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The Structure of Alloys of Lead and Thallium*

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Alloys of lead and thallium have a structure based upon cubic closest packing from 0 to about 87·5 atomic percent thallium. The variation of the lattice constant with composition gives strong indication that ordered structures $PbTl_3$ and $PbTl_7$ exist. In the intermediate ranges, solid solutions of the types $Pb(Pb,Tl)_3$ and $Pb(Pb,Tl)Tl_6$ exist. Interpretation of interatomic distances indicates that thallium atoms present in low concentration in lead assume the same valence as lead, about 2·14, and that the valence of thallium increases with increase in the mole fraction of thallium present, having the same value, about 2·50, in $PbTl_3$ and $PbTl_7$ as in pure thallium. A theory of the structure of the alloys is presented which explains the observed phase diagram, and which in particular accounts for the existence of a maximum melting point at about 63 atomic percent thallium.

1. Introduction

The binary system lead–thallium shows an unusual type of phase diagram. Fig. 1, taken from Hansen (1936), represents in the main the results obtained by Kurnakow & Pushin (1907) and by Lewkonja (1907). The liquidus curve in the wide solid-solution region has a maximum at about 63 atomic percent thallium. The nature of this maximum has not previously been made clear.

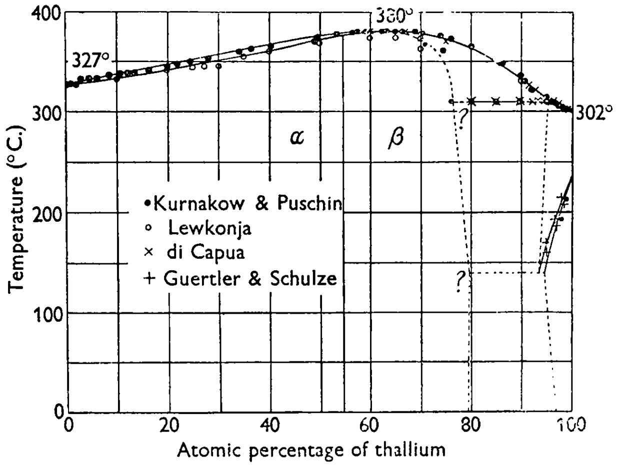

Fig. 1. The phase diagram of the alloy system lead–thallium taken from Hansen (1936).

The electric resistivity was measured by Kurnakow & Schemtschushny (1909) and by Guertler & Schulze (1923), and was found to vary smoothly, with no indication of the presence of a compound such as $PbTl_2$ or Pb_2Tl_3. McMillan & Pauling (1927) prepared X-ray powder photographs of alloys representing ten compositions. The only X-ray diffraction lines shown by the samples with from 0 to 80 atomic percent thallium were those corresponding to the cubic closest-packed arrangement *A* 1, with the lattice constant decreasing from 4·948 kX. for pure lead to 4·858 kX. for 80 atomic percent thallium. Halla & Staufer (1928) reported results from a single crystal of an alloy containing 65 atomic percent thallium which substantiated those of McMillan & Pauling. Ölander (1934) noticed that the lattice constants reported by McMillan & Pauling did not vary linearly with the composition, and he determined the constants for eleven alloys, with greater precision. He was able to represent his values for a_0 by two straight lines intersecting at 54·6 atomic percent thallium, and therefore postulated that below 54·6 atomic percent thallium the alloys are present in a random solid solution, phase α, and above this composition in a partially ordered phase, phase β (Fig. 1). He suggested that the perfectly ordered arrangement of the β phase would conform to the formula $PbTl_7$.

The present investigation was carried out in order to test Ölander's suggestion and to obtain additional information about the nature of these alloys.

2. The preparation and X-ray photography of the alloys

Alloy samples weighing either 100 or 25 g. were prepared by melting weighed amounts of lead and thallium together. The c. p. granular test lead, free from silver, gold and bismuth (Fisher Scientific Company), was indicated by spectroscopic examination to contain approximately 0·005 % iron, 0·001 % thallium and 0·001 % copper. The thallium used was supplied by the Varlacoid Company. Spectroscopic examination showed the presence of approximately 0·01 % lead, 0·005 % iron, and 0·001 % copper.

The meltings occurred in Pyrex tubes under a vacuum of about 10^{-5} mm. Hg. The uniformity of the reguli with respect to composition was achieved by two measures: first, the alloys were kept in the molten state about 100° C. above their melting-points for more than 2 hr.; and secondly, effective agitation was provided by a magnetically driven stirring device.

Twenty-one samples were prepared and investigated.

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All but three of these samples were analyzed chemically and spectroscopically by the Smith-Emery Company of Los Angeles. The chemical analyses (Table 1) agreed with the synthetic compositions to within ±0·3 %. Duplicate 2 g. samples of each of sixteen of the alloys were analyzed and found to have the same composition, showing the alloys to be homogeneous.

Table 1. *Chemical analyses and lattice constants*

Sample	Atomic percent of thallium	Lattice constant a_0 (Å)
1	0	4·947$_4$ ± 0·001
2	4·9 ± 1·0	4·946$_0$ ± 0·001
3	11·2 ± 0·5	4·942$_4$ ± 0·001
4	21·1 ± 0·5	4·934$_7$ ± 0·001
5	30·8 ± 1·0	4·927$_1$ ± 0·001
6	40·6 ± 1·0	4·918$_7$ ± 0·001
7	50·4 ± 0·5	4·908$_6$ ± 0·001
8	53·5 ± 1·0	4·906$_2$ ± 0·001
9	55·4 ± 1·0	4·902$_8$ ± 0·001
10	61·1 ± 1·0	4·897$_4$ ± 0·001
11	64·7 ± 1·0	4·892$_9$ ± 0·001
12	67·6 ± 1·0	4·887$_8$ ± 0·001
13	70·6 ± 1·0	4·885$_5$ ± 0·001
14	75·0 ± 1·0	*A* 4·879$_5$ ± 0·002 *B* 4·874$_0$ ± 0·002
15	77·1 ± 1·0	4·870$_0$ ± 0·002
16	80·5 ± 1·0	4·867$_1$ ± 0·002
17	83·9 ± 1·0	4·863$_6$ ± 0·002
18	87·8 ± 1·0	4·856$_0$ ± 0·002
19	93·4 ± 1·0	4·856$_4$ ± 0·002
20	96·9 ± 1·0	
21	100·0	

In an atmosphere of carbon dioxide, filings from the reguli were screened through a 200-mesh sieve and collected in thin-walled glass capillaries about ½ mm. in diameter. The capillaries were then evacuated and sealed, and the specimens were annealed at 280° C. for 40 hr. and allowed to cool at the rate of about 0·001° C./sec. (It was observed that specimens which were not annealed gave diffuse diffraction lines; the lines were made sharp by the process of annealing as described above.)

A series of powder photographs was taken in a Norelco camera 360 mm. in circumference which holds the film in the Straumanis arrangement and permits a maximum Bragg angle of 87·5°. The copper *K* radiation was filtered through 0·001 in. nickel foil. Eastman No-Screen X-ray film was used throughout. All photographs were taken at room temperature, 26 ± 2° C.

The diffraction patterns for the eighteen samples with between 0 and 87·8 atomic percent thallium correspond in positions and relative intensities of the lines to the *A* 1 arrangement. The photographs for 93·4 and 96·9 atomic percent thallium show this pattern, and in addition the lines of the room-temperature modification of thallium, which has the *A* 3 structure. The sample of pure thallium shows only the latter pattern.

For the alloys containing less than 70 atomic percent thallium the powder photographs showed the reflection 620. For the other alloys in the *A* 1 phase the photographs contained reflections only as far as 600 and 442. The presence of the reflection 620 at Bragg angles varying from 80·7 to 85·5° significantly improves the accuracy of the lattice constants derived from the former photographs.

For each photograph the measurements for the various lines were found to be satisfactorily represented by a straight line when plotted according to the method of Nelson & Riley (1945). This straight line was always drawn through the point representing the diffraction line observed at the maximum Bragg angle. The wavelengths 1·5405 Å for copper $K\alpha_1$, 1·5443 Å for copper $K\alpha_2$ and 1·5418 Å for the unresolved doublet were used. The values of a_0 obtained in this way are given in Table 1.

Two checks of the accuracy of the determinations of the lattice constants were made. Filings of samples 2 and 3 were placed in capillary tubes of two different diameters, and photographs were made and interpreted. For each sample the same lattice constant was obtained from the two photographs. For samples 11 and 14 filings were prepared from two different portions of the 25 g. sample, and powder photographs were prepared. In the case of specimen 11 the lattice constant determined from the two preparations was the same, whereas for specimen 14 values differing by 0·0055 Å were obtained. We believe that the latter variation is due to a small difference in composition, perhaps 0·5 %, in the two samples; the lattice constant is very sensitive to composition in this region.

3. Interpretation of the results

The values found for a_0 are shown in Fig. 2 as a function of composition. They are not linearly dependent upon the composition, but instead can be represented by two smooth curves, one covering the range 0–75 atomic percent thallium, and the other the range 75–87·5 atomic percent thallium. The lattice period of the *A* 1 phase is constant for the alloys with more than 87·5 atomic percent thallium, which indicates that the limit of solubility of thallium in lead is about 87·5 atomic percent. No evidence is provided by our investigation to support Ölander's suggestion of a discontinuity in slope of the lattice-constant curve at 54·6 atomic percent thallium. Our results are compared with those of Ölander and of McMillan & Pauling in Fig. 3. The values of a_0 reported by McMillan & Pauling agree with the new curve to within their estimated error of ±0·1 %, as indicated by the span of the vertical lines. We think that it is likely that the disagreement between our curve and some of the values reported by Ölander is due to a somewhat larger error in his determination than that (±0·02 %) suggested by him.

A reasonable interpretation can be given to the curve of Fig. 2, with its two discontinuities in slope: namely, that there exist ordered phases $PbTl_3$ and $PbTl_7$. Direct evidence from the intensities of X-ray reflections is not obtained for ordering in this case, because of the approximate equality in *f* values of lead and thallium. We can, however, discuss the probable structures of the ordered phases. The powder patterns given by these alloys show no splitting of lines. We estimate that the splitting corresponding to a deviation greater than 0·002 from unity in axial ratio could be detected; accordingly, it is very likely that no superstructure involving deviation from cubic symmetry is present. None of the photographs shows any lines requiring the assumption of a unit of structure larger than the four-atom unit. The near equality in scattering powers of lead and thallium would permit a cubic superstructure based on a larger unit to be present, in case that the atoms were at or very near the positions corresponding to the $A1$ arrangement. However, if the atoms were to be shifted appreciably from these positions (by as much as, say, 0·2 Å) observable diffraction lines requiring the larger unit would be expected.

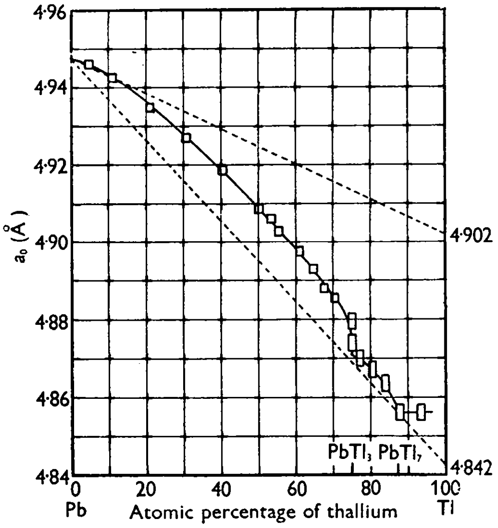

Fig. 2. The lattice-constant curve based on values given in Table 1. The edge lengths of squares and rectangles give the magnitude of uncertainties in a_0 and composition.

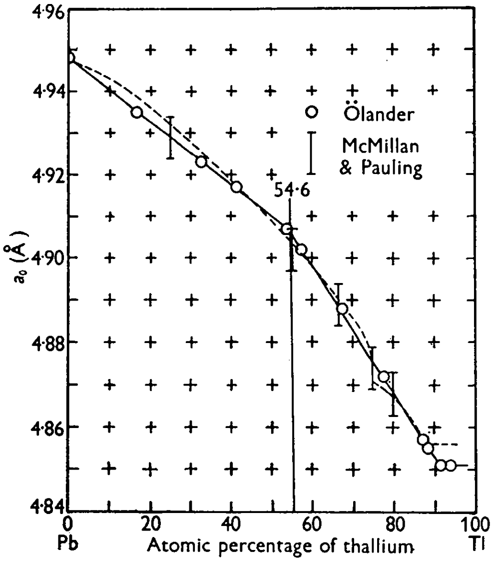

Fig. 3. The two-straight-line result as reported by Ölander. McMillan & Pauling's values are given for comparison. The new lattice-constant curve is also included.

Let us consider the types of superstructure compatible with the assumption that the atoms are completely ordered and occupy with cubic symmetry exactly the points of the $A1$ arrangement. The theory of space groups shows that for two elements, A and B, there exist only two structures compatible with this assumption. These are the structure AB_3 (Fig. 4) and AB_7 (Fig. 5). The structure of AB_3 is the $AuCu_3$ arrangement, with one atom A at 0, 0, 0 and three B at $\frac{1}{2}, \frac{1}{2}, 0$; $\frac{1}{2}, 0, \frac{1}{2}$; and $0, \frac{1}{2}, \frac{1}{2}$. The structure AB_7 is based on a face-centered lattice, the cubic unit containing 32 atoms in the positions indicated. In this structure the atoms B are not all crystallographically equivalent, but are of two types; the structure can in fact be achieved for three elements, A, B and C, and might be realized by a compound ABC_6, as indicated in Fig. 6.

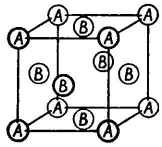

Fig. 4. The structure AB_3.

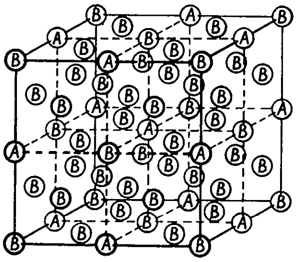

Fig. 5. The structure AB_7. $Z=4$.

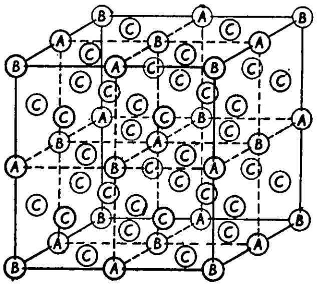

Fig. 6. The structure ABC_6. $Z=4$.

These are the only cubic arrangements provided by the theory of space groups in which every atom occupies an invariant position, and all of the atomic positions are those corresponding to the $A1$ arrangement. Very recently we have found that the cubic phase 'Pt_3Cu' is highly probably also based upon the cubic structure ABC_6 (Tang, 1951).

4. Interatomic distances in the alloys

According to our interpretation the lead–thallium alloys in the range 0–75 atomic percent thallium have the structure $Pb(Pb, Tl)_3$, and between 75 and 87·5 atomic percent thallium they have the structure $Pb(Pb, Tl)Tl_6$. The values of a_0 shown in Fig. 2 indicate that at 75 atomic percent thallium there is nearly complete order, corresponding to the compound $PbTl_3$.

It is possible to discuss the interatomic distances in relation to the valences of lead and thallium. From the system of metallic radii (Pauling, 1949) and the relation

$$D_n = D_1 - 0{\cdot}600 \log n$$

connecting interatomic distance D_n for bond number n with the interatomic distance for a single bond, D_1, which is equal to the sum of the single-bond radii of the two atoms, we calculate for lead in the pure element the valence 2·14 and for thallium in the pure element the valence 2·50, corresponding to lattice constant 4·842 Å for the $A\,1$ structure. It is interesting that a straight line drawn between the lattice constant for pure lead and that predicted for thallium with the $A\,1$ structure passes through the values of a_0 for the compounds $PbTl_3$ and $PbTl_7$, as shown in Fig. 2. At other compositions the observed values of a_0 are larger than those predicted from the linear relation. We conclude that in the intermediate ranges the strain introduced by isomorphous replacement of lead by thallium increases the lattice constants, perhaps by causing thallium to assume a slightly lower valence.

In connection with a discussion of alloys of aluminum and zinc (Pauling, 1949) it was pointed out that an element present in very small quantity in solid solution in another element would have a tendency to assume the valence of the second element. The upper straight line in Fig. 2 is drawn between the value of the lattice constant for pure lead and that calculated for thallium with valence 2·14, equal to that of lead in the state of the pure element. It is seen that it passes through the experimental values of a_0 for the alloys with 4·9 and 11·2 atomic percent thallium, thus supporting the suggestion that in these dilute alloys thallium has assumed the same valence as its solvent, lead.

5. An explanation of the maximum melting point of alloys in the lead-thallium system and related binary systems

We have found it possible to formulate a simple treatment of the lead–thallium alloys that accounts satisfactorily for the existence of a maximum in melting-point displaced from the composition $PbTl_3$ of the ordered structure, and that also accounts in a reasonably satisfactory way for the shapes of the liquidus and solidus curves throughout the range 0—75 atomic percent thallium (Fig. 1). The maximum in these curves occurs at a composition near that for a compound Pb_2Tl_3 or a compound $PbTl_2$. If either of these compounds existed, it would have to be considered as forming solid solutions with lead and with thallium. The data, however, give no evidence for the existence of such compounds.

A very simple treatment can be carried out by assuming that the liquid phase is a series of ideal solutions of lead and thallium, and that in the solid phase isomorphous replacement of thallium atoms in the $PbTl_3$ structure by lead atoms occurs in the way corresponding to the formation of an ideal solution. For the liquid phase the free energy would then be represented by the expression

$$F^0(l) = F^0_0(l) + ax - RT[x \ln x + (1-x)\ln(1-x)].$$

The term ax represents an assumed linear dependence of the free energy of the liquid solution on the mole fraction of thallium, x, and the last term in the expression is the free energy of mixing. For the solid phase in the range $0 \leqslant x \leqslant 0{\cdot}75$ we assume the free energy to be given by the expression

$$F^0(c) = F^0_0(c) + bx - RT[x \ln x + (\tfrac{3}{4}-x)\ln(\tfrac{3}{4}-x) - \tfrac{3}{4}\ln\tfrac{3}{4}].$$

Here the first term is the free energy of pure crystalline lead, the second term an assumed linear dependence on composition, and the third term the free energy of mixing lead and thallium in the atomic positions 0, $\frac{1}{2}$, $\frac{1}{2}$; $\frac{1}{2}$, 0, $\frac{1}{2}$; and $\frac{1}{2}$, $\frac{1}{2}$, 0 of the unit cube. Curves representing these expressions are shown in Fig. 7. The value of a has been put equal to 0 (this simplification does not affect the conclusions drawn below), and the value of b has been taken such as to cause the two curves to osculate at the composition $x = 0{\cdot}63$, as is indicated at the top of the diagram. At a somewhat decreased temperature, represented by the curves in the middle of the diagram of Fig. 7, the curves for liquid and solid intersect in such a way as to permit two common tangential lines to be drawn. Each of these lines, in the region between its points of tangency with the curves, represents a two-phase system, and the points of tangency give the compositions of liquidus and solidus corresponding to the temperature. The curve at the bottom of the diagram corresponds to the temperature

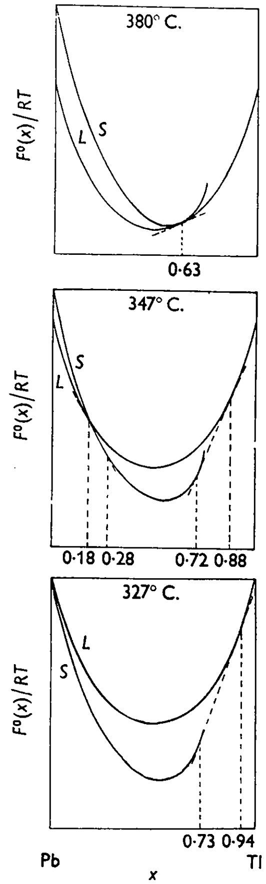

Fig. 7. The free-energy curves and the derivation of the liquidus and solidus curves.

of melting of pure lead; the points of tangency of the straight line at the right side of the diagram give the compositions of liquidus and solidus for the solid solutions of high thallium content.

The phase diagram constructed in this way, with the assumption that the difference in free energy of liquid lead and solid lead, $F^0_0(l)-F^0_0(c)$, is a linear function of the temperature, and that the other parameters remain unchanged, is shown as Fig. 8. It is seen that it is qualitatively similar to the phase diagram for the lead–thallium system in the range 0–75 atomic percent thallium.

This simple theory is unsatisfactory, in that the rate of change of the difference in free energy of liquid and crystalline lead predicted by the Clausius–Clapeyron equation leads to a temperature scale for Fig. 8 four

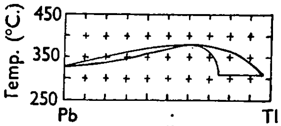

Fig. 8. The phase diagram derived from the free-energy curves in Fig. 7.

times as great as that in Fig. 1. This lack of agreement is eliminated if the assumption is made that the free energy of the crystalline phase depends in a more striking way on the characteristics of the ordered phase PbTl$_3$. In PbTl$_3$ each lead atom is surrounded by twelve thallium ligates, with the configuration corresponding to the cubic closest-packed arrangement, and each thallium atom is surrounded by eight thallium ligates and four lead ligates, the latter lying in an equatorial plane. It is not unreasonable to assume that the ordering is the result of a special stability of this configuration of eight thallium atoms and four lead atoms about each thallium atom. If we assume that a stabilizing contribution to the free energy of the crystalline phase is made by each thallium atom with this configuration, and that the thallium and lead atoms are distributed at random among the points 0, $\frac{1}{2}$, $\frac{1}{2}$; $\frac{1}{2}$, 0, $\frac{1}{2}$ and $\frac{1}{2}$, $\frac{1}{2}$, 0, we conclude that a term cx^9 should be included in the free-energy expression for the crystal. A similar term might also be included in the free-energy expression for the liquid, but it is found to be so small in comparison with that in the crystal as to permit its neglect. We accordingly replace the expression in equation (2) by an expanded expression, obtained by adding the term cx^9 on the right side of this equation. When this is done, it is found that suitable values of b and c can be determined such as to make the maximum melting-point occur at $x=0{\cdot}63$, as observed, with the temperature coefficient of $F^0_0(l)-F^0_0(c)$ equal to the value given by the Clausius–Clapeyron equation

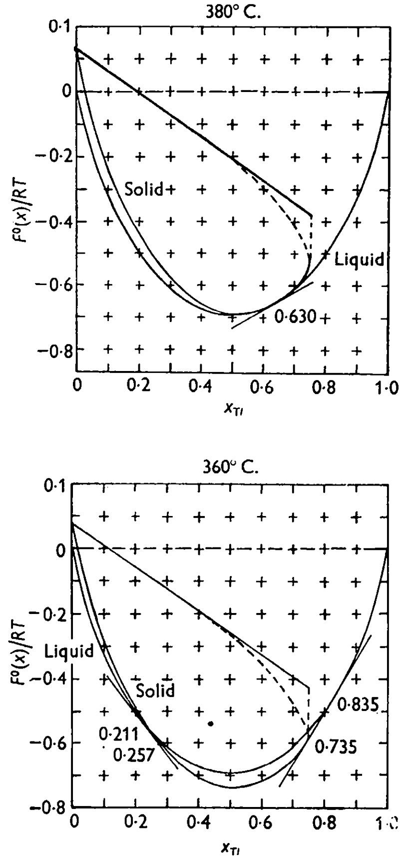

Fig. 9. The free-energy curves calculated with the inclusion of the term cx^9 for the solid phase.

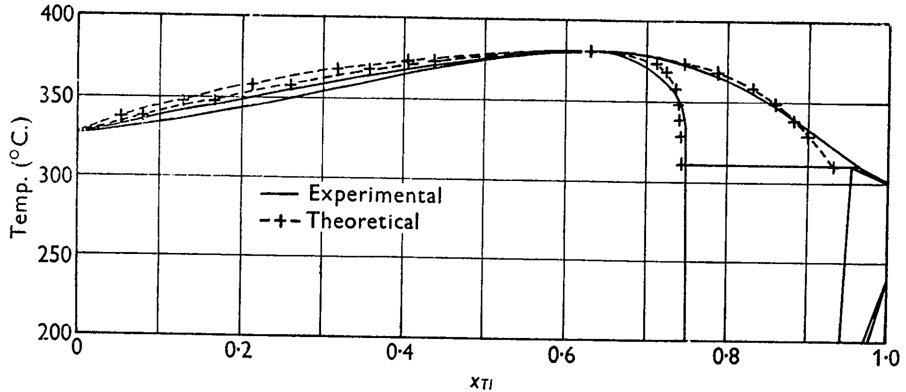

Fig. 10. The theoretical phase diagram derived from the free-energy curves in Fig. 9 is compared with the experimental one.

with the observed heat of fusion of lead, 1·3 kcal.mole^{-1}. Some free-energy curves calculated in this way are given in Fig. 9, and the corresponding phase diagram is represented in Fig. 10. The discrepancy in the lead-rich region between the theoretical liquidus and solidus curves and the experimental ones is probably due to the fact that the occupancy of the position 0, 0, 0 by lead atoms alone could not be retained at very small percentages of thallium; the dilute alloys may well have a random or nearly random replacement of lead atoms by thallium atoms in all positions.

There seem to be many binary metallic systems in which there are phases of this sort. In the sodium–lead system there are two such phases. One of them, based on the ideal structure Na_3Pb, extends from 27 to 30 atomic percent lead, with its maximum at about 28 atomic percent lead; and the other, corresponding to the ideal composition $NaPb_3$, extends from 68 to 72 atomic percent lead, with maximum at about 70 atomic percent. The intensities of X-ray reflection have verified that in the second of these phases sodium atoms occupy the positions 0, 0, 0, and the other three positions in the unit cell are occupied by lead atoms isomorphously replaced to some extent by sodium atoms (Zintl & Harder, 1931). These two phases are interesting in that the ranges of stability do not include the pure compounds Na_3Pb and $NaPb_3$.

It seems likely that there are many other phases of this sort. Among them is probably the γ phase of the mercury–thallium system, extending from 21 to 32 atomic percent thallium, and with maximum melting-point at 28 atomic percent thallium; this phase, which usually is described as having the ideal composition Hg_5Tl_2, presumably should be described as having the ideal composition Hg_3Tl.

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Physical Properties of Crystals: The Direct-Inspection Method

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The independent non-zero components of physical properties of crystals can be obtained by *direct inspection* in all crystal classes in which one can find Cartesian orthogonal co-ordinates that do not transform into linear combinations of themselves under the symmetry operations, i.e. in the groups S_2–$\bar{1}$; C_{1h}–m, C_2–2, C_{2h}–$2/m$; C_{2v}–$2mm$, D_2–222, D_{2h}–mmm; C_4–4, S_4–$\bar{4}$, C_{4h}–$4/m$, C_{4v}–$4mm$, D_{2d}–$\bar{4}2m$, D_4–42, D_{4h}–$4/mmm$; C_3–3, S_6–$\bar{3}$, C_{3v}–$3m$; T–23, T_h–$m3$, T_d–$\bar{4}3m$, O–432, O_h–$m3m$.

The method is applied to a general third-order tensor (polar or axial) in C_3, S_6, C_{3v}, T_d, O, O_h; to a fourth-order polar tensor t_{rs} (r, $s = 1, 2, 3, 4, 5, 6$) in C_4, S_4, C_{4h}, C_3, S_6, T, T_h (correcting the erroneous results of Pockels on photoelastic constants); and to a sixth-order polar tensor $t_{ikl} = t_{ilk}$ (i, k, $l = 1, 2, 3, 4, 5, 6$) in monoclinic and orthorhombic groups and in C_{4v}, D_{2d}, D_4, D_{4h}.

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Some of the components of tensor properties of matter are zero in crystalline bodies and some are equal between themselves owing to the symmetry of the system. This reduction is additional to the reduction of components of a general tensor of a given order,

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