JOURNAL OF SOLID STATE CHEMISTRY **30**, 65–78 (1979)

The Crystal Structure of the Cation-Disordered Phase $(Tl_{0.75}Pb_{0.25})_4Cl_5$

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Received July 10, 1978; in final form November 3, 1978

The 3:1 compound in the $TlCl–PbCl_2$ system crystallizes in the noncentrosymmetric space group $P4_12_12\ (D_4^4)$ or its enantiomorph $P4_32_12\ (D_4^6)$. Lattice constants are $a = 8.450(1)$ Å and $c = 14.927(1)$ Å. Single-crystal X-ray diffraction data were collected using Ag$K\alpha$ radiation. The structure was determined by analysis of Patterson and difference Fourier syntheses. Least-squares refinement of 41 parameters with 402 unique data converged with $R_w = 0.036$. In the structure the 12 Tl(I) and 4 Pb(II) ions are disordered over two eightfold sites. The formula is therefore appropriately written as $(Tl_{0.75}Pb_{0.25})_4Cl_5$. A difference in size of the two positions suggests a preferential concentration of Pb(II) in the smaller site. The disordering of aliovalent cations together with a three-dimensional network of face-sharing polyhedra of cations surrounding the anions of the structure suggests $(Tl_{0.75}Pb_{0.25})_4Cl_5$ as a particularly favorable case for enhancement of chloride ion conductivity by doping with TlCl. Irregularities in the coordination polyhedra about the cations can be explained by the presence of stereochemically active lone-pair electrons of the cations. The structure of $(Tl_{0.75}Pb_{0.25})_4Cl_5$ is similar to that of the alloy Zr_5Si_4.

Introduction

In recent years, high-power infrared lasers, particularly the CO_2 laser operating at 10.6 μm, have become of increasing technological importance and utility. Although many suitable window materials are available, Si, Ge, and II–VI compounds such as CdSe, for example, little work has been done to develop materials of sufficient birefringence for use in polarizing prisms or as phase-matching materials. A recent study at NBS (*1*, *2*) on heavy metal halides showed that mercurous chloride single crystals could be grown of a size and perfection suitable for prism polarizers with transmission to at least 16 μm. However, there is also a need for noncentrosymmetric crystals with large birefringence which may exhibit second harmonic generation and allow optical mixing in the infrared. As an extension of the previous study, a survey of the system $TlCl–PbCl_2$ was conducted.

Previous work in this system by Korreng (*3*) identified the compounds $3TlCl\cdot PbCl_2$ and $TlCl\cdot 2PbCl_2$ A 1:1 compound reported by Bergman and Tapchanyan (*4*) has not been confirmed in the present study. Instead, another phase which melts incongruently has been identified as occurring at about the 11:4 ratio. The first X-ray diffraction study of this system was reported by Kelsey and Katz (*5*), but they made no attempt to grow single crystals or identify the unit-cell dimensions of the phases, nor did they report values of the d-spacings. Some interplanar spacings were reported by Il'yasov *et al.* (*6*), but the patterns were not indexed. The unit-cell dimensions of $3TlCl\cdot PbCl_2$ and $TlCl\cdot 2PbCl_2$ and their corresponding

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0022-4596/79/100065-14 $02.00/0

Printed in Great Britain

bromides were determined in the course of the present work with the aid of single-crystal data (*7*). Since the systematic absences observed for the 3:1 chloride compound imply that it is noncentrosymmetric, we decided that the crystal structure of this material should be investigated.

Experimental

Crystals of the congruently melting phase $3TlCl{\cdot}PbCl_2$ were synthesized from the melt by the Bridgman technique. Single-crystal X-ray diffraction photographs indicated that the crystals have Laue symmetry $4/mmm$. Reflections ($h00$) and ($0k0$) with $h, k \neq 2n$ and ($00l$) with $l \neq 4n$ are systematically absent from the photographs, implying that the space group is one of the enantiomorphic pair $P4_12_12$ (No. 92, D_4^4) and $P4_32_12$ (No. 94, D_4^6). Lattice constants refined from the indexed powder diffraction pattern[1] are $a = 8.450(1)$ Å and $c = 14.927(1)$ Å. The calculated density is 6.215 g/cm^3, assuming that the unit cell contains four formula units.

A crystal was ground to a slightly prolate ellipsoid of revolution with a mean radius of 0.059 mm. The linear absorption coefficient, μ, is 347.33 cm^{-1} for Ag$K\alpha$ radiation which was used to collect the diffraction data, and $\mu\bar{r}$ is 2.06.

The intensity data were collected with an automated quarter-circle diffractometer. A Si(Li) detector system was used to select the signal from the $K\alpha$ component of the diffracted beam. Data were collected in the θ–2θ scan mode in the range $0° < 2\theta \leq 35°$. The scan range was $(3.0 + \tan\theta)$ degrees 2θ. The scan rate was 1°/min, and backgrounds were measured at each end of the scan for 80 sec. Data in two full octants of reciprocal space were collected. Thus, in general, each unique reciprocal lattice point under Laue symmetry $4/mmm$ is represented by four equivalent measurements.

Low-angle backgrounds could not be resolved from the main beam below $2\theta = 5°$. Reciprocal lattice points with $2\theta < 5°$ were, therefore, excluded from the refinement. It was found impossible to resolve background settings from neighboring peaks for a few additional data. Background values for these data were obtained from a plot of average background versus ($\sin\theta/\lambda$).

The estimated standard deviations in intensity, $\sigma(I)$, were based on counting statistics and an instrumental instablility factor:

$$\sigma(I) = S^{1/2} + (T_S/T_B)B^{1/2} + 0.02S,$$

where S is the scan count, B is the total background count and T_S and T_B are scan and total background times, respectively. Lorentz and polarization corrections were applied to the data. The $\sigma(F)$ were calculated from $\sigma(I)$ using

$$\sigma(F) = (I + \sigma(I))/Lp^{1/2} - F.$$

The 1598 recorded data were then merged into a unique set of 466 reflections in accordance with Laue symmetry $4/mmm$ (see below). The R factor for internal agreement is 0.053. The estimated standard deviation of the mean structure factor $\bar{F}_j$ was calculated from equal contributions of the individual $\sigma(F_i)$ values and the deviation Δ_i of each F_i from $\bar{F}_j$:

$$\sigma(\bar{F}_j) = \frac{1}{2}\left[\frac{\sum_i^n \sigma^2(F_i)}{n} + \frac{\sum_i^n \Delta_i^2}{n}\right]^{1/2}.$$

In a few cases (e.g., 833, 448) the agreement between equivalent reflections was poor, possibly because of errors in assessing the background intensity. In these cases the above equation yielded a large $\sigma(\bar{F})$. The averaged data were corrected for absorption

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[1] See NAPS document no. 03374 for 8 pages of supplementary material. Order from NAPS % Microfiche Publications, P.O. Box 3513, Grand Central Station, N.Y. 10017. Remit in advance in U.S. funds only $5.00 for photocopies or $3.00 for microfiche. Outside the U.S. and Canada add postage of $3.00 for photocopy and $1.00 for microfiche.

assuming an ideal sphere. Correction factors varied from 3.59 to 3.84.

Solution and Refinement of the Structure

Analysis of a Patterson synthesis calculated for $3TlCl \cdot PbCl_2$ indicated that the 12 thallium and 4 lead ions are disordered over two sets of eightfold (8*b*) sites of the space group. The 20 chloride ions appeared in a subsequent difference Fourier synthesis occupying two eightfold (8*b*) sitesets and one fourfold (4*a*) siteset. Because of the apparent disorder, we write the formula $(Tl_{0.75}\,Pb_{0.25})_4Cl_5$. Least-squares refinement of the structure was carried out using the program CRYLSO (*8*). The weights employed in the least-squares analysis were $w = 1/\sigma^2(\bar{F})$. Atomic scattering factors were calculated using the coefficients of Cromer and Mann (*9*) for neutral atoms. Because of the similarity of scattering factors for Tl and Pb, the disordered metal ions were represented in the calculation by the scattering factor for thallium. Correction was made for the real part of the anomalous dispersion (*10*). The imaginary part of the anomalous dispersion included in a refinement using data averaged in accordance with point group 422 failed to discriminate between the two possible enantiomorphic structures. The refinement reported here is based on data averaged in accordance with the Laue group. Space group $P4_12_12$ has been chosen for presentation of the structure.

Convergence was achieved for positional and anisotropic thermal parameters for the five independent atoms and a scale factor (Table I). An isotropic extinction parameter was allowed to vary in the final cycles, but it did not become significantly different from zero. In all, 41 structural parameters were refined using 402 data with $\bar{F}_0 > \sigma(\bar{F}_0)$. Final values of the residuals are $R = 0.052$ and

$$R_w = \left[\frac{\sum w\,(\bar{F}_0 - kF_c)^2}{\sum w\bar{F}_0}\right]^{1/2} = 0.036$$

The standard deviation of a reflection with unit weight is 1.43. A difference Fourier synthesis revealed holes of $-1e^-/\text{Å}^3$ at the metal sites. These holes are the only feature in the map to exceed in magnitude $0.2e^-/\text{Å}^3$.

Description of the Structure

(*a*) *Stacking of Puckered 3^2434 Nets of Cations*

The structure of $(Tl_{0.75}Pb_{0.25})_4Cl_5$ is most simply described by considering first the arrangement of the cations. These lie in four puckered layers which are centered about $z = \pm 1/8$, $\pm 3/8$. Deviation from the average plane of each layer are ±0.70 Å for the cations in site 1, *M*1, and ±0.43 Å for the cations in site 2, *M*2, In each layer the

TABLE I

FINAL VALUES OF ATOMIC PARAMETERS FOR $(Tl_{0.75}Pb_{0.25})_4Cl_5$[a]

Atom	Position	x	y	z	$10^2U_{11}^{b}b$	10^2U_{22}	10^2U_{33}	10^2U_{12}	10^2U_{13}	10^2U_{23}
$M1^c$	8*b*	0.3067(2)	0.0066(2)	0.07832(8)	5.0(1)	5.2(1)	3.31(7)	1.25(6)	−0.16(6)	0.12(6)
$M2$	8*b*	0.8193(2)	0.8787(2)	0.1538(1)	4.21(8)	5.7(1)	5.0(1)	−1.12(7)	−0.47(7)	0.98(7)
Cl1	4*a*	0.342(1)	x	0	3.9(4)	U_{11}	4.9(7)	−0.6(5)	0.6(4)	$-U_{13}$
Cl1	8*b*	0.348(2)	0.974(1)	0.4755(6)	9.5(8)	6.9(7)	4.3(6)	1.6(5)	1.3(6)	−0.8(5)
Cl3	8*b*	0.188(1)	0.012(1)	0.874(1)	5.0(6)	5.5(6)	9.5(7)	0.1(6)	−1.7(6)	−1.8(5)

[a] Estimated standard deviations in parentheses pertain to the final digit in all cases.

[b] The U_{ij} have dimensions Å². The expression for the thermal factor is:
$\exp -[(2\pi^2)\,(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

[c] "*M*" represents a cation Tl(I) or Pb(II).

cations lie at the nodes of a puckered 3^2434 net (Figs. 1 and 2a), an arrangement found in many alloys (*11*), in certain oxides such as euxenite and M'-fergusonite (*12*), and in some halides such as Cs_3CoCl_5 (*13*). In most cases the nets are composed of anions or the larger alloy component, unlike $(Tl_{0.75}Pb_{0.25})_4Cl_5$.

The *quasi*-squares of the nets are centered within the layers by Cl3 ions. The remaining chloride ions, Cl1 (siteset $4a$) and Cl2, lie in layers centered at $z = 0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$, midway between the cation nets. These intervening layers of chloride ions are composed of nearly linear strings parallel to the cell diagonal in which the Cl1–Cl2 distance is 3.76(2) Å and the Cl2–Cl2 distance is 4.53(2) Å. Two strings per layer cross the unit cell, equally spaced along the diagonal of the cell, 6.0 Å apart. Adjacent strings are staggered as shown in Fig. 2b so that the chloride layer can be described as a 3^6 net with considerable elongation in the direction normal to the strings. Cations from adjacent net layers are puckered toward the centers of two-thirds of the triangles between chloride strings. This can be seen in Fig. 2c. The distances of neighboring cations to the mean plane of the chloride ion layer are 1.17 Å and 1.44 Å for $M1$ and $M2$, respectively.

Successive cation layers are stacked in such a way as to complete irregular octahedra about Cl1 and Cl3 ions, the octahedra about Cl3 ions being highly distorted. Because the 4_1 operator which relates successive nets of cations does not coincide with any of the *quasi*-symmetry elements of the nets, the relationship between nets is complicated. A simple relationship between nets can be seen, however, if the puckering is temporarily disregarded and the internodal disstances are made equal in projection. Successive nets are then related by translation of one triangle altitude along the cell diagonal (Figs. 1 and 2c). If the internodal distance is l, then the unit cell edge, a, is $((1/\sqrt{2})\ (1+\sqrt{3}))$ or $1.9319l$, and the translation relating nets at $\frac{1}{8}$ and $\frac{3}{8}$ is $\{1/a\ (l\sqrt{6}/4,\ l(\sqrt{6}/4)\}$ or (0.3170, 0.3170). This translation brings a pair of triangles from the two nets into an approximately antiprismatic relation but shifted so that the

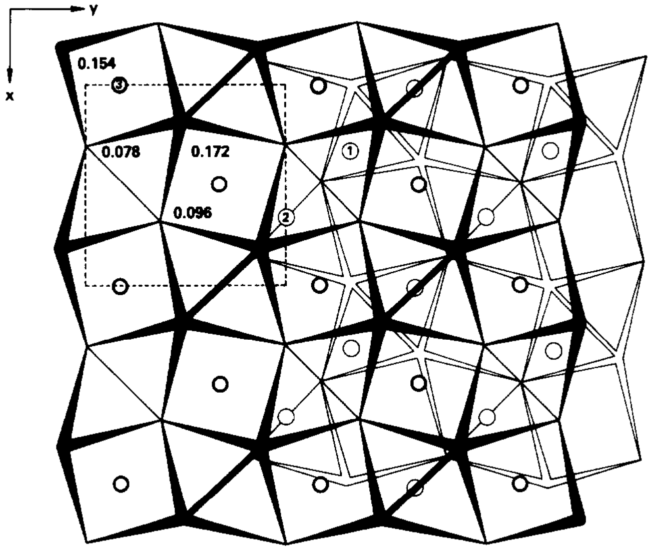

FIG. 1. The puckered 3^2434 net of cations centered about $z = \frac{1}{8}$. Cl3 ions center the squares. The 3^2434 net of cations at $z = \frac{1}{8}$ appears in the right half.

apex of each triangle of the pair lies directly opposite the base of the other. Therefore, a pair of faces of the octahedron formed between the two triangles is vertical, parallel to c. If the octahedron is to be regular, then the triangle faces within the nets must be puckered from the mean plane of the nets by rotation of 19° 28′ about the common edge of the triangles.

Based on this model, the value of c is $2\sqrt{3}l$ and c/a is 1.7932. The value of c/a determined for $(Tl_{0.75}Pb_{0.25})_4Cl_5$ is 1.766. The magnitude of the puckering for the model is $\pm c/24$; the fractional displacement of any node from the mean net plane is 0.0417. The puckering of the nets in $(Tl_{0.75}Pb_{0.25}(_4Cl_5$ follows this pattern for preserving the geometric quasi-regularity of the Cl1 octahedron. The mean fractional displacemnt from the net plane observed in $(Tl_{0.75}Pb_{0.25})_4Cl_5$ is 0.0377.

A set of coordinates for the geometric model of the structure derived above appears in Table IIA. The similarity of these idealized coordinates to those of $(Tl_{0.75}Pb_{0.25})_4Cl_5$ is close despite the apparent complexity of the structure and the many degrees of freedom.

(*b*) *Coordination of the Chloride Ions*

Interionic distances in $(Tl_{0.75}Pb_{0.25})_4Cl_5$ are found in Table III and on Figs. 3 and 5. Mean values of the chloride ion-cation distances for the two octahedrally coordinated chloride ions Cl1 and Cl3 are 3.16 and 3.20 Å, respectively; average edge lengths are 4.466 and 4.526 Å, respectively. The larger values observed for the Cl3 octahedron reflect the severe distortion of this polyhedron: Each of the cations which caps

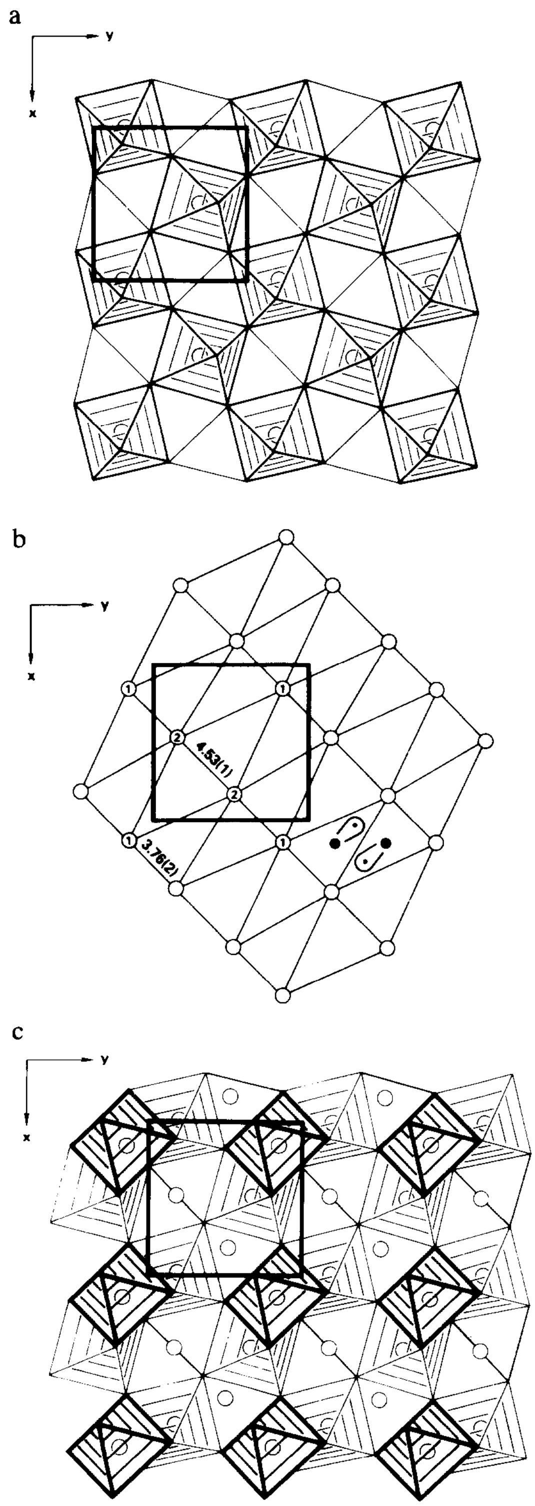

FIG. 2. Structural layers. (a) The layers of cation octahedra about Cl3 at $z = \frac{1}{8}$. (b) The linear strings of Cl1 and Cl2 ions in the layer at $z = \frac{1}{4}$. Projected cation sites and lone-pair orbitals are indicated. (c) The layers of cation octahedra about Cl3 at $z = \frac{1}{8}$ and about Cl1 octahedra at $z = \frac{1}{4}$.

TABLE II

A. COORDINATES FOR THE IDEALIZED GEOMETRIC MODEL OF $(Tl_{0.75}Pb_{0.25})_4Cl_5$

Atom[a]	Position	*x*	*y*	*z*
S1	8*b*	0.3170	0	1/12
S2	8*b*	0.8170	0.8661	1/6
L1	4*a*	0.3415	$\equiv x$	0
L2	8*b*	0.3170	0	1/2
L3	8*b*	0.1831	0	7/8

B. ATOMIC POSITIONAL PARAMETERS FOR Zr_5Si_4 FOM PFEIFER AND SCHUBERT (*30*)

Atom	Position	*x*	*y*	*z*
Si1	8*b*	0.308	0.945	0.062
Si2	8*b*	0.790	0.859	0.175
*Zr*1	4*a*	0.326	$\equiv x$	0
Zr2	8*b*	0.350	0.003	0.465
Zr3	8*b*	0.141	0.004	0.874

[a] "S" refers to the smaller component; "L" refers to the larger component.

TABLE III. ITERIONIC DISTANCES[a]

Atom type	Distance (Å)[b]
*M*1[c]-Cl2	2.89(1)
-Cl3	3.01(1)
-Cl1	3.08(2)
-Cl3	3.17(1)
-Cl1	3.17(2)
-Cl3	3.21(2)
-Cl2	3.30(1)
-M2	3.839(2)
-Cl2	3.90(1)
*M*2-Cl3	3.10(1)
-Cl1	3.22(2)
-Cl2	3.23(1)
-Cl2	3.26(1)
-Cl3	3.26(1)
-Cl3	3.42(2)
-Cl2	3.49(1)
-*M*1	3.839(2)
-Cl2	3.87(1)
Cl1[d]-*M*1	3.08(2)
-*M*1	3.17(2)
-*M*2	3.22(2)
-Cl3	3.61(2)
-Cl3	3.67(2)
-Cl2	3.76(2)
-Cl2	3.89(2)
Cl2-*M*1	2.89(1)
-*M*2	3.23(1)
-*M*2	3.26(1)
-*M*1	3.30(1)
-*M*2	3.49(1)
-Cl1	3.76(2)
-*M*2	3.87(1)
-Cl3	3.87(1)
-Cl1	3.89(2)
-*M*1	3.90(1)
Cl3-*M*1	3.01(1)
*M*2	3.10(1)
-*M*1	3.17(1)
-*M*1	3.21(2)
-*M*2	3.26(1)
-*M*2	3.42(2)
-Cl1	3.61(2)
-Cl1	3.67(2)
-Cl2	3.87(2)

[a] Distances and standard deviations were calculated using the program BONDLA (*8*). Parameter interactions, ignored in calculating the standard deviations, were small.

[b] Standard deviations in parentheses apply to the final digit in all cases.

[c] "*M*" represents a cation Tl(I) or Pb(II).

[d] Each distance occurs twice.

the square of the 3^2434 net is involved in one short edge, 3.839(2) Å, and one long edge, 5.252(2) or 5.531(2) Å. The average parameters of the less distorted Cl1 octahedron are close to those observed in epitaxially grown NaCl-type TlCl in which the Tl–Cl distance is 3.15 Å and the Tl–Cl distance is 4.45 Å (*14*). In the normal CsCl-type, TlCl polymorph the distances are 3.328 and 3.843 Å, respectively (*15*). Although the average Cl–*M* distance for Cl1 is also close to the average Cl–Pb distance observed in $PbCl_2$ (*16*), direct comparison is unwarranted because of differences in coordination. The overall average octahedron parameters observed in $(Tl_{0.75}Pb_{0.25})_4Cl_5$ are 3.19 Å for Cl–*M* and 4.506 Å for *M–M*.

In the coordination of Cl2 five cations, a triangle from one net, the common triangle edge from another net, approach Cl2 at distances of 2.89(1) to 3.49(1) Å with an average of 3.23 Å. These five nearest cation neighbors of Cl2 do not form a closed polyhedron. Next-nearest neighbors are

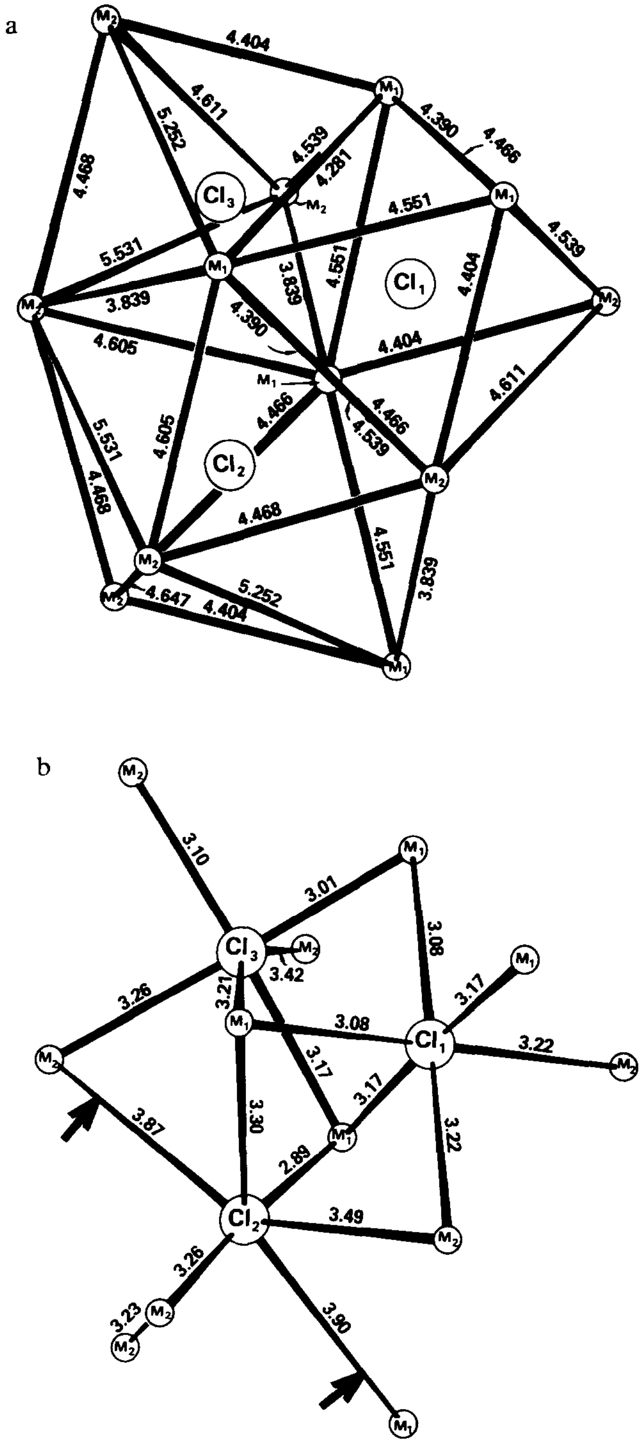

FIG. 3. The cation polyhedra about the chloride ions. (a) Standard deviations in edge lengths (Å) are 0.002 Å. (b) Standard deviations in Cl-*M* distances (Å) are 0.01 to 0.02 Å; approximate centers of lone-pair electron density (see text) are indicated by arrows.

chlorides at 3.76(2), 3.87(2), 3.89(2) and 4.02(2) Å. Two additional cations occur at distances of 3.87(1) and 3.90(1) Å. Inclusion of these two cations in the coordination of Cl2 along with the five nearest cations gives a distorted pentagonal bipyramid of cations surrounding Cl2. The average Cl–*M* distance to the seven cations is 3.42 Å.

The arrangement of the cation octahedra about Cl1 and Cl3 is shown in Figs. 2a and c. These octahedra and the bipyramid about Cl2 are shown in Fig. 3. The locations of the Cl2 bipyramids are also evident in Fig. 2c. It should be noted that the cation polyhedra which surround the chloride ions share faces to form a three-dimensional network of face-sharing polyhedra.

(*c*) *Coordination of the Cations*

Each cation *M*1 or *M*2 is surrounded by seven chloride ions at mean distances of 3.12 and 3.28 Å, respectively. The seven chloride ions are followed by another cation at 3.839(2) Å and another chloride ion at 3.90(1) Å for *M*1 and 3.87(1) Å for *M*2. Beyond this are cation–cation distances beginning a 4.281(2) and 4.404(2) Å. The mean seven-coordinate *M*–Cl distance for both cations is 3.20 Å. Using an appropriately weighted average of seven-coordinate Tl(I)[2] and Pb(II) ionic radii, 1.55 and 1.23 Å, respectively, plus the ionic radius for six-coordinate chloride, 1.81 Å, one obtains the value 3.28 Å (*17*).

The seven nearest chloride ion neighbors of each cation form irregular figures about each cation, which are open on one side (Fig. 4). Both figures can be derived from a pentagonal bipyramid by distortion of one of the axial vertices such that two of the edges to the pentagonal plane become well over 5 Å in length, 5.28(2) and 5.80(2) Å for *M*1, 5.28(2) and 6.11(2) Å for *M*2.

If the eight chloride ions and the near-neighbor cation and its four other neighbors are included, one has a fully triangulated figure composed of 12 chloride ions surrounding a pair of cations (Fig. 5). The polyhedron surrounding each cation is related both to the bisdisphenoid and to the bicapped triangular prism. It can be derived from a distorted bisdisphenoid by moving one of the edges such that four vertices become nearly coplanar, giving a quadrilateral face with edge lengths in the range 3.87(1) to 4.21(2) Å and a shorter diagonal length of 5.28(2) Å. This polyhedron has, in addition to this quadrilateral face, 10 triangular faces. Pairs of these polyhedra share quadrilateral faces. The average *M*-Cl distances for eight-coordination are 3.22 and 3.37 Å for *M*1 and *M*2 and the overall average is 3.29 Å. A weighted average of Shannon's radii (*17*) for eight-coordinate metal ions, 1.59 Å for Tl(I) and 1.29 Å for Pb(II), plus the ionic radius for six-coordinate chloride. 1.81 Å, gives 3.33 Å. Clearly, the agreement is better for eightfold coordination of the metal ions than for sevenfold. The mean lengths of the 17 edges are 3.98 and 4.17 Å.

Discussion

(*a*) *Cation Disorder*

The crystal structure of $(Tl_{0.75}Pb_{0.25})_4Cl_5$ presents an unusual instance in which the space group *requires* Tl(I) and Pb(II) to be disordered, even at the stoichiometric composition. It is not uncommon for disordering of Tl(I) and Pb(II) to accompany nonstoichiometry, as in the terminal solid solutions indicated on the phase diagram for the system Tl_2S–PbS (*18*). Presumably, thallium–lead disorder in complex sulfide minerals such as Hutchinsonite, $(Tl, Pb)_2As_5S_9$, also implies nonstoichiometry. In this compound the larger of the two cation sites has the (7 + 1)-coordination which

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[2] The seven-coordinate Tl(I) radius used was the average of the tabulated six- and eight-coordinate radii for Tl(I).

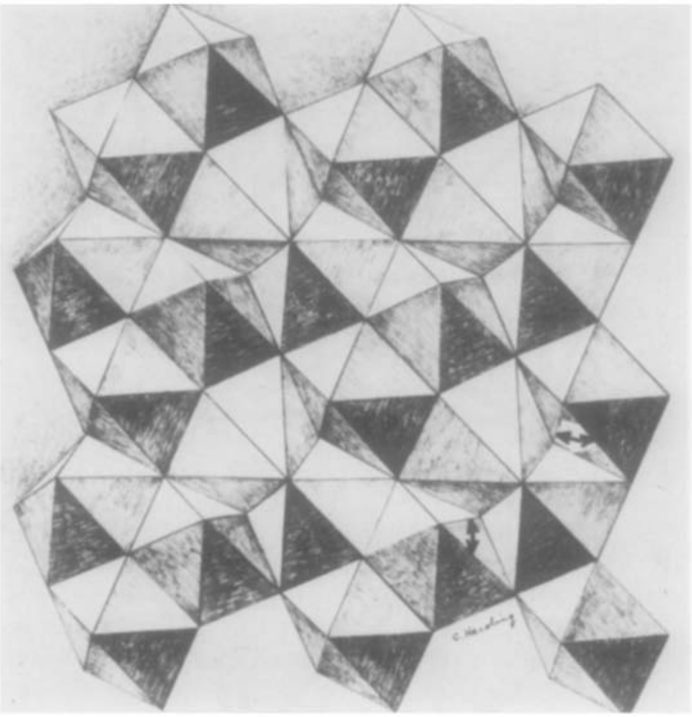

FIG. 4. The layer of distorted pentagonal bipyramids of chloride ions about the cations centered at $z = \frac{1}{8}$. Long edges are indicated by arrows.

characterizes both cation sites in $(Tl_{0.75}Pb_{0.25})_4Cl_5$ (*19*). This site is thought to contain mainly thallium ions. The smaller site, thought to contain mainly lead ions, has sevenfold coordination by sulfur.

The difference in size of the two cation sites in $(Tl_{0.75}Pb_{0.25})_4Cl_5$, evidenced by the discrepancy in average M–Cl distances, may similarly represent a concentration of Pb(II) in the smaller site, $M1$. If we assume that all of the Pb(II) is concentrated in one site we calculate expected eight-coordinate M–Cl distances (*17*) of 3.25 Å for $(Tl(I)_{0.5}Pb(II)_{0.5})$–Cl and 3.40 Å for Tl(I)–Cl. The difference, 0.15 Å, is exactly that found between the average M–Cl distances of the two metal sites, 3.22 and 3.37 Å. This suggests a substantial preferential occupation of site $M1$ by Pb(II) and site $M2$ by Tl(I).[3] Perhaps the formula is better written $Tl_2(Tl_{0.5}Pb_{0.5})_2Cl_5$. Because thallium and lead are practically indistiguishable with Ag$K\alpha$ radiation, no attempt was made to determine the real distribution of cations over the two sites. It may be, however, that the orthorhombic distortion seen in the bromide analog (*7*), Tl_3PbBr_5 (space group $P2_12_12_1$, $a = 8.561(2)$, $b = 9.301(2)$, $c = 15.430(4)$), occurs with an ordering of the thallium and lead ions. Solid solutions of Tl_3PbCl_5 and Tl_3PbBr_5 are tetragonal at room temperature up to 75% bromide, after which they are orthorhombic (*7*).

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[3] The discrepancy is probably too large to arise solely from polyhedral distortion (*17, 20*). Moreover, calculation of a distortion parameter, $\frac{1}{8}\sum (\Delta R/\bar{R})^2$, for the two sites indicates that the larger $M2$ site has the lower distortion, so defined.

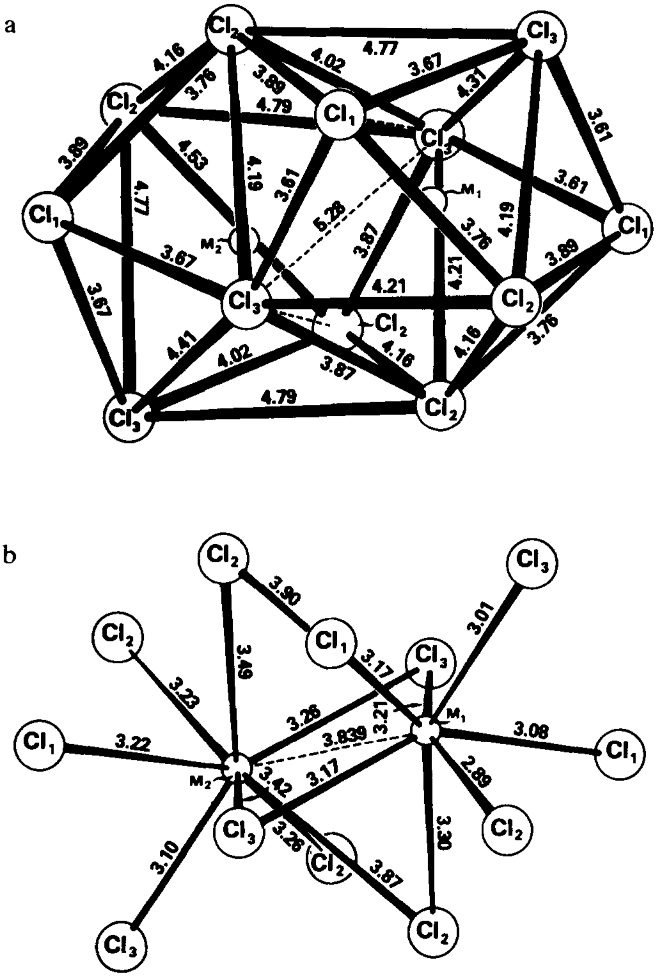

FIG. 5. Coordination polyhedra of chloride ions about a close pair of cations. Standard deviations (q) in edge lengths (Å) and (b) in *M*–Cl distances (Å) are 0.01–0.02 Å.

The tetragonal structure with disordered cations of mixed valence suggests the possibility of variable composition. Compositions rich in TlCl would be of particular interest, since charge compensation would probably occur by formation of anion vacancies. This is significant because electrical conduction in divalent lead chloride and bromide is reported to occur predominantly through the motion of anion vacancies (*21–23*). Schoonman (*24*) reports experiments in which the conductivity of $PbBr_2$ is enhanced by about one order of magnitude through incorporation of 2×10^{-2} mole% TlBr.

In addition the polyhedra of cations in $(Tl_{0.75}Pb_{0.25})_4Cl_5$ which surround the chloride ion positions share faces to form a three-dimensional network. It is plausible, therefore, that the cation structure of $(Tl_{0.75}Pb_{0.25})_4Cl_5$ should be favorable to the mobility of anion vacancies, much as the anion structures of the silver and cuprous halide-based solid electrolytes are favorable to the mobility of cations (*25*). Although the high levels of conductivity observed in the latter materials would not be expected, $(Tl_{0.75}Pb_{0.25})_4Cl_5$ doped with TlCl or other monovalent chlorides might well exhibit unusually high levels of chloride ion conductivity.

(*b*) *Lone-Pair Electrons*

A plausible explanation for the irregular nature of the chloride ion polyhedra surrounding the cations is the presence of stereochemically active lone-pair electrons (*26, 27*) in the vicinity of the open sides of the distorted pentagonal bipyramids of chloride ions. In each of the distorted bipyramids, three vertices are involved in the two long edges. The line which connects a cation with its eight nearest chloride ion neighbor is nearly perpendicular to the plane of the three vertices involved in long edges for each distorted bipyramid surrounding a cation. Points on these lines are roughly the same distance from the three involved vertices in each case. Thus, it seems likely that the orbital which contains lone-pair electrons is directed toward the eighth nearest chloride ion neighbor of each cation. This would explain the discrepancy in the M–Cl distances between the seven nearest chloride ion neighbors of each cation, which average 3.20 Å, and the eighth chloride ion neighbor at 3.90 and 3.87 Å for $M1$ and $M2$, respectively. Since these two long distances also appear in the pentagonal bipyramid of cations surrounding Cl2, the discrepancy is also explained for that polyhedron.

Andersson and Åström (*28*) have given several examples of oxides and oxyfluorides in which lone-pair electrons from an ion such as Pb(II) fill in an open anion layer, being roughly the same size as an oxide or fluoride ion. Based on the geometry of the anion layers, these authors locate the effective center of lone-pair density approximately 1 Å from the nucleus of the cation. If we assume that the center of lone-pair density in $(Tl_{0.75}Pb_{0.25})_4Cl_5$ is 1.0 Å from each cation nucleus along the line which joins the cation and its eighth nearest chloride ion neighbor, then the distances to other ions in the structure are reasonable. In particular, the distances to the three chloride ions involved in the long bipyramid edges and to the eighth nearest chloride ion of the metal ion are all in the range 2.9 to 3.1 Å for both metal ions. It is reasonable to conclude that the effective centers of lone-pair density are in the vicinities of these sites, shown by arrows in Fig. 3b. Evidently, the lone pair is large enough to distort the chloride ion polyhedron about each cation, but not sufficiently large to occupy a full chlorided position. Consequently, an additional chloride ion can be packed into the opening on the polyhedron surface created by the lone pair. Because of the lone pair, this additional chloride ion cannot approach the cation so closely as the other chloride ions do.

The observation of Andersson and Åström (*28*) that lone-pair electrons in fluorides and oxyfluorides pack like anions would suggest that the lone pairs in $(Tl_{0.75}Pb_{0.25})_4Cl_5$ should reside in the vicinity of the open planes of chloride ions. Moreover, they should occupy *quasi*-symmetric sites in those planes such as the centers of the triangles described above. In fact, the sites calculated above do lie closer to the open chloride ion planes than do the cations, and in projection they do lie along the central axes of two-thirds of the elongated triangles of chloride ions in the planes (Fig. 2b). They do not, however, fill in the layer to make it a close-packed net or some other highly symmetric net. Considering, again, the discrepancy in size which must exist between the lone-pair electrons and the chloride ions, that is not surprising.

(*c*) $(Tl_{0.75}Pb_{0.25})_4Cl_5$ *and* Zr_5Si_4

Reference to "Crystal Data" (*29*) for possible analogous structures revealed a single group of entries in the space group $P4_12_12$ with similar axial ratios and numbers of atoms, namely, Zr_5Si_4 ($Z = 4$, $a = 7.122$ Å, $c = 13.000$ Å, $c/a = 1.825$) and isostructural compounds of germanium and hafnium (*30*). In this structure the silicon atoms occupy two 8*b* sitesets and the zirconium atoms two 8*b* sitesets and one 4*a* siteset of the space group. The coordinates (Table IIB) are similar to those of the compound $(Tl_{0.75}Pb_{0.25})_4Cl_5$ with the silicon atoms corresponding to the thallium and lead ions and the zirconium atoms to the chloride ions. The structure of the alloy is in many respects geometrically similar to that of the salt. It can be built up in the same way from rumpled 3^2434 net layers of silicon atoms with zirconium atoms centering the squares.[4] The zirconium atoms in the intervening layers lie in nearly linear strings roughly parallel to the cell diagonal. The puckering of the Si nets follows the pattern noted above in $(Tl_{0.75}Pb_{0.25})_4Cl_5$, and the mean fractional displacement from the net plane is 0.057.

The main structural differences between the two compounds lie in the details of the coordination about the smaller component. In the alloy where coulombic repulsion of like ions is not important, the nearest neighbor of each silicon atom is another silicon atom at 2.47 Å. This Si–Si distance is comparable to the average six-coordinate distance in the high-pressure form of silicon analogous to white tin, 2.482 Å (*31*). Scaled up to the unit cell of $(Tl_{0.75}Pb_{0.25})_4Cl_5$, the hypothetical distance is 2.88 Å compared with the observed distance 3.839 Å between the corresponding cations of the salt (cf. 3.843 Å for the Tl–Tl distance in CsCl-type TlCl (*15*)).

Even though the differences in the details of coordination mean that $(Tl_{0.75}Pb_{0.25})_4Cl_5$ cannot be considered strictly isostructural with Zr_5Si_4 and its isotypes, the similarities in coordination and in the basic arrangement of the structural elements are greater than those necessarily implied by the term "isopuntal." It is not unusual to find such correspondences between metallic alloy and ionic structures. They are to be expected for simpler, high-symmetry structures such as the CsCl structure, the normal form of TlCl. Such correspondences are more difficult to explain for structures such as $(Tl_{0.75}Pb_{0.25})_4Cl_5$ in which the atoms or ions are in positions of low symmetry and have irregular coordination polyhedra. There are, however, many well-known examples of pairs of structures which fall into the latter category.

Consequently it is likely that the structure of the congruently melting 1:2 phase in the TlCl–$PbCl_2$ system (diffraction symbol *mmmP**n*, $a = 8.953$ Å, $b = 12.482$ Å, $c = 7.919$ Å) should have an alloy analog as well. An obvious suggestion might be Zr_5Si_3, which reportedly has the hexagonal Mn_5Si_3 structure (space group $P6_3/mcm$, $a = 7.886$ Å, $c = 5.558$ Å) (*32*) However, although the symmetries are formally compatible, the metrics do not appear to work out well. Since the ratio of average cation to anion size is different for $TlPb_2Cl_5$, zirconium–silicon may not be the appropriate system for a structural analog in this case. We note that Zr_2Si does not have the $PbCl_2$ structure (*33*). Moreover, ZrSi does not have the CsCl-type structure of normal TlCl, but instead has the structure of a thallium salt with a larger halide, namely, TlI (*34*). In this connection, Pfeifer and Schubert (*30*) have discussed relationships between the structures of ZrSi and Zr_5Si_4.

(d) $(Tl_{0.75}Pb_{0.25})_4Cl_5$ *and* Cs_3CoCl_5

The structure of $(Tl_{0.75}Pb_{0.25})_4Cl_5$ does not closely resemble that of either TlCl or $PbCl_2$. One chloride structure which has certain features in common with $(Tl_{0.75}Pb_{0.25})_4Cl_5$ is that of Cs_3CoCl_5 (*13*). This structure is formally similar to that of Cr_5B_3 (*35*), much as $(Tl_{0.75}Pb_{0.25})_4Cl_5$ is similar to Zr_5Si_4.

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[4] Pearson (*11*, p. 772) includes Zr_5Si_4 with "unclassified idiosyncratic structures." Clearly, it can be classified with 3^2434 net structures.

Cs_3CoCl_5 is built up of planar tetragonal 3^2434 layers of chloride ions stacked square upon square with alternating direct and antiprismatic relationships between successive layers. Between each pair of directly related chloride layers lies a 3^2434 net layer of cesium ions related antiprismatically. The squares of the cesium nets are centered by chloride ions as are the metal ion nets of $(Tl_{0.75}Pb_{0.25})_4Cl_5$.

The cesium ions in these layers lie at the center of triangular prisms of chloride ions which are capped on two rectangular faces to give eightfold coordination. Pairs of these chloride ion polyhedra share the remaining rectangular face of each, much as the pairs of eightfold chloride ion polyhedra in $(Tl_{0.75}Pb_{0.25})_4Cl_5$ share a quadrilateral face. In the recently refined isostructural compound Cs_3MnCl_5 (*36*), the Cs–Cs distance through the face is 4.28 Å. This distance corresponds to the common triangle edge of the cesium net. Other Cs–Cs distances in the net are 4.87 Å The Cs–Cs distance in CsCl is 4.123 Å (*37*).

Finally, in Cs_3CoCl_5, all of the chloride ions are surrounded by distorted octahedra of cations. As shown above, three-fifths of the chloride ions are similarly coordinated in $(Tl_{0.75}Pb_{0.25})_4Cl_5$.

Acknowledgments

The authors thank Mr. C. Harding for preparation of Fig. 4. Thanks also to Mr. D. B. Cotts who grew the crystals studied. One of us (P.M.S.) thanks to the National Bureau of Standards and the National Research Council for financial support and hospitality extended under the NBS/NRC Postdoctoral Associateship Program.

References

1. H. S. Parker, AFML-TR-74-56, NBSIR 74-507 (June 1, 1974).
2. R. A. Forman, W. S. Brower, and H. S. Parker, "Mercurous Chloride Prism Polarizers," U. S. Patent 3, 902, 782, assigned to the USA (September 2, 1975).
3. E. Korreng, *Neues Jahrb. Mineral. Geol.* **37**, 117 (1914).
4. A. G. Bergman and T. M. Tapchanyan, *Izv. Sekt. Fiz. Khim. Anal, Inst. Obshch. Neorg. Khim. Akad. Nauk SSSR* **14**, 341 (1941).
5. D. J. Kelsey and L. Katz, *J. Phys. Chem.* **68**, 1584 (1964).
6. I. I. Il'yasov, D. G. Barsegov, I. G. Berikashvili, and L. P. Danilenko, *Russ. J. Inorg. Chem.* **14**, 776 (1969).
7. R. S. Roth, D. B. Cotts, and H. S. Parker, "Program and Abstracts," Ser. 2, Vol. 4, p. 17, Amer. Cryst. Assoc. (January 19–23, 1976).
8. J. M. Stewart, G. J. Kruger, H. L. Ammon, C. H. Dickinson, and S. R. Hall, "The X-ray System," Tech. Rep. TR-192, Computer Science Center, University of Maryland, College Park, (June 1972).
9. D. T. Cromer and J. L. Mann, *Acta Crystallogr. Sect. A* **24**, 321 (1968).
10. J. A. Ibers and W. C. Hamilton (Eds.), "International Tables for X-Ray Cystallography" Vol. IV, pp. 148–151, The Kynoch Press, Birmingham (1974).
11. W. B. Pearson, "The Crystal Chemistry and Physics of Metals and Alloys," pp. 605–633, Wiley, New York (1972).
12. J. Graham and M. R. Thornber, *Amer. Mineral.* **59**, 1026–1034 (1974).
13. H. M. Powell and A. F. Wells, *J. Chem. Soc.* 359–362 (1935).
14. L. G. Schultz, *Acta Crystallogr.* **4**, 487–498 (1951).
15. P. G. Hambling, *Acta Crystallogr.* **6**, 98 (1953).
16. R. L. Sass, E. B. Brackett, and T. E. Brackett, *J. Phys. Chem.* **67**, 2863–2964 (1963).
17. R. D. Shannon, *Acta Crystallogr. Sect. A* **32**, 751–767 (1976).
18. G. Cammeri and L. Fernandes, *Atti Reale Accad. Lincei Sez. I* **1**, 674 (1925).
19. Y. Takeuchi, S. Ghose and W. Nowacki, *Z. Kristallogr.* **121**, 321–348 (1965).
20. I. D. Brown and R. D. Shannon, *Acta Crystallogr. Sect. A* **29**, 266–282 (1973).
21. K. J. deVries and J. H. van Santen, *Physica* **29**, 482 (1963).
22. J. Schoonman and J. F. Verwey, *Physica* **39**, 244 (1968).
23. J. F. Verwey and J. Schoonman, *Physica* **35**, 386 (1967).
24. J. Schoonman, *J. Solid State Chem.* **4**, 466–474 (1972).
25. S. Geller, *in* "Solid Electrolytes" (S. Geller, Ed.), Topics in Applied Physics, Vol. 21, pp. 41–64, Springer-Verlag, Berlin (1977).
26. N. V. Sidgewick and H. M. Powell, *Proc. Roy. Soc. A* **176**, 153 (1940).

27. R. J. GILLESPIE AND R. S. NYHOLM, *Quart. Rev. Chem. Soc.* **11**, 339–380 (1957).
28. S. ANDERSSON AND A. ÅSTROM, *in* "Solid State Chemistry Proceedings of the 5th Materials Research Symposium" (R. S. Roth and S. J. Schneider, Eds.), pp. 3–14, NBS Special Publication 364, National Bureau of Standards, Washington, D.C. (1972).
29. J. D. H. DONNAY AND H. M. ONDIK (Eds.) "Crystal Data, Determinative Tables," Vol. II, p. T-127, National Bureau of Standards, Joint Committee on Powder Diffraction Standards, Washington, D.C. (1973).
30. H.-U. PFEIFER AND K. SCHUBERT, *Z. Metallk.* **12**, 884–888 (1966).
31. J. C. JAMIESON, *Science* **139**, 762 (1963).
32. H. NOWOTNY, H. AUER-WELSBACH, J. BRUSS, AND A. KOHL, *Monatsh. Chem.* **90**, 15–23 (1959).
33. P. PIETROWSKY, *Acta Crystallogr.* **7**, 435–438 (1954).
34. ST.V. NARAY-SZABO, *Z. Kristallogr.* **97**, 223–228 (1937).
35. F. BERTAUT AND P. BLUM, *C.R. Acad. Sci.* **236**, 1055 (1953).
36. J. GOODYEAR AND D. J. KENNEDY, *Acta Crystallogr. Sect. B.* **32**, 631–632, (1976).
37. H. E. SWANSON AND R. K. FUYAT, *Nat. Bur. Stand.* (*U.S.*) *Circ.* **539**, 2, 44 (1953).