly is expected in $[Ag_6Sn_4P_{12}]Ge_6$ at much higher temperatures, e.g. at $\Delta E_0/k \sim 90$ K. At such high temperatures however, the lattice modes are already much more activated and therefore the rather high lattice heat capacities (e.g. 200 J mol^{-1} near 40 K, the maximum of the expected Schottky anomaly) may mask the relatively small contribution ΔC_{Sch} (being less than 11 J mol^{-1} in case of the Sn-compound).

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Zusammenfassung — Die spezifischen Wärmen der *Cluster*-Verbindungen [Ag$_6$M$_4$P$_{12}$]Ge$_6$ (M = Ge, Sn) wurden im Temperaturbereich 2 K bis 300 K bestimmt. Die thermische Zersetzung in die Elemente wurde unter Knudsen-Bedingungen auf einer mit einem Massenspektrometer gekoppelten Thermowaage untersucht. Die Standardentropie, -enthalpie und die Debye-Temperaturen wurden berechnet. Die aus den Knudseneffusionsdaten abgeleiteten Dampfdruckfunktionen dienten zur Berechnung der Bildungswärmen. Die komplizierte Temperaturabhängigkeit der spezifischen Wärme wird für strukturelle Details und unterschiedliche Beiträge qualitativ diskutiert: für $T \leqslant 3$ K ein elektronischer Anteil, in der Ge-Verbindung im Bereich 2 K $\leqslant T \leqslant$ 20 K eine dreifache Schottky-Anomalie ($\Delta E_0/k = 46(2)$ K) sowie Gitterschwingungen, die durch unterschiedliche Abstände d(Ag-Ag) und Massen (Ge und Sn) beeinflusst werden.

Резюме — В интервале температур 2–310 К были измерены теплоемкости кластерных соединений [Ag$_6$M$_4$P$_{12}$]Ge$_6$, где M = Ge, Sn. Термическое разложение их на отдельные элементы было проведено в условиях Кнудсена с помощью термовесов, соединенных с масс-

спектрометром. Из данных теплоемкостей были вычислены такие термодинамические функции, как стандартная энтропия, энтальпия и температуры Дебая. Функции давления паров, выведенные из эффузионных данных Кнудсена, служили для вычисления третьего закона теплообразования. Сложная температурная зависимость удельной теплоемкости количественно обсуждена с учетом структурных деталей и различных вкладов: электронный член ($T \leqslant 3$ K), трехосная аномалия Шоттки ($\Delta E_0/k = 46(2)$ K) в соединени германия (2 K $\leqslant T \leqslant 20$ K), решеточные вклады, затрагиваемые расстояниями Ag–Ag и атомными массами (Ge и Sn) в обоих соединениях.