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The Crystal Structure of NaPb*

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The crystal structure of the intermetallic compound NaPb has been determined by X-ray diffraction methods, with use of both single-crystal and powder specimens. The structure is tetragonal, with space group D_{4h}^{20}-$I4/acd$, and with lattice constants $a_0 = 10{\cdot}580$ Å and $c_0 = 17{\cdot}746$ Å at room temperature. The 32 lead atoms in the unit cell (in $32(g)$: $x = 0{\cdot}0696$, $y = 0{\cdot}1186$, $z = 0{\cdot}9383$; ...; with respect to an origin taken at a center of symmetry) form eight nearly-regular Pb_4 tetrahedra with Pb–Pb bond-lengths of 3·15 and 3·16 Å; the 32 sodium atoms (16 in $16(e)$: $\frac{1}{4}, y, \frac{1}{2}$; ...; $y \approx \frac{1}{8}$; and 16 in $16(f)$: $x, x+\frac{1}{4}, \frac{5}{8}$; ...; $x \approx \frac{1}{8}$; origin as above) are arranged in shells about the Pb_4 tetrahedra, with Pb–Na bond-lengths averaging about 3·48 Å and Na–Na bond-lengths averaging about 3·72 Å. The shell of sodium atoms enclosing each Pb_4 tetrahedron contains 16 sodium atoms, each of which belongs also to shells surrounding other Pb_4 tetrahedra. From the observed bond-lengths the valence of lead in NaPb appears to be about 3·0 and that of sodium about 1·5, there being apparently some electron transfer from lead to sodium.

Introduction

In the binary system sodium–lead there exist a number of phases (intermetallic compounds); Na_4Pb (or $Na_{15}Pb_4$; see below), Na_5Pb_2 (Krohn & Shapiro, 1952), Na_2Pb (or Na_9Pb_4; Krohn & Shapiro, 1952), NaPb, and the β phase, which is ideally $NaPb_3$ (see below) but has a maximum melting point at about the composition represented by the formula Na_2Pb_5. Of these, the structures of only the first and last have as yet been investigated. Zintl & Harder (1936) reported that the actual composition of 'Na_4Pb' corresponds to the formula $Na_{15}Pb_4$, and obtained by X-ray diffraction work a structure based on a body-centered cubic lattice with $a_0 = 13{\cdot}29$ kX. In this structure each of the 16 lead atoms in the unit cube is surrounded by 12 sodium atoms at the vertices of a polyhedron which is a somewhat distorted form of the coordination polyhedron found in hexagonal closest packing. Earlier, Stillwell & Robinson (1933) reported the composition of 'Na_4Pb' to be that represented by $Na_{31}Pb_8$; they found a cubic lattice constant, $a_0 = 13{\cdot}27$ kX., almost identical with that found later by Zintl & Harder, but gave clear evidence for a face-centered cubic lattice rather than a body-centered cubic lattice. (Their composition cannot be correct unless there is some statistical replacement, for 62, the number of sodium atoms in the unit cube, is not divisible by four.) These workers did not determine a structure. It thus appears possible that there are actually two phases of different structure with approximate composition Na_4Pb. Zintl & Harder (1931) found for the β phase a structure based on a simple cubic lattice with $a_0 = 4{\cdot}872$–$4{\cdot}883$ kX., with a sodium atom at each lattice point (0, 0, 0) and lead atoms (or lead atoms statistically replaced by some sodium atoms) at face-center positions (0, $\frac{1}{2}$, $\frac{1}{2}$, etc.).

Our interest in the Na–Pb system has been heightened in recent years by communication and discussions with Drs George Calingaert, Hymin Shapiro, and others of the staff of the Ethyl Corporation Research Laboratories (Detroit, Mich.) who have kindly furnished us with a specimen of NaPb. Our special interest in this compound was enhanced by the fact that it appeared (from powder photographs) to have a complicated structure with a large unit cell, despite the simplicity of its formula. The present investigation of the crystal structure of the compound NaPb was therefore undertaken as part of our program of X-ray diffraction work on the structures of intermetallic compounds, a program in which there is a considerable emphasis on complicated structures with moderate to large unit-cell volumes, and on the coordination of atoms and the configurations of groups of atoms in such structures.

Experimental

Since NaPb reacts very readily with oxygen or moisture, it was necessary to perform all handling operations in an extremely dry and oxygen-free medium, and to protect the specimens during photography by enclosing them in thin-wall pyrex capillary tubes. For these purposes a 'dry box' was used, with an atmosphere of commercial dry nitrogen which was further purified by passage through a hot (450° C.)

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copper foil deoxidizer and subsequent bubbling through a liquid sodium–potassium alloy at room temperature. This method was suggested to us by Dr Hymin Shapiro of the Ethyl Corporation Research Labororatories. The resulting atmosphere within the dry box showed little tendency to attack a sample of sodium–potassium alloy contained in a watch glass, but still attacked samples of NaPb rapidly enough to cause trouble. For this reason it was found necessary to keep the crushed or powdered material, and single-crystal specimens, immersed in paraffin oil which had been dried by shaking with liquid sodium–potassium alloy, first in a large flask to disperse the metal and finally in sealed pyrex tubes which were subsequently opened only in the dry box. Under these conditions, the resulting powder photographs indicated about 10% decomposition of NaPb into the β phase (and, presumably, NaOH), whereas the photographs taken of specimens prepared in the dry atmosphere alone showed over 80% decomposition. Earlier powder photographs taken of material which was powdered under lithium-dried paraffin oil in the presence of room air and then drawn into capillary tubes showed substantially complete decomposition into metallic lead.

The thin-walled pyrex capillary tubes used in the powder work and subsequent single crystal work were prepared by baking them out under vacuum in larger pyrex tubes (each containing a number of the capillary tubes) which were then sealed off and stored for later opening in the dry box. Powder samples were prepared by crushing and grinding a sample of NaPb under dry paraffin oil in an agate mortar; the resulting sludge was drawn by capillary action into the dry capillary tubes (of about 0·2 mm. diameter), the ends of which were then sealed with Plicene cement, using a hot wire. Powder photographs were taken with nickel-filtered copper radiation in a North American Philips powder camera (Straumanis arrangement, 57·30 mm. camera radius). The intensities of all powder lines out to $\sin\theta = 0{\cdot}62$ were estimated by comparison with a powder photograph of $NaZn_{13}$ which had been previously calibrated by the multiple-film technique (Shoemaker, Marsh, Ewing & Pauling, 1952). These intensities were then corrected for Lorentz and polarization factors and multiplied by an empirical scale factor to give values of the 'corrected intensities', denoted G_o^2.

The presence of several lines due to the β phase of the Na–Pb system made indexing of the powder photographs difficult. At the time we did not have the lattice constants previously found by Prof. L. S. Ramsdell to aid us in the indexing of the photographs. We therefore decided to make use of a technique which had been very useful in similar circumstances in work on the σ phase FeCr (Bergman, 1951; Bergman & Shoemaker, 1952). This involves isolation and Laue photography of small fragments of the crushed material in the hope of obtaining a single crystal, from which photographs may be obtained which will give the Laue symmetry and approximate lattice constants. In the present work this technique was successful not only in giving the space group and lattice constants suitable for indexing the powder photographs, but also in giving valuable (though approximate) intensity data for determining the approximate structure.

A specimen of the bulk NaPb alloy was fragmented under dried paraffin oil in the dry box, and several of the more promising-looking fragments, together with the accompanying oil, were drawn into thin-wall pyrex capillary tubes, the ends of which were then sealed with Plicene cement. The capillaries were mounted vertically on a goniometer head and the fragments were examined by Laue photography. After a few trials a fragment was found which was evidently a single crystal, whose c axis was by fortunate accident nearly parallel to the axis of the capillary. Rotation photographs, as well as zero-, first-, and second-layer Weissenberg photographs about the c axis were prepared from this specimen, using unfiltered copper radiation. Evidently the Plicene seal was imperfect, for the crystal decomposed gradually, and after about a week was useless. Moreover, there was some tendency for the crystal to move in the oil. The photographs were therefore of little use for accurate intensity measurements, but were entirely adequate for the purpose originally intended and for yielding an approximate structure. The final determination of both the lattice constants and the atomic positional parameters were based entirely on powder photographic data.

Recently, Dr Gunnar Bergman of this Laboratory prepared an apparently single crystal of NaPb several centimeters long, by drawing the molten alloy into a glass capillary tube and moving it slowly through a temperature gradient. This crystal had its a axis nearly parallel to the axis of the capillary, and rotation and zero-layer Weissenberg photographs about this axis were prepared. Unfortunately, intensity measurements were unreliable owing to absorption effects, although the general agreement between calculated and observed intensities was satisfactory.

The approximate lattice constants determined from the single-crystal measurements were refined by a least-squares treatment of those powder lines which could be unambiguously indexed, and subsequently all powder lines out to a value of $\sin\theta = 0{\cdot}62$ (copper radiation) were satisfactorily indexed. The least-squares technique employed, involving refinement of the lattice constants and simultaneous correction for absorption, was essentially that used by Shoemaker *et al.* (1952) in the parameter refinement of $NaZn_{13}$. The resulting dimensions for the tetragonal cell, together with the probable errors as evaluated from the least-squares residuals, are:

$$a_0 = 10{\cdot}580 \pm 0{\cdot}005,\ c_0 = 17{\cdot}746 \pm 0{\cdot}015\ \text{Å}$$
$$(\text{Cu } K\alpha = 1{\cdot}5418\ \text{Å})\ .$$

With the assumption of 32 NaPb in the unit cell, the calculated density is 6·158 g.cm.$^{-3}$; the density determined from pycnometric measurements in paraffin oil was 6·175 g.cm.$^{-3}$.

The systematic absences, as determined from the single crystal (and powder) photographic data, are hkl with $(h+k+l)$ odd, $hk0$ with h or k odd, $h0l$ with h or l odd, and hhl with $(2h+l) \neq 4n$. These extinctions lead uniquely to the space group $D_{4h}^{20}-I4/acd$, which has 32-fold general positions.

These results are in satisfactory agreement with the unpublished results obtained independently for NaPb some years ago by Prof. L. S. Ramsdell of the University of Michigan and communicated to us recently (Ramsdell, 1951). Professor Ramsdell found the same space group, with $a_0 = 10·5$ Å and $c_0 = 17·6$ Å.

Determination of the structure

Since the average ratio of the scattering powers of lead and sodium is about 9 to 1 (nearly the same as that for carbon and hydrogen) in the range of $\sin\theta$ for which powder data were available, the preliminary work leading toward the structure determination involved the determination of only the lead-atom positions. For this purpose, a Patterson projection on (001) was first computed from the rather poor $hk0$ Weissenberg data. The positions of peaks indicated strongly that the 32 lead atoms are in general positions, and it was a comparatively simple matter to find values for the x and y parameters that would account for the main details of the Patterson projection. An approximate value for the z parameter was subsequently determined from inspection and interpretation of (hkl) powder data. With the origin of coordinates taken at a center of symmetry, the coordinates of the general positions $32(g)$ are

$$0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2} \pm (x, y, z);\ (x, \tfrac{1}{2}-y, \tfrac{1}{2}+z);$$
$$(\bar{x}, y, \tfrac{1}{2}+z);\ (\bar{x}, \tfrac{1}{2}-y, z);$$
$$(\tfrac{1}{4}+y, \tfrac{1}{4}+x, \tfrac{1}{4}+z);\ (\tfrac{1}{4}+y, \tfrac{1}{4}-x, \tfrac{3}{4}+z);$$
$$(\tfrac{3}{4}-y, \tfrac{1}{4}+x, \tfrac{3}{4}+z);\ (\tfrac{3}{4}-y, \tfrac{1}{4}-x, \tfrac{1}{4}+z).$$

The approximate parameters assigned were $x=0·067$, $y=0·121$, $z=0·934$. The structure factors for all reflections within the range of the powder data were calculated for these values. An empirical temperature factor was applied, and values of G_c^2 were obtained:

$$G_c^2 = \sum_i m_i (TF_c)_i^2 ,$$

where T is the temperature factor and m_i is the multiplicity of the ith set of planes; the summation is carried out over all sets of planes contained within the powder line. The agreement between calculated and observed values of G^2 was quite satisfactory, and confirmed the previous indications that the lead atoms occupy one set of general positions 32 (g) with parameters not greatly different from those assumed.

For a preliminary adjustment of the lead parameters, a least-squares treatment of (F_o-TF_c) data was carried out, using only those observed powder lines which were completely resolved and could be indexed unambiguously; for these lines, $|F_o| = \sqrt{(G_o^2/m)}$. The 34 observational equations were weighted according to the method of Hughes (1941). The least-squares formulation employed was that of Shoemaker *et al.* (1952). The resulting improved parameters were $x = 0·070$, $y = 0·118$, $z = 0·938$.

Before proceeding further with the determination of the lead parameters an attempt was made to locate the sodium atoms. On examination of a model of the structure with the lead atoms in place it was found to be impossible to place the sodium atoms in general positions in the unit cell without having absurdly short interatomic distances; however, good packing was obtained by putting the sodium atoms in two sets of 16-fold special positions, as follows (with the origin of coordinates again taken as a center of symmetry):

$$16\ \text{Na}_{\text{I}}\ \text{in}\ 16\,(e);\ 0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2} \pm (\tfrac{1}{4}, y, \tfrac{1}{2});$$
$$(\tfrac{3}{4}, y, 0);$$
$$(\tfrac{1}{4}+y, \tfrac{1}{2}, \tfrac{3}{4});$$
$$(\tfrac{1}{4}+y, 0, \tfrac{1}{4}) .$$
$$16\ \text{Na}_{\text{II}}\ \text{in}\ 16\,(f);\ 0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2} \pm (x, \tfrac{1}{4}+x, \tfrac{5}{8});$$
$$(x, \tfrac{1}{4}-x, \tfrac{1}{8});$$
$$(\bar{x}, \tfrac{1}{4}+x, \tfrac{1}{8});$$
$$(\bar{x}, \tfrac{1}{4}-x, \tfrac{5}{8}).$$

Optimum packing is obtained with values of both y and x of about $\tfrac{1}{8}$. When the structure factors were recalculated including the sodium contributions the improvement between calculated and observed F's was considerable.

For the final refinement of lead-atom parameters a least-squares calculation was carried out using values of G^2 for all powder lines which were either totally resolved or else represented essentially complete degeneracy of two or more sets of planes; that is, only those lines were omitted which, owing to contributions from two or more sets of planes reflecting at slightly different angles, would tend to be diffuse and hence be subject to error in intensity measurements. For this refinement 50 out of a total of 60 observed powder lines were used, and sodium contributions based on y and x parameters of $\tfrac{1}{8}$ were included in the calculations of structure factors. The observational equation for each powder line was of the form

$$\sqrt{w}.\sum_j [\sum_i (m_i T_i^2 \partial F_i^2/\partial \xi_j) \Delta \xi_j] = \sqrt{w}.[G_o^2 - G_c^2] ,$$

where ξ_j is the parameter being adjusted and the summation over i includes all sets of planes contained in the powder line. The final lead parameters, together with the probable error as evaluated from the residuals, are $x = 0·0696 \pm 0·0013$, $y = 0·1186 \pm 0·0012$, $z = 0·9383 \pm 0·0008$.

In an attempt to confirm the locations of the sodium atoms, two 'difference' Fourier summations were carried out in the following way: values of $(F_o - TF_{Pb})$ (where T is the final temperature factor and F_{Pb} is the calculated lead contribution to the structure factor) were obtained for all powder lines which were resolved and could be unambiguously indexed—34 in number. These values were used to construct Fourier summations along the axes of symmetry on which the sodium atoms must lie to conform with space-group requirements; that is, along the lines $(\frac{1}{4}, y, \frac{1}{2})$ and $(x, x+\frac{1}{4}, \frac{5}{8})$. Since only a relatively small number of terms, chosen essentially at random with respect to sodium contributions, were included in these summations, it was anticipated that termination-of-series errors would be very large; hence, similar summations were carried out using values of TF_{Na}—the calculated sodium contributions with the assigned y and x parameters of $\frac{1}{8}$. The results of these calculations are shown in Fig. 1. Both sets of curves show

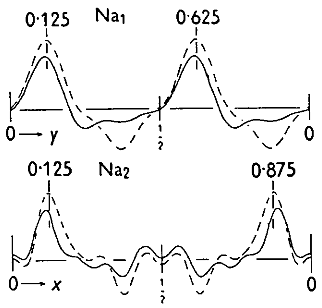

Fig. 1. Fourier summations along the symmetry axes $(\frac{1}{4}, y, \frac{1}{2})$ and $(x, x+\frac{1}{4}, \frac{5}{8})$. The solid lines are obtained from $(F_o - TF_{Pb})$ terms, while the dashed lines are obtained from the calculated values TF_{Na} for the same reflections. All curves are drawn to the same arbitrary scale.

rather large anomalies; yet the over-all agreement between calculated and observed curves is striking—better than might have been expected for atoms as relatively low in scattering power as sodium in the presence of lead. Although the maxima in the observed curves do not agree exactly with those of the calculated curves, it is felt that the deviations are of the same order of magnitude as the experimental error, and no revision of the sodium parameters was attempted. Indeed, the evidence may be regarded as strong that the sodium atoms are very close to the predicted positions.

Table 1 lists the observed and calculated intensity and spacing data for all reflections out to $\sin\theta = 0{\cdot}62$. The lines which are labelled β are attributable to the β-phase structure (see Introduction). The calculated spacings of this phase are reported on the basis of a unit cube with edges of 4·874 kX. (4·883 Å) as determined by Zintl & Harder (1931); the G_c^2 values were obtained by correcting their photometric intensity values (obtained from a sample containing about 30 atomic % sodium) for Lorentz and polarization factors and adjusting with an empirical scale factor.

The final value for the reliability factor $R(G^2)$,

$$R(G^2) = \Sigma|G_o^2 - G_c^2| \div \Sigma G_o^2 ,$$

is 0·145 for the 45 well-resolved powder lines; the corresponding value for $R(F)$ (based on F, rather than G^2, values) would presumably be approximately 0·075. This reliability factor, although considerably lower than expected for single-crystal data, is close to that found in the powder analysis of $NaZn_{13}$. If the contributions of the sodium atoms are neglected in the structure-factor calculations, the value for $R(G^2)$ is increased to 0·19. The final empirical temperature factor is of the form

$$\exp\left[-B \sin^2\theta/\lambda^2\right] ,$$

where $B = 1{\cdot}17$ Å^2. This temperature factor presumably includes an effect of absorption.

Discussion of the results

Projections of the structure along the b and c axes are shown in Figs. 2 and 3. The 32 lead atoms in the unit cell are arranged in eight nearly-regular tetrahedra centered at $0, \frac{3}{4}, \frac{1}{8}$; $0, \frac{3}{4}, \frac{5}{8}$; $0, \frac{1}{4}, \frac{3}{8}$; $0, \frac{1}{4}, \frac{7}{8}$; $\frac{1}{2}, \frac{1}{4}, \frac{1}{8}$; $\frac{1}{2}, \frac{1}{4}, \frac{5}{8}$; $\frac{1}{2}, \frac{3}{4}, \frac{3}{8}$ and $\frac{1}{2}, \frac{3}{4}, \frac{7}{8}$. The Pb–Pb distances along the tetrahedral edges are of two crystallographic kinds, and have values of 3·146 and 3·162(±0·020) Å. Each tetrahedral Pb_4 group is surrounded by sixteen sodium atoms, of which four Na_I are approximately opposite the faces of the Pb_4 tetrahedron and thus form a negative tetrahedron, four other Na_I are nearly opposite the corners of the Pb_4 tetrahedron and form a distorted tetrahedron, four Na_{II} are located at the

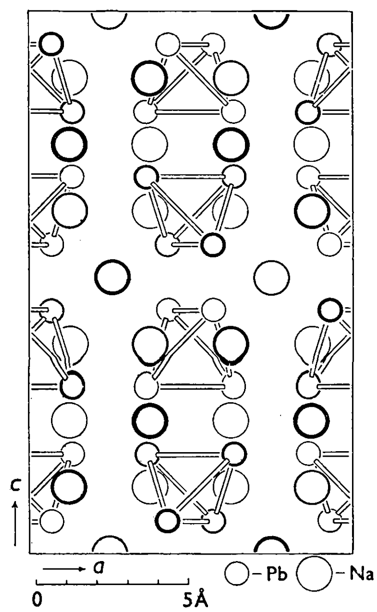

Fig. 2. Projection of the structure along the b axis, showing a complete unit cell. The origin is at the lower left corner.

Table 1. *Spacing and intensity data for* NaPb

(Cu $K\alpha$ radiation)

hkl	$\sin^2\theta$ (calc.)	$\sin^2\theta$ (obs.)	G_o^2	$m(\mathrm{T}F_c)^2$ *
[a]112	0·0182	0·0180[b]	168	188
[a]200	0·0212	0·0206[b]	44	36
(β 100)[c]	(0·0249)	0·0248	9	— (6)
211	0·0284	0·0284[b]	92	18
202	0·0288			57
004	0·0302	—	—	0
220	0·0425	0·0434[b]	184	1
[a]213	0·0435			163
(β 110)	(0·0498)	0·0498	17	— (18)
204	0·0514	—	—	1
[a]312	0·0606	0·0603[b]	70	48
[a]321	0·0709	0·0705[b]	285	320
224	0·0726	—	—	0
215	0·0737	0·0742[b]	456	290
(β 111)	(0·0748)			— (134)
[a]116	0·0785	0·0784[b]	190	202
[a]314	0·0833	0·0832[b]	368	342
400	0·0850	0·0856[b]	375	178
323	0·0860			286
[a]206	0·0891	0·0892[b]	42	66
411	0·0922	0·0925[b]	166	48
402	0·0925			103
(β 200)	(0·0997)	0·0996	158	— (124)
[a]332	0·1031	0·1034[b]	29	24
420	0·1062	0·1071[b]	224	62
413	0·1072			161
[a]422	0·1137	0·1136[b]	43	63
404	0·1151	—	—	0
[a]325	0·1162	0·1159[b]	231	239
217	0·1189	—	—	9
008	0·1206	0·1206[b]	164	147
316	0·1210			77
(β 210)	(0·1246)	0·1247	28	— (49)
[a]431	0·1346	0·1340[b]	61	50
424	0·1364	—	—	1
[a]415	0·1374	0·1371[b]	135	152
[a]208	0·1419	0·1415[b]	60	68
[a]512	0·1456	0·1454[b]	92	111
(β 211)	(0·1495)	0·1498[b]	95	— (57)
[a]433	0·1497			85
406	0·1528	—	—	33
[a]521	0·1559	0·1560[b]	345	263
[a]327	0·1614	0·1614[b]	120	107
228	0·1631	—	—	2
336	0·1634	—	—	9
514	0·1682	—	—	4
440	0·1699	0·1695[b]	31	9
523	0·1710			23
318	0·1737	—	—	0
[a]426	0·1741	0·1747[b]	88	81
219	0·1792	—	—	14
[a]435	0·1799	0·1800[b]	85	82
[a]417	0·1826	0·1834[b]	54	41
532	0·1881	—	—	9
[a]600	0·1912	0·1902[b]	58	36
611	0·1984	0·1992	525	81
602	0·1987			107
1,1,10	0·1991			116
(β 220)	(0·1994)			— (255)
444	0·2001			7
525	0·2011	—	—	28
408	0·2056	0·2054[b]	265	162
516	0·2059			146
2,0,10	0·2097	0·2111[b]	120	51
534	0·2107			103
620	0·2124	—	—	7
613	0·2134	—	—	15

Table 1 (*cont.*)

hkl	$\sin^2\theta$ (calc.)	$\sin^2\theta$ (obs.)	G_o^2	$m(TF_c)^2$
541	0·2196	—	—	10
622	0·2199	—	—	0
604	0·2213 }	0·2219[b]	128	{ 1
[a]329	0·2217 }			{ 113
(β(300+221))	(0·2243)	—	—	— (67)
437	0·2251	—	—	43
[a]428	0·2268	0·2269[b]	137	126
[a]543	0·2347	0·2342[b]	153	176
[a]631	0·2408	0·2403[b]	304	320
3,1,10	0·2416	—	—	46
624	0·2426	—	—	0
419	0·2430	—	—	25
615	0·2436	—	—	2
[a]527	0·2464	0·2467[b]	281	326
536	0·2484	—	—	21
(β 310)	(0·2492)	—	—	— (74)
[a]2,1,11	0·2546	0·2547[b]	140	165
633	0·2559	—	—	2
518	0·2587 }	0·2589[b]	52	{ 0
[a]606	0·2590 }			{ 63
[a]545	0·2648	0·2651[b]	160	165
0,0,12	0·2714	—	—	0
552	0·2730	—	—	19
712	0·2730	—	—	0
4,0,10	0·2735 }	0·2742	413	{ 30
(β 311)	(0·2742) }			{ — (470)
640	0·2761	0·2780	65	92
626	0·2803	—	—	3
721	0·2833 }	0·2834[b]	170	{ 11
642	0·2837 }			{ 116
3,3,10	0·2841 }			{ 6
439	0·2854	—	—	29
635	0·2861	—	—	7
[a]617	0·2888	0·2892[b]	59	65
448	0·2906	—	—	14
2,0,12	0·2927	—	—	1
4,2,10	0·2947 }	0·2956[b]	643	{ 66
714	0·2957 }			{ 497
3,2,11	0·2971 }	0·2972	206	{ 164
723	0·2984 }			{ 9
(β 222)	(0·2991) }			{ — (212)
538	0·3012	—	—	0
644	0·3063 }	0·3065[b]	277	{ 1
[a]529	0·3067 }			{ 267
547	0·3101	—	—	11
608	0·3118	—	—	37
2,2,12	0·3139	—	—	0
[a]732	0·3155	0·3160[b]	130	126
4,1,11	0·3184	0·3180	97	84
(β 320)	(0·3240)	—	—	— (74)
3,1,12	0·3245 }	0·3256	180	{ 168
651	0·3258 }			{ 48
5,1,10	0·3266 }			{ 90
725	0·3286	—	—	37
[a]637	0·3313	0·3314[b]	161	160
628	0·3330	—	—	10
556	0·3334	—	—	28
716	0·3334	—	—	4
734	0·3381	—	—	65
800	0·3398 }	0·3399[b]	94	{ 2
653	0·3409 }			{ 98
646	0·3440	—	—	65
2,1,13	0·3451	—	—	65
741	0·3470 }	0·3474[b]	281	{ 6
811	0·3470 }			{ 10
802	0·3474 }			{ 184
(β 321)	(0·3489)	—	—	— (96)
619	0·3492	—	—	52
4,0,12	0·3564	—	—	5

Table 1 (*cont.*)

hkl	$\sin^2\theta$ (calc.)	$\sin^2\theta$ (obs.)	G_o^2	$m(TF_c)^2$
4,3,11	0·3608	0·3612[b]	174	45
820	0·3611			39
813	0·3621			6
743	0·3621			38
822	0·3686	—	—	21
5,3,10	0·3690	—	—	13
804	0·3700	0·3705[b]	134	0
549	0·3704			5
655	0·3710			85
727	0·3738	—	—	10
736	0·3758	—	—	89
4,2,12	0·3776	—	—	1
6,0,10	0·3797	0·3804[b]	81	55
1,1,14	0·3801			71
5,2,11	0·3821	—	—	9
660	0·3823	—	—	8

* $F_{000} = 14\cdot70 = (Z_{Pb}+Z_{Na})/32\sqrt{10}$.
a. Reflections used in sodium parameter calculations.
b. Reflections included in final least-squares refinement of lead parameters.
c. The reflections marked 'β' are those due to the β phase and should not be confused with Cu $K\beta$ lines, of which none was visible.

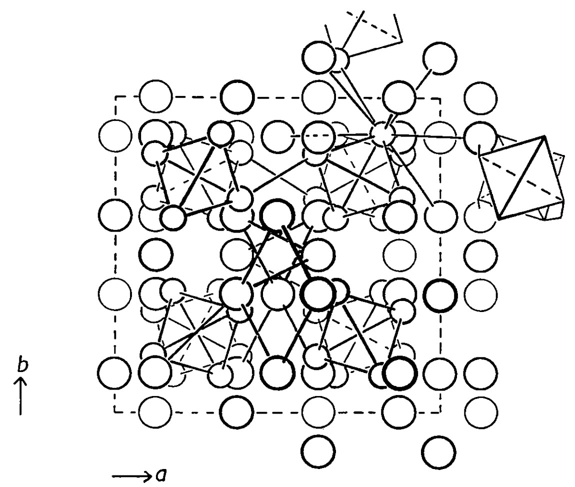

Fig. 3. Projection of the structure along the *c* axis, showing slightly more than a unit cell. The lower left corner has the coordinates $x = \frac{1}{4}$, $y = 0$.

corners of a square and are opposite four edges of the Pb_4 tetrahedron, and four other Na_{II} are arranged in pairs above and below (in the *c* direction) the Pb_4 tetrahedron. Each sodium atom is surrounded approximately tetrahedrally by Pb_4 groups.

Each lead atom has, besides the three other lead atoms in the tetrahedron, eight other near neighbors: four Na_I and three Na_{II} atoms, and one lead atom in an adjacent tetrahedron. Each Na_I atom has twelve near neighbours: three lead atoms in each of two adjacent tetrahedra, one lead atom in each of two more distant tetrahedra, and four equidistant Na_{II} atoms arranged in a distorted tetrahedron. Each Na_{II} atom has eleven near neighbors: two lead atoms in each of two tetrahedra, one lead atom in each of two other tetrahedra, four equidistant Na_I atoms arranged in a distorted tetrahedron, and one Na_{II} atom. Thus, although the packing symmetry around each atom is rather low, the coordination numbers of the various atoms are about the same as for other intermetallic compounds.

The interatomic distances calculated for the assigned parameters are listed in Table 2. The estimated

Table 2. *Interatomic distances and approximate bond numbers in* NaPb

		D(Å)	n
Pb–			
Pb	(2)	3·162	0·52
Pb	(1)	3·146	0·55
Pb	(1)	3·642	0·08
Na_{II}	(1)	3·36	0·25
Na_I	(1)	3·39	0·22
Na_{II}	(1)	3·42	0·20
Na_{II}	(1)	3·48	0·16
Na_I	(1)	3·49	0·15
Na_I	(1)	3·56	0·12
Na_I	(1)	3·62	0·09
			2·86
Na_I–			
Pb	(2)	3·39	0·22
Pb	(2)	3·49	0·15
Pb	(2)	3·56	0·12
Pb	(2)	3·62	0·09
Na_{II}	(4)	3·70	0·07
			1·44
Na_{II}–			
Pb	(2)	3·36	0·25
Pb	(2)	3·42	0·20
Pb	(2)	3·48	0·15
Na_I	(4)	3·70	0·07
Na_{II}	(1)	3·74	0·06
			1·54

probable errors are about 0·02 Å for the Pb–Pb distances, and 0·10 Å for distances involving sodium atoms.

These distances can be discussed by the application of Pauling's system of metallic radii and the equation (Pauling, 1947).

$$D_n = D_1 - 0{\cdot}600 \log_{10} n \,,$$

in which D_n is the observed internuclear separation (the bond distance for bond number n) and D_1 is the sum of the single-bond radii for the two bonded atoms. The single-bond radii are themselves functions of the valences of the atoms. The single-bond radii 1·572 Å for sodium and 1·523 Å for lead correspond to the valences 1 and 2·25, respectively, shown by the elements in the elementary state (Pauling, 1949; in this paper Pauling states that the valence of lead in the elementary state lies between the limits 2·0 and 2·5, with radii 1·540 and 1·506 Å, respectively). The bond orders calculated in this way, however, correspond when summed to valences of about 3·7 for lead and 2·2 for sodium, indicating that the values assumed initially are incorrect. The compound NaPb is one of those for which electron transfer is to be expected (Pauling, 1950); and it is found that the valences 2·9 for lead and 1·5 for sodium are satisfactory. These correspond to the single-bond radii 1·496 Å and 1·506 Å, respectively. These values are calculated by the equations representing the dependence of the metallic radius on the s and p character of the hybrid bond orbitals (Pauling, 1949), with the assumption that the amount of p character of the bond orbital for sodium with valence 1·5 is half way between that for normal sodium, with valence 1, and magnesium, with valence 2. The corresponding values of the bond numbers are given in the third column of Table 2. Their sums are within about 0·1 of the assumed valences, which, in view of the probable errors of the distances, is satisfactory self-consistency.

It is interesting to note that the bonds between each lead atom and its three neighboring lead atoms in the Pb_4 tetrahedron are approximately half bonds, with $n = 0{\cdot}5$. Each lead atom thus devotes about 1·5 valence units, of its total valence of 2·9, to bonds within the Pb_4 tetrahedron. From the consideration of bond numbers it is accordingly appropriate to describe the NaPb crystal as containing Pb_4 complexes, in each of which three covalent bonds resonate among the six Pb–Pb tetrahedral edges.

It is of some interest to see if any support for the above hypotheses can be obtained by comparing electron numbers (numbers of electrons per unit cell) with those corresponding to possible filled Brillouin polyhedra (Pauling & Ewing, 1948). The electron numbers corresponding to the valences discussed above are: 96 for the Hume-Rothery valences of 2 for lead and 1 for sodium, and 141 for respective valences (after electron transfer) of 2·9 and 1·5. On the assumption that the structure factors for electrons vary roughly parallel to those for X-rays, the planes with large structure factors in Table 1 may be examined and volumes in wave-number space may be calculated for various Brillouin polyhedra obtained by the mutual truncation of the corresponding forms. A polyhedron bounded by 60 faces, representing the mutual truncation of the forms {321}, {215}, {116}, {314}, and {400}, has a volume about 52 times that of the reciprocal unit cell, and therefore can accommodate quantum states (of both spins) for about 104 electrons. This provides suggestive agreement with the Hume-Rothery electron number of 96. There is a somewhat larger polyhedron bounded by 32 faces, representing the forms {323}, {206}, and {402}, which contains enough quantum states for about 136 electrons per unit cell, in good agreement with the number 141 which corresponds to valences 2·9 for lead and 1·5 for sodium.

A plausible argument can be made for the supposition that no conclusive interpretation based on Brillouin polyhedra would necessarily be expected; this is that the electrons which form Pb–Pb bonds within a given Pb_4 tetrahedron may be largely localized to the six bonds within that tetrahedron, and hence may show no significant 'free-electron' wave properties associated with relatively free motion (through resonance) from tetrahedron to tetrahedron. In this limited sense, NaPb may be considered as a metallic approach to a 'molecular crystal'. This interpretation may perhaps bear some relation to the reported existence of the ions Pb_7^{4-} and Pb_9^{4-} in liquid ammonia solution of sodium lead alloys (Zintl, Goubeau & Dullenkopf, 1931). In view of the existence of Pb_4 tetrahedra in NaPb, it is possible that the Pb_7^{4-} ion consists of two such tetrahedra sharing a vertex, and that the Pb_9^{4-} ion consists of three such tetrahedra sharing vertices so that a triangle is formed by three edges of the three different tetrahedra.

Quite possibly the presence of Pb_4 tetrahedra in NaPb is largely responsible for the high reactivity of NaPb toward alkyl halides (to form, for example, tetra-ethyl lead). Na_4Pb, which in the structure (for $Na_{15}Pb_4$) reported by Zintl & Harder (1936) contains mutually isolated lead atoms, shows a comparatively small reactivity. That Na_4Pb is a very stable phase is suggested by the fact that its melting point is high (about 385° C.) despite the large atomic proportion of sodium; NaPb melts at a somewhat lower temperature (about 367° C.). The greater reactivity of NaPb towards alkyl halides may be the result of the presence of more highly reactive sodium atoms, to be involved in the production of free alkyl radicals, or more highly reactive lead atoms, to take up the free radicals produced, or both. A greater reactivity for sodium may result from the fact that when sodium atoms are removed from the structure, with consequent exposure of lead atoms, the number of electrons devoted by the lead atoms to bonding is reduced to a lesser extent than in the case of $Na_{15}Pb_4$, since in NaPb such a considerable part of the bonding of a given lead atom is to other lead atoms in the tetrahedron. A greater reactivity for the lead atoms themselves may be expected because of the high asymmetry of the bonding around them, and perhaps also because of bond-angle strain. A rather broad general picture of the reaction of NaPb with an alkyl halide to form, for example, a lead tetra-alkyl, is suggested by these considerations: Free alkyl radicals are produced by the action of sodium atoms on the alkyl halide, and these may attack one or more exposed vertex atoms of a Pb_4 tetrahedron, forming C–Pb single bonds. After two or three alkyl radicals have become bonded to a Pb atom the Pb_4 tetrahedron may become unstable because the necessary increase in the lead valence to a value close to four (and the partial reversal of Pb to Na electron transfer due to the depletion of Na atoms in the neighborhood) would create a strong tendency for the Pb atom to form sp^3 bonds at tetrahedral angles (109° 28′). The consequent disruption of the tetrahedron might give immediately an R_3Pb radical which would take up another free radical to form R_4Pb; or perhaps R_3Pb–PbR_3 (or even $(R_3Pb)_4$) might be an intermediate.

The existence of 'molecular' groups of lead atoms, as Pb_4 tetrahedra in the alloy NaPb and as the reported Pb_7^{4-} and Pb_9^{4-} ions in liquid ammonia solution, must be regarded as an interesting and significant facet of lead chemistry well worthy of further investigation and discussion. It has heightened considerably our interest in the sodium–lead system, and further work on this system is being planned by one of us (D.P.S.) under a separate program.

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