O atoms, three belong to the same *fac* $[Ru(1)(H_2vi)_3]^-$ anion and the last to another independent $[Ru(2)(H_2vi)_3]^-$ anion.

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The Structure of Antiferroelectric Tetramethylammonium Trichlorogermanate(II) at Room Temperature

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Abstract

Below 424 K $[N(CH_3)_4][GeCl_3]$, $C_4H_{12}N^+.Cl_3Ge^-$, crystallizes in a strongly distorted perovskite structure, space group $Pna2_1$, $Z = 4$, with $a = 13{\cdot}069$ (10), $b = 8{\cdot}895$ (5), $c = 9{\cdot}115$ (5) Å. Refinement led to an R of 0·039 for 818 independent reflexions. The structure is characterized by the tendency of bivalent Ge to form discrete $GeCl_3$ groups with pseudo-trigonal-pyramidal geometry. At 424 K, $[N(CH_3)_4][GeCl_3]$ undergoes a structural phase transition to an ionic conducting cubic phase with $a = 6{\cdot}552$ (2) Å. For this phase a model which demands dynamical disorder is proposed.

Introduction

$[N(CH_3)_4][GeCl_3]$ shows unusual physical properties. At 424 K the colourless crystals undergo a phase transition to a cubic high-temperature modification with $a = 6{\cdot}552$ (2) Å and space group $Pm3m$ (Möller & Felsche, 1979). At room temperature the electrical conductivity is of the order of $10^{-9}\ \Omega^{-1}\ mm^{-1}$. This value increases on approaching the transition point by several orders of magnitude to a value of about $10^{-3}\ \Omega^{-1}\ mm^{-1}$. A.c. conductivity, d.c. polarization and NMR investigations (Möller, 1978) confirm that the high conductivity in conjunction with a low value of E_A is due to ionic motion. The present structure determination should facilitate a better understanding of the unusual physical properties.

Experimental

Crystals of $[N(CH_3)_4][GeCl_3]$, suitable for X-ray investigations and also for conductivity measurements, were grown by a convection method from an equimolar solution of $[N(CH_3)_4]Cl$ and $GeCl_2$ in 5 M HCl. Preliminary Weissenberg precession photographs revealed the perovskite-type structure and the systematic extinctions ($0kl$: $k + l = 2n + 1$; $h0l$: $h = 2n + 1$) indicated the possible space groups $Pnam$ and $Pna2_1$. A cube-shaped crystal 0·4 × 0·4 × 0·4 mm was used on a Syntex $P2_1$ autodiffractometer with Mo $K\alpha_1$ radiation to determine the crystal data and to measure the intensities. The lattice constants were obtained by

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Table 1. *Crystal data for* $[N(CH_3)_4][GeCl_3]$

$a = 13{\cdot}069\ (10)$ Å	$Pna2_1$
$b = 8{\cdot}895\ (5)$	$Z = 4$
$c = 9{\cdot}115\ (5)$	$\lambda(\text{Mo } K\alpha_1) = 0{\cdot}70926$ Å
$V = 1059{\cdot}61$ Å^3	$\mu(\text{Mo } K\alpha_1) = 3{\cdot}74\ \text{mm}^{-1}$
$F(000) = 504$	$D_c = 1{\cdot}59\ \text{Mg m}^{-3}$
$M_r = 253{\cdot}10$	$D_m = 1{\cdot}56$

least-squares refinements from 10 reflexions within the range $9{\cdot}68 < 2\theta < 26{\cdot}24°$. The values are listed in Table 1 together with other crystal data. Intensities were collected at room temperature by the θ–2θ technique up to $\sin\theta/\lambda = 0{\cdot}596$ Å^{-1} with a variable scan speed of 2·0–29·3° min^{-1}. Two periodically checked standards showed no significant change of intensities. The reflexions from the quadrants $(+h,+k,+l)$ and $(-h,+k,+l)$ were averaged and gave 1005 reflexions, 801 of which had $I > 1{\cdot}96\sigma(I)$. No absorption correction was applied.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1970). Although the distribution of normalized structure factors was rather centrosymmetric, the structure determination was carried out in the noncentrosymmetric space group $Pna2_1$, which was verified by the successful refinement. The structure was refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$ with anisotropic temperature factors for all atoms. Complex neutral-atom scattering factors were employed (*International Tables for X-ray Crystallography*, 1974). No attempts were made to locate the H atoms. 12 low-angle reflexions of relatively high intensity were suspected to be affected by extinction and were removed from the data set. The final $R_w = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o| = 0{\cdot}039$ for 818 reflexions with $F_o > 3\sigma(F_o)$ and 81 parameters. Unit weights were used. Table 2 lists the final positional parameters and Table 3 important distances and angles.*

Table 2. *Final positional parameters* ($\times 10^4$) *with e.s.d.'s in parentheses*

	x	y	z
Ge	7579 (1)	2520 (1)	7203
Cl(1)	7694 (5)	761 (10)	5329 (7)
Cl(2)	7653 (5)	817 (11)	9043 (6)
Cl(3)	9297 (2)	3073 (2)	7271 (14)
N	4977 (4)	2679 (6)	2180 (22)
C(1)	9647 (7)	740 (8)	2299 (43)
C(2)	9069 (7)	3342 (10)	2346 (46)
C(3)	393 (12)	2627 (29)	787 (21)
C(4)	849 (12)	2767 (30)	3306 (29)

Table 3. *Important distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

(*a*) Bond lengths and angles

Ge–Cl(1)	2·321 (8)	Cl(1)–Ge–Cl(2)	95·2 (3)
Ge–Cl(2)	2·262 (8)	Cl(1)–Ge–Cl(3)	95·8 (3)
Ge–Cl(3)	2·299 (3)	Cl(2)–Ge–Cl(3)	94·7 (3)
N–C(1)	1·475 (10)	C(1)–N–C(2)	109·8 (7)
N–C(2)	1·502 (12)	C(1)–N–C(3)	111 (2)
N–C(3)	1·41 (3)	C(1)–N–C(4)	114 (2)
N–C(4)	1·58 (3)	C(2)–N–C(3)	106 (2)
		C(2)–N–C(4)	111 (2)
		C(3)–N–C(4)	105 (1)

(*b*) Nonbonded distances and angles describing the coordination of Ge^{2+}

Ge–Cl(1)′	4·069 (8)	Cl(1)–Ge–Cl(1)′	176·9 (2)
Ge–Cl(2)′	4·122 (8)	Cl(1)–Ge–Cl(2)′	88·3 (2)
Ge–Cl(3)′	4·322 (4)	Cl(1)–Ge–Cl(3)′	89·6 (2)
Cl(1)–Cl(2)	3·386 (9)	Cl(2)–Ge–Cl(1)′	87·7 (2)
Cl(1)–Cl(3)	3·428 (10)	Cl(2)–Ge–Cl(2)′	176·1 (2)
Cl(2)–Cl(3)	3·354 (10)	Cl(2)–Ge–Cl(3)′	87·1 (2)
Cl(1)′–Cl(2)′	4·670 (13)	Cl(3)–Ge–Cl(1)′	85·1 (2)
Cl(1)–Cl(2)′	4·574 (13)	Cl(3)–Ge–Cl(2)′	86·5 (2)
Cl(1)′–Cl(3)′	4·891 (9)	Cl(3)–Ge–Cl(3)′	174·2 (2)
Cl(1)–Cl(3)′	4·501 (11)	Cl(1)′–Ge–Cl(2)′	88·8 (2)
Cl(2)′–Cl(3)′	4·777 (9)	Cl(1)′–Ge–Cl(3)′	89·4 (2)
Cl(2)–Cl(3)′	4·595 (11)	Cl(2)′–Ge–Cl(3)′	91·4 (2)

(*c*) Angles describing the puckering of the octahedral framework

Ge–Cl(1)–Ge	170·8 (3)	Ge–Cl(3)–Ge	160·5 (1)
Ge–Cl(2)–Ge	172·5 (3)		

(*d*) Nonbonded distances between C and Cl atoms

C(1)–Cl(1)	3·76 (3)	C(3)–Cl(2)	3·63 (2)
C(1)–Cl(3)	3·662 (8)	C(3)–Cl(3)	3·53 (2)
C(2)–Cl(1)	3·65 (2)	C(4)–Cl(1)	3·31 (2)
C(2)–Cl(2)	3·51 (2)	C(4)–Cl(2)	3·80 (3)
C(2)–Cl(3)	3·838 (9)	C(4)–Cl(3)	3·82 (3)

Results and discussion

Figs. 1 and 2 show the essential features of the structure. It is clear that it is of the perovskite type, though strongly distorted. If the ionic radii are assumed to be 1·81 for Cl^-, 0·93 for Ge^{2+} and 2·3 Å for $N(CH_3)_4^+$, the geometric condition for perovskites, $r[N(CH_3)_4^+] + r(Cl)^- \simeq \sqrt{2}[r(Ge^{2+}) + r(Cl^-)]$, is rather well fulfilled. The agreement is even better than in $Cs[GeCl_3]$ (Christensen & Rasmussen, 1965), which also has a distorted perovskite structure. In contrast, the corresponding compound of the Rb^+ ion cannot form the perovskite structure (Messer, 1978) due to the smaller ionic radius. The similarity between the tetramethylammonium and the Cs compounds is evident since both compounds form cubic high-temperature phases, although the value of the lattice constant of the former is increased by about 20% with respect to the latter, *i.e.* 6·552 Å at 438 K for $[N(CH_3)_4][GeCl_3]$ (Möller & Felsche, 1979) and 5·475 Å at 448 K for $Cs[GeCl_3]$ (Christensen & Rasmussen, 1965).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35010 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

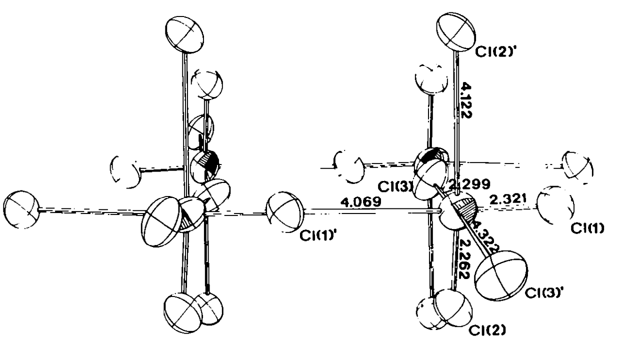

Fig. 1. *ORTEP* plot (Johnson, 1965), showing the distorted octahedral environment of Ge.

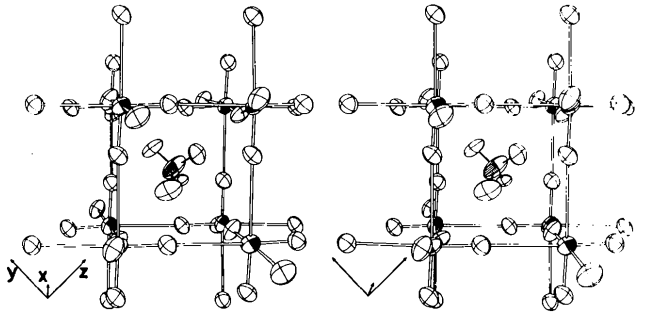

Fig. 2. Stereoscopic view (*ORTEP*, Johnson, 1965) of the structure of $[N(CH_3)_4][GeCl_3]$, showing the tilt system $a^0b^-b^-$ and the arrangement of short and long Ge—Cl distances. The ellipsoids of Ge and N are shaded. N and four C are at the centre.

Table 4. *Dimensions of the* $GeCl_3^-$ *group in trichlorogermanates*(II)

Compound	Ge—Cl bonds	Cl—Ge—Cl angles	Reference
$Cs[GeCl_3]$	2·318 (12) Å	94·5 (3)°	Christensen & Rasmussen (1965)
$Rb[GeCl_3]$	2·307 (4)– 2·319 (5)	94·35 (14)– 94·46 (14)	Messer (1978)
$[N(CH_3)_4][GeCl_3]$	2·262 (8)– 2·321 (8)	94·7 (3)– 95·8 (3)	This work
Pilocarpine trichlorogermanate	2·261 (7)– 2·289 (8)	95·5 (3)– 97·0 (4)	Fregerslev & Rasmussen (1968)

Although the structure was determined by direct methods, an attempt was also made to determine the structure from the rules of Glazer (1975). This failed, and, as we found out later, the reason for this failure was the strong distortion of the Cl octahedra. This irregularity of the octahedra leads to discrepancies between the pseudocubic lattice constants and the assumed tilt system which could not be removed.

The distances and angles describing the distorted octahedral environment of Ge^{2+} are listed in Table 3 and are partly inserted in Fig. 1. The tendency of Ge^{2+} to form trigonal-pyramidal units is obvious. It appears, in good agreement with the assumptions made by Messer (1978), that the Ge^{2+} is mainly $4p^3$ hybridized and that the inert electron pair prefers the 4*s* level. The corresponding bond distances and angles agree well with those of other compounds containing the $GeCl_3^-$ unit (Table 4). The long nonbonded distances, however, are due to the packing conditions of $N(CH_3)_4^+$ and Cl^-. This may be seen from a comparison of the mean nonbonded distances for $[N(CH_3)_4][GeCl_3]$ and $Cs[GeCl_3]$, which are 4·171 and 3·740 Å, respectively. The edge-forming Cl—Cl distances of the octahedron are presented in Table 3(*b*). The values suggest that the environment of Ge^{2+} is best described as a distorted Cl octahedron with two very different opposite triangular faces. The Ge^{2+} cation is not simply off-centred but coordinated by an irregular octahedral environment, due to the formation of covalent Ge—Cl bonds.

Fig. 2 shows a stereographic view of the pseudocubic perovskite unit cell. Following Glazer's (1972) notation, it is obvious that the tilt system is nearly $a^0b^-b^-$. For undistorted octahedra such a tilt system would require $a_p < b_p = c_p$ for the pseudocubic axes. However, in $[N(CH_3)_4][GeCl_3]$, the sum of long and short Ge—Cl distances along the pseudocubic x_p axis is about 0·23 Å longer than along the other two pseudocubic axes (6·621 against 6·390 and 6·384 Å). The arrangement, as shown in Fig. 1, implies that this discrepancy is due to the difference in the lengths of nonbonded Ge—Cl distances. For a better illustration the arrangement of the Ge—Cl bonds (of length 2·3 Å) is presented schematically in Fig. 3. One notices that the arrangement is different for the x_p axis on one side and for the y_p and z_p axes on the other. For a bond along x_p there are, as nearest neighbours, four bonds antiparallel and two parallel. Along y_p and z_p only two bonds are antiparallel, but four are parallel. There is a possibility that this special arrangement along x_p produces some repulsion which is able to separate adjacent octahedra layers along this axis more than

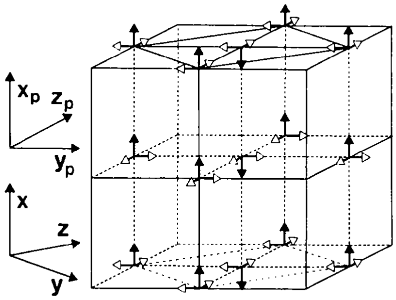

Fig. 3. Schematic drawing showing the arrangement of Ge—Cl bonds along the pseudocubic axes x_p, y_p, z_p. Bonds are represented by arrows. Bonds in the x_p direction are surrounded by four antiparallel and two parallel bonds. Bonds in the y_p and z_p directions are both surrounded by four parallel and two antiparallel bonds. The symbols *x*, *y* and *z* denote the axes of the orthorhombic unit cell.

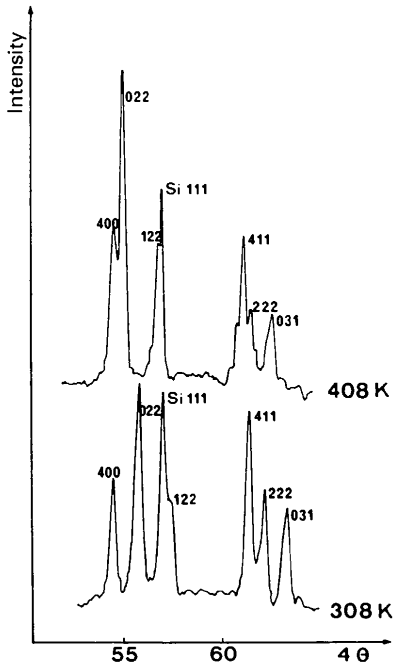

Fig. 4. Microdensitometrically measured group of powder reflexions at 308 and 408 K.

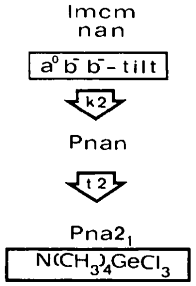

Fig. 5. Group–subgroup relation between the space group of the ideal $a^0b^-b^-$ tilt system and the real space group of $[N(CH_3)_4]$-$[GeCl_3]$, according to Bärnighausen (1975). Space groups are given with their Hermann–Mauguin symbol. The index of the subgroup is given after k or t, which denote *klassengleiche* or *translationsgleiche* subgroups, respectively.

along the other two axes. From a comparison of the lattice constants of the cubic high-temperature phase (6·552 Å) and the pseudocubic axes of the orthorhombic phase, a lengthening of the pseudocubic b_p and c_p axes as the transition temperature is approached is to be expected, whereas the a_p axis remains constant. Powder photographs made at several temperatures confirm this assumption. In Fig. 4 is presented a microdensitometrically measured group of reflexions. The reflexions with $h = 0$ show the strongest shift.

For the cubic phase we propose a model which demands dynamical disorder. It implies antiparallel orientations of Ge–Cl bonds for both the y_p and z_p axes. Consequently, the separation of adjacent layers along these cubic axes must be equal to the separation along a_{cubic} and, therefore, also equal to the separation along $a_{\text{pseudocubic}}$ of the orthorhombic phase.

The space group of the ideal $a^0b^-b^-$ tilt system is *Imcm*, whereas the real space group of $[N(CH_3)_4]$-$[GeCl_3]$ at ambient temperatures is $Pna2_1$. According to Bärnighausen (1975) the symmetry relations may be illustrated as shown in Fig. 5. Structurally the symmetry reduction may be thought of as being produced by (i) ordering of the $N(CH_3)_4$ tetrahedron on the mirror plane at $x = 0$, or by removing Cl(3) from that plane and (ii) by distortion of the octahedra, thus destroying the centre of symmetry at $\frac{1}{4},\frac{1}{4},\frac{1}{4}$.

Within the tetramethylammonium ion the bond lengths and angles deviate from the expected values by up to 4σ (Table 3*a*). It is known in X-ray analysis that the precision for locating lighter atoms in the presence of heavier atoms deteriorates. This probably applies in the present study.

The anisotropic temperature factor coefficients appear quite normal for Ge, Cl and N. The values for the C atoms are unusually high. However, no H atoms have been located for these groups and as no absorption correction has been applied, we do not believe that this finding has physical reality.

There is an important difference between $Cs[GeCl_3]$ and $[N(CH_3)_4][GeCl_3]$. In the former, all Ge atoms are shifted parallel to one face of the octahedron, which leads to distortion and the structure becomes rhombohedral ($R3m$). This would be the cause of the ferroelectric nature of $Cs[GeCl_3]$ (Christensen & Rasmussen, 1965). The corresponding shifts in $[N(CH_3)_4][GeCl_3]$ are antiparallel; therefore, this compound should be antiferroelectric. This assumption is in agreement with the polar point group ($mm2$), which here implies a quadrupled unit cell (with respect to the paraelectric phase). Fig. 6 shows schematically the shifts of the Ge atoms with respect to the centre of an ideal octahedron in the paraelectric cubic phase. For simplicity the shifts are assumed to be in the direction of the cubic body diagonal, *viz* the [120] and [$\bar{1}$20] directions of the actual unit cell. One sees that along all

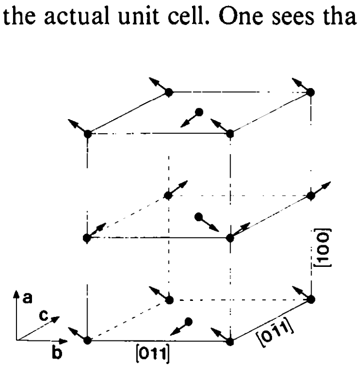

Fig. 6. Schematic drawing showing the antiferroelectric shifts of the Ge atoms with respect to the centres of the ideal octahedra of the cubic high-temperature phase. Directions [011] *etc.* refer to cubic axes.

three axes of the low-temperature phase there is an antiferroelectric stacking of ferroelectric planes.

At 424 K, $[N(CH_3)_4][GeCl_3]$ undergoes a structural phase transition to the cubic phase with $a = 6\cdot552$ (2) Å. The heat of transformation is quite high with a value of 3·1 kJ mol^{-1} (Möller, Wildermuth & Felsche, 1980). It should be noted that the range of thermal stability of the cubic phase is quite narrow. The compound decomposes 22 K above the transition point.

On approaching the transition temperature the ionic conductivity increases by several orders of magnitude. At the moment no mechanism can unambiguously be found for this effect. However, our model suggests possible paths of movement for the Cl atoms. The cubic lattice constant of 6·552 Å does not allow for a bonded Cl atom midway between two Ge atoms, since 3·274 Å is too long for a Ge—Cl bond. Therefore, we assume that this is a mean value for two Cl positions, each being approximately 2·3 Å from a Ge atom. The two Cl positions are separated by a potential barrier. This should not be too high, thus allowing a jumping of the Cl atom from one position to the other. This movement may be combined with a rotation of a $GeCl_3^-$ unit as a whole about a cubic axis, [100] or [111]. As a consequence two or three Cl atoms change axes. A combination of both mechanisms could explain the transport of chlorine. Further research is necessary to find the real mechanism. In this respect it is interesting to note that for the high-temperature phase of $Cs[GeCl_3]$ a type of disorder of the Cl atoms has been found which is in accordance with a double-well model. Furthermore, there is apparently some residual electron density midway between the Cl positions on the *x* and *y* axes (Fig. 4 of Christensen & Rasmussen, 1965).

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Solid–Solid Phase Transitions in $[NH(CH_3)_3]CdCl_3$

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Abstract

Three phases of $[NH(CH_3)_3]CdCl_3$ (TrMCd) have been identified by X-ray diffraction in the temperature range 174 to 415 K. The low-temperature phase is orthorhombic, space group *Pbnm*, with $a = 8\cdot957$ (2), $b = 14\cdot348$ (4) and $c = 6\cdot6873$ (9) Å at 174 K; $Z = 4$. The structure was solved from single-crystal intensities and refined to $R = 0\cdot019$ including isotropically vibrating H atoms. The structure consists of one-dimensional chains of face-sharing $CdCl_6$ octahedra stacked perpendicularly to a nearly hexagonal net. The trimethylammonium ion is located in the free space between the chains and linked to a Cl atom by a hydrogen bond. The phase formed above 342 K is hexagonal, space group $P6_3/m$, $a_{h1} = 26\cdot049$ (5) and $c_{h1} = 6\cdot756$ (1) Å; $Z = 18$. Another hexagonal phase, space group $P6_3/m$, becomes stable in the temperature range 374 to 415 K with lattice constants $a_{h2} = 15\cdot06$ (2) and $c_{h2} = 6\cdot74$ (2) Å; $Z = 6$. Above 415 K, the compound decomposes in the solid state in two steps. The products, $[NH(CH_3)_3]Cd_3Cl_7$ and $CdCl_2$ respectively, have been identified by chemical analysis and powder diffraction. The dynamical behavior of the hydrogen-bonded trimethylammonium ion is responsible for the mechanism of the phase transitions.

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