

*Molecular packing*

Fig. 3 shows a projection of the structure along (001), and Fig. 4 a symbolic representation of the molecular structure in (010) projection.

The molecules are arranged in four identical layers normal to **b**. Within a given layer the molecular net has approximately *pg* symmetry, the corresponding atoms of the different molecules having the same *y* coordinates. The tin atoms themselves are arranged in a regular face centred array. The packing over the crystal structure is very satisfactory. The stacking of phenyl rings (1) and (3) follows the classic pattern for small aromatic hydrocarbons (Robertson, 1933) forming a closely interlocking system. In like manner the carbonyl groups approach one another in a most compact fashion.

Within the asymmetric unit, and between it and its nearest neighbours, there are 102 interatomic separations less than 3.7 Å in length. The shortest such approach is between two oxygen atoms and is 3.00 Å. The shortest distance between a carbonyl carbon atom and an oxygen atom in an adjacent molecule is 3.19 Å; the shortest distance between carbonyl and phenyl carbon atoms in neighbouring molecules is 3.47 Å, whilst

the closest approach of this kind between two phenyl rings is 3.59 Å. All of these distances are compatible with the sums of the van der Waals radii of the atoms concerned.

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Structure and Bonding Model for Na<sub>2</sub>Tl\*

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Na<sub>2</sub>Tl was found to crystallize in the unique space group *C*22<sub>1</sub> with forty-eight atoms per unit cell. The thallium atoms occupy two eightfold sets while the sodium atoms occupy two fourfold sets and three eightfold sets. Precision lattice parameters of  $a_0 = 13.9350 \pm 0.0004$ ,  $b_0 = 8.8797 \pm 0.0003$ , and  $c_0 = 11.6927 \pm 0.0004$  Å were obtained from extrapolation of back-reflection data. The structure parameters were refined with intensity data from 2390 independent reflections taken with Ag *K*α radiation on a General Electric Spectrogoniometer with a scintillation counter detector. In the structure each thallium atom is coordinated to three thallium atoms and nine sodium atoms; the twelve coordinating atoms form a somewhat irregular icosahedron. The thallium atoms themselves form tetrahedra, very nearly regular, with an average Tl-Tl distance of 3.224 Å. The tetrahedra are separated one from another by the sodium sublattice so that there are no direct Tl-Tl bonds between tetrahedra. A molecular orbital bonding scheme, wherein the bonding orbitals are constructed by mixing only the *p* orbitals of thallium, has been postulated to explain the stability of the thallium tetrahedra. The bonding model indicates that Na<sub>2</sub>Tl is related to the structures: NaPb, KSn, KPb, RbSn, RbPb, CsSn, CsPb, KGe, KSi, RbGe, RbSi, CsGe, CsSi, NaSi, NaGe, BaSi<sub>2</sub>, and probably white phosphorus and the metastable allotropes of arsenic and antimony.

## Introduction

The observation of the polyatomic cation, Bi<sub>5</sub><sup>+</sup>, in Bi<sub>6</sub>Cl<sub>7</sub> by Hershaft & Corbett (1963) and the subsequent elucidation of a directional bonding model based on

an LCAO molecular-orbital treatment by Corbett & Rundle (1964) stimulated the interest of the present authors in analogous directional bonding in polyatomic anions. Pearson (1964) and Kjekshus (1964) have given general discussion of this bonding problem and have considered the role of atomic valency in determining coordination and structure in crystals containing directional covalent bonds in the anionic array.

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All too frequently however, such anionic arrays occur in real crystals as extended chains, two-dimensional networks, or three-dimensional sublattices which are not readily tractable to an analysis of the bonding interactions by molecular orbital techniques. The formulation of a bonding model through an LCAO molecular-orbital treatment is most readily accomplished with an atomic array consisting of high-symmetry clusters or islets containing a limited number of atoms and with the clusters definitively separated one from another.

Available structural data for compounds between alkali metals and elements near the Zintl line (as delineated by Laves, 1956) show many anionic configurations indicative of directional bonding within the anionic array. Included are the structures of NaPb (Marsh & Shoemaker, 1953) and of alkali-mercury compounds (Nielsen & Baenziger, 1954; Duwell & Baenziger, 1955, 1960). Since thallium lies between lead and mercury in the periodic chart, the geometries of the thallium arrays in sodium-thallium compounds might also be expected to exhibit directional bonding.

The sodium-thallium phase diagram (Hansen & Anderko, 1958) indicates the existence of four intermediate phases:  $\text{Na}_6\text{Tl}$ ,  $\text{Na}_2\text{Tl}$ ,  $\text{NaTl}$ , and  $\text{NaTl}_2$ . Only the structure of  $\text{NaTl}$  has been reported (Zintl & Dullenkopf, 1932), and it is the prototype of the  $B32$  structure. The crystal structure and thallium coordination in  $\text{NaTl}$  are consistent with the valence rule formulated by Pearson (1964) and Kjekshus (1964). Application of this same valence rule to  $\text{Na}_2\text{Tl}$  indicates that in this latter phase each thallium atom should be coordinated to three other thallium atoms. An investigation of the  $\text{Na}_2\text{Tl}$  structure has now been completed, and the results are herein reported.

### Structure of $\text{Na}_2\text{Tl}$

#### Sample preparation

Thallium was obtained from the Leytess Metal and Chemical Corporation. The supplier's analysis indicated the material to be 99.999 wt. % Tl with impurities 5 ppm Pb and 1 ppm each of Cu, Cd and Zn. This analysis was qualitatively substantiated by spectrographic analysis at this laboratory. Sodium was obtained from the J. T. Baker Chemical Company whose accompanying analysis indicated the material to be 99.996 wt. % Na with impurities present in the following amounts:

Cl	0.0005 wt. %
N	0.002
$\text{PO}_4$	0.0002
$\text{SO}_4$	0.001
Heavy metals (as Pb)	0.0005
Fe	0.0003

The sodium-thallium phase diagram shows  $\text{Na}_2\text{Tl}$  to form at  $154^\circ\text{C}$  by peritectic reaction between liquid

(77 wt. % Tl) and  $\text{NaTl}$ , and solidification of liquid alloys in the composition range 60–77 wt. % Tl when accomplished under equilibrium conditions yields  $\text{Na}_2\text{Tl}$  as the first solid phase. Samples were therefore prepared at 75.5 wt. % Tl, and both quartz and tantalum were used as crucible materials. These crucibles were fabricated with cone-shaped tips, and solidification was induced under a thermal gradient so that the nucleation and solidification occurred at the tips to produce predominantly single-phase alloys of  $\text{Na}_2\text{Tl}$  in the lower portions of the crucibles. The samples were initially homogenized at  $400^\circ\text{C}$  for four hours, the temperature was then reduced relatively rapidly to  $200^\circ\text{C}$ , and subsequent cooling was accomplished at a rate of  $3^\circ\text{C}$  per hour under an average thermal gradient of  $1.75^\circ\text{C}$  per inch.

Each sample was removed from its crucible and the pointed tip was cleaved from the remainder. The tip was then fragmented by a single blow in a diamond mortar. Suitable single-crystalline fragments were transferred to Lindemann glass capillaries and the capillaries were sealed by fusing the capillary ends with a hot wire. All handling operations were conducted under an inert atmosphere of either argon or helium. The samples were exceedingly brittle and the crystalline fragments exhibited bright metallic surfaces. Diffraction patterns from crystals prepared in quartz were found to be the same as for crystals prepared in tantalum, which is interpreted to mean that there was no significant contamination from the crucible materials. Crystalline fragments which were deliberately exposed to either dry or moist air decomposed rapidly.

#### Unit cell and space group

The symmetries in Laue photographs combined with the lattice spacings and symmetries in rotation and Weissenberg photographs indicate that  $\text{Na}_2\text{Tl}$  belongs to the orthorhombic system with  $mmm$  point symmetry. In addition, the extinction conditions which were observed in Weissenberg photographs of layers  $0kl$  through  $6kl$  when combined with the diffraction symmetry indicate the unique space group  $C222_1$ . Cu  $K\alpha$  radiation was employed for symmetry determination and for determination of precision lattice parameters.

Precision lattice parameters were determined with a General Electric Spectrogoniometer equipped with a Single Crystal Orienter and a scintillation counter. The wavelength of the  $K\alpha_1$  line was taken as  $1.54051 \text{ \AA}$ . Forty-eight data points were measured in the range  $151^\circ < 2\theta < 162^\circ$ , the Bragg angle being taken from a  $2\theta$  scan as the midpoint at the half-height of a peak, and no error attributable to the time constant of the apparatus was detected. These data were used with a linear least-squares fit (Williams, 1964) to the Nelson & Riley (1945) extrapolation function to obtain:

$$\begin{aligned} a_0 &= 13.9350 \pm 0.0004, \\ b_0 &= 8.8797 \pm 0.0003, \\ \text{and } c_0 &= 11.6927 \pm 0.0004 \text{ \AA} . \end{aligned}$$

An independent extrapolation against the eccentricity function (Williams, 1964) gave the same results. These lattice parameters correspond to a volume of 1447 Å<sup>3</sup> for the unit cell. On the basis of density considerations in sodium, thallium, NaTl and related compounds, one can estimate ~90 Å<sup>3</sup> as the volume per formula weight of Na<sub>2</sub>Tl. The ratio of the volume of the unit cell to the volume per formula weight indicates that there are 16 formula weights of Na<sub>2</sub>Tl per unit cell.

#### *Trial structure and refinement of parameters*

An initial set of intensity data for *hk0* and *h0l* reflections was accumulated from an irregularly shaped crystal. Relative intensity values were determined by visual judgment of a series of timed exposures (Buerger, 1960) which were recorded on a precession camera with Ag K $\alpha$  radiation. These data were corrected for Lorentz and polarization effects but not for absorption effects.  $P(x, y)$  and  $P(x, z)$  Patterson projections were computed and subjected to the superposition program of Fitzwater, Johnston, Erbeck & Rhyne (1964). Since the thallium atoms control 95% of the scattering power in Na<sub>2</sub>Tl, the thallium coordinates were readily inferred from the superposition analysis. The thallium atoms were indicated to be in two general sets of eightfold multiplicity of the type 8(c) in C222<sub>1</sub>: for Tl<sub>I</sub>,  $x \sim 0.3$ ,  $y \sim 0.05$ , and  $z \sim 0.125$ ; for Tl<sub>II</sub>,  $x \sim 0.05$ ,  $y \sim 0.33$ , and  $z \sim 0.5$ .

These thallium positions were adequate for the determination of the phase relationships among the structure factors, and the electron density projections,  $\rho(x, y)$  and  $\rho(x, z)$ , were generated from which the sodium positions were sufficiently well defined to allow the postulation of a trial structure. However, the two-dimensional *hk0* and *h0l* film data were inadequate for a reliable refinement of atomic coordinates. Therefore a set of three-dimensional intensity data was accumulated from the crystal which had been used in the determination of precision lattice constants. This crystal was also irregular in shape. The intensity data were

measured with a General Electric Spectrogoniometer and Ag K $\alpha$  radiation, the diffracted beam being passed through a palladium filter to a scintillation counter detector.

Intensities for 2390 independent reflections were measured in four octants of reciprocal space. The following procedure was used in order to minimize the effects of irregular geometric absorption:

(1) Each integrated intensity was measured by the  $2\theta$  scan (moving-crystal, moving-counter) technique. A 40 second scan time was used at a rate of 2°  $2\theta$  per minute. If the reflection had a measurable intensity, background counts were made at both extremes of the scan. Background counts were also of 40 seconds duration;

(2) The peak was then scanned in three other octants. If any of the new scan intensities differed by more than 10% from the original scan intensity, additional background counts were made;

(3) If a reflection was unobserved in the octant of strongest intensities, the peak intensity was not measured in the other three octants;

(4) The final integrated intensity of a reflection was taken to be the average scan intensity in the four octants minus the average background intensity.

An absorption correction was then based on an approximation of the irregular crystal as a sphere of mean radius, 0.137 mm. The absorption function (Bond, 1959) for a sphere of this radius and a mass absorption coefficient of  $\mu/\rho = 54.3 \text{ cm}^2\text{g}^{-1}$  was plotted against the Bragg angle  $\theta$ . A linear approximation was found to reproduce the function to within  $\pm 5\%$  in the angular region of the intensity data, 0–30° in  $\theta$ . This linear approximation is

$$A^* = 57.7 - 1.228\theta$$

where  $A^*$  is the multiplicative absorption correction to the measured intensity and  $\theta$  is the Bragg angle. In addition to the absorption correction, the intensity data were also corrected for Lorentz and polarization effects.

Table 1. *Positional and thermal parameters together with their standard deviations*

Atom set	<i>x</i>	<i>y</i>	<i>z</i>	Thermal parameters (Å <sup>2</sup> )
Tl <sub>I</sub> 8(c)	0.2845 ± 0.0001	0.0484 ± 0.0002	0.1320 ± 0.0001	$\beta_{11} = 0.00209 \pm 0.00005$ $\beta_{22} = 0.0117 \pm 0.0002$ $\beta_{33} = 0.0043 \pm 0.0001$ $\beta_{12} = 0.0009 \pm 0.0001$ $\beta_{13} = 0.00098 \pm 0.00008$ $\beta_{23} = 0.0008 \pm 0.0002$
Tl <sub>II</sub> 8(c)	0.0498 ± 0.0002	0.6776 ± 0.0003	0.5270 ± 0.0002	$\beta_{11} = 0.00350 \pm 0.00009$ $\beta_{22} = 0.0167 \pm 0.0004$ $\beta_{33} = 0.0051 \pm 0.0002$ $\beta_{12} = 0.0063 \pm 0.0002$ $\beta_{13} = 0.0021 \pm 0.0001$ $\beta_{23} = -0.0011 \pm 0.0002$
Na <sub>I</sub> 4(a)	0.067 ± 0.002	0	0	$B = 3.6 \pm 0.6$
Na <sub>II</sub> 4(b)	0	0.592 ± 0.004	½	$B = 4.7 \pm 0.7$
Na <sub>III</sub> 8(c)	0.297 ± 0.002	0.194 ± 0.003	0.421 ± 0.002	$B = 4.3 \pm 0.4$
Na <sub>IV</sub> 8(c)	0.126 ± 0.002	0.278 ± 0.002	0.207 ± 0.002	$B = 3.7 \pm 0.4$
Na <sub>V</sub> 8(c)	0.370 ± 0.002	0.405 ± 0.003	0.165 ± 0.002	$B = 5.2 \pm 0.6$

The corrected intensity data were used for refinement of the positional and thermal parameters of the trial structure. The least-squares technique was employed, and reflections were weighted with the finite difference formula of Williams & Rundle (1964). For the weighting scheme non-statistical fluctuations were assigned values of 5%, and unobserved reflections were arbitrarily given a weight of  $10^{-4}$  in order to insure their negligible contribution to the refinement. Of the 2390 independent reflections, 918 had observed intensities, 1479 were unobserved, and three were excluded. These latter three are the 110 and 200 which suffer interference from fluorescent radiation from the palladium filter and the 1,1,10 which is a weak reflection obscured in the fringe of the much stronger 1,1,11 reflection.

Initial refinement of sodium and thallium coordinates with isotropic temperature factors produced a weighted residual of 0.167. At this point twelve observed structure factors were in substantial disagreement with their respective calculated structure factors. A three-dimensional difference density map revealed that the thallium extrema were significantly asymmetric. Final refinement was therefore undertaken with anisotropic thallium temperature factors. This refinement produced a

weighted residual of 0.117 for observed reflections alone and of 0.127 for all reflections, and the maximum discrepancy between observed and calculated values for the twelve previously deviant reflections was reduced to 15%. A difference density map based on the final refined parameters contained no significant extrema. The refined parameters are given together with uncertainties in Table 1, and a comparison of observed and calculated structure factors is shown in Table 2. In the latter Table, unobserved reflections are indicated by asterisks, and for these reflections the tabulated  $F_{\text{obs}}$  represents the minimum detectable intensity estimated from counting statistics. Coordination and bond distances are shown in Table 3.

### Discussion

The nature of the atomic array is indicated by the coordination atmospheres which are shown in Fig. 1. The thallium coordination is irregularly icosahedral for both  $\text{Tl}_I$  and  $\text{Tl}_{II}$ , the irregularity being somewhat more severe for  $\text{Tl}_{II}$ ; this coordination is illustrated in Fig. 1(a). The twelfefold coordinations about  $\text{Na}_I$ ,  $\text{Na}_{II}$ , and  $\text{Na}_{IV}$  and the fourteenfold coordinations about  $\text{Na}_{III}$  and  $\text{Na}_V$  are shown in Fig. 1(b) through (e). The

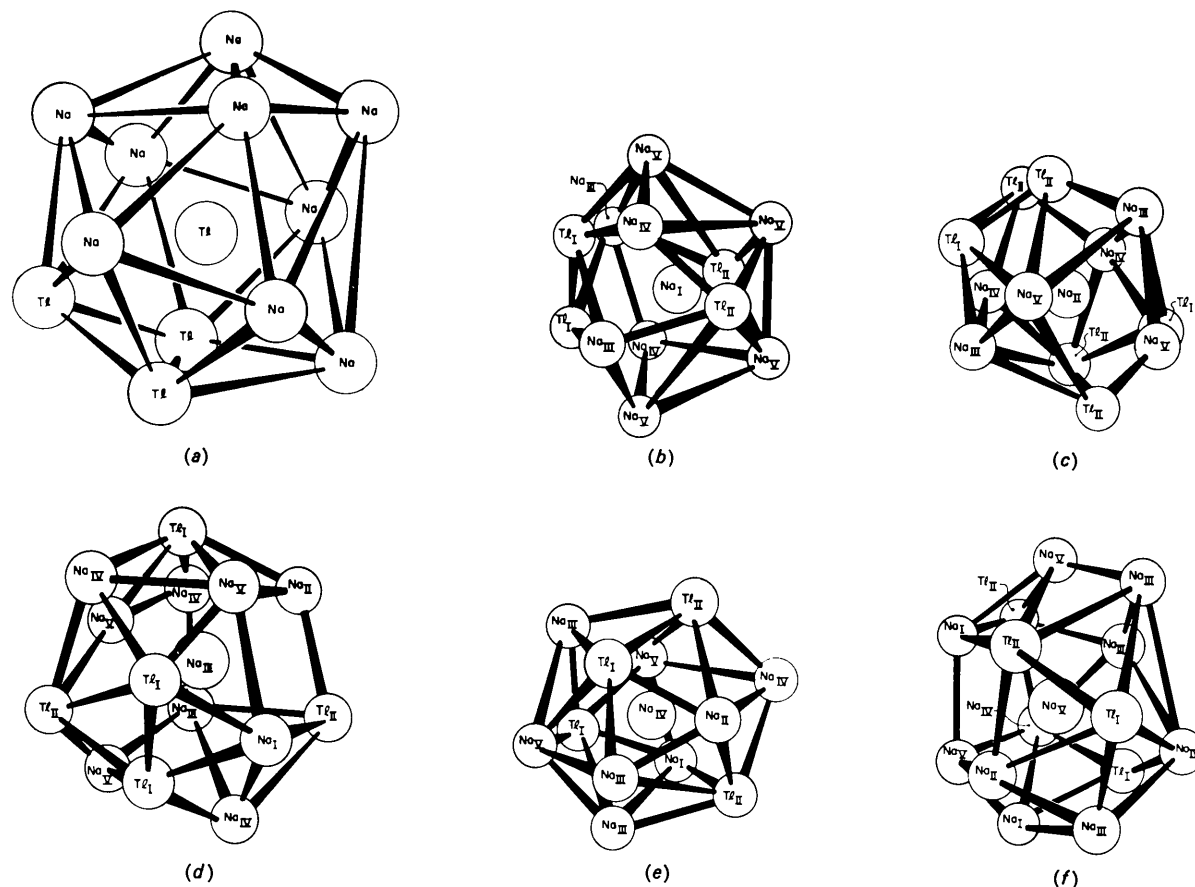


Fig. 1. (a) Thallium coordination as typified by  $\text{Tl}_I$ , and the respective coordinations of (b)  $\text{Na}_I$ , (c)  $\text{Na}_{II}$ , (d)  $\text{Na}_{III}$ , (e)  $\text{Na}_{IV}$ , and (f)  $\text{Na}_V$ .



Table 2 (cont.)

Table with multiple columns containing numerical data, organized in a grid-like structure. The columns are labeled with letters and numbers, and the rows contain various numerical values.



age sodium-sodium distance in  $\text{Na}_2\text{Tl}$  is 3.65 Å, which is only 1.6% shorter than the 3.71 Å distance in elementary sodium, most of the volume contraction must be attributed to the bonding interactions which lead to the tetrahedral thallium arrays. It was therefore decided to attempt an explanation of the general features of the bonding interactions within the thallium tetrahedra in terms of an LCAO molecular-orbital model.

Several simplifying assumptions are incorporated in the bonding model. First, the thallium tetrahedra are assumed to be regular. The small distortion from regularity represented by the actual thallium array should not affect the bonding or antibonding nature of any computed level; rather the distortion should effect an inconsequential lifting of the degeneracy of levels which are multiply degenerate in the regular tetrahedral approximation. Second, only the 6*p* orbitals of thallium are considered to participate in the bonding. This assumption is justified on the basis that the lowest,  $6s^26p^1 \rightarrow 6s^16p^2$ , promotion energy of atomic thallium is 5.6 eV (Moore, 1958). While this separation between *s* and *p* states does not preclude mixing of the 6*s* states into the molecular orbitals, symmetry considerations limit such mixing to molecular orbitals of  $A_1$  and  $T_2$  character. In addition, the magnitude of the *s*-*p* sepa-

ration is sufficiently large that any 6*s* mixing should, as in the case of the regular tetrahedral approximation, raise or lower the levels only slightly without affecting the bonding or antibonding nature of any given level. A final assumption is that the bridging sodium ligands do not participate in the bonding. This is most certainly incorrect. Sodium orbitals would need to be combined with the molecular orbitals of the thallium tetrahedra to form crystal orbitals in a complete and detailed bonding scheme, and it should be emphasized that, on the basis of topological arguments (Kettle, 1966), the sodium atoms in the  $\text{Na}_2\text{Tl}$  structure are in appropriate geometric positions [Fig. 1(b) through (e)] to allow such combination. However, the neglect of sodium orbital participation may be justified as a first approximation on the basis that the short bond distances within the isolated tetrahedra are indicative of strong, directional covalent bonds. Thus the model, while admittedly incomplete, represents an attempt to determine the number of bonding states for comparison with the number of bonding electrons.

Within the foregoing approximations the present problem becomes analogous to the problem of the tetrahedral  $\text{P}_4$  molecule which has been treated by Hart, Robin & Kuebler (1965), and a complete numerical evaluation could in principle be obtained with

Table 3. *Interatomic distances and coordinations\**

Neighbor	Distance	Neighbor	Distance	Neighbor	Distance
Tl <sub>I</sub>		Tl <sub>II</sub>		Na <sub>I</sub>	
Tl <sub>I</sub>	3.204 Å	Tl <sub>I</sub>	3.296 Å	(2) Tl <sub>I</sub>	3.43 Å
Tl <sub>II</sub>	3.296	Tl <sub>I</sub>	3.179	(2) Tl <sub>II</sub>	3.31
Tl <sub>II</sub>	3.179	Tl <sub>II</sub>	3.216	(2) Na <sub>III</sub>	3.44
Na <sub>I</sub>	3.43	Na <sub>I</sub>	3.31	(2) Na <sub>IV</sub>	3.56
Na <sub>II</sub>	3.33	Na <sub>II</sub>	3.40	(2) Na <sub>V</sub>	3.46
Na <sub>III</sub>	3.62	Na <sub>II</sub>	3.61	(2) Na <sub>V</sub>	4.09
Na <sub>III</sub>	3.55	Na <sub>III</sub>	3.68		
Na <sub>III</sub>	3.40	Na <sub>III</sub>	3.73	Na <sub>II</sub>	
Na <sub>IV</sub>	3.29	Na <sub>IV</sub>	3.31	(2) Tl <sub>I</sub>	3.33 Å
Na <sub>IV</sub>	3.13	Na <sub>IV</sub>	3.26	(2) Tl <sub>II</sub>	3.40
Na <sub>V</sub>	3.41	Na <sub>V</sub>	4.20	(2) Tl <sub>II</sub>	3.61
Na <sub>V</sub>	3.44	Na <sub>V</sub>	3.23	(2) Na <sub>III</sub>	3.58
				(2) Na <sub>IV</sub>	3.33
				(2) Na <sub>V</sub>	3.46
Na <sub>III</sub>		Na <sub>IV</sub>		Na <sub>V</sub>	
Tl <sub>I</sub>	3.62 Å	Tl <sub>I</sub>	3.13 Å	Tl <sub>I</sub>	3.41 Å
Tl <sub>I</sub>	3.55	Tl <sub>I</sub>	3.29	Tl <sub>I</sub>	3.44
Tl <sub>I</sub>	3.40	Tl <sub>II</sub>	3.31	Tl <sub>II</sub>	3.23
Tl <sub>II</sub>	3.68	Tl <sub>II</sub>	3.26	Tl <sub>II</sub>	4.20
Tl <sub>II</sub>	3.73	Na <sub>I</sub>	3.56	Na <sub>I</sub>	3.46
Na <sub>I</sub>	3.44	Na <sub>II</sub>	3.33	Na <sub>I</sub>	4.09
Na <sub>II</sub>	3.58	Na <sub>III</sub>	3.53	Na <sub>II</sub>	3.46
Na <sub>III</sub>	3.92	Na <sub>III</sub>	3.52	Na <sub>III</sub>	3.66
Na <sub>IV</sub>	3.53	Na <sub>III</sub>	4.12	Na <sub>III</sub>	3.80
Na <sub>IV</sub>	3.52	Na <sub>IV</sub>	3.66	Na <sub>III</sub>	3.62
Na <sub>IV</sub>	4.12	Na <sub>V</sub>	3.61	Na <sub>IV</sub>	3.61
Na <sub>V</sub>	3.66	Na <sub>V</sub>	3.63	Na <sub>IV</sub>	3.63
Na <sub>V</sub>	3.80			Na <sub>V</sub>	4.23
Na <sub>V</sub>	3.62			Na <sub>V</sub>	4.11

\* Distance

Tl-Tl

Na-Tl

Na-Na

Standard deviation

± 0.003 Å

± 0.02

± 0.03



their self-consistent field procedure. In the present case the primary interest was in the number of bonding states rather than in the quantitative spacing of levels. On this basis a self-consistent field treatment was not attempted but rather the coulomb and resonance integrals,  $\alpha$  and  $\beta_0$  (Daudel, Lefebvre & Moser, 1959), were left as unevaluated constants which when combined give the scaling parameter,  $\beta_0 - \alpha$ , for the energy level diagram shown in Fig. 2. The numerical coefficients of the scaling parameter were determined with overlap integrals evaluated with the use of Slater orbitals (Silver, 1965). Neglect of overlap (simplest Hückel approximation) changes the spacings of the levels somewhat but retains the same sequence of levels and the same number of bonding and antibonding states. For the present purposes this latter consideration is most relevant. With the inclusion of spin degeneracy, the bonding levels would be saturated with a total of twelve electrons per tetrahedron or three electrons per thallium atom. Since each sodium atom has one valence electron and each thallium atom has one  $6p$  electron, the stoichiometry Na<sub>2</sub>Tl has the correct number of electrons to saturate these bonds if the sodium electrons are relinquished completely to the thallium tetrahedra.

This is an extreme interpretation, and the sodium electrons are not likely to be completely localized in the thallium tetrahedra. The neglected participation of the sodium orbitals to form hybridized crystal orbitals could allow appreciable time-average electron density in the sodium sublattice. However, magnetic susceptibility data indicate that there is no significant Pauli paramagnetism which implies that the crystal orbitals deviate markedly from a free-electron approximation. Greiner (1966) has found a temperature-independent diamagnetism with a value of  $-60 \times 10^{-6}$  e.m.u.mole<sup>-1</sup>. The core contributions to this diamagnetism are indicated by Selwood (1956) to be  $-34 \times 10^{-6}$  e.m.u. per g. ion for Tl<sup>+</sup> and  $-5 \times 10^{-6}$  e.m.u. per g. ion for Na<sup>+</sup>, which sums to  $-44 \times 10^{-6}$  e.m.u.mole<sup>-1</sup> for Na<sub>2</sub>Tl. The net difference of  $-16 \times 10^{-6}$  e.m.u.mole<sup>-1</sup> is attributable to the valence electrons, and this excess diamagnetism is the right order of magnitude to be explicable as a Langevin precession of the valence electrons in orbits with dimensions comparable to those of the thallium tetrahedra. Thus, while the magnetic susceptibility data do not unequivocally prove the bonding model, the data are at least in qualitative accord with the model and with the inference that the valence bands arising from the tetrahedral bonding levels are very nearly saturated. On this basis one would speculate that Na<sub>2</sub>Tl is likely to be a poor electrical conductor or even a semi-conductor.

A search of the literature has produced no previously published structure which is isostructural with Na<sub>2</sub>Tl. However, a number of crystal structures were found in which the electronegative species form well-defined isoelectronic tetrahedra. These structures include NaPb (Marsh & Shoemaker, 1953), KSn, KPb,

RbSn, RbPb, CsSn, and CsPb (Hewaidy, Busmann & Klemm, 1964), KGe, KSi, RbGe, RbSi, CsGe, and CsSi (Busmann, 1961), NaSi and NaGe (Witte, Schnering & Klemm, 1964), BaSi<sub>2</sub> (Schäfer, Janzon & Weiss, 1963), and probably white (yellow) phosphorus (Hultgren, Gingrich & Warren, 1935) and, also likely, the metastable allotropes of arsenic and antimony (Wells, 1950). It may be noted from the stoichiometries of these phases that in every instance the number of the  $p$  electrons of the more electronegative species plus the number of valence electrons of the electropositive species, if any, averages to the same three electrons per atom of the species forming the tetrahedra. The bonding in all of these substances is presumably analogous.

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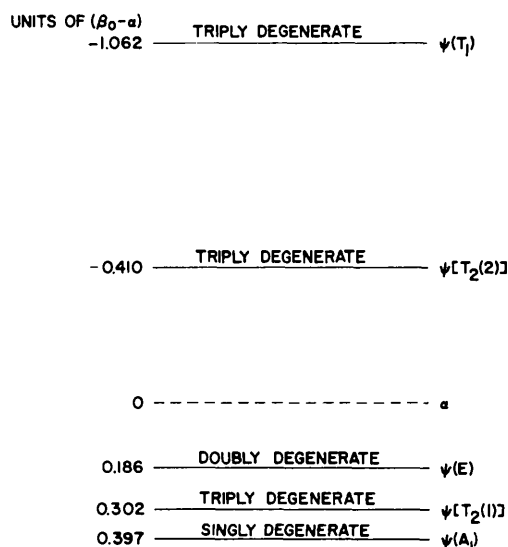


Fig. 2. Energy level diagram for Tl<sub>4</sub> tetrahedra.

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## Determination of the Layer Stacking Sequence of a New Complex Mica Polytype: A 4-layer Lithium Fluorophlogopite\*

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A method of deriving a 'periodic intensity distribution function' that is characteristic of the layer stacking sequence of any mica polytype is given. It is then shown how this function can be directly related to the X-ray diffraction patterns of multi-layer micas so as to establish the particular stacking sequence and thus the structure of the mica polytype. This intensity function is utilized to solve the crystal structure of a newly discovered 4-layer mica polytype, a synthetic lithium fluorophlogopite. This mica is triclinic, space group  $C1$ ,  $a=5.31$ ,  $b=9.19$ ,  $c=40.58$  Å,  $\alpha=\gamma=90^\circ$ ,  $\beta=100^\circ 3'$ . The layer stacking sequence of this polytype involves relative layer rotations of 0, 60, 180, and 120°. Atomic parameters for the 80 atoms in the asymmetric unit are given.

### Introduction

The principal mica polytypes have been investigated by Hendricks & Jefferson (1939), by Heinrich, Levinson, Levandowski & Hewitt (1953), and more recently by Smith & Yoder (1956), who described the six simplest mica polytypes, namely the  $1M$ ,  $2M_1$ ,  $2M_2$ ,  $2O$ ,

$3T$ , and  $6H$  forms. Zvyagin (1961) gave a method of calculating the structure factors of these simple forms. Sadanaga & Takéuchi (1961) gave an elegant analysis of the possible twin operations found in these polytypes. Burnham & Radoslovich (1964) carefully refined the  $2M_1$  muscovite structure.

Ross & Wones (1965) and Takeda & Donnay (1965) have found many more complex polytypes not included among those previously described. Two of these newly discovered polytypes have 4-layer structures. A method of generating all possible structure models for mica polytypes with a given layer repeat has been developed by Ross, Takeda & Wones (1966). Some of the simpler

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