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THE PHASE DIAGRAM OF THE MERCURY-INDIUM
ALLOY SYSTEM

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SUMMARY

The mercury-indium phase diagram has been investigated over the whole composition range from $-78^\circ$C to the melting point of indium, using thermal analysis, X-ray and superconductivity techniques. This is believed to be the first application of superconductivity measurements to phase diagram investigations. A compound, HgIn, of very limited range of composition, melts congruently at $-19.3^\circ$C; and gives rise to eutectics at 61.5 at.% indium and $-31^\circ$C, and at 34.7% indium and $-37.2^\circ$C. The $\beta$ phase extends from 2.5 to 19.1% indium and has a maximum melting point of $-19.2^\circ$C at 14.2% indium. It forms a peritectic or eutectic at a temperature indistinguishable from the melting point of pure mercury with a solid solution in mercury containing some, but less than 0.3%, indium. A transition from face-centred tetragonal to face-centred cubic in the indium-rich solid solutions at about 93% indium gives rise to a peritectic at 108°C. The solubility of mercury in this face-centred cubic phase falls from about 22% at $-31^\circ$C to 13% at $-78^\circ$C.

INTRODUCTION

In the course of studies of superconductivity in mercury-indium alloys certain features of the phase diagram emerged, and encouraged a complete study of the system. Some previous work on portions of the system are summarized by Hansen, and the existence of various compounds has been suggested elsewhere. During the course of the present work Kozin and Tananaeva published the results of a study of the liquidus and solidus. The only other systematic work on the system was the X-ray investigation of the indium-based solid solution by Tyzack and Raynor, who measured lattice spacings and observed a sharp transition from face-centred tetragonal structures (with a slightly composition-dependent axial ratio) to f.c. cubic ones at about 6 at.% mercury.

We have investigated the constitution of the whole system at temperatures between $-80^\circ$C and the melting point of indium, using thermal analysis, X-ray measurements, and measurements of superconducting transition temperature. The latter proved a very powerful method for examining the phase boundaries in the solid state.

MATERIALS AND METHODS

The mercury and indium used in this work were both of a purity stated to be greater than 99.999%; the mercury was "Vacumetal" from Metal Salts Corp., Hawthorne, * On leave from Imperial College, London.

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New Jersey, and the indium, in the form of shot, was obtained from the Indium Corp. of America, Utica, N.Y. Since most of the work was done at or below room temperature, all compositions quoted (always in atomic percentages) are based on the weights of the components used. For the same reason all the alloys were melted in air, and although some superficial oxidation was observed it was always slight. Two low temperature annealing baths were used, one of melting heptaneone (−40°C) and the other of solid carbon dioxide dispersed in acetone (−78°C).

A general survey of the liquidus and solidus was carried out in the early stages of the work using differential thermal analysis. A thick-walled aluminium crucible containing about 50 g of the alloy served as reference temperature for the differential thermocouple and was cooled by raising about it a thick-walled copper cylinder standing in a Dewar vessel containing a small amount of liquid nitrogen. For alloys with melting points above room temperature this crucible was heated in a small tube furnace. The output of the differential copper−constantan couple was amplified and fed to the Y terminals of a potentiometric X-Y recorder, the X terminals being fed directly by a copper−constantan couple located in the wall of the crucible. The X scale of the recorder was calibrated during each experiment with voltages from a Rubicon potentiometer.

![Fig. 1. Low temperature portion of the mercury–indium phase diagram. x, Thermal analysis data; ○, single-phase alloy; □, two-phase alloy; △, alloy containing liquid; ●, boundary from superconductivity measurements.](image)

This arrangement proved very sensitive and was particularly useful in revealing the presence and extent of invariant reactions, but the absolute accuracy of the temperatures given was not very high. All the temperatures shown in Figs. 1 and 2 have therefore been taken from direct temperature–time heating and cooling curves obtained with constantly stirred 50–100 g melts in alumina crucibles, the copper−constantan thermocouple being enclosed in a very thin-walled glass sheath dipping into the specimen. Before and after the series of measurements the couple was calibrated at room temperature, 0°C, and the melting point of pure mercury; and

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during the course of measurements on the indium rich alloys it was again calibrated at the melting point of pure indium and 100°C.

X-ray diffraction data at room temperature were obtained with a G. E. Diffractometer using Cu Kα radiation. To obtain data for the low melting point alloys a special specimen holder was constructed, which could be cooled with solid carbon dioxide and acetone. The specimen was cast directly into the holder and protected against condensation by a stream of dry nitrogen.

The superconducting transition temperatures were measured by monitoring the self-inductance at 1 kilocycle of a coil containing the specimen. (Such a method, relying on the change in the magnetic properties is inherently more reliable than a measurement of the resistivity.) Coil and specimen were directly immersed in a bath of boiling helium for temperatures in the range 1.0°–4.2°K, or suspended in the temperature gradient above the liquid helium for temperatures of 4.2°–5.0°K, the temperature then being measured by a carbon resistance thermometer. Most of the specimens used for the phase boundary determinations had transition widths of about 0.02°K.

**EXPERIMENTAL RESULTS**

*Liquidus and solidus*

The results of thermal analysis are shown in Figs. 1 and 2, and are in good general agreement with those of KOZIN AND TANANAeva. Critical points, with experimental uncertainties, are:

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Invariant reaction

\[ 0.25 \pm 0.2\% \text{ indium}, -38.9 \pm 0.2^\circ \text{C} \]

(probably a peritectic: Liquid \(\sim 0\%\) indium + solid \(\sim 0.2\%\) indium
\[ \rightarrow \text{liquid} + \beta\text{ 2.5\% indium.} \])

First maximum:

\[ 14.2 \pm 0.2\% \text{ indium}, -14.2 \pm 0.2^\circ \text{C} \]

First eutectic:

\[ 34.7 \pm 0.2\% \text{ indium}, -37.2 \pm 0.2^\circ \text{C} \]

Second maximum:

\[ 50.0 \pm 0.2\% \text{ indium}, -19.3 \pm 0.2^\circ \text{C} \]

Second eutectic:

\[ 61.5 \pm 0.4\% \text{ indium}, -31.0 \pm 0.2^\circ \text{C} \]

Peritectic:

Liquid 86.6\% indium + \(\alpha\)T 93.8\% indium \[ \rightarrow \text{Liquid} \]
\[ + \alpha_c 92.7\% \text{ indium}, 108^\circ \text{C} \pm 1^\circ \text{C}. \]

The steepness of the solidus of the \(\alpha_c\) phase made it impossible to obtain reliable solidus temperatures from thermal analysis, and Fig. 2 shows the results of annealing experiments on quenched and homogenized samples in the form of 2 mm thick plates. The presence of more than 1 or 2\% of liquid in grain boundaries was detected at the annealing temperature by the separation of grains under light pressure with a screwdriver. Heating curves of alloys with around 80\% indium after holding for some hours at room temperature revealed thermal arrests near 60^\circ \text{C}, but a long series of experiments showed these to be spurious. They were not seen in heating curves of alloys held overnight at \(-14^\circ \text{C}\) nor in heating curves of alloys thoroughly stirred for as long as possible during cooling. Similar arrests seem to have been observed by Kozin and Tananaeva.8

The phase boundaries in the solid state

Almost all the detailed information that we have obtained on the solid-state constitution has been derived from measurements of the superconducting transition temperatures. The transition temperature of a single phase alloy is normally, like the lattice spacing, a function of composition. In a two-phase region the two transi-
tions of the component phases may, under suitable circumstances, be observed, especially when a small amount of a second phase of higher transition temperature than the major component is present. Since the inductive method used is especially sensitive to the surface of the specimen, the presence of a second phase is more clearly indicated when it is the phase separating during the initial stages of solidification. Figure 3 shows some typical transitions, the ordinate being the mutual inductance of the coil surrounding the specimen and thus a measure of the permeability of the specimen, and Fig. 4 shows the application of such data to the $\alpha_C$ and $\beta$ phases. We believe that this is the first recorded use of superconductivity measurements as a technique for the determination of phase boundaries. Normal annealing times were one week at $-40^\circ$C and four to six weeks at $-78^\circ$C.

The mercury-rich solid solutions

Within the accuracy of the thermal analysis technique the solidus temperatures of alloys with up to 2.5% indium could not be distinguished from the melting point of pure mercury; but superconductivity measurements showed a distinct solubility of indium in mercury to exist, the transition temperature of the mercury-rich phase in alloys of 1–2% indium being about 4.12°K as compared with 4.15°K for pure mercury. The most probable invariant reaction is a very limited peritectic; and from the data for alloys of 0.1, 0.3 and 0.5% indium we would estimate the solubility limit to be between 0.1 and 0.3% indium.

The $\beta$ phase is a substitutional solid solution, and its conductivity gives no indication of ordering. After annealing at $-40^\circ$C the limits of this phase, as indicated by superconductivity data, lie at 2.5 ± 0.2 and 19.1 ± 0.3% indium. No significant change was found after 6 weeks annealing at $-80^\circ$C. A change in slope of the transition temperature–composition curve near 11% indium may, like corresponding effects in lattice spacing curves in other systems, be connected with a change in

![Fig. 4. Superconducting transition temperatures and phase boundaries.](image-url)
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electronic structure; but the X-ray diffraction pattern (see Appendix) is identical in the 7.7% and 14.3% indium alloys.

The HgIn compound

Superconductivity data show this compound to have an extremely limited composition range, well annealed alloys of 49.5 and 50.5% indium having indistinguishable transition temperatures (3.81°K). Results for these alloys after short periods of annealing at −40°C suggest, however, that while the liquid + solid boundary on the indium-rich side is accurately vertical a slight slope exists on the mercury-rich side, for the 49.5% indium alloy then has a range of transition temperatures from 3.63° to 3.81°K. The compound is evidently ordered for it has an electrical conductivity of the same order as that of pure mercury at 4.2°K, and unlike the other phases is not ductile at −80°C. It has an X-ray diffraction pattern (see Appendix) which we have not yet been able to solve, but which is clearly not the simple CsCl structure shown by LaHg and MgHg.

The indium-rich solid solutions

One of the most interesting features of the diagram is the occurrence of a two-phase region (and the consequent peritectic) between the tetragonal and cubic solid solutions. This had not previously been reported in this system or the related In−Tl and In−Cd systems, and TYZACK AND RAYNOR had concluded that the tetragonal/cubic transition was of second order in these systems; but MOORE, GRAHAM, WILLIAMSON AND RAYNOR considered the reproducibility of two-phase tetragonal + cubic indium-thallium alloys strongly suggestive of a first order change.

Recent work on In−Cd alloys shows a peritectic and an even narrower two-phase region. In the present system X-ray methods showed an alloy of 93% indium to be single-phase cubic after quenching from 85°C, but two-phase after holding at room temperature for six weeks. At about −78°C it was wholly tetragonal, having presumably transformed martensitically. The superconductivity data indicated that the 92% alloy also became tetragonal on cooling to liquid helium temperature. X-ray examination at room temperature showed no second phase in the cubic 92.5% alloy or the tetragonal 94% alloy but the axial ratio of the tetragonal phase in the 93% alloy was significantly less (1.038) than that of the 94% alloy (1.042), indicating that the limit of the tetragonal phase must lie at slightly less than 94.0% indium.

In the f.c. cubic solid solution range the lattice spacing is almost composition-independent, and even had it been possible to make accurate parameter measurements below room temperature a determination of the solid solubility by the lattice-spacing method would not have been possible. Fortunately, however, the superconducting transition temperature is very strongly dependent on composition, and its behaviour has been used to detect the shape of the boundary, as shown in Fig. 4. Annealing times of more than 50 days were needed to produce equilibrium at −78°C, and it is therefore not possible to use the technique to establish whether the boundary will intersect the cubic/tetragonal transition at lower temperatures.

DISCUSSION

Mercury and indium have rather similar atomic sizes and the general form of the

diagram is much what one might therefore have predicted, with extensive ranges of solid solubility. A rather surprising feature however is the occurrence of the equiatomic ordered compound of negligible range of composition. It is conceivable that this owes its existence to zerovalent behavior of mercury, with the localization of two electrons in the 6s shell as an inert pair. The stability of such a pair has been strikingly emphasized by the existence of the semi-conducting CsAu compound.

The mercury–thallium system, with which comparisons might be profitable, shows no equiatomic compound but a simple close-packed solid solution in the 20–30% thallium region.

In view of the occurrence of the β-mercury structure as the extensive secondary solution of the mercury–cadmium system, an attempt was made to fit the diffraction pattern of the mercury-rich mercury–indium secondary solid solution to this structure, but without success. It would seem therefore that the stability of both mercury structures is related to the presence of an electron/atom ratio of 2.0.

ACKNOWLEDGEMENTS

We are very grateful to Mr. M. A. Jensen for his assistance with the superconductivity measurements and for informing us of the results of conductivity measurements, to Mrs. S. Hillhouse for the preparation of many of the alloys, to Mr. D. Hamilton for a translation of the paper of Kozin and Tananaeva, and to Dr. B. T. Matthias for many sceptical discussions. This work was financially supported in part by the U.S. Air Force Office of Scientific Research, and the U.S. Office of Naval Research.

REFERENCES

1 M. F. Merriam and M. A. Jensen, to be published.

APPENDIX

X-ray diffraction results for β and HgIn

Although reproducible results of low-temperature X-ray measurements could be obtained, it did not prove possible to solve the structures. Table I gives the plane spacings for the two phases, with rough estimates of intensities; but it should be noted that the use of a solid sample which was not necessarily either fine-grained or random in grain orientations makes these intensity estimates rather unreliable, although they are based on the results of a number of different experiments. The β phase spacings in alloys of the 7.7% and 14.3% indium were the same to one part in 1,000, and can be reasonably well accounted for with a tetragonal unit cell of \[ a = 3.88 \text{ kX}, \ c/a = 1.34. \]
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**TABLE I**

X-RAY DIFFRACTION DATA FOR $\beta$ AND HgIn PHASES

<table>
<thead>
<tr>
<th>Plane spacing (°26)</th>
<th>Intensity</th>
<th>Plane spacing (°26)</th>
<th>Intensity</th>
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</thead>
<tbody>
<tr>
<td>4.983</td>
<td>medium</td>
<td>4.48</td>
<td>medium</td>
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<tr>
<td>3.735</td>
<td>v. strong</td>
<td>3.00</td>
<td>medium</td>
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<tr>
<td>3.490</td>
<td>medium</td>
<td>3.735</td>
<td>strong</td>
</tr>
<tr>
<td>2.781</td>
<td>v. strong</td>
<td>3.504</td>
<td>medium</td>
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<tr>
<td>2.408</td>
<td>strong</td>
<td>5.100</td>
<td>weak</td>
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<tr>
<td>2.002</td>
<td>medium</td>
<td>3.080</td>
<td>weak</td>
</tr>
<tr>
<td>1.741</td>
<td>strong</td>
<td>2.846</td>
<td>v. strong</td>
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<tr>
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<td>v. weak</td>
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<tr>
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<tr>
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<td>1.912</td>
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<td>strong</td>
</tr>
<tr>
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<td>medium</td>
<td>1.210</td>
<td>medium</td>
</tr>
<tr>
<td>1.102</td>
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<tr>
<td>1.109</td>
<td>weak</td>
<td>1.109</td>
<td>weak</td>
</tr>
</tbody>
</table>

*Note added in proof*

G. JANG (Z. Metallk., 53 (1962) 612) has recently examined the liquidus and solidus of the Hg–In alloys by thermal analysis, and suggests the existence of compounds of very limited composition range forming peritectically at Hg$_4$In and Hg$_2$In$_3$. Our superconductivity data cannot be reconciled with the existence of the latter compound, for $T_c$ remains constant at that of the HgIn phase over the range 25–49% In, nor could we detect any variation in the temperature of the first arrest in heating curves for alloys of 35–45% indium. The existence of Hg$_4$In also seems rather unlikely, although we did observe slight anomalies in the cooling curves of the 17, 18.5, and 20% indium alloys near $-21^\circ$C, and ascribed these to the rapid change of slope in the $\beta$ solidus curve at this temperature. In well annealed alloys of 19.5, 20, and 21% indium the superconducting transition of the indium-rich $\beta$ phase is observed at the value corresponding to 19.1% indium; and although a higher temperature transition is also observed in the 21% alloy it seems very likely that this is due to the small amounts of the HgIn phase present, its value of $T_c$ having been depressed slightly by a small particle size.

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