Thermochimica Acta, 31 (1979) 13–19

ANOMALIES IN THE ENTHALPY OF FREEZING IN ALPHA-PHASE INDIUM–LEAD, DUE TO BRILLOUIN-ZONE EFFECTS

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(Received 22 May 1978)

ABSTRACT

The enthalpy of freezing has been measured with DTA using electrical calibration for 33 compositions of indium–lead in the range 6.9–7.9 at.% lead, at which range the electron–lattice interaction causes anomalies in several physical and structural properties. Enthalpies of mixing, ΔH^s_m, have been calculated. The results reveal three maximum and minimum pairs corresponding to partial shift of the Fermi surface to higher Brillouin zones in three steps at 7.1, 7.2 and 7.3–7.4 at.% lead. These details in the overlapping have not been found earlier. The observed change in ΔH^s_m in the steps is about 1 meV atom^{-1}.

INTRODUCTION

When a tetravalent metal such as lead is alloyed to trivalent indium, more conduction electrons occupy the energy levels of the solid. At certain electron-to-atom ratios Z, the expanding Fermi surface crosses the Brillouin-zone boundaries, which are determined by the crystal lattice. The interaction of the Fermi surface with the boundaries causes changes in the position of the boundaries, thus causing changes in the tetragonality of the indium-based lattice and promoting stresses. These stresses are relieved after the Fermi surface has jumped across the boundary. The changes in different properties of the alloy, due to this interaction between the electrons and the lattice, are called Brillouin-zone effects. In recent years numerous investigations have revealed such effects in indium-based alloys of tin, cadmium, lead and mercury; the studies have concerned superconducting critical temperature[1–5], lattice parameters[1–4, 6, 7], electrical resistivity[8], thermoelectric power[9] and electronic specific-heat capacity[5, 10].

The variations in the total electron plus lattice energy cause changes in the enthalpy of mixing in the solid state, ΔH^s_m, which can be determined from the measured enthalpy of freezing, ΔH, from the enthalpy of mixing in the liquid phase, ΔH^l_m, and from the specific heats in the solid and liquid phases. For the indium–lead

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system the enthalpy of mixing in the solid state has been studied by Heumann and Predel[11] using DTA and by Yoon and Hultgren[12] using liquid tin calorimetry. In a study concerning the whole binary system, measured points are usually at intervals of 5–10 at.%. The Brillouin-zone effects can be found, however, only when several measurements are performed in a narrow composition range, in the indium-based alloys in the range 0–10 at.% of alloying metal. Thus, in the case of the indium–tin system, earlier measurements performed in this laboratory revealed a minimum and maximum pair in ΔH_m^s at about 8 at.% tin[13]. The curve was drawn with 20 measured points between compositions 7.03 and 9.15 at.% tin.

Because DTA has proved to be a valuable tool in studies of anomalous behaviour of solids in narrow composition ranges, research was continued with other indium-based alloys for which Brillouin-zone effects have been reported, in the present case lead as the alloying element.

EXPERIMENTAL

The enthalpy of freezing was measured with DTA, using electrical calibration. This method has been presented by Heumann and Predel[14]. Samples of about 10.5 g were weighed with an accuracy of 0.1 mg. The calculated composition cannot be considered true for more than three numbers because during the first melting of the sample, indium easily adheres to the wall of the sample tube above the meniscus edge as a small speck of about 1 mg. The starting materials were indium bars of 10 mm diameter and of 5N5 purity, obtained from Kawecki-Billiton, Arnhem, The Netherlands, and lead in the form of wire and of 5 N purity from Koch-Light Laboratories (Ltd.), Colnbrook, Bucks., England. The weighed samples were placed in a flat bottomed glass tube with an internal diameter of 14 mm and a height of 110 mm. This in turn was inserted in another, bottomless glass tube fitted in a copper block. The bottom of the sample tube was in contact with the copper block. Nitrogen of 5 N purity was allowed to flow slowly through the sample tube at ambient pressure. Before measurements the sample was heated to 350°C and kept molten for 16 h. During the phase transition the average cooling rate was 1 °C min^{-1}.

The temperature of the sample and the temperature difference were followed with NiCr–Ni thermocouples. The cooling rate was regulated by means of thyristors. The calibration energy was fed to the sample with a spiral of insulated resistance wire. Three calibration peaks were registered both before and after the phase transition. A Goerz Servogor RE 512 integrating recorder was used. The calibration factor at the temperature of the phase transition was calculated with linear regression analysis.

The indium or alpha-phase extends to 12 at.% Pb[11]. The solidus and liquidus have a common minimum at 2.5 at.% Pb; the corresponding temperature is 0.16°C below the melting point of indium. At the composition 8 at.% Pb the difference between the liquidus and solidus temperatures is about 0.4°C; thus conditions exist for the quantitative use of DTA. Pure tin of 5N5 purity, delivered by Kawecki–Billiton, was used to check the calibration and corrections. The measured value for the enthalpy of fusion, 7.245 kJ mole^{-1}, is in good agreement with the value obtained in our earlier measurements (7.190 kJ mole^{-1})[13] and also with the other published values (Predel[15], 7.257 kJ mole^{-1}, Alpaut and Heumann[16], 7.240 kJ mole^{-1}).

During the phase transition differentiation takes place and therefore a result cannot be counted to the calculated composition of the sample. In each grain and in the whole sample indium enriches in the parts that solidify last. The differentiation has a smoothing effect on the curve.

At least four measurements were performed with every sample to diminish the influence of random errors. When a new measurement gave a result which did not fit the curve already drawn, more measurements were performed at neighbouring compositions.

TABLE 1

MEASURED VALUES FOR THE ENTHALPY OF FREEZING

Composition (at.% Pb)	*ΔH (kJ mole^{-1})*	*FSD (%)*
6.897	3.237	1.0
7.005	3.215	1.0
7.071	3.185	2.0
7.090	3.170	1.6
7.114	3.102	1.2
7.118	3.212	2.0
7.123	3.246	1.1
7.137	3.232	2.1
7.148	3.134	2.1
7.186	3.118	1.8
7.201	3.190	1.1
7.210	3.261	2.2
7.221	3.288	1.6
7.229	3.240	2.2
7.238	3.202	2.2
7.248	3.188	2.3
7.255	3.196	3.2
7.264	3.180	1.3
7.281	3.162	3.0
7.303	3.194	1.4
7.320	3.146	0.7
7.341	3.117	0.4
7.348	3.258	2.1
7.355	3.236	1.9
7.371	3.287	2.7
7.385	3.216	2.6
7.401	3.167	0.4
7.405	3.212	1.3
7.431	3.201	2.5
7.499	3.180	2.8
7.655	3.206	1.3
7.875	3.196	0.6
7.898	3.201	2.0

RESULTS

The arithmetic mean values for the enthalpy of freezing, ΔH, and the fractional standard deviation (FSD) are given in Table 1. The enthalpy of mixing in the solid state, ΔH^s_m, is calculated according to the relation

$$\Delta H^s_m = x_{In}\Delta H_{In}(T) + x_{Pb}\Delta H_{Pb}(T) + \Delta H^l_m - \Delta H(\text{obs})$$

where $\Delta H(T)$ is the enthalpy of freezing at the approximate temperature T of freezing for an alloy; $T = \frac{1}{2}(T_{\text{liquidus}} - T_{\text{solidus}})$ and $\Delta H(T)$ is calculated from the equation

$$\Delta H(T) = H(T_0) + c_{\text{solid}}(T_0 - T) - c_{\text{liquid}}(T_0 - T)$$

where T_0 is the melting point of the pure component. The specific heats are given[17] as follows

$$\text{indium } c_{\text{solid}} = \left(24.3 + 0.01\frac{T}{\text{K}}\right) \text{kJ (K mole)}^{-1}$$

$$c_{\text{liquid}} = 31 \text{ kJ (K mole)}^{-1}$$

$$\text{lead} \quad c_{\text{solid}} = \left(24.1 + 8.45 \times 10^{-3}\frac{T}{\text{K}}\right) \text{kJ (K mole)}^{-1}$$

$$c_{\text{liquid}} = 31.6 \text{ kJ (K mole)}^{-1}$$

The enthalpy of mixing in the liquid phase, ΔH^l_m, is calculated from the equation[18]

$$\Delta H^l_m = (3.85x_{Pb} + 3.24x^2_{Pb} + 2.82x^3_{Pb} + 3.77x^4_{Pb} + 1.55x^5_{Pb}) \text{ kJ mole}^{-1}$$

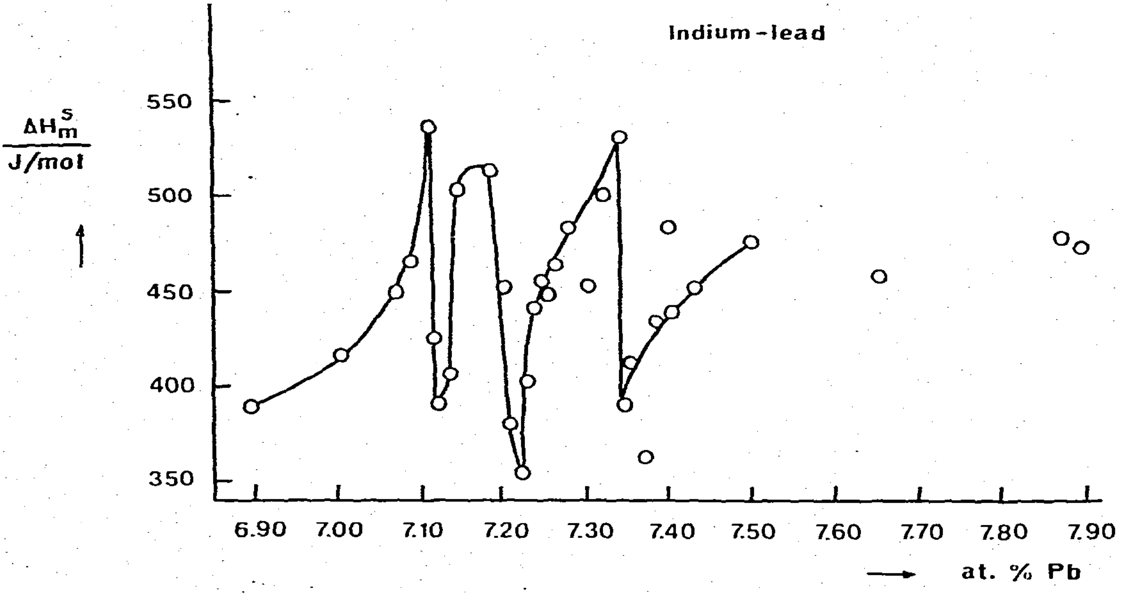

Fig. 1. The dependence on composition of enthalpy of mixing in the solid state for indium-lead alloys.

For the enthalpies of freezing for the pure components at their melting points the following values were used: indium 3.297 kJ mole^{-1} (obtained in this study), lead 4.871 kJ mole^{-1} (ref. 14). The variation of the enthalpy of mixing in the solid state is given in Fig. 1.

DISCUSSION

The whole series of points is located below the curve of Heumann and Predel[11]. Yoon and Hultgren[12] reported the heat of formation for $x_{Pb} = 0.10$ to be (0 ± 150)J mole^{-1} at 315 K.

Tyzack and Raynor[6] measured the lattice parameters between 0 and 7 at.% Pb and Moore et al.[7] between 7 and 10 at.% Pb. Altogether these measurements show a slight bend at 3 at.% Pb and a sharp maximum at 7 at.% Pb in c/a. Merriam[3] observed the dependence of superconducting transition temperature and found a bend at 7.5 at.% Pb. The existence of the bend has been confirmed in later studies; for the composition corresponding to the bend Preece and King[4] give the value 7 at.% Pb and Lambert et al.[5] the value 9 at.% Pb. Merriam[1] also found fluctuations in lattice parameters in the range 6.5–8.0 at.% Pb. Preece and King[4] performed lattice parameter measurements at liquid nitrogen temperature to obviate the strong diffuseness of Debye–Scherrer lines present in films taken with samples at room temperature. Their results show a rather slow change in lattice parameters and in axial ratio, for which there is a broad maximum at 8 at.% Pb. The compositions with which Preece and King[4] performed measurements in the interesting range are 6.5, 7.1, 7.7 and 8.0 at.% Pb.

Thomas and Reitz[9] found anomalies in the thermoelectric power of indium–lead alloys at 6–10 at.% Pb. Carriker and Reynolds[8] observed anomalies in the residual resistivities in directions perpendicular to the c-axis at 3.5 and 7.0 at.% Pb.

The tetragonality of indium has been explained by an energetically favourable situation between the Fermi surface and the Brillouin-zone boundaries of the distorted *fcc* lattice. The free-electron model for the Fermi surface of indium consists of holes in the first zone corners and electrons in the second, third and perhaps fourth zone, too. The four Brillouin zones have common corners which are important in connecting the various parts of the Fermi surface. According to Goodenough[19], when approaching the Brillouin-zone the Fermi surface causes it to contract. After the overlap there is a reverse effect. The total energy is minimized by adjustments in the electronic and lattice energies. These changes affect various properties, as mentioned above. Thomas and Reitz[9] and also Carriker and Reynolds[8] explain their results by initiation of overlapping of the Fermi surface across the faces perpendicular to the c-axis to the second zone at the composition 7 at.% Pb. Merriam[1] interpreted his observations as being due to interaction and overlapping of the Fermi surface with the second and third zones on common points and considered the lattice parameter variations to confirm the predictions of Goodenough concerning the interaction.

Preece and King[4] explain the overlap as taking place from the first zone corners to the fourth zone at 7 at.% Pb. They criticize the lattice parameter values of Merriam because they would mean great volume changes which are not predicted by Goodenough's theory. Taking into account the different results from observations of the Fermi surface of indium, Lambert et al.[5] estimate the structure to consist of a second-zone surface and third-zone tubes. They explain the observed anomalies to be due to the overlap to the third zone taking place at $Z = 3.09$.

The anomalies in ΔH_m^s show that the overlap takes place in several steps of the order of 1 meV atom^{-1} each. The steps may, however, the substantially smoothed by the differentiation during freezing. The actual extremities may have not been detected. The step found in the study of indium–tin alloys at 8.10 at.% tin was 1.2 meV atom^{-1} (ref. 13). Only one step was found, but the present study has shown that a large number of samples is needed to determine all the steps. Four samples, as in the study of Preece and King[4], are not enough.

The observed compositions, at which different steps in overlapping occur, are not directly comparable with those observed at low temperatures because of the temperature broadening of the electron distribution and also because of the dependence of tetragonality on temperature.

The difference in the composition of the anomalies in the cases In–Pb and In–Sn is due to other factors but not the valency of the alloying element. The atomic volume and the potential can be taken into account by considering the first reciprocal lattice vectors in connection with the mean pseudopotential of the alloy[20]. It is, however, evident that the rapid changes in physical and structural properties which have been observed at 7–9 at.% Pb are due to electronic effects.

Because of the mutual interaction of electrons, the difference in the electron energies at different compositions could also be detected by studying other than valence electrons. Two indium–tin samples with compositions 8.10 and 8.31 at.% Sn, corresponding to maximum and minimum in ΔH_m^s were studied with a precision X-ray fluorescence spectrograph in order to determine the energy of the In$L\alpha_1$ (L_3–M_5) transition. The results showed that within the accuracy of the method no shift in the M_5 energy level could be detected. Another possibility is to measure the energy of the Compton electrons from different samples.

ACKNOWLEDGEMENTS

The authors are indebted to Professor Markus Pessa for the spectrographical work and to Dr. Ensio Laine for his comments.

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