The System Indium - Lead - Tin

by

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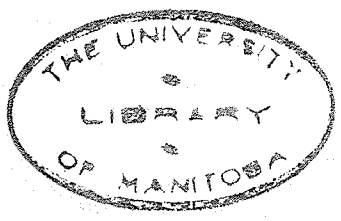

To Dr. A.N. Campbell

who with infinite patience guided
me in this my first venture into
the field of research.

Acknowledgments

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Abstract

A study of the system Indium-Tin-Lead was started using thermal and X-ray analysis. The following conclusions resulted:

1. The system In-Pb-Sn has no true ternary eutectic point.

2. There is a slight depression of melting point on addition of Pb to In but the depression is not as large as previously recorded.

3. The positions of the peritectics cannot be found readily in the ternary system by thermal analysis alone. There is a need for further work on this system using X-ray and optical metallographic methods to determine the nature of the solid phase.

4. The phase of In-Sn has a simple hexagonal structure as suggested by Fink.

5. The phase of In-Sn does not have the tetragonal I-lattice with two atoms per cell proposed by previous authors although the correct structure has not yet been deduced.

6. The eutectic temperature of the In-Sn system was found to be 118.8° not 117° as other authors had reported.

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Origin of the Problem

Indium, a semi-precious metal is found associated with zinc in the Sullivan mine of Consolidated Mining and Smelting Co. Ltd. near Kimberley, B.C. Although the indium content of the original ore is generally very small (.001 - .1%), in the smelting operations for recovery of the base metals the indium becomes concentrated in various by-products. Therefore, these complex by-products could serve as a source of the metal.

Unfortunately due to its high price and a lack of knowledge of its properties in alloys, indium is not very widely used today. Hence Consolidated Mining and Smelting Co. Ltd. during the last ten years has sought data on the various alloys of indium.

In 1950 the company had several In-Sn-Pb alloys investigated by the Battelle Memorial Institute for possible uses as corrosion-resistant solders.

Because of this it was decided that a complete phase equilibrium investigation of the system In-Sn-Pb would be a suitable topic for research under the Cominco Fellowship.

INTRODUCTION

The prime objective of a research of this nature is the determination of the equilibrium diagram of the system under investigation. This phase diagram when completed will show the changes that the components of the system will undergo when the variables (temperature and composition) are altered. The diagram will also show the regions in which the various phases are stable.

Since these changes are associated with variations in the physical properties of the system, the alterations can be detected by the measurement of those properties. Consequently the investigator has many tools at his disposal to determine the equilibrium diagram.

In this investigation the methods used were thermal and X-ray analysis. Therefore, a brief description of both methods will be given.

Thermal Analysis

The phase changes which occur in a system are generally associated with a heat effect. Hence if the system is subjected to heating or cooling, heat will be absorbed or evolved at the temperature of the transformation. Any temperature measuring method which has as its object the determination of the temperature of this transformation is called a "thermal analysis" method.

The main method of thermal analysis is the study of cooling or heating curves. These curves are constructed by plotting temperature against time. If a transformation occurs on heating or cooling a characteristic break will be observed in the resulting curve. If the transformation occurs with increasing temperature then the system will absorb heat and if it occurs with a decreasing temperature then heat will be evolved (Le Chaletier's Principle). Thus, if the rate of heating or cooling is known the presence of the transformation can be observed.

Because cooling curves were used exclusively in this investigation a brief discussion of their application will be given here.

Suppose the system under investigation is heated to a temperature considerably above that of the surrounding atmosphere and then the source of heat is removed. It will be observed that the rate of cooling

will be considerably greater at the beginning than at the end. In fact, it has been observed that the rate of cooling is proportional to the temperature differential between the system and the atmosphere around it. This is expressed by Newton's equation:

$$q = k\,(t_2 - t_1)$$

q = heat evolved

t_2 = temperature of system

t_1 = temperature of atmosphere

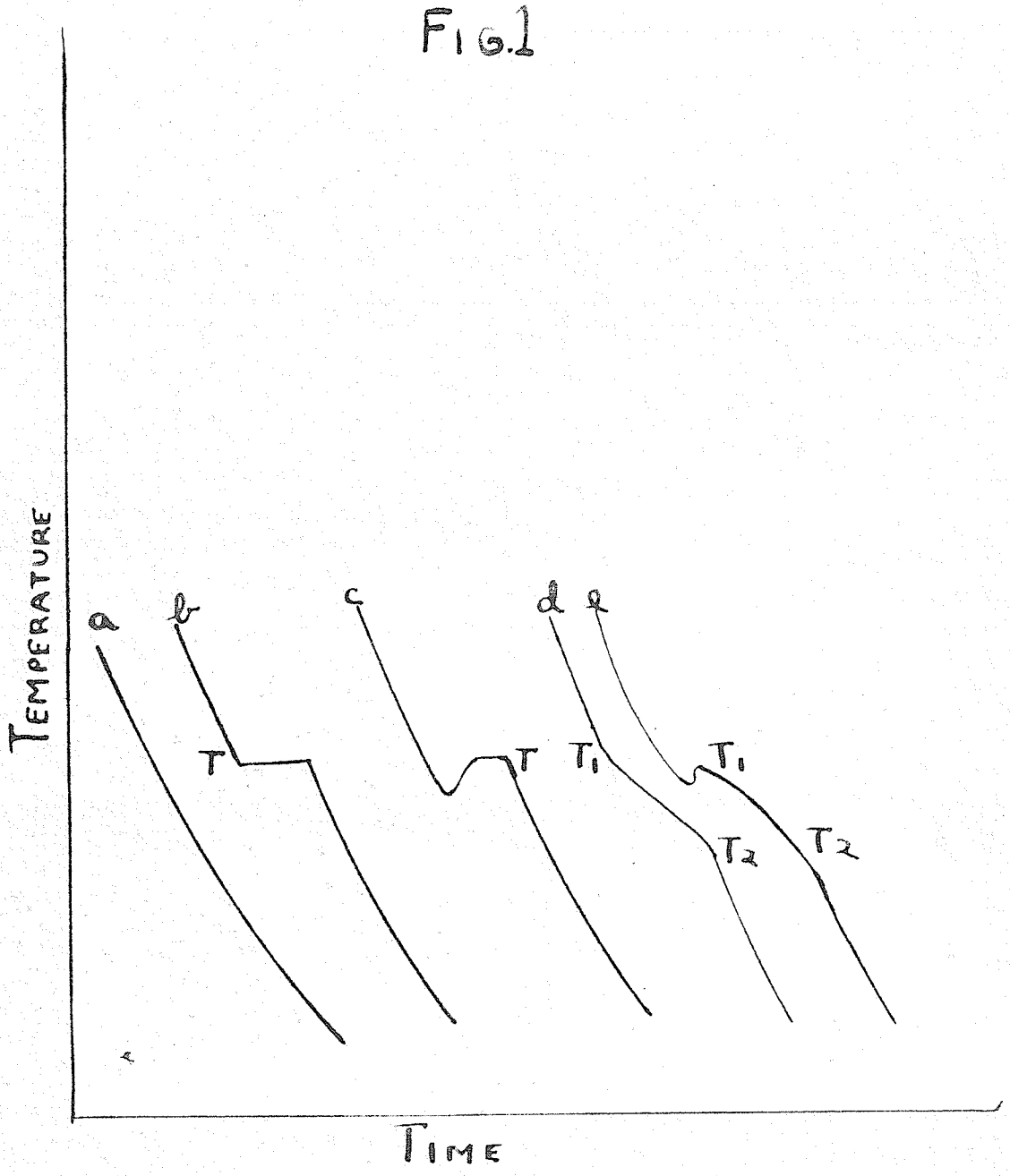
k = constant

The cooling curve of a substance which undergoes no transformation is given in Figure 1 (a).

If on cooling a temperature is reached for which the degree of freedom is zero, the temperature must remain constant until the number of phases has been reduced by one. The temperature can only fall on the disappearance of a phase.

Suppose a pure substance undergoes a liquid-solid transformation at a temperature T. Let the cooling begin at a temperature greater than T. When the system has cooled to this prescribed temperature, solid begins to settle out and the system is thus invariant. Thus the temperature must remain constant until the liquid has completely disappeared. On the cooling curve a horizontal is observed, the temperature of which can be read easily as shown in Figure 1 (b).

FIG. 1



In actual practise the curve is subject to two modifications - supercooling and a rounding off at the end of the transformation as shown in Figure 1 (c). Supercooling is the phenomenon of the liquid existing at a temperature less than the melting point and is represented by the small depression in the figure. The rounding at the end of the transformation is due to two causes.

1. The quantity of liquid remaining is insufficient to maintain a rate of evolution of heat great enough to keep the temperature constant.

2. The specific heat of the solid is less than that of the liquid and hence has a tendency to cool at a greater rate.

Let us consider a system in which there are more than m components present, (m being the number of components required for invariance when one solid phase is formed from the liquid). During the formation of that one solid phase the temperature does not remain constant but falls gradually. In such a case, because heat is being evolved the cooling curve has a slope different from that observed when no transformation takes place.

When a solid is formed on cooling the transformation temperature does not remain constant because the

compositions of both the liquid and solid phases are undergoing continuous change. This case is illustrated in Figure 1 (d).

The freezing point (the temperature at which solid first appears) is given by T_1. The melting point (the temperature at which the last drop of liquid disappears) is given by T_2. The determination of T_1 is relatively easy to make but because of the rounding off at the end of the transformation, the determination of T_2 is subject to considerable error.

To make a more accurate determination of T_2 possible, Plato[24] suggested that the rate of cooling be maintained at a constant value throughout the cooling of a system which undergoes no transformation. This method is often referred to as Rectilinear Cooling (figure 2 (a)).

For a pure substance which undergoes a transformation at the temperature T, the ideal linear cooling curve is as shown in Figure 2 (b). The melt cools linearly until the temperature T is reached (the freezing point) solid begins to separate out and continues to separate out at constant temperature until all liquid is gone. Then, because the temperature of the furnace is less than that of the system, the system's rate of cooling is large until the two rates are again

equal. This quick cooling is represented by mn in the diagram. In actual practise supercooling and a rounding off at the end of the transformation occur resulting in a curve of Figure 2 (c).

In the case of a solid solution being formed from the melt the ideal linear cooling curve is as shown in Figure 2 (d).

Here solidification begins at the temperature T_1 and continues to the temperature T_2 where liquid no longer exists. The determination of both T_1 and T_2 would be easy in such a case.

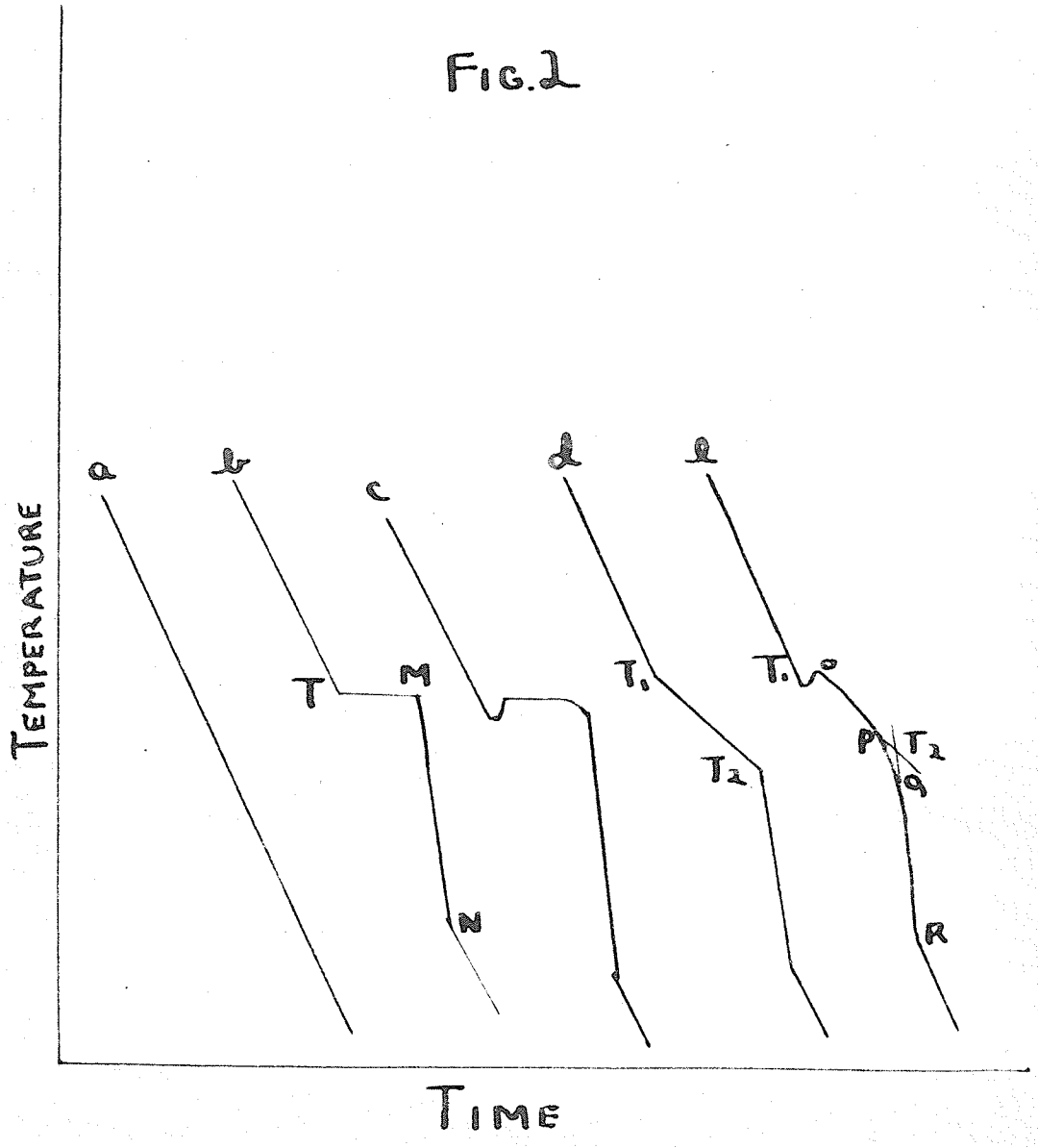
In actual practise the resulting cooling curve is modified by the two effects previously noted.

Tammann (31) has shown that the true melting point can be determined accurately by extending the two straight lines op and qr until they intersect at the point T_2. The ordinate of T_2 is the true melting point.

METHOD OF X-RAY ANALYSIS

X-rays can be used to identify and determine the structure of the solid phases in a given region. Since in this investigation X-rays were used only to determine crystal structure, this discussion will be confined to that phase of their use.

FIG. 2



The X-ray beam is directed on the sample which can either be a single crystal or a powder rolling. The powder rolling is obtained by forming a cylindrical rod of powder of the solid held together by a suitable binder. Bragg has shown that the conditions for reflection to occur from a given set of lattice planes are

$$n\lambda = 2 d \sin \theta$$

where n = a whole number

λ = wave length of the incident X-rays in Å units

d = interplanar spacing in Å units

θ = the angle between the planes and the incident X-rays

As a result, reflections occur only at definite values of θ. Consequently an X-ray pattern results on an enclosing film when X-rays are directed at a sample. Because these resulting reflections are characteristic for a given crystalline material, the method can be used for identification. The method can also be used to determine the structure of the crystal since the position and intensity of the arcs are functions of the internal structure.

To determine the structure of a crystal it is necessary to index and measure the intensities of the various lines on an X-ray photograph. By indexing is meant the

assigning of the Miller indices of the planes of the crystal to each observed line. From the systematic absences, if any, of certain types of reflections, the possible space group of the crystal can be found. From this and any information that can be gained by other means, a structure is proposed. The intensities of the lines are calculated for the proposed structure and compared with the values observed. If they agree, the proposed structure is the correct one; if not another structure is proposed and the intensities calculated on it. This process is continued until reasonable agreement between calculated and observed intensities indicates that the correct structure has been found.

PREVIOUS INVESTIGATIONS

The Pure Metals

TIN

Tin is a soft bluish-white metal which has a melting point of 231.9 ± .1°C. It exists in two allotropic forms, the α, a grey cubic form, and β, a white tetragonal form. The transition point for $\alpha \rightarrow \beta$ tin is 13.2°C. The existence of a third allotrope has been suggested by many workers; eg. Degens (5) who reported the transformation temperature to be at 161°. The present belief is that no γ tin exists but that the effect noted at 161° was due to impurities in the tin (12).

α tin has the diamond structure with a cube edge of 6.46 A.

β tin has a body-centred tetragonal lattice with the lattice constants

$a = 5.83$ Å $\qquad\qquad$ $c = 3.182$ Å

INDIUM

Indium is a very soft, silvery white metal which has no allotropic forms. The literature value of melting point of this metal has shown considerable variation since its discovery in 1863. The first reported melting point was that of C. Winkler (37) who reported a temperature of 176° C. Later workers placed the value

at 154-155°. The generally accepted value of 156.4°C is due to the work of Roth et al (28). In 1947, H.M. Davis (4) reported the melting point to be 157.3°C, but this value is not generally accepted. As a result of these variations the phase diagrams of indium systems have undergone considerable alteration.

Indium crystals are face-centred tetragonal with cell dimensions

$$a = 4.594 \text{ Å} \quad \text{and} \quad c = 4.951 \text{ Å}$$

LEAD

Lead is a heavy, bluish-grey metal with a melting point of 327.4° ± .1°.

It is generally believed that polymorphism does not exist in lead. However, E. Cohen and W.D. Hilderman (3) from density and chemical action studies thought polymorphism did exist and that the transition temperature was near 50°. E. Janecke (14) from a study of pressure-temperature heating and cooling curves found evidence of transition temperature between 59 and 62°. Because various other authors do not confirm these results the transition temperature is thought to be non-existant.

Lead crystallizes with a face-centred cubic lattice with a cell edge of 4.9379 Å.

The System of Pb-Sn

The system of Pb-Sn is the basis of most soft solders. Hence it would be expected that the system should receive much study. This has been the case for the literature on this system is extensive. Therefore, only a brief outline of the most important points will be presented here.

The fact that tin and lead could be alloyed in all proportions was known as early as the time of the Romans. However, the first modern research on this subject was done by Roberts-Austin (26) in 1897. He reported that the eutectic composition of the system was 69 Wt % tin and a temperature of 180°. He also claimed that in the solid state lead and tin are nearly mutually insoluble.

The errors in Roberts-Austin's report were pointed out by Rosenhain and Tucker (27) who used thermal analysis, differential thermal analysis and microscopic analysis.

Their work showed the eutectic at 180°C. and at a composition of 62.93 Wt % tin. They found that lead could dissolve up to 16 Wt % tin at 182.5°C and 18% at 149°C. These authors pointed out the heat evolution which occurred at 149°C. The liberation of heat was noticed for alloys containing 18-63 Wt % tin to be 149°C and for those containing 8-18% tin to be at

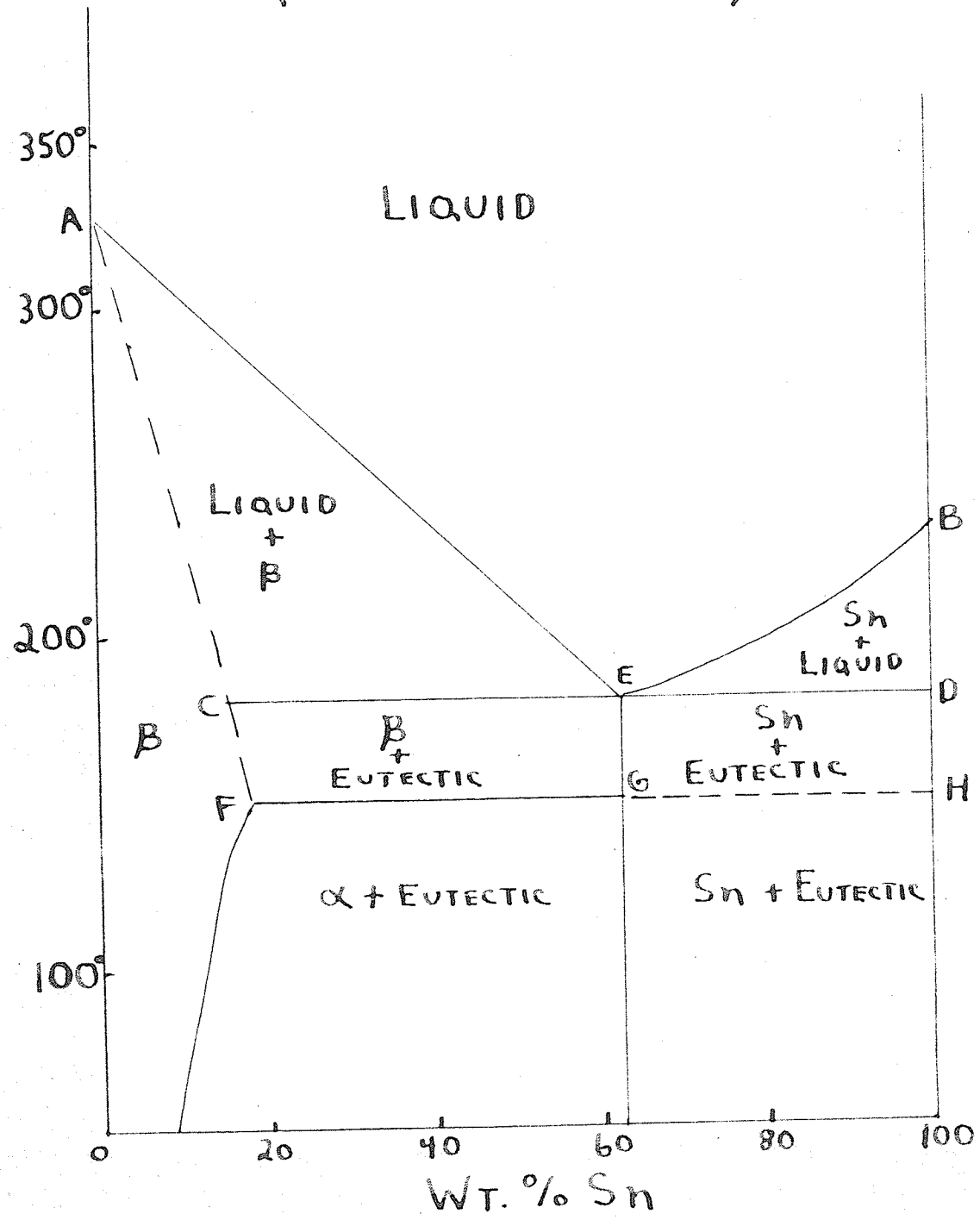
a slightly lower temperature. As a result of these observations Rosenhain and Tucker's diagram contained a line at 149°C.

Degens (5) was the next major worker to publish on this system. His work showed that lead and tin were completely miscible in the liquid state but that solution was incomplete in the solid state. He placed the eutectic at 181° with a composition of 24.4 at % lead. The solid solubility of lead in tin according to him extended to 0.21 at % lead while that of tin in lead extended to 88 at % lead.

The thermal effect noted by Rosenhain and Tucker was observed by Degens to occur at 146°. This thermal effect was of maximum duration at 57 at % lead which corresponds to a composition of Pb_4Sn_3. In trying to determine the cause of the transformation he noted that on cooling large masses of tin a break in the cooling curve occurred between 160-164°C. Pure tin also showed a decided volume change at 161°C. This was determined by use of an air dilatometer. The presence of the change in Pb-Sn system was also found dilatometrically to occur at 146°. Thus the results of Rosenhain and Tucker were partially confirmed.

In the early 1910's the presence of the thermal effect was fairly well substantiated but its cause was attributed to various factors. The main theories

FIG. 3
Pb-Sn SYSTEM
(ROSENHAIN AND TUCKER)



were those of Rosenhain and Tucker, and of Degens. These first authors attributed the heat effect to an allotropic transformation of an α solid solution to a β solid solution. The β form was thought to contain less tin and hence the heat effect was due to the precipitation of that metal.

Degens claimed that the cause of the heat effect was compound formation.

Mazzatto (21) in 1912 pointed out that the line CF should not exist in the diagram of Rosenhain and Tucker. He realized that a heat effect did occur but he attributed it to supersaturation due to lack of equilibrium during the cooling. Hence the separation of one component would occur explosively at a lower temperature when the supersaturation ended.

The next major work on this system was that of N. Parravano and A. Scortecci (23) who in 1920 by means of electric conductance measurements, determined the solubility of tin in lead. Their results showed that the solubility decreased from 14.5 wt % at 175° to 1.5 wt % at 25°C. These workers claimed that the thermal effect was due to supersaturation. Thus the diagram of this system was described as being of type V of Roozeboom's classification of solid solutions.

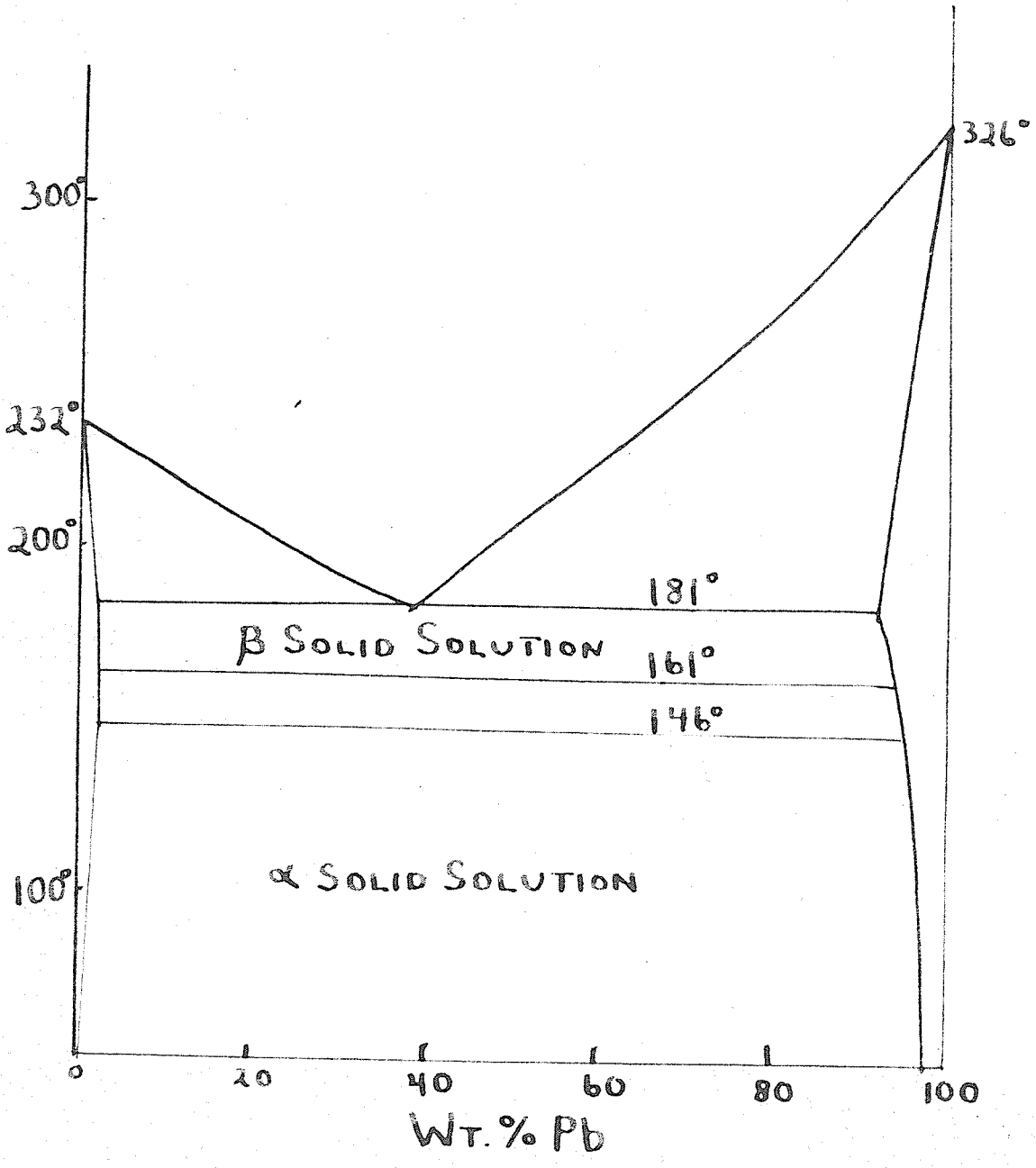
In 1921 Jeffery (15) published his diagram based

on electrical conductances with very slow rates of cooling. He reported no line of thermal halts at 149° and assumed therefore that his slow rate of cooling allowed equilibrium to be maintained at all times. Other workers, he claimed, used too fast rates of oooling and hence supersaturation occurred, followed by precipitation at the temperature from 145-150°. The eutectic as determined by Jeffery's method occurred at 183±.3°C with a composition of 66 wt % tin. The solubility of lead in tin was determined to be 3 wt % at 183° and of tin in lead to be 16.5 wt % at the same temperature.

In spite of the evidence to the contrary, many complicated diagrams were published on this system. Some of these diagrams eg. Mellor's (22) in "A Comprehensive Treatise on Inorganic and Theoretical Chemistry" showed the presence of two extra lines at 161° and 146°. The line at 161° corresponded to transformation of $\gamma \rightarrow \beta$ tin while that at 146° corresponded to transformation of β solid solution to α solid solution.

In 1930, K. Honda and H. Abe (13), using a differential thermal analysis method decided that the heat effect which occurred, according to them, at about 160° was due to a rapid decrease in solubility of tin-rich phase in the lead-rich solid solution with decreasing temperature. Consequently the hori-

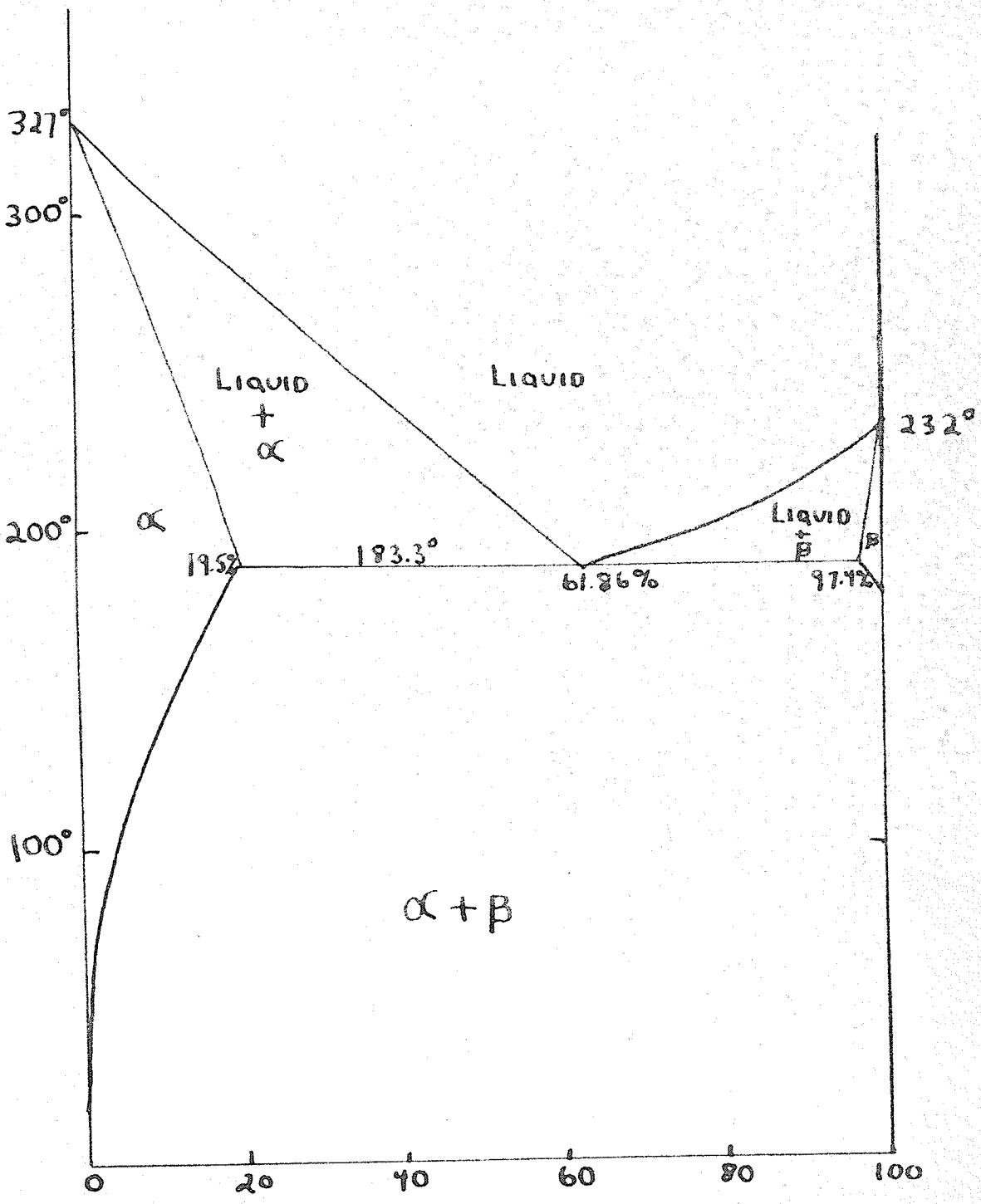
FIG. 4.
Pb-Sn SYSTEM
(MELLOR)



zontal line at about 160° in previous diagrams should be omitted. Instead a sudden inflection should occur in α phase boundary at 160° at 18 wt % tin. They reported the eutectic composition to be 66 wt % tin.

In 1932, Stockdale (30) brought out his diagram which is the basis of most modern diagrams. By means of four methods, thermal, differential thermal, micrographic, and a modified electral conductance method, he determined the eutectic to be at 183.3°C with a composition of 61.86 wt % tin. The solubility of lead in tin was found to be 2.6 wt % at 183°C while tin is soluble in lead to 19.5%. The solubilities at room temperature were found to be very small. Because the evolution of heat occurring at 150° in lead-rich alloys varied with the previous history of the specimen; it is suggested that it may be due to separation of tin in some form other than white tin. The precipitated form is then converted to white tin with evolution of heat. Stockdale stated that Honda and Abe's point of inflection on the lead-rich solid solubility boundary did not exist. Hence, their explanation is not sound according to him.

Most later results are in agreement with the



Wt. % Tin

Pb-Sn System

(Stockdale)

Fig. 5

diagram proposed by Stockdale, but the nature of the heat evolution is not yet fully understood.

The System of In-Pb

The first published work on this system was that of Kurnakow and Puschin (17) who by use of thermal analysis reported that Indium and Lead formed an unbroken series of solid solutions. The addition of a small quantity of lead to indium caused a very slight rise in the melting temperature which was determined as 154.0° for the pure metal.

After 10 at % Pb had been added the rise in temperature became more rapid.

N. Kurnakow and S. Shemtschushny (18) in 1909 confirmed the earlier thermal analysis results by means of electrical conductance measurements.

The presence of an unbroken series of solid solutions was explained by Haughton and Ford (9), who noted that although the two end members did not crystallize in the same habit, the tetrogonal indium crystal lattice differs from the face centred cubic lattice of lead by an elongation of 6% of one of the axes. Thus indium could be thought of as a slightly dissorted cubic lattice which sould form an isomorphous series with lead.

In 1926 van Liempt (19) pointed out that from

X-ray analysis, the Pb-In system should not be regarded as one in which there exists a continuous series of mixed crystals.

The truth of van Liempt's work was brought out by Ageev and Ageeva(1) who used thermal and X-ray analysis in their investigations. They claimed that the assumption of an unbroken series of solid solutions was not correct for the elements had only limited solubility in one another. They reported a peritectic transformation occurred at 32 at % lead and 154°C. The physical properties were in agreement with this modified diagram.

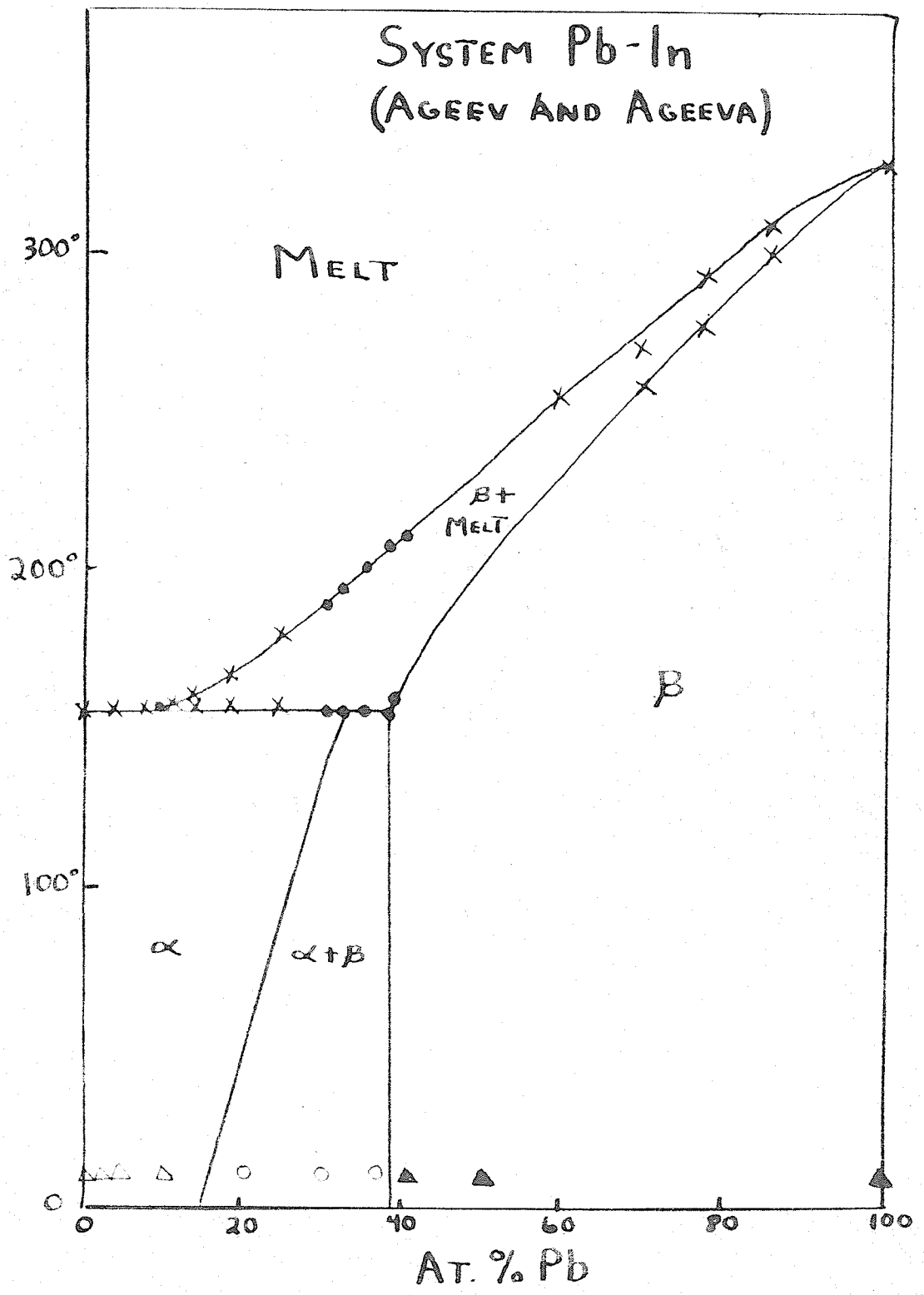
The diagram which is presently accepted is that of S. Valentiner and A. Habestroh who published a series of four papers on this system.

The first paper (35), published in 1938 (which did not acknowledge the work of Ageev and Ageeva) claimed that the only work done on this system prior to their own was done by Kurnakow and Puschin. Hence they claimed they were first to notice that lead and tin did not form an unbroken series of solid solutions. They used thermal and X-ray analysis.

According to them, indium can be introduced into the lead lattice with a resulting falling lattice constant until 30 at % lead is attained. Then at this composition a face-centred tetragonal crystal of

△ α Indium Lattice
▲ β Lead Lattice
○ α+β
● Thermal Arrest
× Kurnakow's Results

Fig. 6



18.75 at % lead separates out. The lattice constants of this crystal, which may be thought of as having a formula of $In_{26}Pb_6$, are a = 4.87Å and $\frac{c}{a}$ = 0.93.

It was observed that on further decreasing the lead content below 20 at % lead, the $In_{26}Pb_6$ crystals were not stable below 159°C. Instead a transformation to $In_{30}Pb_2$ occurred. The lattice constants of this latter crystal were found to be a = 4.59 Å and $\frac{c}{a}$ = 1.08. Thus the diagram of the system had to be modified considerably in the light of these new results.

Valentiner pointed out that the upper composition limit of $In_{26}Pb_6$ had been determined by thermal analysis to extend to 40 at % lead while that of $In_{30}Pb_2$ extended to 30 at % lead. He attributes this to incomplete equilibrium caused by too rapid cooling.

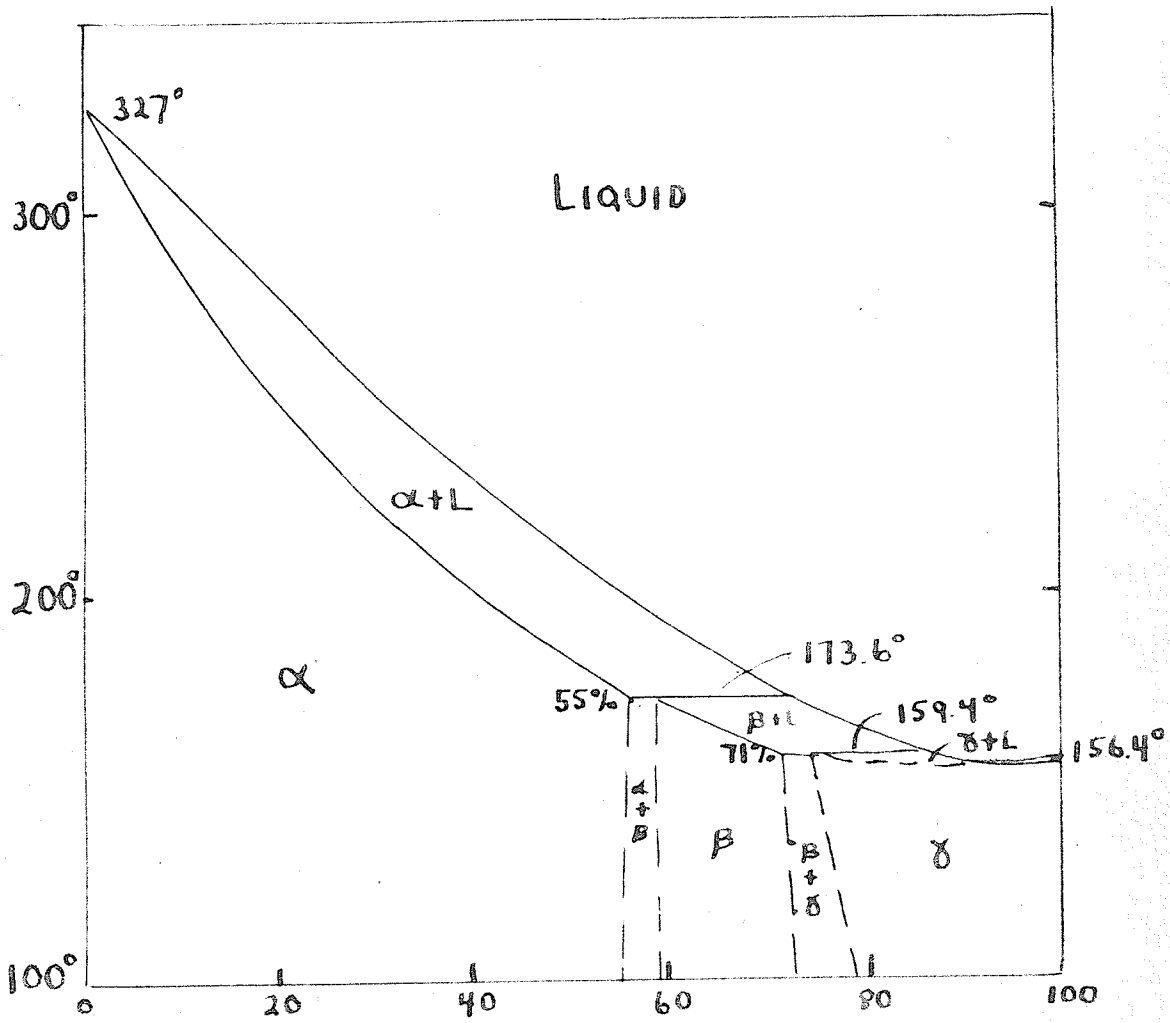
In their next paper Valentiner and Habestroh (36) acknowledged the work of Ageev and Ageeva. They noted that the results were not in agreement but claimed that the disagreements were due to faulty interpretation of X-ray photographs by Ageev and Ageeva.

In 1940, Valentiner (33) published the results of hiselectrical resistance studies on the Pb-In system. The results confirmed the assumption that an unbroken series of solid solutions did not exist.

In 1948 Klemm (16) et al. published their results on the study of this system. They used X-ray and thermal analysis to obtain their results, which agreed very closely with those of Valentiner. They determined the limits of the miscibility gaps to be 8-12 at. % lead, and 27-30 at. % lead. However, for the β phase they claimed a face centred tetragonal crystal with $\frac{c}{a} = 0.98$. Because they did not obtain any heterogenous solids they concluded that the heterogenous areas must be small. These workers also determined the position of the solidus with great care by means of heating curves. The alloys were kept just below their melting points for 1-2 days and then were slowly heated. They claimed that the position of the solidus could in this manner be obtained with greater accuracy. Any other method of determination was subject to error because of sluggish transformations.

In the Metals Handbook (39) there is given a diagram of this system. The diagram which is credited to an unpublished work by H.M. Davis and G.H. Rowe agrees closely with the preceding works; however a depression of melting point is claimed on addition of lead to indium. Ludwick (20) in her book, "Indium", also shows that depression. In the diagram in the latter book the depression appears to be about one degree. Hence a small disagreement has appeared in the modern diagram of the In-Pb system.

FIG. 7



WT. % In

Pb-In SYSTEM

(DAVIS AND ROWE)

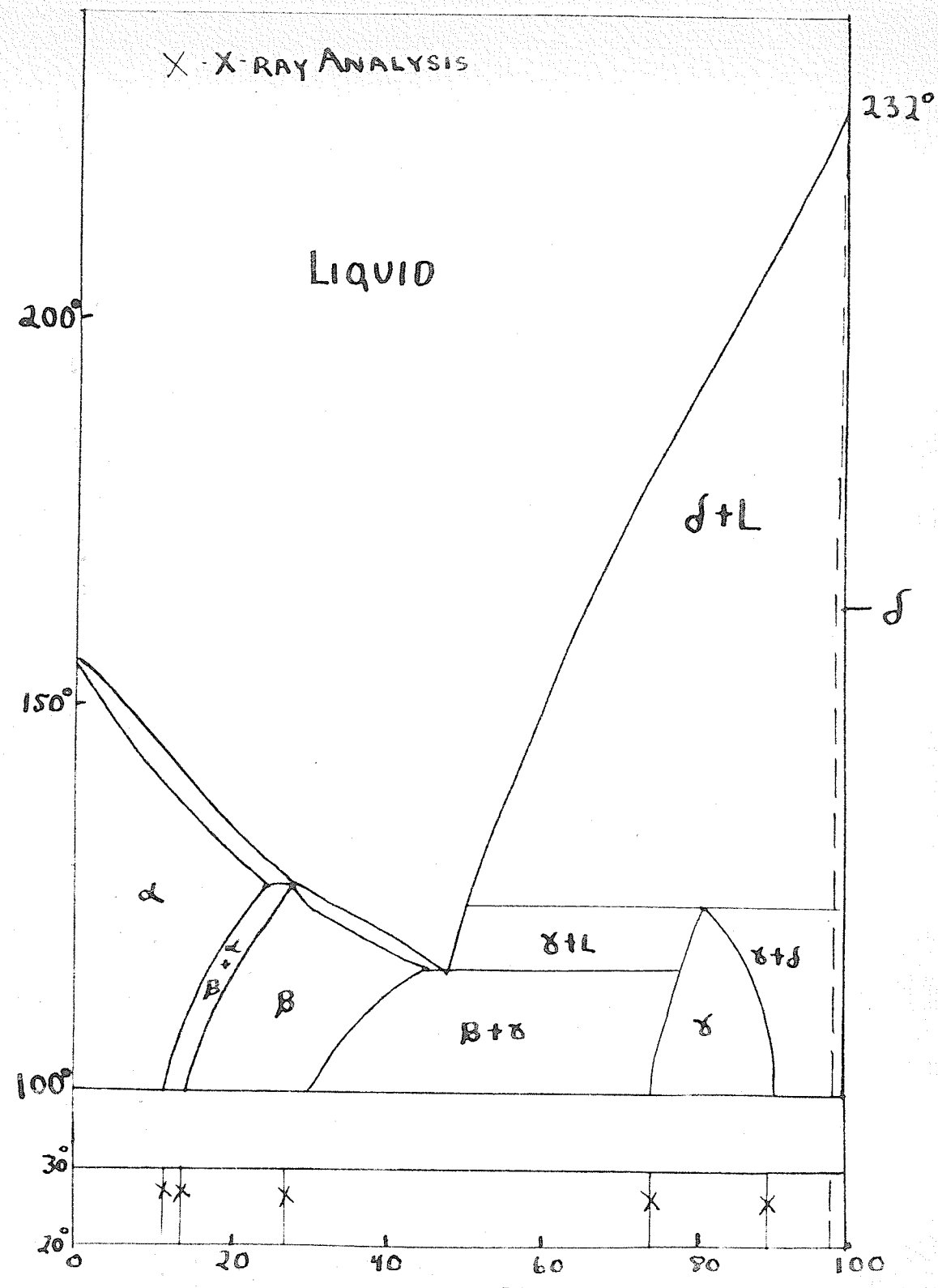
The System In-Sn

The first research on this system was done by Heycock and Neville (11) who stated that indium dissolved rapidly in molten tin. They also observed that Indium depressed the melting point of tin at least up to 1% In.

No further investigation was done on this system until 1939 when Fink et. al. (6) published their results. By means of thermal analysis they determined a large portion of the liquidus and a small portion of the solidus. These authors were the first to report that indium and tin did not form an unbroken series of solid solutions and that a peritectic occurred at 126° at a composition of 28 at % tin. The eutectic at a temperature of 116°C corresponded to a composition of 48.5 at. % tin. The fact that tin is soluble in indium up to 10 Wt. % and that indium is only slightly soluble in tin were also noted.

These same authors (7) published a second paper on this system in 1945 in which they completed their phase diagram. This diagram showed the presence of a series of four solid solutions, the regions of which was determined by X-ray and density measurements. Their results showed that the α solid solution extended to 13 at. % tin, the β solid solution for 14-28 at. % tin while that of the γ phase was stable

FIG. 8



In-Sn System
(Fink et. al.)

from 75 - 90 at. % tin at room temperature. The δ phase extended to 3.3 at. % indium at 20° and to only 1.3 at. % indium at 126°. The peritectic temperatures of the β and γ phases were found to be 124.5° and 126°C respectively.

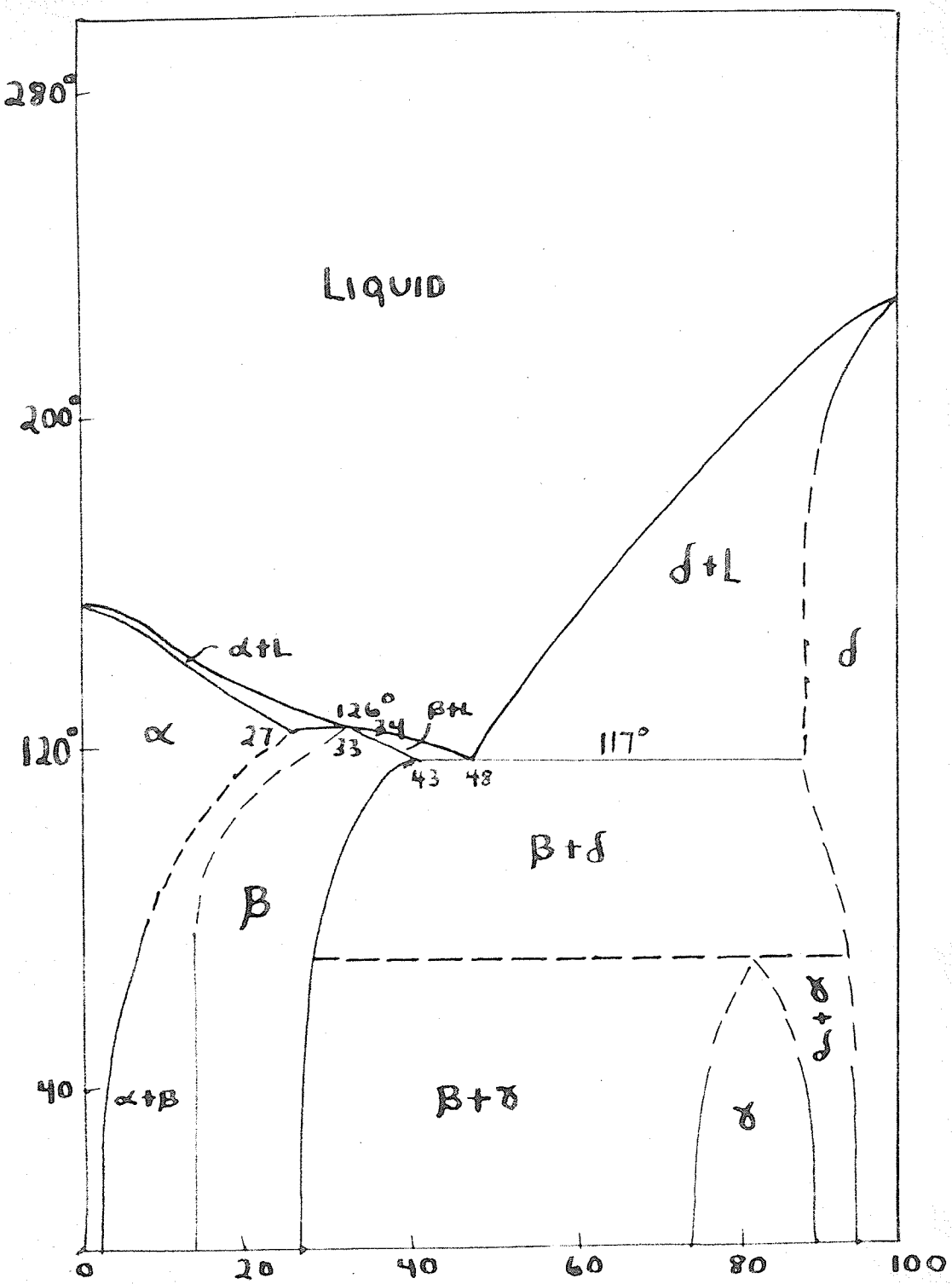
S. Valentiner (33) published the results of his investigation on this system in 1940. By thermal analysis he determined the position of the liquidus and the eutectic horizontal. His results disagreed with those of Rink et al. in that he found no peritectic transformation on the liquidus, and that the eutectic horizontal went beyond the limits set by Fink et al. The eutectic horizontal in fact passed right through the γ region.

Valentiner (34) did further work on this system using X-ray and electrical conductance measurements. By means of these methods he was able to find the β and γ phases of Fink et al. However, Valentiner made no attempt to determine their areas of existence, but did attempt to determine their structure.

Rhines et al. (25) were the next workers to publish on this system. For the determination of the diagram they used precise thermal and metallographic methods. They set the limits of the four solid solutions at 20° as

α	0-3 wt. % tin
β	14-27 wt. % tin
γ	75-88 wt. % tin
δ	95-100 wt. % tin

FIG. 9



WT. % Sn

In-Sn System

(Rhines et. al.)

Thus the results of Rhines et al. agreed quite closely with those of Fink et al. However, Fink et al. had four alloys with arrests at 124° on cooling. Hence they placed the peritectic temperature for the γ phase at that temperature. Rhines et al. on the other hand, did not observe any thermal arrests in this region. Hence, in their diagram they omit this line. Instead they proposed that the γ phase must undergo peritectoid decomposition at a temperature above 80°C. However, they did not determine the exact temperature.

Rhines et al. investigated the liquidus very thoroughly and found that the curves did not fall smoothly but that three inflection points were observable. These inflection points occurred at 17, 34 and 80 wt. % tin and suggested peritectic transformations. However only one (34%) has been associated with a peritectic.

Valentiner, Rhines et al. and Fink et al. agreed that the eutectic temperature of the system was in the neighborhood of 117°C and basically agreed on the general diagram of the system.

The crystal structures of the two phases (β and γ) were investigated by Valentiner. He proposed a face-centred tetragonal lattice for β phase and the body-centred tetragonal structure of white tin for γ phase. Fink et al. disagreed with Valentiner on the lattice of γ phase and proposed instead a simple hexagonal

lattice with one atom per unit cell, that is, a structure with a primitive hexagonal packing. Fink et al. were unable, however, to confirm this unusual structure by intensity measurements for lack of good photographs although their indexing on the primitive hexagonal lattice was very satisfactory. They pointed out that for the β phase, their body-centred tetragonal lattice with two atoms per cell was simply a smaller cell of the same lattice, the F-lattice with four atoms per cell, that Valentiner had proposed, the one cell being related to the other by a rotation of the a axis through 45°. Hence both authors agree on this structure.

E. Orlamunder in the paper by Klemm et al, confirmed Valentiner's tetragonal F-lattice for the β phase but disagreed with Valentiner's proposed structure for the γ phase although she proposed no substitute for it. Orlamunder evidently was unaware of the work done by Fink et al. on this system.

Thus the exact structure of the γ phase is still in doubt while that of the Beta phase seems to be agreed upon at least by those three groups of authors.

The System of In-Sn-Pb

The only previous work that has been reported on this system is that of Grymko and Jaffee (8). While their work dealt primarily with the corrosion-resistant properties of In-Sn-Pb solders, they mention that the liquidus of an alloy of composition 37.5 wt. % lead, 37.5 wt % tin and 25 wt % indium is at 181°C while the solidus is at 134°.

No other data could be found on this ternary system.

Experimental Procedure

Purity of Materials

The metals used in this investigation were analyzed by the companies supplying them.

Lead (Merck Reagent Grade)

Maximum Impurities

Antimony	0.005%
Silver	0.002%
Total Foreign Metals	0.05%

Indium supplied by the Consolidated Mining and Smelting Company Limited (marked Tadanac 99.95 + Indium)

	Batch I	Batch II
Tin	.015%	.015%
Nickel	.002%	<.001%
Lead	.014%	.016%
Copper	<.001%	.003%
Cadmium	<.001%	<.001%
Iron	-----	<.001%

Tin Vulcan "Commercial" Tin Batch #73

Iron	0.0020%
Antimony	0.0023%
Lead	Trace
Copper	Trace
Tin	99.9957% (by difference)

Method of Chemical Analysis

The composition of the alloys was determined after each run. Although oxidation was generally very slight, it was thought necessary to analyze because of the dangers of preferential oxidation.

The sampling of an alloy in which solid solutions occur is generally the cause of inaccuracy in the determination of the composition. Hence, it was decided to sample the alloy while it was in the molten state. The method of sampling was as follows:

The alloy, which was in an alundum crucible, was heated about 25° above the liquidus and then stirred with an alundum rod. An alundum tube with an internal diameter of 1/16 of an inch and an external diameter of 1/8 inch was placed in the melt and mild suction applied. A core of the alloy was thus drawn up into the tube where it solidified. The tube was broken away and the whole core weighed out for analysis. It was thought necessary to use the entire core because of concentration gradients within the tube.

When the temperature of the melt was below 175° Pyrex capillary tubes of internal diameter of 2 mm. were used instead of the costly alundum tubes. The glass tubes were found to be very satisfactory and broke away from the core very cleanly. However, if the

temperature of the melt was above 200° the glass had a tendency to adhere to the metal. Thus the use of glass tubes was limited to the lower temperatures.

Two methods of chemical analysis were used in this investigation.

1. For use in regions where indium content was low.

A 1.5 - 2.0 gram sample was weighed out. Around this sample a piece of platinum foil was wrapped. The sample was then placed in a 250 ml. Erlenmeyer flask which was connected to a water condenser. 75 mls. of conc. Hydrochloric acid were added and the Erlenmeyer placed in a water bath. The flask was heated at 100° until solution was complete. This generally took five hours. The purpose of the condenser was to prevent loss of the volatile $SnCl_4$. The platinum foil was to speed up solution by formation of an electrotytic cell.

When solution was complete, the contents of the Erlenmeyer were poured into a 500 ml. volumetric flask while still hot. The Erlenmeyer and condenser were then washed several times with boiling water and the solution made up to 500 ml. by addition of hot water.

While the solution was still hot aliquot portions were drawn off for analysis of tin and indium.

Tin was determined by a method (slightly modified)

suggested by Scott (29). The aliquot portion of the solution containing from .2-.3 gs. of tin was placed in a 250 ml. Erlenmeyer. To this 1 gram of 200 mesh antimony powder was added, followed by 100 ccs. of air-free water and 50 ccs. of conc. Hydrochloric acid. The method as given by Scott was then followed. The iodine solution had previously been standardized using tin treated exactly in the same way.

Indium was determined by means of a Sargent Heyrovsky Polarograph.

The method of determination of indium as outlined by Tuxworth (32) proved unsatisfactory in the analysis of this three component system. Hence it was necessary to modify the procedure. The revised method is as follows:

A portion of the alloy sample was diluted until the concentration of indium was .0001 - .0002M. The last solution was buffered with ammonium acetate. About 10 mls. of this solution were placed in the polarographic cell. To remove the oxygen, a stream of hydrogen was passed through the solution for ten minutes. Then a polarogram was taken with span voltage set at 2.0 Volts and the shunt rationof 5. The resulting polarogram was compared with a polarogram determined previously using solutions of know indium concentrations. In each case five or six curves were made on each solution to increase accuracy.

The lead content of the sample was determined by difference.

2. In the regions of high indium content a method suggested by the Consolidated Mining and Smelting Company Limited was used. An outline of this method follows.

A sample weighing between 1 - 1.5 grams was dissolved in 1: 5 $\ddot{H}NO_3$ in a 150 ml. beaker. The beaker was then placed in a water bath maintained at 95-100° for four hours. Following this prolonged digestion, the metastannic acid was filtered off, washed ten times with hot 1 : 10 Nitric acid. The metastannic acid was then ignited to SnO_2 in a porcelain crucible.

The lead was determined by the standard method of precipitation as $PbSO_4$ washing with ethyl alcohol and drying at 110° for one hour.

Indium was determined by difference.

Thermal Analysis

Apparatus

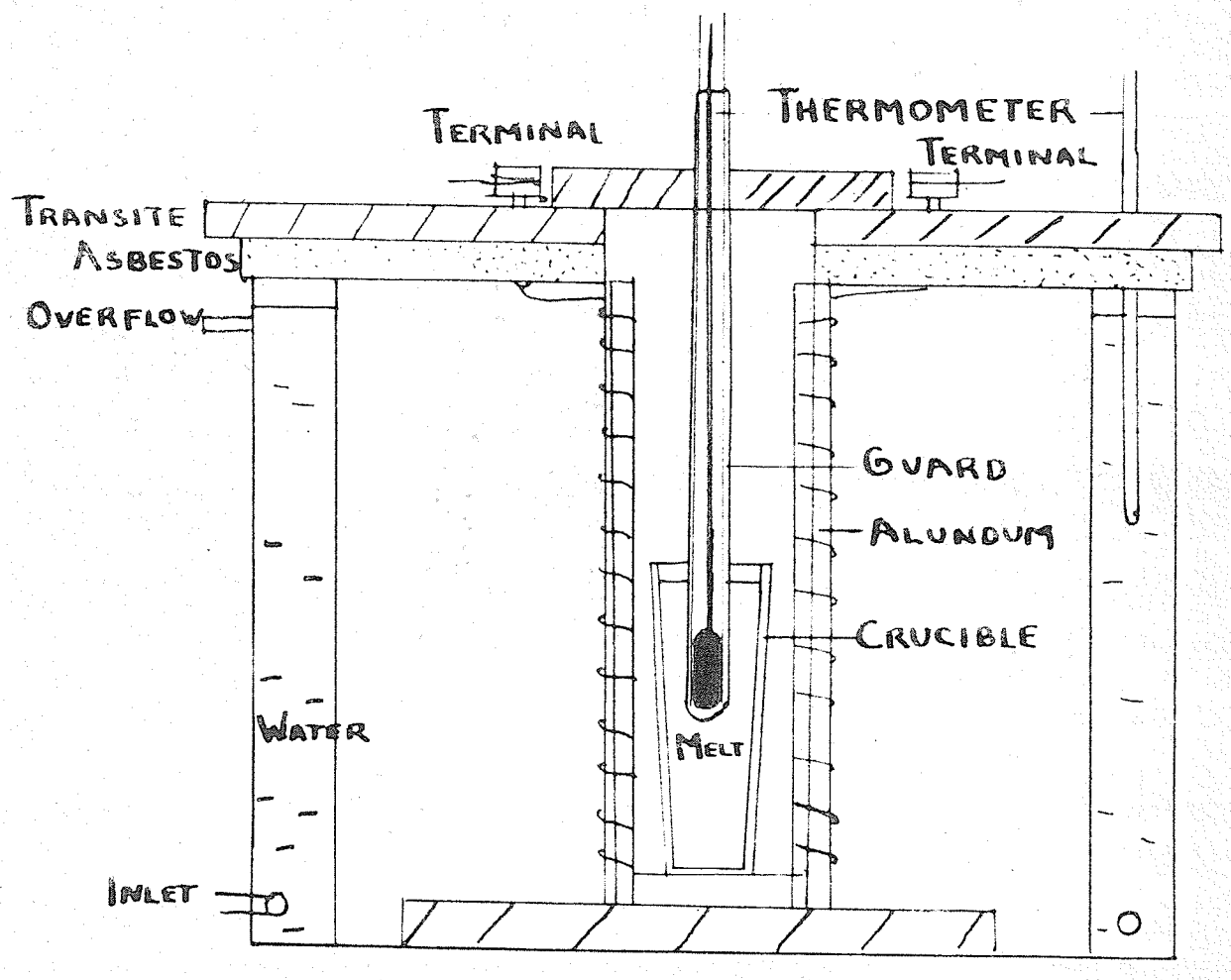
The furnace used for this investigation was constructed in the following manner.

Thin sheets of asbestos soaked in water glass were wrapped around a hollow alundum tube which had external and internal diameters of 5.5 and 4.5 cms. respectively. The height of the alundum tube was 16.5 cms. A base of asbestos cement was constructed for the tube. No. 22 guage (B and S) Nichrome wire of length sufficient to have 25 ohms resistance was wrapped tightly around the covered tube and across the base. Care was taken not to have the wire overlapping at any point. The Nichrome wire was then covered with several sheets of asbestos soaked in water glass. The whole core was then dried in an oven for 24 hours at 110°C.

A circular tank 25.5 cms. in diameter and 18 cms. in height was constructed of #24 guage copper sheet. At the centre of this tank another circular copper tank of 21.3 cms. diameter and of the same height was silver soldered. Water passed through the space between the two copper sheets. The inlet and outlet for the water were placed as shown in the diagram. To ensure circulation of the water the entering water was led into the water

Fig. 10

Cross Section of Furnace



space by means of a copper tubing in which holes were cut every 5 cms. This copper tubing with the end closed off was bent into a circular shape, placed at the bottom of the water space and connected to the water inlet. The temperature of the water was kept constant at 25°C by regulating the flow of tap water by hand. The purpose of the outer water space was to maintain a constant atmosphere so that linear cooling could be achieved.

The furnace core was placed on a 1 cm. thick section of asbestos board at the centre of the two tanks. The top was cut from Transite 7 mm. thick to which 1 cm. of asbestos board had been cemented.

A hole 5.5 cms. in diameter was cut in the centre of the Transite board. The leads to the furnace were brought out as shown in the diagram.

A cover of 5/8 inch Transite asbestos board was constructed for the furnace core. A hole was drilled in this so that the thermometer and protective casing could pass through.

The melts were contained in alundum crucibles 8.2 cms. high, the external diameter at the base being 3.1 cms. while that at the top was 3.4 cms.

Temperature measurements were made by means of 0-201° (76 mm. immersion) mercury in glass thermometer.

The divisions were 0.2° apart. To protect the bulb of the thermometer it was snugly enveloped in a pyrex tube which had the lower end sealed off. The thermometer was calibrated against a platinum thermometer using an oil bath. To ensure that errors introduced by the protuding stem would be compensated for, the thermometer was placed in the oil to the same depth as it would be when used in the melt. The air space between the cover and the oil was adjusted so that it equalled the depth of air space in the furnace. Consequently, the conditions of calibration were identical with those of actual use, and the error involved in the stem protuding should be a minimum.

The greatest correction term was .2° hence, the temperatures should be accurate to ± .2°C.

Thermal Analysis

Method

1. Determination of Position of Eutectic Trough

The terminals of the furnace were connected in series to a 25 ampere ammeter and to a power source. The current was regulated by means of a bank of rheostats and a Variac. Later the bank of rheostats was replaced by another Variac to give greater ease in shifting from one rate of cooling to another.

Linear cooling was obtained by the following method. A copper block with a hole drilled in it of sufficient size to contain the protecting tube of the thermometer was placed in the furnace core. The size of the block was such that it approximately equalled the heat capacity of the melt and crucible for a typical run.

The thermometer bulb, properly protected, was placed in the copper block. The current was adjusted by trial and error by means of the external bank of rheostats until a temperature of 200° was maintained in the furnace when the Variac was set at 100.

The Variac setting was lowered one division a minute and the resulting temperature recorded. A plot of temperature against time was then made. Corrections were made on the Variac settings and the process repeated.

By repeating this method several times a linear plot was obtained from 200 to 100°. The duration of such a run was approximately 100 minutes.

Since this rate of cooling (1° per minute) was thought to be too great for those alloys melting at lower temperatures a slower rate was used for them. The upper temperature was 180° while the lower limit was 80°. The time required was 150 minutes.

This method of obtaining linear cooling may seem rather tedious, however it is far superior to the previously used method of straight resistance adjustments to cut down the current.

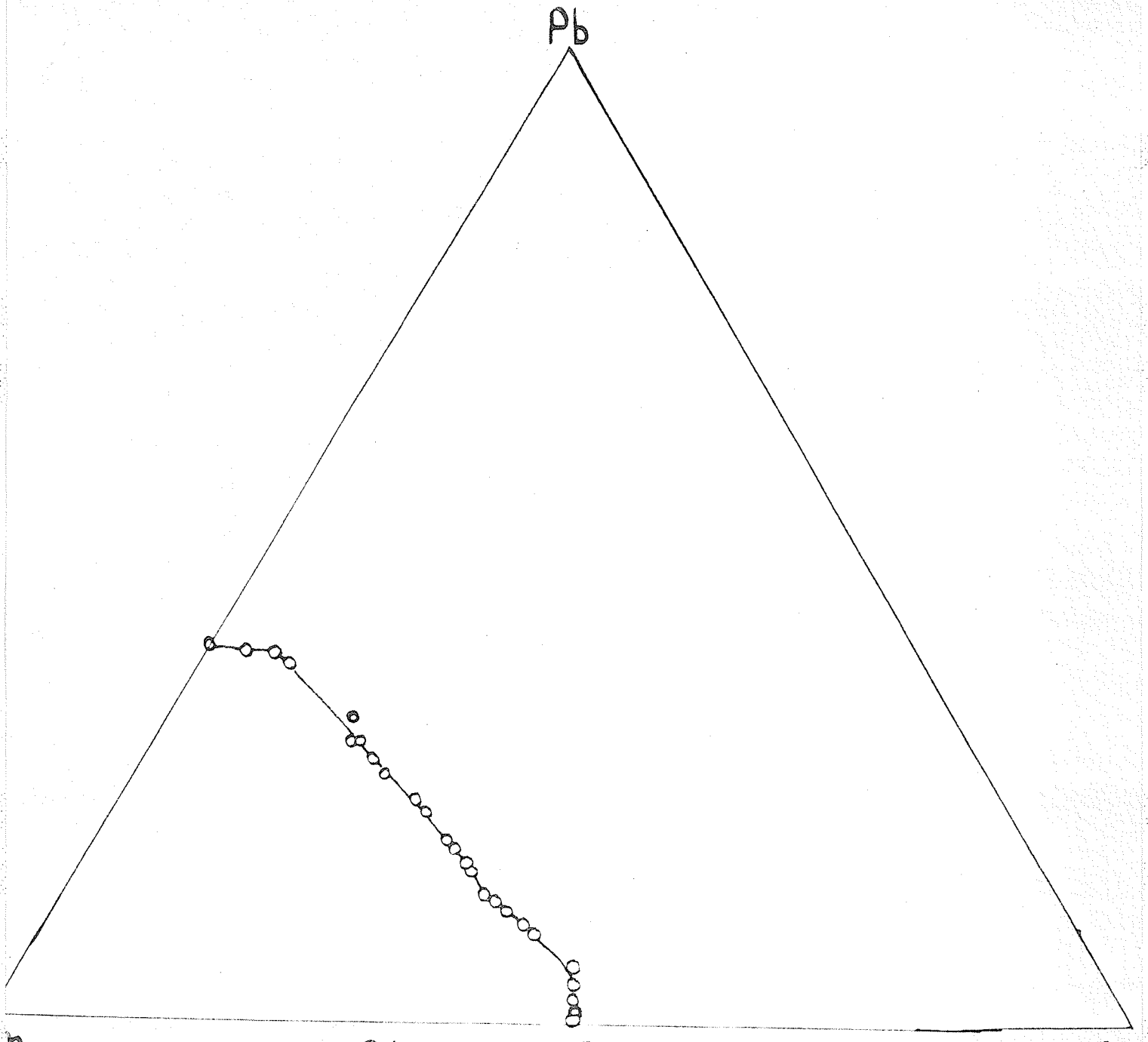
When linear cooling had been achieved from 200-100° as outlined in the preceding paragraphs actual runs were made. The first alloy was the Pb-Sn eutectic. This was made up according to Stockdale's results (28). The alloy was prepared by melting the tin in an alundum crucible similar to the one previously described and adding the correct amount of lead to the molten tin. The lead sank below the surface of the tin and consequently did not oxidize to such an extent as it would have if it had been heated directly. The temperature of the alloy was raised to about 250°C until all the lead had dissolved. The melt was stirred using an alundum rod and the current set at the value required to maintain

200° as previously determined. When 200° had been reached the alloy was cooled linearly. To ensure that equilibrium is attained the alloy was heated to 200° stirred and let stand for two hours and then cooled linearly. Since the results were identical with those attained for the first run, the melt was assumed to be homogeneous. The weight of melt was approximately 150 grams.

To the eutectic mixture four grams of indium were added and the process repeated using a maximum temperature of 200°. The procedure was then repeated increasing the amount of indium every trial, but making sure the alloy was of such a composition as to be in the eutectic trough. This determination was easily made by an examination of the cooling curve. If by adding indium the alloy was out of the trough small amounts of tin were added until the alloy on cooling gave the characteristic trough curve.

Thus the path of the trough was determined in the Pb-Sn side of the diagram. When it became obvious that the trough was heading directly toward the In-Sn eutectic, it was decided to investigate the position of the trough starting from that point.

Consequently, that eutectic mixture was made up according to the composition as determined by Rhines et al (25). The temperature of the binary eutectic was determined by means of thermal analysis using two mercury in



POSITION OF EUTECTIC TROUGH

FIG. 11.

glass thermometers and two different batches of the eutectic mixture. Altogether six determinations were made in determining the eutectic temperature.

The path of the lower end of the trough was then investigated by adding lead and the required amounts of tin.

B. Investigation of Pb-In System

The diagram of the Pb-In diagram as given in "Indium" by Maria Ludwick (20) showed that the presence of a depression of 1° is noted on addition of lead to pure indium. The presence of this depression was checked by the use of a Beckmann thermometer. The bulb of the thermometer was protected by a Pyrex test-tube drawn out so that the bulb of the thermometer fitted snugly into the tube. To ensure better thermal contact a small quantity of paraffin oil was placed in the test-tube.

The Beckmann thermometer in the pyrex test-tube was first placed in a crucible containing 130 grams of pure indium in a furnace in which the current was adjusted so that the temperature remained at 158.5°. The furnace was then shut off and the alloy allowed to cool. The Beckmann readings were recorded every 10 seconds. Hence the temperature of solidification could be obtained by the standard method of graphical

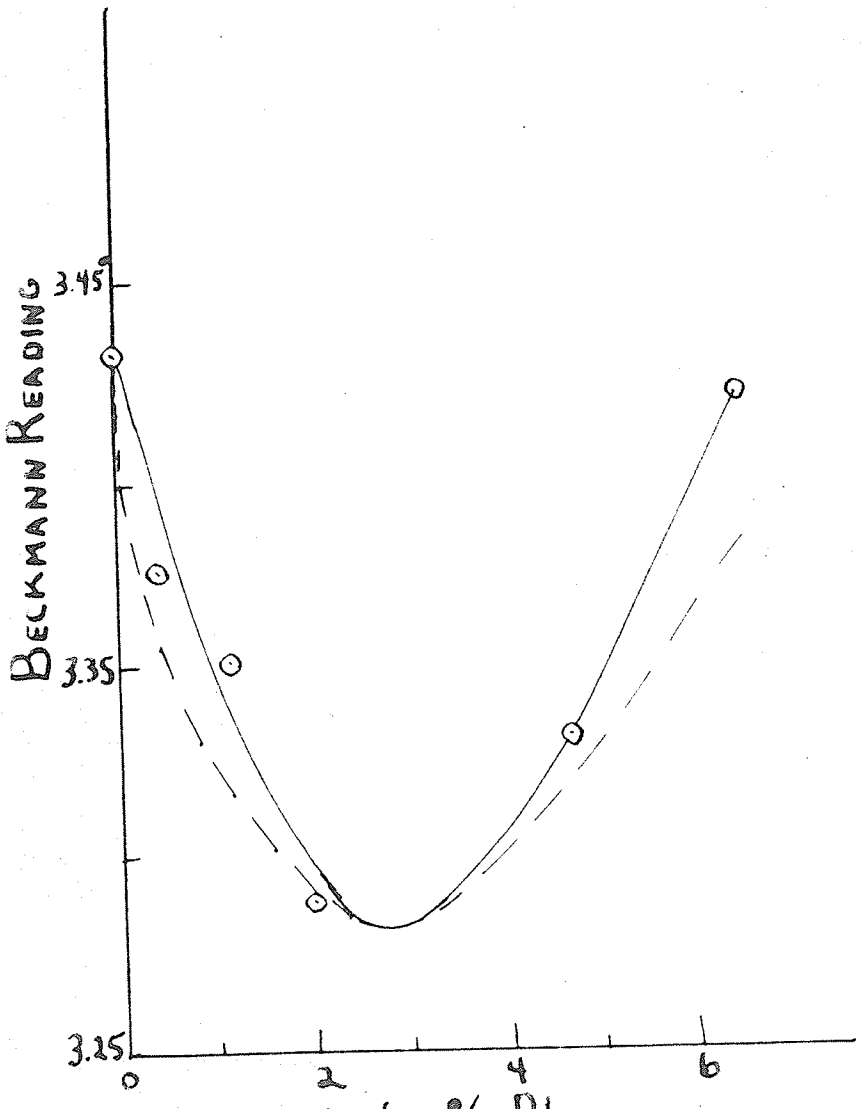


FIG 12
In-Pb

plotting. When three determinations had been made on the pure indium a small quantity of lead was dissolved in the indium. After solution of the lead had been accomplished the alloy was allowed to stand at a temperature of 180° for two hours to ensure equilibrium. Stirring was done several times during this interval. The alloy was then cooled to 158.5° and stirred. Since no solidification was observed at this temperature and since no thermal effects were observed by the use of 0-201° C thermometer in the range 175-158, the alloy was assumed to be homogeneous. The solidification point of the alloy was then determined. This was done three times for each addition of lead. The process was repeated for four more additions of lead and the temperatures of solidification noted.

The temperature of solidification of the last alloy was measured on the calibrated 0-201° thermometer and hence the absolute values of all the results were determined.

C. Peritectic Investigation

The next undertaking in this research was a study of the peritectics of the binary systems and their influence on the ternary diagrams. The first peritectic made up was that of the γ phase of In-Sn diagram.

Alloys were made up corresponding to desired composition and after suitable treatment to ensure equilibrium were allowed to cool linearly. The cooling curves of the three mixtures were then compared to see if the presence of the peritectic was easily determined. Following this a small quantity of lead was dissolved in the peritectic mixture and the cooling curve determined. Since the peritectic halt was not too easily observed in the binary, its presence in the ternary was not able to be determined by thermal analysis only.

This process was repeated for the two In-Pb peritectics but with only one could the peritectic halt be seen to be great enough to warrant further thermal analysis. That one at 172.4° according to Davis (4) was seen to give a noticeable halt at 172.0°. Consequently a small quantity of tin was added to that mixture and a cooling curve determined.

Since the peritectic reaction was so small in the binary it was not expected to be large enough to be distinguished in the ternary. This was found to be the case.

D. Liquidus Determination

To complete the liquidus it was necessary to determine the temperature at which solidification began for those alloys whose compositions differed from those of the

trough. The process involved here was the determination of the cooling curve for alloys made up of the desired composition.

It was necessary to determine the shape of the liquidus in the region of high lead content. The temperature of the liquidus in such a region would have been too high for the previously calibrated thermometer to be used so consequently another means was used.

A chromel-alumel thermocouple was connected to a voltmeter which read up to 1800 millivolts in 10 millivolt intervals. The thermocouple was placed in a sample of pure lead and its melting point determined. Since the melting point of lead was accurately known to be 327.3°C, the voltage corresponding to this on the thermocouple voltmeter was recorded. The experiment was repeated uding the desired composition. The voltage at which solidification began was noted. The temperature of this was determined on the basis of the melting point of pure lead and the reading corresponding to zero temperature difference across the thermocouple. The cool leads of the thermocouple were immersed in an oil bath maintained at 28.9 ± .1°C by means of mercury regulator and relay.

X-Ray Analysis

Apparatus

The apparatus used for taking the X-Ray pictures was a North American Phillips X-ray unit with a simple Debye Camera of 57.3 mm. diameter.

The radiation used was copper with a nickel filter.

Method

Since the exact structures of the β and γ phases of In-Sn system were not known, it was decided to investigate their structures by means of X-rays.

An attempt to obtain a single crystal of the γ phase was made. The following method was used:

The metals in the desired proportions were placed in a small Pyrex test-tube which was then evacuated and sealed off. The tube was heated and shaken until complete solution of the two metals was obtained. The Pyrex tube was placed in a furnace set for 220°. This temperature was maintained for five days. Following this the furnace temperature was lowered 5° a day until a temperature of 110° was reached. This temperature was maintained for one week.

Because the metals were so soft no usable crystals were obtained and therefore it was decided to abandon the single crystal method and sttempt the powder rolling method. For this the alloy previously prepared was used.

With a triangular file using very light pressure, filings were obtained. These filings were examined under a microscope and the large particles removed. The remaining small particles were made into a rolling using "Nuskin" as the binding agent in the standard manner. An X-ray diffraction picture was taken of the rolling using the apparatus previously mentioned.

The resulting picture was read to determine if the γ phase was the only phase present. In order to get a better diffraction picture the following method was attempted. An alloy of the desired composition was melted and by means of suction drawn up into a very small capillary tube of Pyrex glass. This was kept at 110° for ten days. The glass tube was then carefully broken away and small sections of the core preserved. These were rolled until uniform and of diameter .02 cms. An X-ray picture was taken of the resulting wire which was found to consist solely of the γ phase. However, because of preferred orientation the picture was much more spotty than the powder rolling and hence was rejected.

Using the powder rolling previously prepared and three layers of X-ray film a picture was taken in the Debye Camera. The exposure time for this picture was ten hours. The purpose of the three films was to obtain a better measurement of intensity. Since the film

would absorb a fairly substantial proportion of the X-rays, only the strongest lines would appear on the outermost film while very weak lines would be observable on the inner film.

The intensities and spacings of the lines were read visually by two persons and the results averaged. The intensities and spacings were then compared with those which would have resulted if the simple hexagonal structure were the true structure.

The picture of the β phase was obtained by preparing a rolling of the correct composition according to Fink et al and using the filing technique as outlined above. Only one film was used however.

Experimental Results

Thermal Analysis

Table 1

A - Determination of Eutectic Trough

Alloy No.	Solidification Temperature (°C) Start	Finish	Sn %	Composition by Wt. In %	Pb %	In + Pb %	Further Halts on Cooling
Pb-Sn Eutectic	183.3	183.3	61.9	----	38.1	0	----
1	177.6	174.8	59.5	2,9	37.6	7.2	----
2	170.7	164.5	57.0	5.8	37.2	13.5	----
3	164.7	159.1	56.1	7.7	36.2	17.6	----
4	147.7	134.9	54.1	17.3	28.6	37.7	----
7	135.9	130.8	51.8	25.9	22.3	53.6	----
8	134.3	129.4	51.5	27.4	21.1	56.5	----
9	132.7	128.0	51.1	28.9	20.0	59.2	----
10	131.2	126.4	50.9	30.3	18.8	61.7	----
11	130.0	126.0	51.1	31.1	17.8	63.6	----
12	129.0	126.0	50.7	32.2	17.1	65.3	----
13	128.3	125.7	50.2	33.5	16.3	67.2	----
14	127.1	125.1	50.1	34.6	15.3	69.4	----
15	125.9	124.5	50.3	36.6	13.1	73.6	----
16	124.9	123.6	49.8	38.0	12.2	75.7	----
17	124.5	121.5	49.4	38.9	11.7	77.4	----
18	118.7	118.7	48.7	51.3	----	100.0	----
19	118.9	118.7	48.4	51.1	0.5	98.9	----
20	119.6	118.8	47.4	50.0	2.6	95.0	----
21	120.3	119.6	46.8	49.3	3.9	92.7	----
22	121.7	120.0	45.8	48.3	5.9	89.2	----

Table 1 (cont'd)

Alloy No.	Solidification Temperature (°C) Start	Finish	Composition by Wt. Sn %	In %	Pb %	In/Pb %	Halts on Cooling
23	122.6	121.4	48.1	42.8	9.1	82.4	-----
25	123.9	122.5	48.2	42.0	---	8.0	-----
26	118.8	118.8	48.7	51.3	---	100.0	-----
27	118.8	118.8	48.7	51.2	0.1	99.8	-----
30	150.3	133.3	53.2	15.8	31.0	33.8	136.8-7.3
31	147.1	133.8	53.4	18.2	28.4	40.3	137.1
32	144.6	132.8	53.5	20.0	26.5	43.0	137.3
33	142.0	131.9	53.6	21.8	24.6	47.1	137.2

Whether a given composition was in the eutectic trough was very easily accomplished by observation of the cooling curve.

In the case of a composition being in the trough on cooling a curve of fig. 13 (b) was obtained. It was found that for all alloys whose composition could be represented in the trough had a horizontal at the beginning of solidification. This horizontal was largest for those alloys whose composition approached that of the two end binary eutectics and was a minimum for those which were far removed from the eutectics. If on cooling a melt, a point of inflection was noted above the temperature of this horizontal the alloy was not in the trough and consequently its composition had to be altered until the point of inflection was removed. This is given in fig. 13 (a).

It should be noted that this method of determination of trough is only applicable to those alloys whose composition is close to that represented by the trough. If the composition is too far removed, prior precipitation causes insufficient liquid to cause the apparent horizontal.

FIG. 13

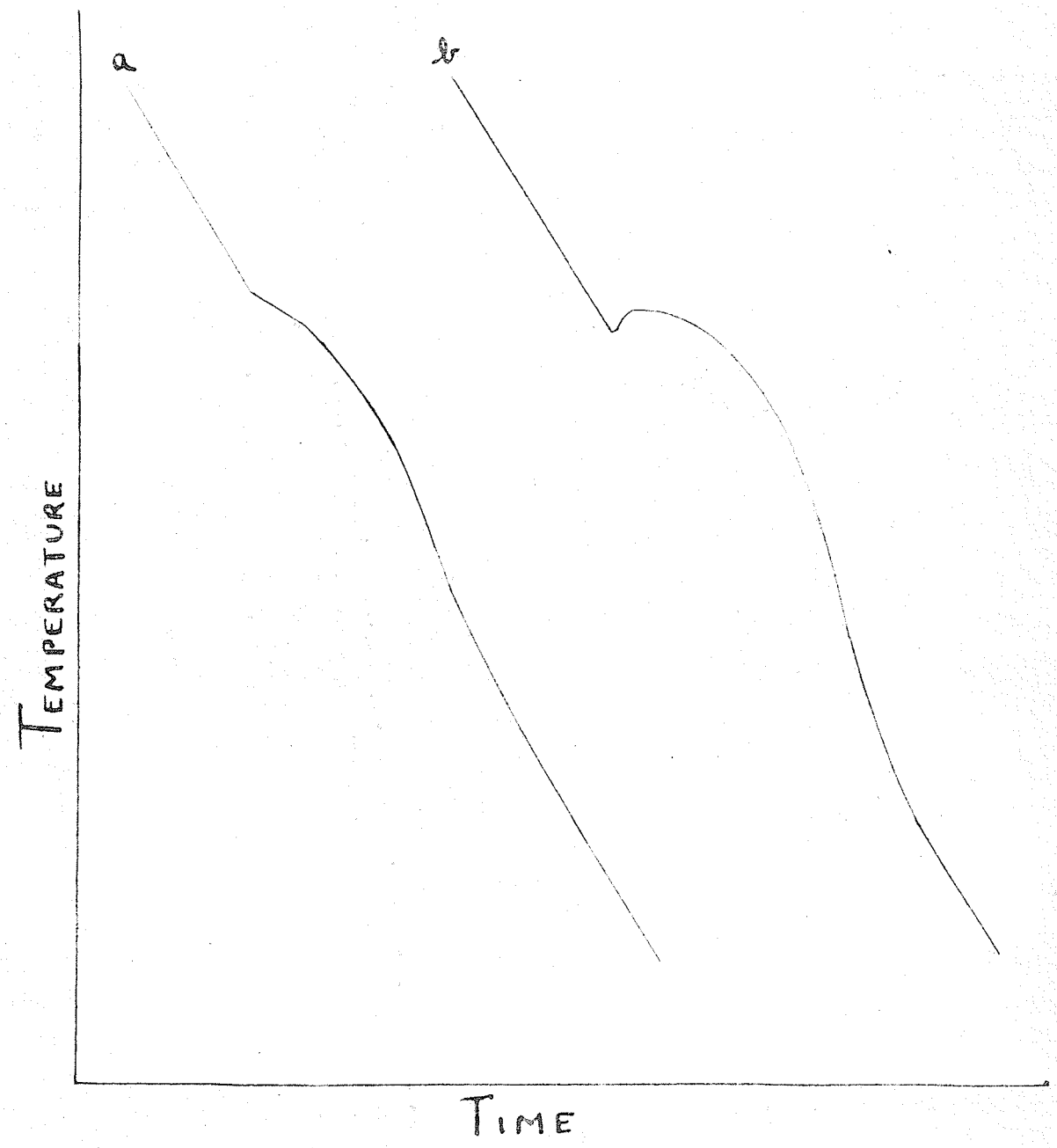


Table 2

B. Effect of small quantities of lead on the melting point of indium.

Alloy No.	Composition Wt. %		Melting Point			
	In	Pb	Trial 1	Trial 2	Trial 3	Mean
53	100.	0	3.435	3.378	3.480	3.431
54	99.59	0.41	3.368	3.380	3.375	3.374
55	98.87	1.13	3.348	3.342	3.370	3.353
56	97.95	2.05	3.308	3.292	3.268	3.289
57	96.83	3.17	3.296	3.270	3.278	3.281
58	95.30	4.70	3.330	3.342	3.322	3.331
59	93.57	6.43	3.408	3.423	3.435	3.422

Beckmann setting of $3.422^{\circ} = 156.5^{\circ}$

Melting point of pure indium was therefore = $156.5^{\circ}C$.

Table 3

C. Peritectic Investigation

1. Peritectic Investigation of In-Pb System

Alloy No.	Solidification Begins	Solidification Ends	Peritectic Halt	Comp.(% Wt) Sn	In	Pb
35	193.6	162.1	173.3	---	56.4	43.6
60	166.0	159.6	-----	---	74.5	25.5

2. Peritectic Investigation of In-Sn System

36	127.3	125.9	-----	32.2	67.8	----
37	127.9	126.5	-----	31.2	68.8	----
38	128.5	126.5	-----	30.4	69.6	----

Table 4

D. Investigation of Liquidus

Alloy No.	Solidification Begins	Solidification Ends	Trough Temp.	Comp. by Wt. % Sn	In	Pb
39	157.9°C	132.3°C	145.6°C	62.2	17.0	20.8
40	179.6	129.0	140.7	70.8	12.5	16.7
42	154.7	125.6	143.7	35.7	34.7	29.6
43	131.6	128.8	-----	28.6	65.6	5.8
44	140.4	133.7	-----	25.4	58.0	16.6
45	152.3	136.6	-----	22.6	51.8	25.6
46	172.3	137.7	153.8	20.1	46.0	33.9
47	177.5	138.5	152.3	19.3	44.4	36.3
48	123.6	121.5	-----	38.0	61.9	0.1
49	125.9	123.4	-----	36.4	59.3	4.3
50	127.5	125.6	-----	34.0	62.0	4.0
51	128.9	126.6	-----	31.6	64.7	3.7
52	130.6	127.8	-----	29.0	67.6	3.4
61	155.4	145.2	-----	10.1	67.0	22.9
62	241.0	-----	-----	21.5	14.2	64.3

Table 5

Results of X-ray Studies Cu-Ni radiation

γ Phase 81.75% Sn by weight

2θ	d obs.	d calc.	h k i l	I obs.	I calc.
30.05	2.97	2.992	0001	2.5	4.25
32.35	2.77	2.781	$10\bar{1}0$	10	11.6
44.55	2.03	2.037	$10\bar{1}1$	10	12.8
57.35	1.604	1.606	$11\bar{2}0$	4.5	4.21
62.20	1.490	1.496	0002	0.5	1.20
66.00	1.413	1.415	$11\bar{2}1$	7	6.31
67.35	1.388	1.390	$20\bar{2}0$	3.5	3.05
71.70	1.314	1.317	$10\bar{1}2$	5	5.49
75.45	1.259	1.261	$20\bar{2}1$	5	5.00
89.55	1.094	1.095	$11\bar{2}2$	4	3.97
94.25	1.051	1.051	$21\bar{3}0$	4	3.74
98.35	1.018	1.018	$20\bar{2}2$	4	3.72
-----	-----	0.997	0003	0	0.62
101.9	0.992	0.992	$21\bar{3}1$	7	7.48
110.2	0.939	0.939	$10\bar{1}3$	3.5	3.87
112.45	0.927	0.927	$30\bar{3}0$	1.5	1.96
*120.6	0.887	0.885	$30\bar{3}1$	4.5	4.39
*126.8	0.861	0.860	$21\bar{3}2$	9	9.91
*130.2	0.849	0.847	$11\bar{2}3$	6	5.30
*143.1	0.812	0.810	$20\bar{2}3$	7.5	7.35
*146.4	0.805	0.803	$22\bar{4}0$	3	4.02
*154.8	0.789	0.788	$30\bar{3}2$	9	10.9
*165.1	0.777	0.775	$22\bar{4}1$	9	18.9

* refers to the α_1 line

Table No. 6

Results of X-ray Studies Cu-Ni radiation

β phase In-Sn		24.99% Sn by Weight			
2θ	d obs.	d calc.	h k l	I obs.	I calc.
33.15	2.70	2.717	101	10	10
36.85	2.44	2.449	110	3.75	4.1
41.35	2.182	2.191	002	5	1.6
53.15	1.722	1.731	200	1.75	2.1
56.4	1.629	1.633	112	6.5	3.8
63.7	1.459	1.460	211	5.5	6.0
69.3	1.354	1.358	202	2	2.6
69.9	1.344	1.346	103	5	2.6
77.9	1.255	1.224	220	.25	1.0
87.6	1.113	1.116	301	.75	1.8
89.7	1.092	1.096	004	1.50	2.1
92.8	1.064	(1.063 (1.069	(113 (222	4	5.0
100.9	0.999	1.000	114	2	1.7
103.8	0.979	0.980	312	2	3.4
110.7	0.936	0.938	321	1.5	3.5
112.6	0.926	0.926	204	1.5	1.8
116.7	0.905	0.906	303	1	1.8
130.2	0.849	0.850	105	3	2.3
137.6	0.826	0.825	411	3.5	5.4
141.4	0.816	0.816	224	3.5	4.6
146.7	0.804	(0.805 (0.802	(402 (323	3.5	10.7
✱ 166.2	0.776	0.775	---	9	----

✱ denotes α_1 line.

The X-ray intensities were calculated using the expression as given by Bunn(2). Additional information was obtained from other references (10 and 40).

I calc. = (k) (Angle Factor) (T) (A_p) (F^2)

I calc. = intensity as calculated

k = arbitrary constant so chosen that

I calc. = I obs. for the line $20\bar{2}1$

$F^2 = A^2 + B^2$ - Structure Amplitude

A and B are calculated as follows

$A = \Sigma f \cos 2\pi(hx + ky + lz)$

$B = \Sigma f \sin 2\pi(hx + ky + lz)$

The term f is the Thomas Fermi scattering factor which is a function of the angle θ and the atomic number of the element in question. Since in this case a very simple structure was being dealt with, the value of f was taken as a weighted mean between the literature values of indium and tin whose atomic numbers are 49 and 50 respectively. A plot of f against $\frac{\sin\theta}{\lambda}$ was drawn. The values of f at the desired angles θ were then read off.

h k l are the Miller indices of the plane in question

xyz are fractions of unit cell lengths.

If a centre of symmetry exists and if all atoms are equivalent as they are in this case B = 0 and

$A = \Sigma f \cos 2\pi$

hence $F^2 = f^2$

Angle Factor = $\frac{1 + \cos^2 2\theta}{\sin^2\theta \cos\theta}$

$T = e^{-B^1(\frac{\sin\theta}{\lambda})^2}$ where B^1 = arbitrary constant taken as 3 in this case.

A_p = Absorption Factor = μr

where $\mu = \mu m P$

μm = mass absorption coefficient for the radiation used.

P = density of alloy

A_p is a function of θ but the function is known. Hence the values of A_p were determined at various values of θ by a plotting of the literature values of A_p against θ.

r is the radius (in cm.) of the powder rolling.

P is the number of equivalent planes of the type in question.

I observed values were the mean of two readings, one done by Dr. R.B. Ferguson and the other by the author.

The values of d calc for the γ phase, hexagonal, were calculated from the following equation.

$$\frac{1}{d^2} = \frac{4}{3a^2}(h^2 + hk + k^2) + \frac{l^2}{c^2}$$

the values of a and c being the unit cell dimensions as determined by Fink et al.

The values of d calc for the β phase, tetragonal, were calculated from the following equation:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Discussion of Results

Thermal Analysis

A. Determination of Eutectic Trough

From Table I of the Experimental Results it can be seen that no true ternary eutectic was found in the system In-Sn-Pb. Instead the eutectic trough extends from the Pb-Sn eutectic to the Sn-In eutectic. The temperature of the liquidus at first falls rapidly from 183.3° C then less rapidly until the temperature of 118.7°C is reached. It appears as if two peritectics are present in this trough - one at 134°, the other at 126°. The presence of these was not determined by true peritectic halts but rather as cessation of solidifcation at a definite temperature for a range of composition along the trough. The presence of these horizontals can be seen readily by observation of the plot of $\frac{\text{weight of indium}}{\text{Wt. of indium + Wt. of lead}}$ (fig. 12)

The exact nature of these temperature horizontals can not be obtained readily from thermal analysis alone. Consequently X-ray and general metallographic methods should be applied to this system to determine the presence of the solid phases. However, there appears to be a great similarity between the binary Pb-In diagram (fig.7) and this diagram.

For alloys 30,31,32,33 it was observed that there was a point of inflection on the cooling curve at approximately 137°. This point could be due to two causes:

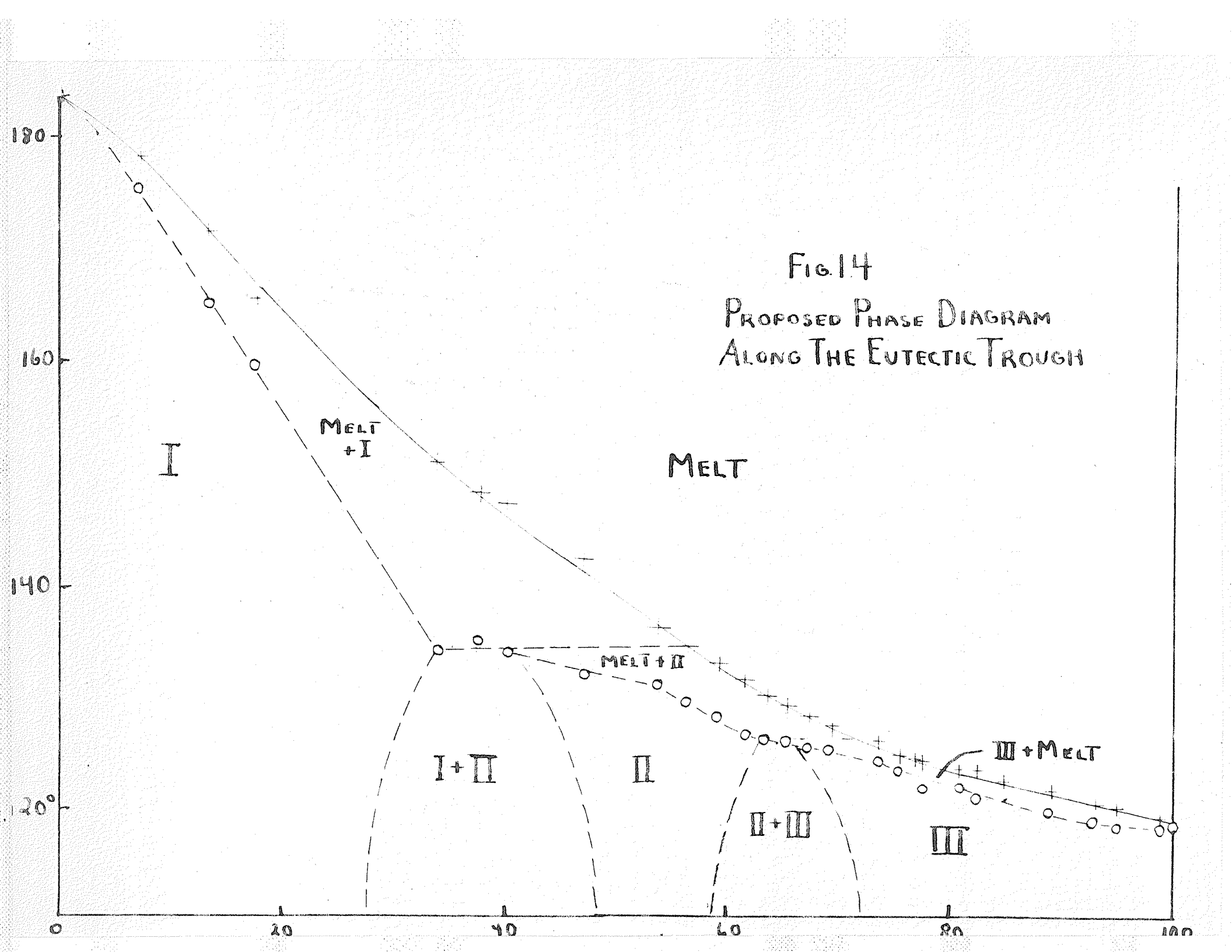


FIG. 14

PROPOSED PHASE DIAGRAM
ALONG THE EUTECTIC TROUGH

1. a peritectic point

2. the thermal effect noted in the Pb-Sn diagram might extend into the body of the ternary system and appear at a slightly lower temperature.

This heat evolution is very small and does not last for longer than two minutes with a cooling rate of 0.6° / minute. However, it was noted for these four alloys and was found to be reproducible within .3° for them.

The Pb-Sn eutectic was found to be 183.3° which is very good agreement with Stockdale's value (28). However, the temperature of the In-Sn eutectic is several degrees higher than that determined by other workers. The generally accepted value is 117° but was found in this investigation to be 118.7°. The cooling curve of the eutectic (made up according to Rhine's value) showed no halts at other temperatures. To ensure that no mistake had been made in making up the alloy, another sample (no. 26) was prepared. The eutectic point of this mixture was found to be 118.9°C. Consequently, it appears as if the eutectic value may be higher than previously thought.

B. Investigation of Pb-In System

From the results it can be seen that a depression does exist which however is not as large as previously suggested. The depression appears to be about .15° and not 1° as suggested by Ludwick. The accuracy of the

method employed is generally not too great, largely because of supercooling but in this determination supercooling never exceeded .2° and was generally about .05-.1°. There was considerable variation noted in the melting point of pure indium. However, it was noted that the melting occurred sharply in the three trials indicating the high purity of the indium used.

C. Peritectic Investigation

The peritectic which occurs at 173.6° according to Davis was found as a slight halt at a temperature of 173.3°. However, the heat evolved with this transformation appeared to be so small, that on addition of tin the effect was no longer noticeable and consequently the path of the peritectic in the ternary system could not be followed by thermal analysis alone.

The peritectic which occurs at 159.4° was not observed as a halt but rather as a cessation of solidification of alloy no. 60. The temperature was found to be 159.6°.

The peritectic of the β phase of the In-Sn diagram was not determined as a horizontal on subjecting alloys 36, 37, 38 to thermal analysis but these three alloys had solidi at 125.9, 126.5 and 126.5° which agrees with the generally accepted value of 126.°C.

Because of a lack of sufficient heat evolution accompanying these transformations, the investigation by thermal analysis of the positions of the peritectics in the ternary system had to be abandened.

D. Liquidus Investigation

The liquidus was found to be fairly smooth as shown by Fig. 15. A large number of points were spotted around on the surface to determine the position of the liquidus, but no irregular areas were found. A solid model of the system was constructed from Plaster of Paris and is shown in Plate I.

A large number of determinations were made in the neighbourhood of the 126° peritectics in the In-Sn diagram to determine the nature of the surface but no irregularity was observed that could not be accounted for by the shape of the binary curve.

The value of the liquidus as given by Grymko and Jaffee (8) does not appear to agree too well with these results. It appears that the freezing point for composition of 37.5% Pb, 37.5% Sn, 25% In is lower than their value of 181°C.

X-ray Analysis

a) γ Phase

From Table 5 there appears to be quite good agreement between the values of d calc. and d observed as well as between I calc. and I observed. Consequently, Finks proposed simple hexagonal structure seems to be correct.

b) β Phase

The crystal structure of this phase has been thought of as face centred tetragonal, however the observed values and those calculated from this proposed structure do not agree in all cases. The d values as calculated using Finks values for the constants appear to agree quite closely. However, although the intensity readings are generally in agreement there are several gross offenders. For example the line at 41.35° to which the value (.002) has been assigned has an intensity three times as great as that calculated. Consequently, the assigned structure may not be quite correct for the two values should agree quite closely.

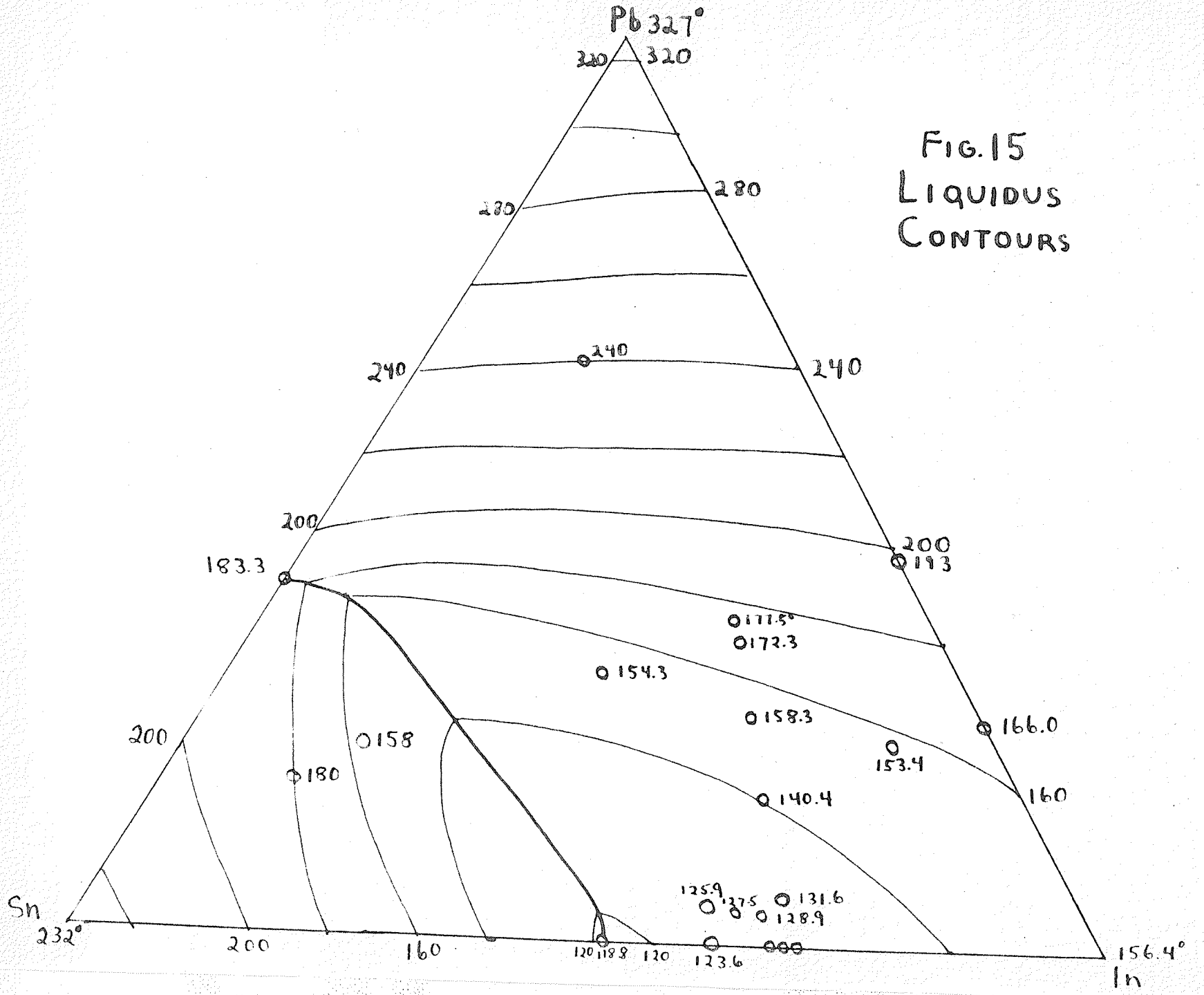
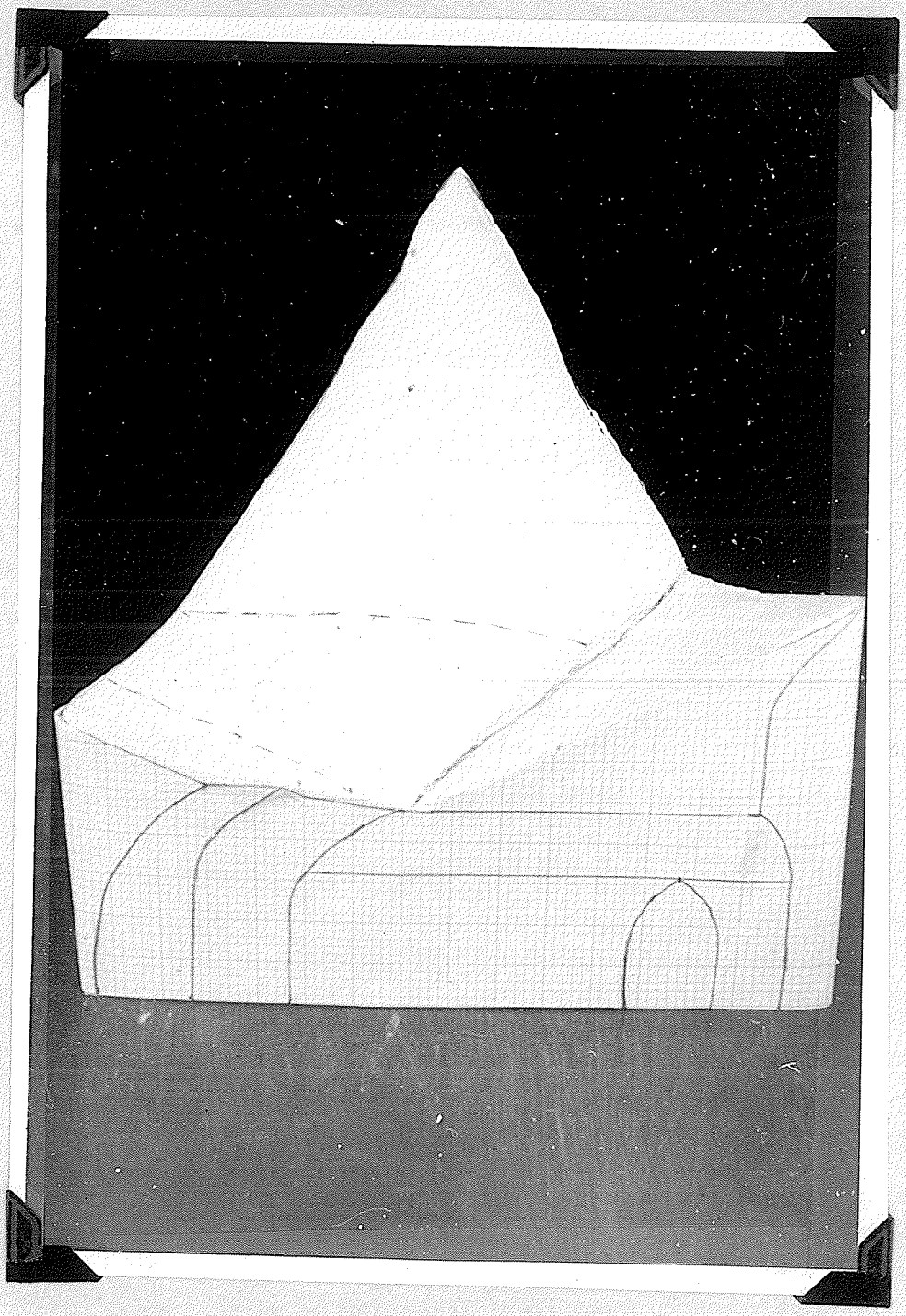


FIG. 15
LIQUIDUS
CONTOURS



Summary

1. The system In-Pb-Sn has no true ternary eutectic point.

2. There is a slight depression of melting point on addition of Pb to In but the depression is not as large as previously recorded.

3. The positions of the peritectics cannot be found readily in the ternary system by thermal analysis alone. There is a need for further work on this system using X-ray and optical metallographic methods to determine the nature of the solid phase.

4. The γ phase of In-Sn has a simple hexagonal structure as suggested by Fink.

5. The B phase of In-Sn does not have the tetragonal I-lattice with two atoms per cell proposed by previous authors although the correct structure has not yet been deduced.

6. The eutectic temperature of the In-Sn System was found to be 118.8° not 117° as other authors had reported.

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