Thermochimica Acta, 160 (1990) 63–70
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THERMAL BEHAVIOUR OF THE TETRACHLOROGALLATES(III) OF GALLIUM, POTASSIUM AND INDIUM, $A^I[GaCl_4]$ A^I = Ga, K, In, AND OF $Ga[AlCl_4]$

GERD MEYER, THOMAS STAFFEL and MANFRED IRMLER

Institut für Anorganische Chemie und Sonderforschungsbereich 173,
Universität Hannover, Callinstrasse 9, D-3000 Hannover (F. R. G.)

SUMMARY

The chlorides $Ga[GaCl_4]$, $K[GaCl_4]$, $In[GaCl_4]$ and $Ga[AlCl_4]$ were synthesized and their thermal behaviour was investigated by Guinier-Simon powder X-ray diffraction in various temperature ranges. Three structure types are relevant: I: $GaCl_2$ type, II: $GaAlCl_4/KAlCl_4$ type, III: baryte ($BaSO_4$) type. $In[GaCl_4]$ is monomorphic (III), its crystal structure has been refined at ambient temperature, $Ga[GaCl_4]$ and $Ga[AlCl_4]$ are dimorphic (I, II) and $K[GaCl_4]$ is trimorphic (I, II, III). Transition temperatures and thermal expansion coefficients have been determined. Mechanisms for the first-order ($I \rightleftarrows II$) and second-order ($II \rightleftarrows III$) phase transitions are considered.

INTRODUCTION

Ternary chlorides of trivalent gallium, $A^I[GaCl_4]$, are well known for a number of monovalent cations. Of these, the alkali metal cations (Li^+-Cs^+) are the most simple and may be complemented by the much more interesting inert-pair cations Ga^+ , In^+ , and Tl^+ (ref. 1). As this group of compounds contains isolated tetrahedral anions, $[GaCl_4]^-$, throughout, their individual structures must depend upon size and shape of the counter cation A^+. For example, the structure types of $NaAlCl_4$ (ref. 2), $KAlCl_4/GaAlCl_4$ (refs. 3,4), $GaCl_2$(= $GaGaCl_4$) (ref. 5) and baryte that are important in this connection, may all be viewed at as if they contain rows of tetrahedra arranged parallel to one crystallographic axis.

Furthermore, as temperature may be regarded as comparative to isomorphic substitution, polymorphic transitions between such closely related structural types are expected. This has indeed been observed for the example of $K[GaCl_4]$ (ref. 6). Three modifications were detected although the structure of $KGaCl_4$-I remained unclear. Quite recently, a structure determination of $Ga[AlCl_4]$ (ref. 4) revealed that this is isostructural with $KGaCl_4$-II. $In[GaCl_4]$ belongs to the baryte-type of structure (ref. 1). A refinement from single crystal data is reported below.

Therefore, a closer inspection of the thermal behaviour of the tetrachlorogallates(III), $A^I[GaCl_4]$ with A^I= Ga, K, In, appeared promising in order to decide

0040-6031/90/$03.50 © 1990 Elsevier Science Publishers B.V.

whether the observed topological relationships within this structural family are only formal or if the compounds are also thermodynamically connected through phase transitions. Ga[$AlCl_4$] was included in this study for comparison.

EXPERIMENTAL DETAILS

Starting materials were KCl (E. Merck, suprapur), aluminium (Johnson-Matthey, 99.999%), gallium (Aldrich, 99.999%), $GaCl_3$ (Aldrich, 99.99%), and indium (Koch-Light, 99.999%) which were all used without further purification. $AlCl_3$ (E. Merck, p.a.) was sublimed in a sealed Duran tube where a few grains of aluminium had been added. $InCl_3$ (Riedel-de Haen, 99.999%) was sublimed in an HCl gas stream. $GaAlCl_4$ and $KGaCl_4$ were prepared as previously described (refs. 4,6). $GaCl_2$ was obtained from mixtures of gallium and $GaCl_3$ in a 1:2 molar ratio (e.g., 141 mg Ga, 712 mg $GaCl_3$) in a sealed Duran tube under argon at 200°C/4 days. For $InGaCl_4$ an analogous route as for $GaAlCl_4$(ref. 7) was used. The reaction of $InCl_3$ and gallium in a 4:3 molar ratio (e.g., 450 mg $InCl_3$, 106 mg Ga) in a sealed Duran tube under dry argon at 400°C results in a clear colourless melt of $InGaCl_4$ and molten indium metal. They separate on solidification upon cooling and may be separated mechanically in a dry box. Single crystals were selected therefrom and sealed in thin glass capillaries for further investigation. For details of the data collection and structure refinement processes see Table 1.

Powder samples of $KGaCl_4$, $GaGaCl_4$, $InGaCl_4$ and $GaAlCl_4$ were investigated by X-ray diffraction utilizing the Guinier-Simon technique (ref. 8) (camera FR 553, Enraf-Nonius, Delft, Cu-K_α radiation). Temperature controlled patterns were recorded at various heating or cooling rates and film speeds, respectively, in order to determine the transition temperatures. Lattice constants were determined from Guinier-Simon patterns at defined temperatures using low-quartz as an internal standard for calibration and refined by least-squares techniques (ref. 9).

RESULTS AND DISCUSSION

A previous study had clearly shown that $KGaCl_4$ is thermally trimorphic (ref. 6). A single crystal study of Ga[$AlCl_4$] (ref. 4) revealed that $KGaCl_4$-II is isostructural and, hence, has the same structural topology as $KAlCl_4$ (ref. 3) although this was thought to be non-centrosymmetric. Furthermore, the present study has shown that a low-temperature form of $GaAlCl_4$ exists ($GaAlCl_4$-I) which is isotypic with $GaGaCl_4$ which, in turn, is at higher temperatures isostructural with $GaAlCl_4$. Fig. 1 gives a summary of the results.

Therefore, three structure types have to be considered to describe the polymorphism of the chlorides $A^I[GaCl_4]$ (A^I = Ga, K, In) and of Ga[$AlCl_4$]:

TABLE 1

$InGaCl_4$: Crystallographic data and their determination

Lattice constants (pm):
a = 1091.6(2), b = 708.3(1), c = 931.6(2) pm, V_m = 108.4(1) $cm^3 \cdot mol^{-1}$.

Crystal system: orthorhombic, *Space group:* Pnma (No. 62), Z = 4.

Data collection: Four-circle diffractometer Philips PW 1100, Mo-K_α radiation, graphite monochromator, λ = 71.07 pm, ω-scan, scan speed: 0.15°/s, scan width: 4.5°, $3° \leq \Theta \leq 30°$, F(000) = 581, μ = 78.9 cm^{-1}.

Data corrections: Background, polarization and Lorentz factors, absorption: Φ scan, ΔΦ = 10°, Θ = 7.21° (hkl: -2 -1 -2), absorption coefficients 0.833 and 0.994.

Data statistics: Intensities of 4512 reflections measured of which 1128 were symmetrically independent (R_{int} = 0.048).

Structure determination and refinement: Program system SHEL-X 76, scattering factors from Cromer et al., In positions by direct methods, Ga and Cl positions from successive difference Fourier maps, full-matrix least-squares refinement, R = 0.084, R_w = 0.049, w = $0.901\ \sigma^{-2}(F_o)$.

Atomic parameters

		x/a	y/b	z/c
In	4c	0.8138(1)	0.25	0.6888(2)
Ga	4c	0.9327(2)	0.25	0.1878(2)
Cl1	8d	0.9252(3)	0.4969(4)	0.3248(4)
Cl2	4c	0.7724(5)	0.25	0.0537(6)
Cl3	4c	0.6009(5)	0.25	0.4312(6)

Thermal parameters (U_{ij} in pm^2)

		U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
In	4c	648(11)	1580(20)	1307(15)	0	0.0(14)	0
Ga	4c	412(11)	366(11)	344(10)	0	-38(12)	0
Cl1	8d	843(24)	603(24)	940(24)	-345(22)	-145(22)	90(23)
Cl2	4c	996(42)	1133(56)	827(36)	0	-534(33)	0
Cl3	4c	1062(48)	1609(72)	1220(49)	0	-693(40)	0

I: The $GaCl_2$ type (orthorhombic, Pnna, Z=4) (ref. 5).

II: The $KAlCl_4$ type (monoclinic, $P2_1$, Z=4) (ref. 3) or the $Ga[AlCl_4]$ type (monoclinic, $P12_1/n1$, Z=4) (ref. 4).

III: The baryte ($BaSO_4$) type (orthorhombic, Pmnb, Z=4), e. g., $In[GaCl_4]$.

Unit cell settings were chosen such that the relationships between the lattice constants are b>c>a in all three cases.

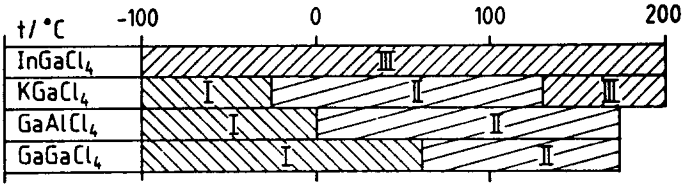

Fig. 1. An overview of the stability ranges of three modifications of $AMCl_4$ type compounds dependent upon temperature.

TABLE 2

Lattice constants and distances (pm) for the three modifications of $K[GaCl_4]$

$KGaCl_4$- t/°C	I -50	II +75	III +140
a/pm	728.5(2)	720.1(2)	712.7(2)
b/pm	988.9(2)	1057.2(3)	1078.4(3)
c/pm	962.1(2)	936.3(3)	942.7(3)
β/°	90	93.24(2)	90
V_m/cm^3mol^{-1}	104.4(1)	107.2(1)	109.1(1)
$d(K^+-Cl^-)$/pm	321.7 (2x) 322.6 (2x) 322.9 (2x) 326.8 (2x)	319.6 319.6 327.9 330.9 331.7 331.9 359.9 364.2 390.7	334.2 334.6 (2x) 339.7 (2x) 346.9 389.7 (2x) 403.9 (2x) 433.2 (2x)
$\bar{d}$/pm [C.N.]	323.5 [8]	341.8 [9]	373.6 [12]
$d(Ga^{3+}-Cl^-)$/pm	221.1 (2x) 222.4 (2x)	213.2 215.5 218.3 219.5	213.3 214.2 218.4 (2x)
$\bar{d}$/pm	221.8	216.6	216.1

Table 2 gives a comparison of the lattice constants of $KGaCl_4$ for three different temperatures together with interatomic distances between Cl^- and K^+ and Ga^{3+}, respectively. For these calculations, crystallographic data (especially the atomic parameters) were taken for $KGaCl_4$–I from $GaCl_2$ (ref. 5), for $KGaCl_4$-II from $GaAlCl_4$ (ref. 4), and for $KGaCl_4$-III from $InGaCl_4$ (Table 1).

Thermal behaviour of $InGaCl_4$, $KGaCl_4$, $GaAlCl_4$ and $GaGaCl_4$ was followed at different temperature ranges. Table 3 reports lattice constants at typical temperatures for these four chlorides. The isotropic ("cubic", volume) thermal expansion coefficients, γ, calculated from the temperature dependences of the molar volume are summarized in Table 4. This shows an interesting result: For $In[GaCl_4]$ which does not undergo a phase transition, $\gamma = 19 \cdot 10^{-5}K^{-1}$ is observed. Expansion coefficients for the other compounds "oscillate" with respect to this "mean" value. For the $GaCl_2$-type form I γ is always around 15 to $17 \cdot 10^{-5}K^{-1}$ and for the modifications II and III at about 23 to $25 \cdot 10^{-5}K^{-1}$. This reflects that the transition II⟶III is second-order (equal expansion coefficients!) and I⟶II is a first-order transition at which the thermal expansion coefficient rises abruptly. Fig. 2 illustrates the dependence of the molar volume upon temperature for the example of $KGaCl_4$. Although this shows a rather small volume discontinuity at the first-order phase transition at about -25°C and, of course, none at the second-order phase-transition temperature (~130°C), the changes of the lattice constants with temperature are rather dramatic as Fig. 3 shows.

TABLE 3

A comparison of lattice constants of tetrachlorogallates(III) at typical temperatures

compound	form	t/°C	a/pm	b/pm	c/pm	β/°
$InGaCl_4$	III	+50	708.5(2)	1092.5(2)	931.4(2)	
$KGaCl_4$	I	-50	728.5(2)	988.9(2)	962.1(2)	
	II	+75	720.1(2)	1057.2(3)	936.3(3)	93.24(2)
	III	+140	712.7(2)	1078.4(3)	942.7(3)	
$GaAlCl_4$	I	-20	720.2(3)	973.0(3)	952.9(2)	
	II	+50	716.3(1)	1021.7(1)	926.8(1)	93.22(1)
$GaGaCl_4$	I	0	722.7(2)	970.7(2)	954.8(2)	
	II	+100	721.5(2)	1027.4(4)	932.1(2)	93.43(2)

TABLE 4
Isotropic (volume) thermal expansion coefficients, γ, of $AMCl_4$ type compounds

	temperature range [°C]	$\gamma \cdot 10^5$ [K^{-1}]
$In[GaCl_4]$	+ 50 to +225	19.3
$K[GaCl_4]$-I	-150 to - 40	14.9
-II, -III	- 25 to +200	23.6
$Ga[AlCl_4]$-I	-160 to - 20	15.1
-II	+ 25 to +170	24.8
$Ga[GaCl_4]$-I	- 60 to + 40	17.0
-II	+ 70 to +145	24.7

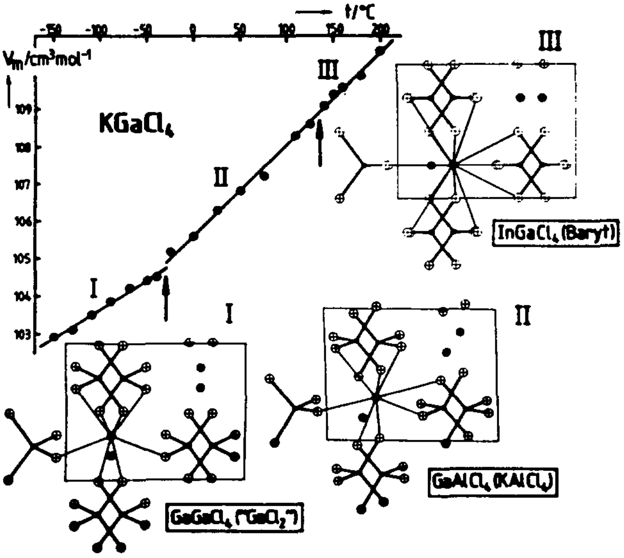

Fig. 2. Dependence of the molar volume, V_m, of $KGaCl_4$ upon temperature and a comparison of the crystal structures of the three modifications viewed onto (010).

Despite these dramatic changes of the lattice constants, the topological changes of the crystal structures are rather straightforward. Fig. 2 shows (in part) analogous projections parallel (010) of the crystal structures of the three modifications of $KGaCl_4$. There one views onto rows of tetrahedra $[GaCl_4]^-$ of which only two are shown that are (dis-)continuously rotated parallel to [001] with rising temperature, moving on from modification I to III. Their internal integrity, i.e., their distances and angles, is thereby almost unchanged. The driving force for

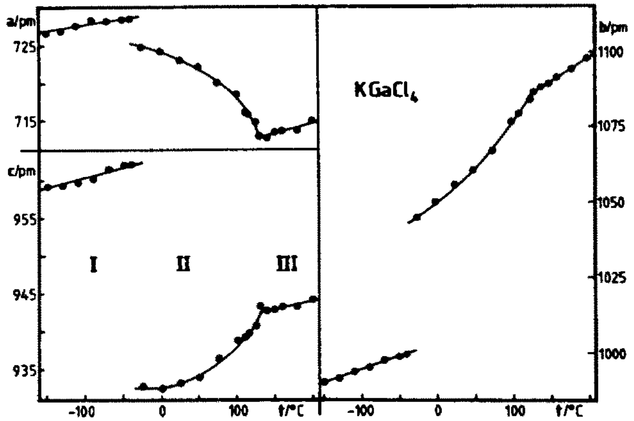

Fig. 3. Dependence of the lattice constants of $KGaCl_4$ upon temperature.

the phase transitions is the demand of the monovalent cation (K^+, ...) for the "right" coordination polyhedron at temperature:

The coordination polyhedron in the low-temperature $GaCl_2$-type $KGaCl_4$-I is a very strict dodecahedron with eight almost equal distances as is so typical for this structure type. There seems to be only little freedom for change with temperature for this dodecahedron so that a first-order phase transition to a less strict structure type appears to be a necessity.

In the $GaAlCl_4$-type $KGaCl_4$-II, the polyhedron for K^+ may be derived from a trigonal prism with two fairly long-distant caps and an additional (ninth) far-away ligand, cf. Table 2, hence a coordination number (C.N.) of 6+2+1.

The high-temperature modification, $KGaCl_4$-III, belonging to the baryte type allows for a coordination number of 12. For $KGaCl_4$-III, C.N. = 6+2+2+2 is a much better description.

Another important feature of the successive phase transitions I→II→III in $KGaCl_4$ which is evident from Fig. 2 is that the monovalent cations (K^+, ...) need to be "transported" from one mirror plane, parallel to (100) in I, to another, parallel to (001) in III. Again, this appears to be necessary to allow for a coordination sphere increasing with temperature. The mean distance K^+-Cl^- increases rather dramatically from 324 (I, -50°C, C.N. 8) to 342 (II, +50°C, C.N. 6+2+1) to, finally, 374 pm (III, +140° C, C.N. 6+2+2+2) if all 8, 9 and 12 distances are taken into account with unit weights.

ACKNOWLEGDEMENTS

This work has enjoyed considerable support from the Deutsche Forschungsgemeinschaft, Bonn, (Schwerpunktprogramm "Kristallstruktur und Eigenschaften") and from the Fonds der Chemischen Industrie, Frankfurt/Main.

REFERENCES

1 G. Meyer and E. Schwan, Z. Naturforsch., 35b (1980) 117.
2 a) N.C. Baenziger, Acta Crystallogr., 4 (1951) 216.
  b) W. Scheinert and A. Weiss, Z. Naturforsch., 31a (1976) 1354.
  c) G. Mairesse, P. Barbier and J.P. Wignacourt, Acta Crystallogr., B 35 (1979) 1753.
3 G. Mairesse, P. Barbier and J.P. Wignacourt, Acta Crystallogr., B 34 (1978) 1328.
4 Th. Staffel and G. Meyer, Z. anorg. allg. Chem., 552 (1987) 108.
5 a) G. Garton and H.M. Powell, J. Inorg. Nucl. Chem., 4 (1957) 84.
  b) H. Schmidbaur, R. Nowak, W. Bublak, P. Burkert, B. Huber and G. Müller, Z. Naturforsch., 42b (1987) 553.
6 G. Meyer and E. Schwan, Z. anorg. allg. Chem., 468 (1980) 82.
7 R.K. McMullan, and J.D. Corbett, J. Am. Chem. Soc., 80 (1958) 4761.
8 A. Simon, J. Appl. Crystallogr., 3 (1970) 11.
9 J. Soose and G. Meyer, SOS: Programme zur Auswertung von Guinier-Aufnahmen, Giessen 1980.