On the Dubious Existence of a Second Na_4Pb Phase ($Na_{31}Pb_8$)[1]

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The crystal structure of a phase of composition $Na_{15}Pb_4$ was reported in 1936 by Zintl and Harder[2] (hereinafter designated Z and H). It has a body-centered cubic lattice, with $a_0 = 13.29$ kX. ($= 13.32$ Å.), with 16 Pb atoms and 60 Na atoms per unit cube. However, it was claimed previously by Stillwell and Robinson[3] (hereinafter designated S and R) on the basis of X-ray powder photographs that a phase to which they assigned the composition $Na_{31}Pb_8$ has a *face*-centered cubic lattice with $a_0 = 13.27$ kX. ($= 13.30$ Å.), and with 78 atoms (2×39) per unit cube (77.2 from observed density). (The number 78, being indivisible by four, is inappropriate to a face-centered cell, however.) In part because of the substantial identity of the lattice constants there has been some confusion as to whether it is the S and R result or the Z and H result that represents the phase commonly referred to as Na_4Pb, or whether, perhaps, the two results both represent existing phases of nearly this composition. Taken at face value as representing the same single phase, the two reported powder diagrams are mutually exclusive; one cannot be interpreted to give the other result, despite the fact that the two have some spacings in common (though with very different relative intensities). Moreover, previous thermal analysis work[4,5] does not indicate the existence of more than one phase in this region. Since the Z and H lattice is supported by a plausible structure ($D8_6$, represented also by $Cu_{15}Si_4$)[6] that provides agreement with observed intensities, and since the S and R lattice is supported by no plausible proposed structure and by no subsequent experimental confirmation, it must be the S and R result rather than the Z and H result that must be subject to any doubt that may exist. In our program of work on the structures of alloys in the Na–Pb system it appeared desirable to confirm or reject the S and R result, particularly in view of the fact that the S and R phase is frequently listed among the so-called gamma alloys (*e.g.*, Cu_5Zn_8, D82 and $Cu_{31}Sn_8$, D84).[7] As originally pointed out by S and R, with assumed Na and Pb valences of one and four, respectively, the formula $Na_{31}Pb_8$ yields the Hume-Rothery electron:atom ratio of 21:13, characteristic of the gamma alloys. It is, however, difficult to see how the S and R phase can be nearly as closely related, structurally, to the gamma alloys as these are to each other; the basic gamma alloy structure is based on a body-centered 52-atom cubic unit, while $Cu_{31}Sn_8$, which is face-centered cubic with twice the cell edge and eight times as many atoms (416), is apparently a superstructure on the 52-atom unit. The $Na_{15}Pb_4$ structure, with close to the same electron-atom ratio, shows no particular resemblance to the gamma alloy structure.

Experimental

A number of alloys were prepared with the compositions, as determined by subsequent analysis (which in all cases checked well with the intended compositions), given in Table I. These were prepared by melting together the constituents (approximately 30 g. Na, 80 g. Pb) under argon in an Aquadag-coated steel bomb sealed with a soft copper gasket, in an electric furnace at 420°. The Na used was Mallinckrodt analytical reagent grade, and the Pb was J. T. Baker C.P. analyzed (Ag-free). The bomb contained a welded-in tapered thermocouple well extending from the bottom to about the center.

TABLE I

Na_4Pb ALLOY PREPARATION AND POWDER PHOTOGRAPHY

Powder film no.	Analysis (at. % Na)[a]	Heat treatment[d]	Substances other than $Na_{15}Pb_4$ (Z and H) identified as present in small amount[b]
1001 1002	79.59 ± 0.05	B	None
1003	79.59 ± .05	D	(Pb), (Na_9Pb_4 and/or Na_5Pb_2)
1004	79.59 ± .05	C	(Na_9Pb_4 and/or Na_5Pb_2)
1005	83.21 ± .29	D	Na^c
1006	83.21 ± .29	C	Na^c
1007	83.21 ± .29	B	Na^c
2064 2071	80.33 ± .17	A	(Na^c)
2099 2101	78.11 ± .04	A	Na_5Pb_2
2111 2114	86.62	A	(Pb), (Na_9Pb_4 and/or Na_5Pb_2), Na^c
2137	80.33 ± .17	AE	Na_9Pb_4, Na_5Pb_2, Pb, (Na^c)
1031	80.33 ± .17	AF	Na_5Pb_2, Na_9Pb_4, Pb, (NaPb), (Na^c)

[a] Presented with average deviation of two or three results from the mean. For comparison: $Na_{15}Pb_4 = 78.95$, $Na_{31}Pb_8 = 79.49$, $Na_4Pb = 80.00$ at. % Na. [b] Listed in decreasing order of apparent amount present, from lines present on powder photographs. Parentheses indicate trace amounts. [c] Though it did not appear in photographs, Na was present in excess as was apparent from mechanical properties. Na probably segregated out in grinding alloy and filling capillaries. [d] A = annealed at about 280° for about 60 hours in accord with S and R procedure; B = quenched from the melt by immersing the bomb in cold water; C = quenched by dropping a fused silica tube containing the molten alloy into liquid nitrogen; D = slowly cooled from the melt without annealing: cooling curve taken; E = alloy ground with oil in presence of air; F = slurry (E) allowed to stand in air two hours before capillary filled.

The alloys were treated as summarized in Table I. Specimens for X-ray powder work were prepared by grinding the alloy with paraffin oil that had been dried by prolonged agitation (> 20 days) with liquid Na–K alloy, and drawing the slurry by capillary action into thin-wall Pyrex capillary tubes, about 0.3 mm. in diameter, that had been baked out under vacuum and subsequently exposed only to dry-box atmosphere prior to completion of filling and sealing operations. The filled capillaries were sealed with plicene. Materials handling and specimen preparation were carried out in a vacuum-tight box that was filled with welding-grade argon after having been evacuated to about one micron pressure. Powder photographs were taken with

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[1] This work was done under a Grant-in-Aid from the Ethyl Corporation, Chemical Department, Baton Rouge, Louisiana.

[2] E. Zintl and A. Harder, *Z. physik. Chem.*, **B34**, 238 (1936).

[3] C. W. Stillwell and W. K. Robinson, THIS JOURNAL, **55**, 127 (1933).

[4] C. H. Mathewson, *Z. anorg. Chem.*, **50**, 171 (1906).

[5] G. Calingaert and W. J. Boesch, THIS JOURNAL, **45**, 1901 (1923).

[6] Strukturbericht (*Z. Krist.*), *III*, 62, 366 (1933–35); *IV*, 138 (1936); F. R. Morral and A. Westgren, *Ark. Kem. Mineral. Geol.*, **11B**, 6 (1934).

[7] Strukturbericht (*Z. Krist.*), *I*, 497, 536, 547 (1913–1928); A. J. Bradley and J. Thewlis, *Proc. Roy. Soc. (London)*, **A112**, 678 (1926); A. Westgren and G. Phragmén, *Z. Metallkunde*, **18**, 279 (1926).

nickel-filtered copper Kα radiation in a North American Philips 114.59-mm. powder camera, Straumanis arrangement.

All photographs gave good patterns corresponding to the Z and H body-centered cubic structure ($Na_{15}Pb_4$) with spacings in good quantitative agreement with those previously reported and with intensities in good agreement as far as discernible. Only a few weak lines were found that could not be accounted for in this way; in most cases the substances giving rise to them could be identified as metallic lead or other alloys[8] in the system (see Table I). No evidence was found for the presence of the S and R phase; although in film 1003 and again in film 1004 a weak line was observed that could correspond to it, the line could be interpreted as a Na_9Pb_4 line or a Na_5Pb_2 line, and other lines required by the S and R phase were absent. The photographs of samples that had been exposed to air showed partial decomposition to Na_9Pb_4 and Na_5Pb_2 as well as to metallic lead.

The cooling curve for specimen 1003 showed a thermal arrest at 375°, and no other arrests or breaks. The cooling curve for specimen 1005 showed a thermal arrest at 364° and one at 97.6°, and no other arrests or breaks. These temperatures are approximate, having been measured with an uncalibrated thermocouple. (According to Mathewson[4] the maximum melting temperature in this region is 386° at the composition Na_4Pb, and the temperature of the eutectic with lead is 97°; the range of homogeneity at low temperatures is given as 78.5 to 80.0% Na.)

Discussion

In our experimental work we failed completely to duplicate the results of Stillwell and Robinson. Despite wide variation in initial composition and heat treatment the only phase obtained in quantity was the Z and H phase ($Na_{15}Pb_4$), together with small amounts of Na_5Pb_2 at the lowest Na concentration and excess Na at the highest Na concentration. Other substances were present only in very small or trace amounts, except when the alloy was exposed to air. This result appears to rule out the existence of an S and R face-centered phase stable at room temperature. If the alloy had been obtained by S and R through the accidental supercooling of a phase stable at a higher temperature we should expect a break in the cooling curve since the transformation must be rapid enough to take place in our fast quenching (treatment C, Table I). The conclusion appears inescapable that the results given by S and R differ from those obtained by Z and H and by us not in any essential difference in the structure of the alloy prepared but in the way in which diffraction data were obtained. In the work of S and R, the X-ray beam was diffracted by a single piece of the alloy, which was kept covered with mineral oil to prevent oxidation. The inference is strong that it was a non-rotating piece so oriented that the surface presented to the beam was smooth. Such a smooth surface might be that presented by the alloy to the wall of the iron crucible during preparation and annealing, or else the solidified free surface. In either case, or even with a cleaved surface (especially with incomplete protection from the air), a surface layer containing lead compounds other than Na_4Pb can easily raise. With copper Kα radiation the absorption coefficients for lead and its compounds are so high (for metallic lead, μ = 2600 cm.$^{-1}$) that a film a few microns thick suffices to prevent material beneath the film from receiving or diffracting the X-rays.

This result receives support from the failure of all of our attempts to devise a plausible structure containing 76 or 80 atoms in a face-centered cubic unit cell with a_0 = 13.3 Å. that would yield calculated powder intensities in accord with those reported by S and R. In particular, all possible structures in which the 16 Pb atoms are in *ordered* positions in a face-centered cubic cell have been ruled out by exhaustive trial and calculation based on the Pb atoms alone (since the Na atoms have relatively small scattering power). There are three possible ordered arrangements of 16 Pb atoms: (I) in positions 16(e) in T^2 or T_d^2 (*xxx*, . . .; *x* values were investigated at intervals of 0.015); (II) in positions 16(c) in T_h^4, O^4 and O_h^7; and (III) in positions 16(a) in O_h^8 or combinations of eight- and/or fourfold positions in ten other space groups.[9] Attempts to construct a *disordered* structure to the above requirements have not succeeded, though the search cannot be described as altogether exhaustive. The most promising structure ((IV), with space group T_d^2, 80 atoms per unit cube), which was arrived at via several different paths, can be obtained by placing a gamma-phase 26-atom grouping (4A + 4B + 6C + 12D)[7] at each lattice point, with sharing of the D atoms between pairs of groupings. Packing is reasonably satisfactory, and distances are normal or only slightly shorter than expected. With Pb atoms as A (or B) in ordered arrangement the lead atoms are in Pb_4 tetrahedra, as in NaPb,[10] but this assignment, being a case under arrangement (I) above, fails to fit the S and R data. Disordered versions of this structure with statistical assignment of Pb to A and B, or to all four positions, also fail. No other suitable structure based on resemblance to the gamma phase structure has been found. Other attempts, based on a cubic closest packed substructure with a subcell edge (4.43 Å.) equal to one third of the S and R cell edge, failed to yield a plausible structure containing as few as 80 or 76 atoms per unit cube. This line of attack was suggested by the fact that all lines predicted by the subcell with spacings within the S and R experimental range are in fact reported by S and R, accounting for 9 out of the 26 reported lines (out of the 68 possible in the range Σh^2 = 24 through 224). The possibility that the S and R data are due to a non-cubic structure, specifically tetragonal or hexagonal, was examined with Hull-Davey charts, but no promising indications were obtained.

The S and R spacings have been compared with those of all other known alloys in the Na–Pb system and with Na and Pb themselves, as well as of a large number of their compounds (oxides, hydroxides, carbonates, plumbates, etc.), largely with the aid of the Hanawalt index,[11] in an attempt to find an alternative interpretation of the S and R data. No significant agreement, constituting a possible basis for an identification, was obtained.

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(8) I. T. Krohn, R. C. Werner and H. Shapiro, THIS JOURNAL, **77**, 2110 (1955); D. P. Shoemaker, N. Weston and J. Rathlev, work in progress.

(9) "International Tables for X-Ray Crystallography," The Kynoch Press, Birmingham (England), 1952.

(10) R. E. Marsh and D. P. Shoemaker, *Acta Cryst.*, **6**, 197 (1953).

(11) J. Hanawalt, H. W. Rinn and L. K. Frevel, *Ind. Eng. Chem., Anal. Ed.*, **10**, 457 (1938).

In summary, it appears overwhelmingly probable that the S and R data apply not to an alloy of approximate composition Na_4Pb but to some other substance or substances as yet unidentified, and possibly of unknown constitution and structure.

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The Reaction of Chlorosilanes with Benzaldehyde

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Rochow and Gingold[1] recently stated that they did not succeed in combining chlorosilanes with aldehydes, including benzaldehyde, to form siloxanes, even on boiling for 3–4 days, the starting products being obtained again in unchanged form. In this respect I wish to report on work carried out on this reaction, though with different scope and aims.

Silicon tetrachloride reacts with benzaldehyde on being allowed to stand at room temperature, the reaction being expressed by the gross equation

$$SiCl_4 + C_6H_5COH \longrightarrow (SiCl_2O)_n + C_6H_5CHCl_2$$

If $SiCl_4$ is allowed to stand together with benzaldehyde, after a few weeks these liquids which mix well show an increase in viscosity which is somewhat accelerated by exposure to daylight. Demixing occurs in two phases after 2–3 months. This phenomenon is caused more rapidly at elevated temperatures. Likewise, in the gaseous phase $SiCl_4$ reacts with benzaldehyde within the sense of the above equation. The lighter one of the two layers consisted chiefly of excess benzaldehyde and benzal chloride as well as a small quantity of chloropolysiloxane while the heavy phase consisted to the major part of chloropolysiloxane. The latter was obtained as a residue in the fractional distillation. The determination of the molar weight estimate resulted in values between 1800 and 2000. The chlorine values of these polysiloxanes, calculated on hydrolyzable chlorine, were correspondingly around 60% with the silicon values around 26%. The index n in the formula $(SiCl_2O)_n$ thus appears to be in the order of 15.

While always an excess of benzaldehyde reacted with $SiCl_4$ in all the cases examined, the reaction did not proceed beyond the formation of a chloropolysiloxane. It appears to be probable, however, that the reaction will proceed to the formation of SiO_2 with sufficiently long periods of exposure or more critical conditions.

As shown by orientating qualitative experiments, the reaction is not limited to $SiCl_4$ but also proceeds in a corresponding manner in the case of organochlorosilanes, *e.g.*, phenyltrichlorosilane.

The reaction appears to take place in two stages. In a first stage the $SiCl_4$ will add on the CO double link of the aldehyde

$$Cl_3SiCl + O{=}CHC_6H_5 \longrightarrow Cl_3SiOCHClC_6H_5 \quad (1)$$

This product seems to react relatively rapidly with a further SiCl link to form

$$Cl_3SiOCHClC_6H_5 \longrightarrow Cl_3SiOSiCl_3 + C_6H_5CHCl_2 \quad (2)$$

No such products as result from equation 1 were isolated.

The apparent discrepancy with respect to the work of Rochow and Gingold can satisfactorily be accounted for by these two authors only having tried triphenylchlorosilanes with benzaldehyde.[2] In the case of this silane the reaction is strongly inhibited for steric reasons, and the reactivity of the SiCl linkages is unfavorably influenced by the three phenyl groups.

This suggestion is supported by the observed fact that already the $PhSiCl_3$ reacts with benzaldehyde somewhat slower than $SiCl_4$.

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[1] E. G. Rochow and K. Gingold, THIS JOURNAL, **76**, 4852 (1954).

[2] Private report by Prof. E. G. Rochow.

Phase Diagram of the System $KNbO_3$-$KTaO_3$ by the Methods of Differential Thermal and Resistance Analysis

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$KNbO_3$ and $KTaO_3$ both exhibit the ABO_3 perovskite structure, but have widely separated Curie points. The unit cell size of both compounds, in the cubic state, differs only slightly.[1] On the basis of this, and the isomorphic nature of tantalum and niobium compounds, a strong possibility for solid solution interaction between the meta salts was seen to exist. If such an interaction takes place, it might be possible to prepare dielectric ceramics with Curie points ranging between 13 and 688°K., the Curie temperatures of $KTaO_3$ and $KNbO_3$, respectively.[2,3] Resolution of the diagram would provide needed information for the preparation of the necessary ceramic materials.

The solidus curve of a solid solution is generally more difficult to determine than the liquidus curve. The graphical extrapolation method employed by Tammann[4] and later modified by Campbell and Prodan[5] was found inapplicable because of the difficulties in attaining reasonable equilibrium throughout the cooling range. The standard heating curve techniques are at best laborious, and if not performed with the utmost care tend to give low results.[6] If applicable, quenching methods are invaluable, but in this system the tendency for crystallization to occur, even with small charges,

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[2] J. K. Hulm, B. T. Matthias and E. A. Long, *Phys. Rev.*, **79**, 885 (1950).

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[6] G. W. Morey, Jr., *Wash. Acad. of Sci.*, **13**, 326 (1923).