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THE LOW-TEMPERATURE REGION OF THE LEAD-INDIUM PHASE DIAGRAM

Eckhard Nembach

June 1968

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Submitted to Transactions of the
Metallurgical Society of AIME

UCRL-18284
Preprint

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

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Inorganic Materials Research Division, Lawrence Radiation Laboratory, University of California, Berkeley, California

ABSTRACT

The phase-diagram of the system Pb-In has been investigated below room temperature, using mainly x-ray diffraction. In accordance with thermodynamic measurements by T. Heumann and B. Predel,[3] a segregation occurs at low temperatures, though not in the form of a miscibility gap.

1. Introduction

The phase diagram of the system lead-indium has been the subject of extensive investigations,[1,2] but recently T. Heumann and B. Predel[3] concluded from their thermodynamic data that a new feature should occur below room temperature. The maximum values for the enthalpy and entropy of mixing are reached at a composition of 50 at.% Pb and are +400 cal/g-atom and +1.7 cal/g-atom degree, respectively. From this the authors estimated that a miscibility gap should occur below 30°C, centered at 50 at.% Pb. Resistivity measurements seemed to support this view. These authors proposed the phase diagram outlined in Fig. 1. Three phases exist at 30°C; the tetragonal In-phase with $c/a > 1$, the tetragonal intermediate phase α_1 with $c/a < 1$ and the face-centered cubic Pb-phase. We[4] observed, during an investigation of the superconducting properties of Pb-In alloys, that aging a specimen with 50 at.% Pb for 14 days at -18°C decreased the superconducting transition temperature about 0.13°K and tripled the transition width. In this paper, we report the results of an investigation of the low temperature portion of the Pb-In phase diagram. Superconductivity and x-ray methods have been used.

2. Specimen Preparation

The materials were provided by the American Smelting and Refining Company. According to the manufacturer their purity was 99.999%. The weighed amounts of the constituents were sealed in quartz tubes under an atmosphere of 10 Torr helium, mixed for 24 hrs in a rocking furnace at 380°C, quenched in ice-water and homogenized at 20-30°C below the solidus line, established by T. Heumann and B. Predel. The annealing times were 144 hrs for specimens containing less than 30 at.% Pb and 36 hrs for the remainder.

3. Superconductivity Experiments

The specimens were quenched from the homogenization treatment into ice-water and their superconducting transition temperatures T_c measured. The procedure used has been described in Ref. 4. The transition was detected by the change of the mutual inductance of two coaxial coils containing the sample. T_c was defined as the temperature at which 50% of the total change in inductance had occurred. Then the specimens with lead contents between 38 and 75 at.% were aged for 7 days at temperatures between -30°C and 40°C. If this treatment caused T_c to change by more than 0.005°K or the width of the transition to increase by more than 0.002°K, it was concluded that the specimen had undergone a phase change and no longer consisted only of the f.c.c. Pb-phase, as it did immediately after homogenizing. The result is shown in Fig. 2. From this one can estimate the extension of the f.c.c. phase. The x-ray measurements were based on these preliminary results.

4. X-ray Experiments

Because of the softness of the material, relatively coarse powders (75μ) had to be used, which were filed in a helium atmosphere from homogenized specimens. The powders were annealed at least 30 min at temperatures between 120° and 160°C, depending on their concentration, and quenched in ice-water. Then their x-ray patterns were taken at -178°C, using a Picker diffractometer, model 3488K. In this way the following relation was established for the f.c.c. Pb-phase:

$$a = 4.6970 + 0.002469\ C \text{ for } 40 \leq C \leq 75 \qquad (1)$$

where a is the lattice constant (Å) and C is the at.% of Pb. The coarseness of the powder made it impossible to use lines with $\theta > 75°$, therefore a was averaged from lines with $45° \leq \theta \leq 75°$. Relation (1) is very similar to the one found by T. Heumann and B. Predel at room temperature.

Following this, homogenized specimens with compositions between 15 and 56 at.% Pb were aged for at least 10 days at temperatures between -27°C and +25°C. The aging temperatures were chosen in accordance with the superconductivity results. Since an aging time of only 7 days gave the same results, obviously the aging time of 10 days was sufficient to produce the equilibrium phases. Then the x-ray patterns were again taken at -178°C. Three types of x-ray patterns were found: 1) those containing only lines of the tetragonal α_1 -phase, 2) those containing only lines of the f.c.c. Pb-phase, or 3) those containing lines of the α_1 and the f.c.c. Pb-phase. However, lines belonging to two f.c.c. phases, differing only in lattice constant, have never been observed

in a sample. This shows that the miscibility gap, proposed by T. Heumann and B. Predel, does not exist.

The boundary between [only Pb-phase] and [Pb-phase + α_1] was established by calculating the concentration of the f.c.c. phase from its lattice constant, using Eq. (1). This procedure was not possible for the phase boundary between [only α_1] and [α_1 + Pb-phase], because the lattice constant of α_1 could not be measured accurately enough. Low intensity made it impossible to use lines with $\theta > 34°$.

Therefore another method has been used. Specimens with lead contents between 15 and 28 at.% Pb were first annealed above 100°C. This treatment produced specimens containing only the α_1-phase. If the subsequent aging below room temperature resulted in the formation of the f.c.c. phase, the (111)- x-ray-line of this phase could be observed as well as the (111)-line of the tetragonal α_1 phase. The limit of detection of the former line was about 0.3% of the intensity of the latter. The results are again plotted in Fig. 2, together with the suggested phase diagram.

No attempt has been made to investigate the range of stability of the α_1 phase in the low concentration region as previous work[5-7] has shown that it is very difficult to establish equilibrium even above room temperature.

5. Conclusions

The results of this x-ray study shows that a narrowing of the stability ranges of the α_1 and the f.c.c. phases in the Pb-In-system occurs below room temperature. This is in agreement with T. Heumann and B. Predel's thermodynamic data, which suggested a segregation of lead and indium because of the high positive enthalpy of mixing. However, the miscibility gap, proposed by these authors, does not exist.

It seems surprising that an intermediate phase (α_1) should occur in a phase-diagram which shows also a tendency for segregation of the constituents. However, α_1 differs from the (In)-phase only in c/a, the change of the mean atomic volume being less than 0.2%, and ordering does not occur. According to C. Tyzack and G. V. Raynor[5] the existence of the α_1 - phase is primarily due to an interaction of the Fermi surface with a Brillouin boundary, but not to a tendency of ordering, which is usually the reason for the occurrence of intermediate phases.

This work was performed under the auspices of the United States Atomic Energy Commission.

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FIGURE CAPTIONS

Fig. 1 The low temperature region of the In-Pb phase diagram as outlined by T. Heumann and B. Predel. (In) tetragonal, $c/a > 1$; α_1 tetragonal, $c/a < 1$; (Pb) f.c.c. The miscibility gap is dashed.

Fig. 2 Results of the superconductivity and x-ray measurements:

low temperature aging did change ● } the superconducting properties
did not change O

phase boundary from lattice constant measurements ▽,

x-ray lines of two ▣ } phase detectable
of only one □

X points on the phase boundaries given by T. Heumann and B. Predel.

— Phase boundaries based on this investigation

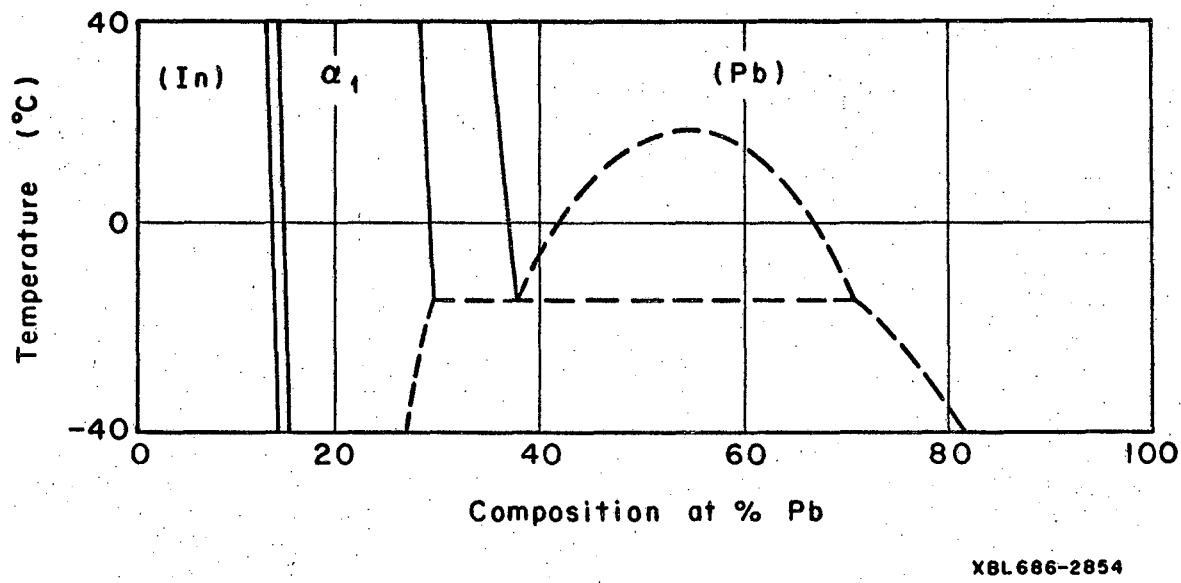
40
0
-40
Temperature (°C)
(In)
α_1
(Pb)
0
20
40
60
80
100
Composition at % Pb
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Fig. 1

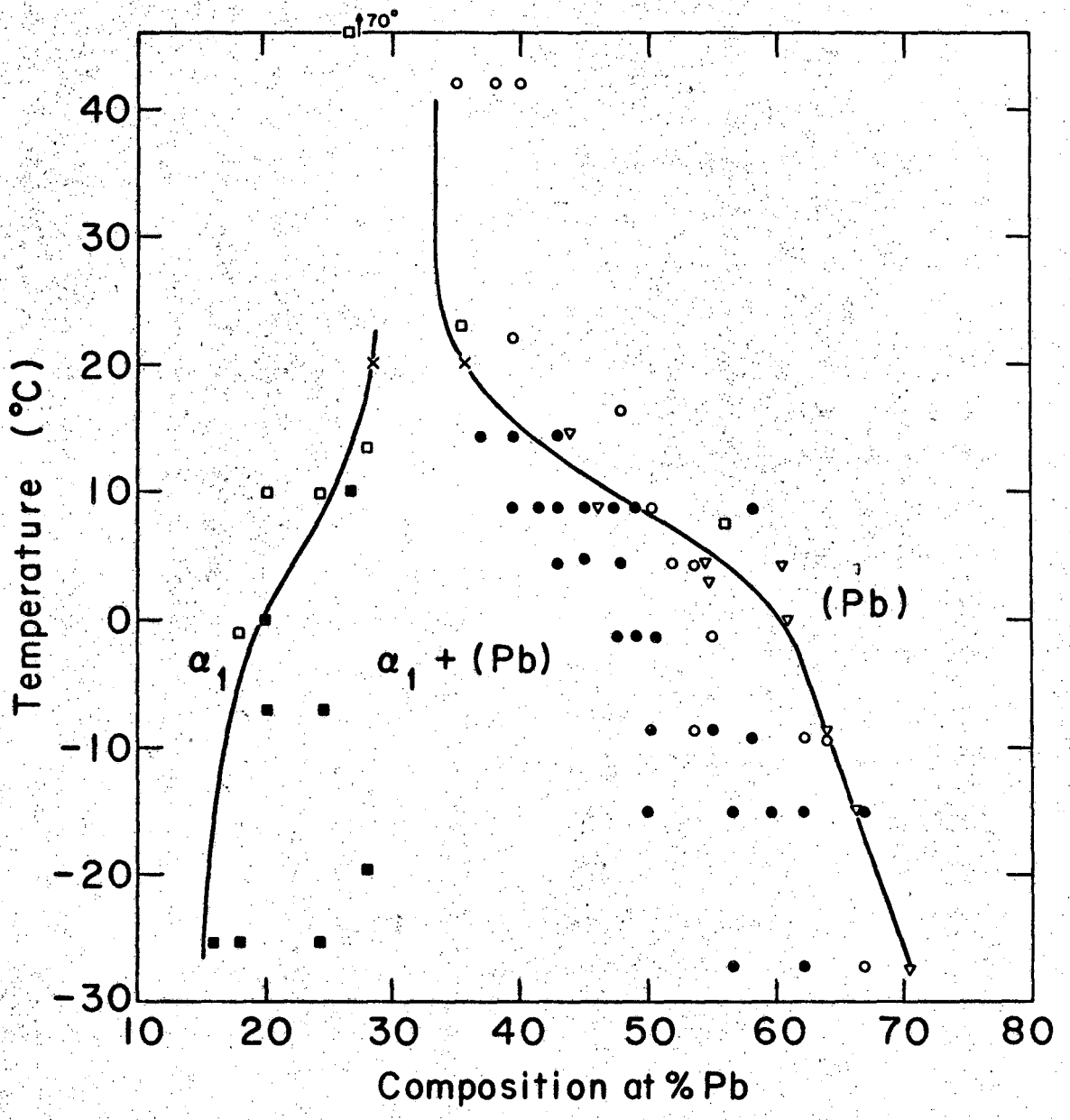

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Fig. 2

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