Conclusion

The intensity of a diffracted x-ray beam has been found to be decreased by surface irregularities of the target in proportion to their magnitude and to the coefficient of absorption of the target material for the wave length involved. This effect was studied for grids of various size and powdered particles of metals and compounds of various diameter. For accuracy in quantitative chemical analysis based on x-ray spectroscopy attention must therefore be given to the fineness of the powdered samples, more especially when $L\alpha$ radiation is involved.

SCHENECTADY, NEW YORK RECEIVED JULY 20, 1932
PUBLISHED JANUARY 11, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Sodium-Lead Alloys. The Structure of the Compound Known as Na_4Pb

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A number of recent investigations have shown that when copper, silver or gold is alloyed with cadmium, zinc, tin or aluminum, the same types of crystal structures often occur in each binary alloy even though the empirical formulas of the compounds differ. The type structure of any specific compound seems to depend upon the ratio between the number of atoms and the number of valence electrons in the molecule.[1]

The behavior of binary alloys of these three metals is fairly consistent and it is of considerable interest to know whether similar relations hold for alloys in which the first group metal is an alkali metal. The only x-ray study of such alloys which has been reported is that for the lead rich end of the sodium-lead system, up to 32 atomic per cent. of sodium.[2] An extension of the data for this system is therefore desirable. The present paper presents an analysis of the crystal structure of the compound usually designated as Na_4Pb.

Experimental Part

The alloy was prepared by melting together in an iron crucible the theoretical quantities of sodium and lead, making due allowance for the evaporation of some sodium. Cooling curves showed the initial break at the melting point of the compound Na_4Pb indicated in the equilibrium diagram.[3] The alloy was annealed for sixty hours at 280–300° in an atmosphere of argon.

A Mueller tube and CuK_α radiation were used for obtaining the diffraction patterns. The camera was essentially the Debye–Scherrer type tipped on edge so that it rested on the curved surface instead of on the base of the cylinder. With this arrangement the specimen may be mounted at the center of curvature and kept covered with mineral oil

(1) Westgren and Phragmen, *Trans. Faraday Soc.*, **25**, 379 (1929).
(2) Zintl and Harder, *Z. physik. Chem.*, **154**, 79 (1931).
(3) Calingaert and Boesch, THIS JOURNAL, **45**, 1901 (1923).

to prevent oxidation during the exposure. The x-ray beam is thus diffracted from the surface of a single piece of the alloy and good patterns may be obtained in a relatively short time. There are several obvious sources of error in this type of camera, but repeated calibration with pure metals has demonstrated that the maximum error in the determination of the interplanar spacings is 0.5%, and in general the error is somewhat less.

Complete diffraction data for the compound are listed in Table I. The values in column II are average values from four different films made from four different specimens of the alloy.

TABLE I

DIFFRACTION DATA FOR THE COMPOUND Na_4Pb ($Na_{31}Pb_8$)

Int.	Cm.	$\sin^2\theta$	d_{hkl}	$h^2+k^2+l^2$	a_0
vs	3.96	0.0802	2.719	24	13.30
m	4.23	.0914	2.547	27	13.25
m	4.61	.1071	2.353	32	13.30
m	4.91	.1215	2.209	36	13.25
w	5.70	.1609	1.920	48	13.30
s	5.95	.1746	1.843	52	13.29
s	6.23	.1887	1.772	56	13.27
w	6.38	.1991	1.726	59	13.25
s	7.08	.2410	1.569	72	13.30
m	7.28	.2538	1.528	76	13.30
vw	7.76	.2839	1.445	84	13.23
s	8.35	.3233	1.354	96	13.28
w	8.53	.3356	1.329	99	13.21
w	8.74	.3505	1.301	104	13.28
w	8.97	.3655	1.274	108	13.26
m	9.46	.4003	1.217	120	13.31
m	9.65	.4140	1.197	123	13.29
w	9.86	.4287	1.176	128	13.30
w	10.23	.4564	1.140	136	13.29
w	10.54	.4791	1.112	144	13.33
w	11.06	.5157	1.072	152	13.21
m	11.93	.5782	1.013	171	13.25
w	12.31	.6057	0.9894	180	13.27
w	13.06	.6570	.9500	195	13.25
w	14.23	.7347	.8983	216	13.21
w	14.56	.7560	.8855	224	13.27
					Av. 13.27 ± 0.035 Å.

Discussion

The analysis indicates a face-centered cubic lattice in which $a_0 = 13.27 \pm 0.035$ Å. The error indicated is 0.5%, the maximum error established by the calibration of the camera. It is evident that most of the values for a_0 are well within this limit.

The structure of this phase suggests that it is analogous to the γ-phase of the copper, silver and gold alloys. Of these, Cu_5Zn_8, Cu_9Al_4 and $Cu_{31}Sn_8$ are typical examples. These are similar in that they have cubic structures

with large unit cells and in each the ratio of valence electrons to atoms is as 21:13. They differ in detail. Thus Cu_5Zn_8 is body-centered cubic and contains 52 atoms in the unit cell;[4] Cu_9Al_4 is simple cubic and contains 52–49 atoms per unit cell;[5] $Cu_{31}Sn_8$ is face-centered cubic, containing 416 atoms per unit cell.[6] In order that the number of molecules in a unit cell may be a whole number, Bernal[7] assigns the formula $Cu_{41}Sn_{11}$ to this copper–tin phase.

If it is assumed, as it was for the γ-phase of the copper–tin system, that the more exact formula for the compound Na_4Pb is $Na_{31}Pb_8$, then the 21:13 value for the ratio of valence electrons to atoms is satisfied. The density of $Na_{31}Pb_8$ has been determined as 3.31 at 25° and from this value the number of atoms in the unit cell has been calculated as 77.2. This is sufficiently close to 78 to indicate that there are two molecules in the unit cell.

Another check is furnished by the data of Zintl.[2] He has reported a face-centered cubic structure (Na_2Pb_5 and Na_4Pb_9), containing four atoms in the unit cell in which $a_0 = 4.872 - 4.883$ Å. The side of the unit cell of $Na_{31}Pb_8$ is about 2.72 times as long as the above and the volume of $Na_{31}Pb_8$ is therefore twenty times that of the smaller cell. From these figures the number of atoms in the unit cell of $Na_{31}Pb_8$ has been calculated as 80, which agrees significantly with the value 77.2 determined from the density.

We are grateful to Dr. G. Calingaert of the Ethyl Gasoline Corporation, who prepared the alloys for this study, and to Dr. G. L. Clark of this Department, who suggested a study of sodium–lead alloys.

Summary

Diffraction data for the compound usually designated as Na_4Pb have been analyzed. The analysis indicates that the structure of this compound is face-centered cubic, with $a_0 = 13.27 \pm 0.035$ Å. There are 78 atoms in the unit cell. It is apparently analogous to the familiar γ-phase of copper, silver and gold alloys and its more exact formula is therefore $Na_{31}Pb_8$.

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RECEIVED JULY 23, 1932
PUBLISHED JANUARY 11, 1933

(4) Bradley and Thewlis, *Proc. Roy. Soc.*, (London) **A112**, 678 (1926).
(5) Bradley, *Phil. Mag.*, **6**, 878 (1928).
(6) Westgren and Phragmen, *Z. anorg. allgem. Chem.*, **175**, 80 (1928).
(7) Bernal, *Nature*, **122**, 54 (1928).