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THERMAL STUDY OF THREE IN-TL ALLOYS IN THE NEIGHBORHOOD
OF THE F. C. C. TRANSITION;
HEAT CAPACITIES FROM 5-300°K

by

Robert Gerald Schwartz

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HEAT CAPACITIES FROM 5-300°K

by

Robert Gerald Schwartz

An Abstract of
A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

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Iowa State University
Of Science and Technology
Ames, Iowa

1970

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THERMAL STUDY OF THREE IN-TL ALLOYS IN THE NEIGHBORHOOD
OF THE F.C.T.-F.C.C. TRANSITION;
HEAT CAPACITIES FROM 5-300°K¹

Robert Gerald Schwartz

Under the supervision of B. C. Gerstein
From the Department of Chemistry
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The heat capacities and thermodynamic functions of three In-Tl alloys, having compositions of 34.6, 28.9 and 18.8-at. % Tl, have been measured from 5-300°K. In this temperature range, the 28.9-at. % Tl alloy transformed martensitically from f.c.t. to f.c.c., while the 34.6-at. % Tl alloy remained f.c.c. and the 18.8-at. % Tl alloy remained f.c.t. The entropy at 298°K was found to be 61.6 ± 1.6 eu, 61.4 ± 2.0 eu, and 61.1 ± 1.6 eu for the three alloys, respectively.

The alloy that transformed from f.c.t. to f.c.c. exhibited the expected deviations from normal heat-capacity behavior. While no alloy exhibited anomalous behavior below 195°K, above 195°K all alloys exhibited anomalous 5-8% rises in heat capacity, occurring over a 25° to 35°K range, depending on the alloy composition. This rise in heat capacity was irreversible in the 28.9 and 34.6-at. % Tl alloys, but reversible in the 18.8-at. % Tl alloy. This behavior was corrobo-

¹U.S.A.E.C. Report IS-T-362. This work was performed under Contract W-7405-eng-82 with the Atomic Energy Commission.

rated by the anomalous thermal expansion coefficients of f.c.c. and f.c.t. alloys reported by previous investigators.

The anomalous behavior of the f.c.t. alloy is believed to correlate with the "rubber-like" to plastic mechanical property changes previously observed in f.c.t. alloys. No mechanical property data for f.c.c. alloys exists, but because the heat capacity of the f.c.c. alloys is similar to the heat capacity of the f.c.t. alloy, it is believed that the "rubber-like" to plastic mechanical property changes should exist in f.c.c. alloys as well.

The cause of the "rubber-like" to plastic change is not known.

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INTRODUCTION

Through the advancement and application of knowledge gained from experimental research, the realization of environmental control necessary to man's existence is being made possible. Contributing to this realization is the knowledge gained from learning to alter the intensive properties of materials. Exploring the behavior of materials, such as the In-Tl alloy system, and seeking explanations for their behavior, would seem, then, to be of prime importance in developing the ability to intelligently design materials that possess desirable intensive properties.

The In-Tl alloy system (Figure 1)¹ has exhibited anomalous behavior both in the thermal expansion coefficients of the f.c.c. alloys (Pahlman and Smith, 1968) and in the mechanical properties of the f.c.t. alloys (Burkhart and Read, 1953; Basinski and Christian, 1954). The causes of the behavior were not known, but knowledge of the heat capacities of the f.c.c. and f.c.t. alloys could lead to an understanding of them.

The martensitic f.c.t.-f.c.c. transformation has been of considerable interest to previous investigators.² The investigation of the transformation by heat-capacity measurements

¹Figure taken from Pahlman and Smith (1968).

²See Literature Review.

Figure 1. Phase diagram of the In-Tl alloy system

would yield further information about the transformation and further correlations about the alloy system's behavior would be obtained.

For these reasons the heat capacities and thermodynamic functions of three In-Tl alloys having compositions of 34.6, 28.9, and 18.8-at. % Tl, respectively, have been measured from 5-300°K. Through the region measured (Figure 2)¹ the 28.9-at. % Tl alloy transformed from f.c.t. to f.c.c. while the 34.6-at. % Tl alloy remained f.c.c. and the 18.8-at. % Tl alloy remained f.c.t.

Hopefully, then, with the additional knowledge about the behavior of the system and the correlations thus obtained, it might be possible to suggest ways of altering the alloy properties, thus making it possible to effectively design an alloy for predetermined uses.

This paper is divided into four major parts: Literature Review, Experimental Procedure, Results, and Discussion.

¹Figure taken from Pahlman and Smith (1968).

Figure 2. Phase diagram of the In-Tl alloy system in the neighborhood of the f.c.t.-f.c.c. transition

LITERATURE REVIEW

The literature review will be divided into three parts: F.C.T.-F.C.C. Transformation, Physical Properties, and Specific Studies. These divisions are somewhat artificial as several investigations fall into several of the categories.

The investigations on the delineation of the In-Tl phase diagram (Figure 1) have been described by Hansen (1958) and Elliott (1965).

F.C.T.-F.C.C. Transformation

Other studies that have further delineated the f.c.t.-f.c.c. portion of the phase diagram (Figure 2) are those of Merriam et al. (1967) and Pahlman and Smith (1968). Merriam et al. as part of their general study of the electronic structures of alloys, measured the superconducting temperature of 0.045 to 99.2-at. % Tl In-Tl alloys. They reported the delineation, at 3°K, of the region in which the f.c.t.-f.c.c. transformation occurs. Pahlman and Smith, interested in the correlations between thermal expansion behavior and the transformation, used the thermal expansion behavior to further delineate the f.c.t.-f.c.c. region.

Guttman (1950) and his co-workers Bowles, Barrett, (and Guttman) (1950), studied the f.c.t.-f.c.c. portion of the phase diagram by x-ray diffraction and metallographic techniques, and characterized the f.c.t.-f.c.c. transformation as

martensitic, occurring with a double shear mechanism, with twinning occurring on transformation from f.c.c. to f.c.t.

Wechsler et al. (1953), proposed a theory of the martensitic transformation, that made possible the calculation of the observed crystallographic features of the transformation. Burkhart and Read (1953) successfully applied this theory to the In-Tl alloy system and also studied the hysteresis associated with the transformation. They also suggested a mechanism that did not involve a double shear mechanism as proposed by Bowles et al. (1950).

Basinski and Christian (1954b, 1956), because of questions raised about the nature of the mechanism, reinvestigated, crystallographically, the martensitic transformation. They concluded that the double shear mechanism of Bowles et al. was correct.

The thermodynamic order¹ of the martensitic transformation in the In-Tl alloy system has been investigated and debated since Guttman's (1950) work. On the basis of his x-ray investigations of the crystal structures of the In-Tl alloys, he concluded that it was second order, because of the lack of an equilibrium two phase region between the phases.

A literature review of this topic is found in Hansen (1958). In addition to the investigations cited in Hansen, Predel (1954), Pahlman and Smith (1968), and Pollock and King (1968) have also

¹ Stout (1948) and Franzen and Gerstein (1967) discuss the order concept in binary systems.

investigated the nature of the order of the transformation.

Predel, using dilatometric and DTA techniques, measured the volume and enthalpy changes associated with the martensitic transformation in a 20.5-at. % Tl alloy. The volume change was found to be $0.0260 \pm 0.0006 \text{ cm}^3/\text{g-atom}$, with the enthalpy change $0.49 \pm 0.03 \text{ cal/g-atom}$. Pahlman and Smith, on the basis of their thermal expansion data, concluded the transformation was first order.

Pollock and King (1968) have suggested that the phase diagram should not be considered an equilibrium phase diagram in the delineation of the f.c.t.-f.c.c. portion of the phase diagram.

Physical Properties

Early investigations by Meissner et al. (1932) have shown that In-Tl alloys were superconductors with superconducting temperatures ranging from 3.4°K in pure In to 2.37°K in pure Tl. Merriam et al. (1967) have studied the superconducting temperatures of alloys from 0.045 to 99.2-at. % Tl alloys. Included in their publication are references to previous work in this area.

Because of anomalous behavior in the In-Pb system (Tomasch, 1958), Tomasch and Reitz (1958) measured the thermoelectric power of 0-15-at. % Tl alloys at 77 and 273°K in order to compare the In-Tl system with the In-Pb system. They found the thermoelectric power of the In-Tl alloys was a smooth function

of composition at both temperatures of measurement.

In an investigation of structure stability in In-Tl alloys, Novotny and Smith (1965) measured the single crystalline elastic constants of f.c.c. In-Tl alloys from 200-350°K. They found that the elastic constants were linear functions of temperatures, within the precision of their measurements. However, the elastic shear constant was found to be smaller than expected.

In an investigation of In-rich alloys and electronic structures, Yonemitsu et al. (1965) measured the Hall coefficients and electrical resistivities of 0 to 10-at. % Tl alloys at 110°C and found that the Hall coefficient varied monotonically with concentration.

Predel and Emam (1967) measured the density of liquid In-Tl alloys and found that the systems approached ideal behavior in the liquid state.

Predel and Mohs (1969) measured the enthalpy of mixing of 15-40-at. % Tl alloys at 100°C and found that the behavior of the alloy system approached ideal behavior as well.

De Morton (1968, 1969) has investigated the elastic and anelastic behavior of 10-25-at. % Tl alloys. On the basis of his measurements of the internal friction and shear modulus of the alloys, De Morton concluded that f.c.c. and f.c.t. alloys can undergo stress induced ordering either through a Tl-cluster reordering (Zener, 1948) or, as proposed by De Morton (1969), through a lattice rearrangement. Reordering was found to be a

function of Tl concentration, increasing with increasing Tl concentration in the alloys and apparently independent of the martensitic transformation.

Specific Studies

Heat capacities of In-Tl alloys have not, to date, been reported above 5°K, although the heat capacities of In (Carter, 1962) and of Tl (Hicks, 1938; Larikov et al., 1966) have been determined in the range 5-450°K and 12-500°K, respectively. While the heat capacity of Tl exhibits normal behavior in this range, anharmonic contributions to the heat capacity of In appear to become appreciable above 260°K. There were several studies of the In-Tl system directly relevant to the present investigation.

One was the study of Pahlman and Smith (1968) who measured the thermal expansion of four single-crystalline In-Tl alloys in order to determine whether the expansion behavior of such alloys would correlate with the f.c.t.-f.c.c. transformation. Two of the alloys transformed from f.c.t.-f.c.c. or f.c.c.-f.c.t. in the temperature range studied, while the other two alloys remained f.c.c. from 4.6-270°K.

From their data, obtained by interferometric techniques (Pahlman and Smith, 1968), Pahlman and Smith calculated the thermal expansion coefficients for each alloy. The results of the calculations are shown in Figure 3.

The coefficients of the non-transforming f.c.c. alloys were anomalous both in the 70-100°K and 200-240°K regions. The coefficients of the alloys experiencing the transformation

Figure 3. Thermal expansion coefficients of In-Tl alloys and copper

were also anomalous in the 200-240°K region. No data were available for the f.c.t. phase in the region 70-100°K.

The alloys that transformed exhibited the expected hysteresis, characteristic of martensitic transformations. The fact that the two coefficients of thermal expansion, measured both on heating and cooling, do not coincide, appears to be due to apparatus problems because of the transformation and not of anomalous behavior of the samples. The infinities in the coefficients also appeared to be apparatus problems. The apparatus difficulties appeared to be caused by the speed of the transformation and the rate at which the data were taken.

The expansion coefficient of oxygen-free, high conductivity Cu was also determined by Pahlman and Smith as a check on their apparatus, and is shown in Figure 3. The Cu results indicated that the apparatus was operating properly in other than the transformation regions.

The lattice heat-capacity, associated with normal mode lattice vibrations, would be expected to exhibit anomalous behavior correlated with anomalies in the expansion coefficients, unless, as Pahlman and Smith (1968) have suggested, the Grünesen parameter, γ , is not constant at low temperature.

Swenson (1968) has shown that

$$\gamma = \beta B_s V/C_p$$

where $\beta = 3\alpha$ $V = \text{volume.}$

$B_s = \text{adiabatic bulk modulus}$

An anomalous variation of α would imply anomalous behavior in the heat capacity and/or γ . If γ is not constant at low temperatures, it would be possible for the heat capacity to continuously increase without exhibiting anomalous behavior.

At high temperature, γ is usually constant, and variations in α would imply variations in the heat capacity.

Pahlman and Smith indicated that the anomalous behavior of α was not understood, and that heat-capacity measurements might yield information about the cause of such behavior.

Pahlman (1968) explored the possibility that the behavior was caused by magnetic effects, an order-disorder phenomena, or Fermi surface geometry. No correlations were obtained to explain the alloy behavior.

Burkhart and Read (1953) studied the effect of bending stress on an 18-at. % Tl f.c.t. alloy which had the "banded twin" martensitic structure. They observed that above 268°K, the alloy was plastic in behavior, in that once bent it remained bent. Below 263°K, however, the alloy behaved in a "rubber-like" manner. By "rubber-like," they meant that the alloy would deform when stressed, but would return to its original position when the stress was removed. The alloy exhibited this behavior to at least 197°K, the lowest temperature of their observations.

In the 263-268°K range, the alloy would behave plastically if deformed for a "long" period of time, but it would behave in a "rubber-like" manner if deformed for a "short" period of

time. "Long" and "short" were not defined, nor was the method of investigation in determining the range 263-268°K. They also made the following observations on the alloy behavior. At 298°K, when pulled in tension, the alloy clicked. When bent, a twinning cry could be heard and upon application and removal of axial stress, a single twin interface was observed to traverse the crystal. At temperatures between 197-298°K, using Laue and metallographic techniques, during the bending stress one set of twins was observed to grow at the expense of another, but on removal of the stress the original twin structure could be reattained. The alloy readily bent but only so far. The alloy then became rigid and further bending was difficult. In the "rubber-like" region the alloy would spring back to its original configuration, whereas in the plastic region the alloy would remain in its stressed position.

Two mechanisms were proposed to explain this behavior. One mechanism involved stabilization of twin interface movements. It was proposed that at higher temperatures the twin boundaries were stabilized, consistent with a Zener (1948) relaxation which involved a stress induced reordering of the Tl atoms. At lower temperatures, stabilization would not occur and "rubber-like" behavior would result. They reasoned that slower diffusion rates at lower temperatures would prevent the Tl atoms reordering.

The second mechanism was also based on diffusion, but this time impurities would migrate to the grain boundaries

during the stress, and then the impurities would "lock in" to stabilize the new lattice configuration. At lower temperatures, the impurities would not migrate, and stabilization would not occur.

The 263-268°K region would be the temperature range in which diffusion would not take place as quickly as at high temperatures. Thus, a "longer" time would be necessary to produce a plastic behavior. Below 263°K diffusion would then occur too slowly to produce the stabilization necessary for the plastic behavior.

Basinski and Christian (1954a) investigated the behavior of an 18.5-at. % Tl alloy from 298°K to 77°K. They confirmed the results of Burkhart and Read (1953) and also observed the identical alloy behavior for compression stresses at all temperatures. They found the transition from "rubber-like" to plastic behavior occurring at 273°K. They also observed that as the alloy passed through the martensitic transformation, superelastic effects were observed. For a discussion of these effects and other alloy systems that exhibited them, see Barrett and Massalski (1966). Basinski and Christian pointed out that the superelastic effects do not appear to be related to the "rubber-like" behavior below 0°C.

They suggested that in Burkhart and Read's work what was observed was not a twin boundary movement on return of the alloy to its original configuration, but actually a new growth of twins, resulting from nuclei left in the original lattice

position. The explanation for the phenomenon was left with the statement that further work was needed to find the cause.

This "rubber to plastic" transition is not new; it had previously been found in the orthorombic phase of the Au-Cd alloy system (Chang and Read, 1951).

In summarizing the available information on the In-Tl alloy system from 5-300°K, it seems fair to state that there is a decided lack of knowledge of the properties of the alloys through the entire temperature range and in particular from 150-250°K. Thus, only limited correlations to the alloy behavior can be made, using Pahlman and Smith's data and the observations of Basinski and Christian and Burkhart and Read.

In view of these reported properties, it might be expected that anomalous behavior would be exhibited in the heat capacities of all three alloys, corresponding to the "rubber-like" to plastic transformation. It is not known whether the heat capacity from 60-100°K of the f.c.c. alloys would also be anomalous. The martensitic transformation would be expected to deviate from normal lattice behavior in a manner consistent with the properties of the martensitic transformation.

EXPERIMENTAL PROCEDURE

Alloy Preparation

The alloys were prepared from "five-nines" percent purity In obtained from Cominco American and "five-nines" percent purity Tl obtained from Leico Industries. The In and Tl were obtained in bulk form.

Special handling

As Tl is highly toxic, (Browning, 1969) special precautions had to be taken in its handling: skin contact, vapor inhalation, and ingestion had to be avoided. Polyethylene gloves were worn at all times to insure against skin contact and a lab coat, which was laundered after each use, was worn when working with Tl or an alloy.

One hood was used exclusively for In and Tl work in order to help insure against accidental contamination of other work areas. All tools that were used were stored in the hood. Waste metal and contaminated materials were placed in a large polyethylene bag, which was disposed of by burying.

The Tl metal was stored in a desiccator to help prevent oxidation, because it oxidizes when in contact with the atmosphere, and as a safeguard against accidental contamination. The metals and alloys were stored in the same area, which was appropriately marked.

Preparation

The three alloys were prepared with alloy 1 having a composition of 34.6-at. % Tl, alloy 2 having a composition of 28.9-at. % Tl and alloy 3 having a composition of 18.8-at. % Tl. Through the 5-300°K region, then, alloy 1 remained f.c.c., alloy 3 remained f.c.t., while alloy 2 transformed from f.c.t. to f.c.c. (Figure 2).

Tl was cleaned with concentrated H_2SO_4 in order to remove surface oxides and other surface impurities.¹ The container in which the alloy was made was a 45-mm diameter vycor tube, 50-cm long. This size container was chosen to facilitate mixing of the components in the "rocking furnace"² in which the alloys were made. After the metals were placed in the tube, it was evacuated with a forepump for a period of 10-12 hours, and sealed. The tube was then placed in the rocking furnace.

Because In melts at 156°C and Tl at 303°C, the melts were mixed at 375°C for 2-3 days. The alloy melt was then quenched and the ingot was removed from the tube by cracking the vycor, taking all necessary precautions against Tl contamination. The ingot was then cleaned in concentrated H_2SO_4 in order to remove the oxides and other impurities on the surface.

¹J. Pahlman, ISU (Private communication).

²An electrical resistance furnace that has a motor attached to it which can move the furnace through an angle of 120°.

The alloy was machined to fit the calorimeter can (Figure 4)¹ in a "special handling room" which was designed to insure minimum contamination to the machinist and the outer world.

The final weights of the three alloys were alloy 1-399.6g, alloy 2-352.5g, and alloy 3-366.5g. A mole of alloy was taken to be an Avogadro's number of atoms. The atomic weights of In and Tl were taken to be 114.82g and 204.37g, respectively.

Alloy 1 was annealed in the calorimeter can at room temperature for approximately two and a half weeks. Alloy 2 was machined, and placed inside a vycor tube. The tube was then placed in a 345°K oil bath and the alloy was annealed for one week. Alloy 2 was also annealed for approximately two weeks in the can at room temperature. Alloy 3 was machined and then annealed in the oil bath for 17 days in a vycor tube.

Alloy Analysis

Metal samples for major constituent analysis by wet chemical analysis were taken from the top, side, and bottom of alloys 1 and 2, and the top and bottom of alloy 3. In was determined by EDTA titration, in the presence of Tl, by masking Tl with ascorbic acid, xylenol orange serving as an indicator. Tl was determined by titrating with KBrO_3 with no masking of

¹Taken from Schwartz et al. (ca. 1970).

Figure 4. Calorimeter can

the In required, methyl orange serving as an indicator (Tschetter and Banks, ca. 1970).

Annealing of the alloys did not appear to affect major constituent analyses results, as analysis results of alloy 3, annealed for 17 days at 65°C were within 0.01% of analysis results before annealing.

The results of the analyses are given in Table 1.

Table 1. Major constituent analysis results

Alloy		In(Wt %)	Tl(Wt %)
1	Top	51.56	48.58
	Middle	51.56	48.56
	Bottom	51.48	48.62
2	Top	58.19	41.87
	Middle	^a	42.02
	Bottom	58.11	41.92
3	Top	70.86	29.20
	Bottom	70.92	29.15

^aNot determined.

The analytical results for alloys 1 and 2 indicated the possibility of concentration gradients. This indication is a bit tenuous, however, as the precision of the analyses was 0.1% for In and Tl. A trend was nevertheless indicated in the analytical results.

Since the alloys analyzed to greater than 100 wt. %, it seemed reasonable¹ to approximate wt. % from the value of average In and average Tl in each alloy divided by the total wt. %.

Mass spectrographic analyses were performed on the pure metals and the alloys with oxygen and hydrogen being determined by other methods. The results are found in Table 2. It is felt that alloy 1 has greater impurity levels in B and Si due to its being remade five times. These impurities were thought to have resulted from the vycor. The Be, Sc, C and N values may be considered upper limits because of the mass spectrographic precision. All elements, except as noted, not listed are considered to be at levels low enough to be undetectable by mass spectrographic techniques.

Initially, mass spectrographic analysis for elements from Sc on were performed on machining turnings of the alloys. The results from the two analyses differ in Fe content in alloy 1, V and Fe in alloy 2, and Cu and Fe in alloy 3. Y, Mo, and La were also reported in alloy 1 in the second analysis. The differences were thought to be due to inhomogeneities in the alloys or surface contamination due to the cutting tools. The Y, Mo, and La results tend to substantiate the latter hypothesis.

Hydrogen content was determined by vacuum fusion analysis. Table 3 lists the results of these analyses for the alloys and metals. The samples of alloys used for analysis were taken from machining turnings obtained from the billets used in the

¹R. Bachman, ISU (Private communication).

heat-capacity measurements, and indicate maximum impurity content.

Table 2. Minor constituent analysis results (at. ppm)

Element	Alloy 1	Alloy 2	Alloy 3	In	Tl
Be	7	0.2	0.9	0.04	0.2
B	50	0.2	0.3	0.2	0.06
C	130	60	130	70	80
N	40	10	30	30	20
F	0.02	0.05	0.03	0.01	0.05
Na	3	2	2	2	1
Ag	30	10	20	20	5
Al	20	6	50	1	4
Si	400	100	150	20	5
P	1	0.2	1	0.1	0.2
Cl	10	4	5	5	2
K	10	4	5	5	2
K	6	1	6	7	3
Ca	30	2	10	4	1
Sc	0.7	0.8	0.7	2	-
Ti	2	5	2	0.4	8
V	10	0.3	0.3	0.2	2
Cr	2	1	3	2	10
Mn	1	0.3	1	0.3	1
Fe	200	14	30	6	50
Co	0.1	0.3	0.1	0.1	20
Ni	1	5	2	0.8	40
Cu	15	3	90	2	20
Fn	70	3	140	6	20
Se	0.3	0.05	0.3	-	2

Table 3. Hydrogen analysis results

		At. PPM
Alloy	1	.17 $\pm$.05
	2	.12 $\pm$.05
	3	.04 $\pm$.02
Metal	In	.07 $\pm$.03
	Tl	.04 $\pm$.02

Oxygen content was determined by neutron activation analysis. The results of the analyses are shown in Table 4. Again the analyses were performed on machining turnings and the results again should indicate maximum oxygen content of the alloys measured.

Table 4. Oxygen analysis results

Alloy	At. PPM
1	175 $\pm$ 30
2	94 $\pm$ 18
3	121 $\pm$ 15

The results of the analyses indicate that alloy 1 was 99.97-at. % pure, alloy 2 was 99.98-at. % pure, and alloy 3 was 99.95-at. % pure with respect to non-metals; alloy 1 was 99.92-at. % pure, alloy 2 was 99.98-at. % pure, and alloy 3 was 99.96-at. % pure with respect to metals. In was 99.98-at. % pure and Tl was 99.98-at. % pure with respect to metals. In was 99.98-at. % pure and Tl was 99.98-at. % pure with respect to non-metals, with oxygen not being determined.

As a further check on the purity of the samples, photomicrographs at 250X were made of a representative portion of each alloy, after electropolishing with a 33% HNO_3 , 67% NaOH polishing agent, at room temperature. These pictures are shown in Figure 5.

34.6-at. % Tl

28.9-at. % Tl

18.8-at. % Tl

Figure 5. Photomicrographs (250X) of the alloys

All three alloys exhibited cracks in the grains and grain boundaries. The 34.6-at. % Tl alloy exhibited a rippled surface. These effects are thought to be due to the softness of the metals and the polishing techniques. No impurities were seen in the grain boundaries.

The 18.8-at. % Tl alloy exhibited the expected twinning due to the martensitic transformation. Also, no second phase or incomplete transformation was indicated in the photomicrograph.¹

Heat-Capacity Measurements

An adiabatic calorimeter of the Westrum design (Westrum, 1961) was used for the heat-capacity measurements. The circuitry of the calorimeter (Skochdopole, 1954; Gerstein, 1960), manual adiabatic shield control (Skochdopole, 1954; Gerstein, 1960), and automatic adiabatic shield control (Rulf, 1970), have been described previously.

A platinum resistance thermometer calibrated by the National Bureau of Standards was used for temperature determination. The calibration of the thermometer and the determination of the precision and estimated accuracy of the calorimetric measurements have been described previously (Gerstein et al., 1969).

¹D. Peterson, ISU (Private communication).

The sample container was a gold-plated copper can that has also been previously described and is shown in Figure 4. The main new feature was a non-metallic seal (Ashworth and Steeple, 1968), which replaced the traditional solder seal (Gerstein, 1960), for sealing the top to the can. Sample-to-container thermal contact was enhanced by the use of Apiezon T grease. No exchange gas was used, but to facilitate heat transfer from the heater well to the top of the can, a copper spring was inserted between the well and the can top, a technique previously described (Gerstein et al., 1966).

The standard interrupted heating method for making adiabatic heat-capacity measurement was used, and has also been described previously (Westrum et al., 1968).

An IBM 360/65 computer was used to calculate $Q/\Delta T$, $C_p(T)$, and the thermodynamic functions in a manner previously described (Gerstein, 1960).

X-Ray Measurements

The intensities of the (2,0,0), (2,2,2), and (4,2,0) reflections at angles of $2\theta=37^\circ$, $2\theta=68^\circ$, and $2\theta=93^\circ$, respectively, of a polycrystalline sample of the 34.6-at. % Tl alloy were measured at 13 temperatures in the 120-300°K region.

A 20x25mm sample of alloy, 1mm thick, was cast in a graphite mold from a melt, made from machining turnings of the alloy.

The apparatus used was a vertical diffractometer, equipped with a low temperature-high vacuum attachment made by the Materials Research Corporation.¹ The attachment was equipped with a dewar for refrigerant, a heater for temperature control, and a copper-constantan thermocouple for temperature determination.

As standard x-ray techniques (Cullity, 1956) were used, no description of them will be given. Cu radiation was used. The intensities of the diffracted beams were recorded on chart paper and standard techniques were used to integrate the area under the curves.

The alignment of the diffractometer was sensitive to the weight of the low temperature-high vacuum attachment. In order to evaluate this sensitivity, the peak intensities were measured at three different diffraction angles.

The measurements were taken both when the sample was being cooled to 120°K, and when it was being heated to 270°K. The precision of temperature control was $\pm 2^\circ\text{K}$. The accuracy of temperature determination was estimated to be $\pm 3^\circ\text{K}$.

A check on the operation of the apparatus was made by measuring the intensity as a function of temperature of one reflection in a standard sample. The peak chosen was the (4,4,0) β peak. The sample was polycrystalline Si. The measure-

¹Model X-86NC.

ment procedure for the standard sample was the same as that described for the In-Tl alloy.

RESULTS

Heat-Capacity Measurements

The data for the heat-capacity measurements from 5-300°K of the three alloys measured are listed in tabular form in Appendix I. The average temperature, the temperature interval, and the experimental heat capacity, uncorrected for curvature, of each data point are listed for each alloy. The heat capacities of each alloy, obtained from a graphical smooth-curve fit of the data, with no curvature correction made, are listed in tabular form in Appendix II. Curvature corrections were not made because the corrections were either less than 0.1% of the smooth-curve heat capacity or because non-equilibrium conditions existed, as in the 195-300°K regions of the alloys and the martensitic region of the 28.9-at. % alloy (70-100°K).

The heat capacity of each alloy was graphically extrapolated to 0°K, in order to obtain the thermodynamic functions. The smooth-curve values of the heat capacity, along with the standard entropy, the standard enthalpy, and the standard free energy are also listed in tabular form in Appendix II.

The alloys are superconducting and the extrapolation to 0°K does not include the superconductivity contribution to the heat capacity. The smooth curve of alloy 2, through the 70-100°K region, was obtained by extrapolation of the smooth curves below and above this region.

Based on these approximations, the entropy at 298°K is estimated to be 61.6 ± 1.6 eu for alloy 1, 61.4 ± 2.0 eu for alloy 2, and 61.1 ± 1.6 eu for alloy 3.

The precision of measurements was such that for more than 95% of the points, the experimental data points deviated from the smooth curve for alloy 1 by no more than $\pm 0.2\%$ above 30°K, $\pm 0.6\%$ from 15-30°K, and $\pm 10\%$ below 15°K. For alloy 2, except for the 70-100°K region, the deviations were $\pm 0.2\%$ above 20°K, $\pm 0.7\%$ from 10-20°K, and $\pm 4\%$ below 10°K. For alloy 3, the deviations were $\pm 0.2\%$ above 20°K, $\pm 0.8\%$ from 10-20°K, and $\pm 2.0\%$ below 10°K.

The heat capacity of the addenda had been previously measured (Schwartz et al., ca. 1970) and was found to be 16% of the total heat capacity at 10°K, 42% at 100°K, and 51% at 300°K.

There are three main regions of interest from 5-300°K: the martensitic f.c.t.-f.c.c. transformation region in alloy 2; the 5-195°K region, and the 195-300°K region in all alloys. Because the 34.6-at. % Tl alloy exhibited no anomalous behavior below 200°K, the 28.9-at. % Tl alloy was made such that the transformation occurred below 100°K (Figure 2).

Martensitic region

The experimental heat-capacity points for the f.c.t.-f.c.c. transition region, delineated by the 70-100°K region in alloy 2, are plotted in Figure 6. The smooth curve was obtained by extrapolation from the smooth curves above 100°K and below 70°K, as mentioned previously.

Figure 6. Experimental heat-capacity data for the 28.9-at. % Tl alloy, 70-100 K

The thermal histories of the measurements are shown in Table 5a.

Table 5a. Thermal history of the heat capacity measurements for the 70-100°K region of the 28.9-at. % Tl alloy

Data points	Calorimeter	
	Cooled to	Heated to
4625-4628	5°K	300°K
4638-4644	48°K	300°K
4714-4721	5°K	99°K
4723-4741	48°K	97°K
4743-4810 ¹	48°K	99°K
4861-4863	48°K	74°K

The results possibly indicate irreversible behavior in the 82-86°K and 88-95°K regions. Deviations from a smooth curve appear to be reproducible and outside the usual $\pm 0.2\%$ deviation from a smooth curve in this region. The lone point at 93°K (Figure 6) was not found to be in error because of a data-taking error, a calculation error, or calorimeter problems, so it was included with the data. However, the other heat-capacity data through this region does not indicate the heat-capacity behavior to be discontinuous in this manner. The experimental data does not suggest that the smooth curve heat-capacities below 70°K lie on a different smooth curve than above 100°K.

¹The arrow in Figure 6 indicates a split in the 4743-4810 data. The calorimeter was held at this temperature for 10 hours.

5-195°K

The second region of interest is the region below 195°K. The smooth curves of the data for this region were of the normal sigmoid shape in all three alloys except for the 70-100°K region in alloy 2 (Figure 7).

195-300°K

The smooth curves for the three alloys from 195-300°K are plotted in Figure 8. A 5-8% rise in the heat capacity has been observed in all three alloys. The rise in heat capacity increased with increasing Tl concentration. In alloy 1 the rise was 1.8 Joules/mole-°K; in alloy 2, 1.75 Joules/mole-°K; and in alloy 3, 1.4 Joules/mole-°K. The temperature range over which this behavior occurs appears also to be increasing with Tl concentrations: for alloy 1, 34°, for alloy 2, 35°, and for alloy 3, 25°. The heat capacities through this region are irreversible for alloy 1 and 2 and are outside the $\pm 0.2\%$ deviation from a smooth curve as expected for the region. Alloy 3 exhibited reversible behavior.

The thermal histories of the measurements of the heat capacities of alloy 1 and 2 are given below. There would appear to be a correlation between the rate at which the heat capacities were measured and the rate of rise of the heat capacities through the region.

The high curve in alloy 1 (Figure 8) included a 9 hour temperature hold at 205°K and measurements from 205-239°K in

Figure 7. Smooth curve heat capacities of the alloys

Figure 8. Smooth curve heat capacities of the alloys, 190-300°K

3 hours. The middle curve included a 2-1/2 hour temperature hold at 210°K and measurements from 210-240°K in 2-1/2 hours. The low curve measurements were made from 200-245°K in 4 hours.

The high curve in alloy 2 (Figure 8) includes a 2 hour temperature hold at 215°K and then measurements from 215-239°K in 1-1/2 hours. The middle curve represents measurements from 193-239°K in 3-1/2 hours. The low curve represents measurements from 197-243°K in 3 hours.

Alloy 1 and 2 exhibited anomalous behavior in the 240-300°K region, again, with the effect increasing with increasing Tl concentration. The deviations from a smooth curve are greater than 0.2% and are reproducible. Alloy 3 exhibits no deviation from a smooth curve, outside the expected $\pm 0.2\%$ precision of the measurements.

Alloy 3 exhibited reproducible behavior in the 196-221°K region. The thermal histories of the measurements were such that the alloy was held at 200°K and 206°K for 4 hours and 11 hours respectively. The data through the region were taken in approximately two and a half hours, except as noted above.

Figure 9 shows the correlation between these data and previous work (Pahlman and Smith, 1968). The solid lines represent the data of this work. A rise of the heat capacity calculated from thermal expansion coefficient data indicated a rise of the heat capacity in alloys near the at. % of those measured.

Figure 9. Comparison between the heat capacities calculated from thermal expansion data and the measured heat capacities

18.8-at. % alloy

With respect to the 18.8-at. % Tl alloy which transformed martensitically between 380-390°K, (see Figure 2) the photomicrographs indicated no second phase and no incomplete transformation in the sample. This would seem to indicate that at high temperatures, near the m.p. of the alloys, the martensitic transformation would appear to be complete even for polycrystalline, non-homogeneous alloys.

X-Ray Measurements

The weight of the x-ray attachment caused alignment difficulties with the diffractometer at the lower angles of reflection, $2\theta=37^\circ$ and $2\theta=68^\circ$. The only results that are presented are the results for the $2\theta=93^\circ$ reflection.

The results are shown in Figure 10. A change in the rate at which the integrated intensity was increasing, with decreasing temperature, was found in the 200-210°K region.

The results of the measurement of the Si, $2\theta=92.8^\circ$ reflection, are also shown in Figure 10. Normal behavior was found through the entire region measured. Deviations from the straight line drawn through the data would indicate the precision of the measurements.

Figure 10. X-ray measurement results for the 34.6-at. % Tl alloy and Si

DISCUSSION

The discussion of the results of the heat capacity measurements is presented in three sections: Martensitic Region, 5-195°K Region, and 195-300°K Region. The 28.9-at. % Tl alloy transformed from f.c.t. to f.c.c., while the 34.6-at. % Tl alloy remained f.c.c. and the 18.8-at. % Tl alloy remained f.c.t. in the region measured (Figure 2). The 5-195°K and 195-300°K regions refer to the behavior of all three alloys while the martensitic region refers only to the 28.9-at.% Tl alloy.

Martensitic Region

The general properties of martensitic transformations are discussed in many metallurgy texts¹ with the text by Reed-Hill (1964) citing the In-Tl transformation as a specific example.

The properties of the martensitic f.c.t.-f.c.c. transformation in the In-Tl system are listed below:

The transformation is:

1. diffusionless, occurring by a double-shear mechanism, proceeding with a single interface in a single crystal, producing twinning on transformation from f.c.c. to f.c.t.
2. irreversible, in the sense that the transformation on heating occurs at higher temperatures (hysteresis)

¹Avner (1964), Christian (1965), and Barrett and Massalski (1966) are some of the many texts that describe martensitic transformations.

than on cooling.

3. reproducible, in the sense that the same transformation path through the alloy can be reproduced, both on cooling and heating, provided the manner in which the alloy is cooled and heated remains approximately the same.
4. athermal, in that the transformation stops when heating or cooling is stopped. Stabilization occurs if too much time has elapsed before continuing with cooling or heating.
5. non-equilibrium in nature, in that no two phase region with phases of different composition co-existing in equilibrium has been observed.

The deviations of the heat capacity data (see Figure 6) in the region of the expected f.c.c.-f.c.t. transformation were possibly caused by the relief of strains in the alloy, the strains being produced by the martensitic transformation on cooling from f.c.c. to f.c.t. and now associated with the f.c.t.-f.c.c. transformation. If the entire alloy would have transformed from f.c.c. to f.c.t., all strains would have been relieved by twinning. However, as the alloy was inhomogeneous and polycrystalline, it would be expected that strains from the transformation would not all be relieved by twinning. The strains would then be present when transforming from f.c.t. to f.c.c. The reproducibility of the deviations would correlate with the reversibility of the path of the transformation.

The possibility also exists that what had been observed in the 70-81°K region were deviations from the smooth curve due to lack of precision in the heat-capacity measurements. The deviations shown in Figure 6 were not randomly scattered about the smoothed curve, as would be expected for random errors, however. This would indicate that the deviations represented the behavior of the alloys rather than problems in the measurement technique.

The data taken after allowing the sample to remain in the center of the expected transformation range for a period of 10 hours (arrow, Figure 6) did not reproduce the previous data through the 81-95°K region. This behavior would not be inconsistent with the In-Tl athermal martensitic nature and stabilization effects inherent in this transformation. There is also the possibility that normal deviations from a smooth curve were being observed: scatter off a smooth curve that lay between the two sets of data and marked the In-Tl transformation.

In summary, the In-Tl phase diagram (Figure 2) indicates that the alloy should experience the f.c.t.-f.c.c. transformation between 80-100°K. The heat capacity data for this alloy seemed to indicate a transformation occurring over either a 24° region, 72-96°K, or a 14° region, 82-96°K. The wider range would be consistent with the expected behavior of a polycrystalline, inhomogeneous alloy undergoing the transformation.

It might have been expected that the heat capacity of the f.c.t. alloy would be different than the heat capacity of the f.c.c. alloy; that is, the heat capacity of the f.c.t. alloy should lie on a different curve than that of the f.c.c. alloy. The small ΔH of transformation (0.5 cal/g-atm)¹ would indicate that perhaps no heat-capacity change would be observed. There was no indication that the data below 70°K scattered around a different smooth curve than the data above 100°K .

The simplest model of an alloy in which the behavior is near ideal, for both components, is the regular solution model in which the chemical potential of the i^{th} component is given

$$\text{by}^2 \quad \mu_i^a = \mu_i^{o,a} + RT \ln X_i^a + X_j^{a2} w^a$$

Since In and Tl are both IIIA elements, there exists the possibility that such a model might have some relevance in describing the thermodynamic behavior of the alloy. To this end, such a model has been invoked in an attempt to fit the heat-capacity results through the martensitic transformation region.

The molar heat capacity of a binary alloy in a two phase region is given by:

$$\bar{C}_P^{C,T} = X_C \bar{C}_P^C + X_T \bar{C}_P^T$$

¹Predel, 1964.

²Lewis and Randall, 1961.

C and T are phase C and phase T; X_C and X_T are the mole fractions of the phases; and $\bar{C}_P^C$ and $\bar{C}_P^T$ are the molar heat capacities of each phase.

Assuming a regular solution chemical potential for the system, the molar enthalpy for phase C, is given (Lewis and Randall, 1961) by:

$$\bar{H}^C = x_1^C \bar{H}_1^O + x_2^C \bar{H}_2^O + x_1^C x_2^C (w^C - \frac{T \partial w^C}{\partial T} \Big|_P)$$

$\bar{H}_1^O$ and $\bar{H}_2^O$ are the standard state enthalpies of component 1 and 2 and are assumed to be the enthalpies of the pure components. x_1^C and x_2^C are the mole fractions of components 1 and 2 in phase C. The w^C is the chemical potential interaction parameter for phase C.

For a two phase region, $\partial x_1 / \partial T \Big|_P \neq 0$ and $x_1^C + x_2^C \equiv 1$, the heat capacity of phase C is now given by:

$$\begin{aligned} \bar{C}_P^C (= \frac{\partial \bar{H}^C}{\partial T} \Big|_P) &= x_1^C \bar{C}_{P1}^O + (1 - x_1^C) \bar{C}_{P2}^O - x_1^C (1 - x_1^C) \frac{\partial^2 w^C}{\partial T^2} \Big|_P \\ &+ \frac{\partial x_1^C}{\partial T} \Big|_P [(\bar{H}_1^O - \bar{H}_2^O) + (1 - 2x_1^C)w^C - \frac{T \partial w^C}{\partial T} \Big|_P] \end{aligned}$$

If the assumption is made that w is approximately constant and $w \equiv w^C \equiv w^T$, where T represents a second phase, the heat capacity through the two phase region for an In-Tl alloy¹ is given by:

¹C is now identified as the f.c.c. phase and T as the f.c.t. phase.

$$\begin{aligned}
\bar{C}_P^{C,T} = & X_C [X_{In}^C \bar{C}_{P,In}^O + (1 - X_{In}^C) \bar{C}_{P,Tl}^O + \frac{\partial X_{In}^C}{\partial T} \Big|_P (\bar{H}_{In}^O \\
& - \bar{H}_{Tl}^O) + (1 - 2X_{In}^C)w] + X_T [X_{In}^T \bar{C}_{P,In}^O + (1 \\
& - X_{In}^T) \bar{C}_{P,Tl}^O + \frac{\partial X_{In}^T}{\partial T} \Big|_P (\bar{H}_{In}^O - \bar{H}_{Tl}^O) + (1 - 2X_{In}^T)w].
\end{aligned}
\tag{1}$$

A computer program was written for the IBM 360/65 computer in order to calculate the heat capacity of the In-Tl system using (1). The data consisted of $X_{In}^C(T)$, $X_{In}^T(T)$, $C_{P,In}(T)$, $C_{P,Tl}(T)$, and $\partial X_{In}^T / \partial T \Big|_P$, and $\partial X_{In}^C / \partial T \Big|_P$.

By choosing an initial alloy concentration, the values of $X_{In}^C(T)$ and $X_{In}^T(T)$ were determined from the phase diagram. The lever rule (Moore, 1966) was then used to calculate $X_C(T)$ and $X_T(T)$. The partial derivatives were determined graphically from the phase diagram. The calculation was carried out over the 50-64°K region, for a 29.7-at. % Tl alloy, so that the derivatives could be assumed constant through the region (Figure 2). Because the exact values of $(H_{In}^O(T) - H_{Tl}^O(T)) (= \Delta H^O)$ were not known this quantity and w were varied in the calculation. The heat capacity of the 28.9-at. % Tl alloy was used for the heat capacity to be matched in the 50-64°K region. The error in assuming the 28.9-at. % Tl alloy heat capacity for a 29.7-at. % Tl alloy is estimated to be 0.1% or less.

In order to match the heat capacity of the alloy through the two phase region, w had to vary with temperature. For ΔH° values of 400, 700, and 1000 Joules/mole, w varied from 7.1×10^3 to 16.6×10^3 , 6.8×10^3 to 16×10^3 , and 6.1×10^3 to 15.2×10^3 Joules/mole, respectively.

The dependence of w on temperature is shown in tabular form in Table 5b. The ΔH° value used for this calculation was 400 Joules/mole. The dependence of w on temperature is representative of the behavior of w for the heat capacity through this region.

Table 5b. Dependence of w on temperature ($\Delta H^\circ = 400$ Joules/mole)

$T(^{\circ}\text{K})$	$w(10^3 \text{ Joules/mole})$
50	7.1
52	8.1
54	1.1
56	10.1
58	11.5
60	13.2
62	14.9
64	16.0

Except for the 70-100 $^{\circ}$ K region in the 28.9-at. % Tl alloy, the heat capacities of all three alloys were found to deviate from the sum of the In and Tl heat capacities, multiplied by the appropriate mole fractions. These deviations from the Newmann-Kopp Rule (Gopal, 1966) are listed in Table 6.

Table 6. Alloy heat-capacity deviations from the Neumann-Kopp Rule (Joules/mole)

T	Alloy (at. % Tl)		
	18.8	28.9	34.6
20	- 0.9	- 1.1	- 1.4
50	- 1.0	- 1.4	- 1.6
100	- 0.5	- 0.5	- 0.7
150	- 0.2	- 0.03	- 0.1
200	0.06	0.1	0.15
300	1.1	1.2	1.0

The appropriate corrections had to be made to the calculated heat capacities through the two phase region, to take into account the deviations in the 28.9-at. % Tl alloy. This effectively has removed the approximation that $\partial^2 w / \partial T^2 = 0$ and replaced it with the actual experimental deviations from ideal behavior.

The results of the calculation show that for a regular solution approximation, w must vary fairly rapidly as a function of temperature in order for the calculated heat capacities to match the experimental ones through the two phase region. This would seem to imply that for other types of behavior, other than monotonically increasing values of the type approximated, w should also vary as a function of temperature, in an appropriate manner. In regions where the deviations from the Neumann-Kopp Rule were less for the alloy, w would vary less and also be smaller.

The calculation was attempted in order to determine how w did vary as a function of temperature. This purpose was fulfilled. The calculation was a zeroth order attempt to define the interactions in the system, through a regular solution approximation, and the results should be viewed as qualitative only.

5-195°K Region

No anomalous behavior was observed in the 34.6-at. % Tl alloy.¹ It would seem that Pahlman and Smith's conjecture that the Grüneisen γ varied at the low temperatures with the heat capacity increasing normally, would appear to be correct (see Literature Review). At higher temperature γ is usually regarded as constant (Swenson, 1968) and it might then be expected to see heat-capacity deviations if the expansion coefficient varied.

The following points are to be made about the 5-195°K behavior.

1. The heat capacity of a polycrystalline alloy might obliterate the effect observed in the single crystal alloys.

¹See Figure 7.

2. Electrical resistivity data (Stout and Guttman, 1952) did not indicate any anomalous behavior in the 60-77° K region. However, it might be expected that if no anomalous behavior is observed in the heat capacity of the alloys, none would be observed in the resistivity.
3. Time does not appear to be a factor in the cause of the anomaly, as Pahlman and Smith switched to a liquid nitrogen bath at 100°K and re-equilibrated at 90°K. Both sets of their data agreed between 90-100° K. Thus it would be expected that the long times necessary for heat capacity measurements would not be so long that the effect had occurred and would have been unobservable. If this were the case it should have been observed by Pahlman and Smith.

195-300°K Region

The heat capacities of the alloys through the 195-300°K region exhibited anomalous rises (Figure 8), with which the x-ray data for the 34.6-at. % Tl alloy and the Pahlman and Smith data for the f.c.c. alloys correlate (Figure 2).

The data of Pahlman and Smith indicate anomalies in the f.c.c. alloys. The "rubber-like" behavior and change to plastic behavior was exhibited (Burkhart and Read, 1953; Basinski and Christian, 1954a), as previously reported, in f.c.t. alloys. It would seem then, that since the heat ca-

capacities in the f.c.c. alloys behave like the heat capacity in the f.c.t. alloy, it would be reasonable to conclude that the "rubber-like" behavior would also exist in the f.c.c. alloys.

Pahlman (1968) had considered the possibility of magnetic effects, order-disorder effects, and Fermi surface geometry on the behavior of the alloy system. He had concluded that no simple correlations existed between the alloy behavior and the above effects. Perhaps, a change in short range order is occurring. Previous work¹ on the alloy system has indicated that stress induced ordering occurs in the system and possibly a reordering of Tl clusters is occurring from 195-235°K which may be associated with the "rubber-like" to plastic changes.

It is doubtful, in light of the impurity analyses, if an impurity could be responsible for the anomalies. This would imply that Pahlman and Smith would have had the same impurity problems. Though possible, this would seem to be unlikely.

If hydrogen content was responsible for the behavior of the alloys, then, for example, 10 ppm by weight, hydrogen would act as a heat sink for a heat capacity rise of 1.75 Joules over a 35°K range. This amount of hydrogen was 0.17 ± 0.05 -at. %. It would not seem reasonable to assume that this amount of hydrogen would be responsible for the effect. To support this assumption, no hydride has been observed in the alloys in any

¹Literature review.

previous x-ray¹ work. All other impurities are an order of magnitude or greater, less in percent than the hydrogen. Impurities would seem to be ruled out.

Other points to be made are:

1. The effect was observed to be present in both polycrystalline and single crystalline alloys.
2. There was no evidence in previous x-ray work that the In-Tl lattice is long-range ordered. It would seem then that the heat capacity anomalies for the three alloys are not the beginning of a long range order-disorder transformation.
3. The rises would appear not to be caused by quenching or machining strains, as once relieved, these strains should not return.

The results of heat-capacity measurements on the 28.9 and 34.6-at. % Tl alloys in the 200-235°K region (Figure 8) appear to depend upon how fast the heat capacities were measured through the region in question. The limiting value of the heat capacities through this region was not able to be measured in times necessary for meaningful measurements. This time dependence would seem to imply a diffusion controlled mechanism, or at least, a mechanism which has diffusion associated with it. The diffusion of the metal atoms would thus explain the non-reproducible behavior of the 28.9 and 34.6-at. % Tl alloys. The

¹D. Bailey and J. Smith, ISU (Private communication).

2

18.8-at. % Tl alloy exhibited the rise in heat-capacity beginning at 195°K, but the results were reproducible in the temperature range 195-300°K.

The heat capacities of the 28.9 and 34.6-at. % Tl alloys also exhibited anomalous deviations from smooth curve behavior in the region 235-300°K (Figure 8). In this range, the heat capacities of these alloys were not monotonically increasing functions of temperature. The data follow the smooth curve as drawn in Figure 8, which would serve to indicate that the effect is real, and not an artifact of the measurement. Again, the 18.8-at. % Tl alloy does not exhibit this behavior, other than normal scatter off the smooth curve as drawn in Figure 8. The causes of the behavior of the alloys are not known.

The rises of the heat capacities of all three alloys in the neighborhood of 200°K would seem to be associated with the transformation from "rubber-like" to plastic behavior observed in the f.c.t. alloy and believed to exist, on the basis of the heat-capacity measurements, in the f.c.c. alloys as well. It is not clear from previous work that the onset of the mechanical property changes in the alloys does not begin at temperatures lower than 263°K¹. The heat-capacity data suggests that it does. The possibility exists that the "rubber-like" behavior does not exist in the f.c.c. alloys and the rises are due to another cause.

¹See Literature Review.

Different mechanisms have been proposed to explain the behavior of the mechanical property changes of both the f.c.t. In-Tl alloys and the Au-Cd orthorombic phase alloys. On the basis of the heat-capacity measurements, it would appear that another explanation for the behavior of the f.c.c. alloys is needed and perhaps only observation of the behavior have been made but the actual cause has not been determined.

Because the only two alloy systems that are known to exhibit this anomalous mechanical behavior also have a martensitic transformation associated with a phase change, it would be fair to suggest that the properties of the alloy that are responsible for producing a martensitic transformation also produce the anomalous mechanical behavior.

Future Work

It would be worthwhile to measure the heat capacity of a single-crystal of an In-Tl alloy that transforms martensitically in the temperature range of the measurements. This would alleviate the polycrystalline interferences to the transformation and perhaps yield a more definitive heat capacity than the one measured. The only problem with this suggestion is that single crystals of the size needed for the type of calorimetry described in this investigation need to be on the order of 30 to 50g, to yield meaningful data with presently available

instrumentation. Attempts to grow single crystals of a 28.9-at. % Tl alloy have to date met with no success.

Perhaps the definitive way to study the alloy system is to use inelastic neutron diffraction to study the optical and accoustical modes of the lattice vibrations (Gopal, 1966). Unfortunately, In has a sufficiently large neutron capture cross section so that no meaningful results would be expected for a measurement of this type. However, x-ray diffuse reflectance, though less sensitive to small changes in vibrational modes than the inelastic neutron diffraction method, might well yield the desired information about the two types of vibrational modes.

The study of the short-range order parameter as a function of the diffracted x-ray beams would yield information about the change of the short range order of the alloys in the 150-250°K region, and might serve to indicate whether a change in short range order was occurring in the anomalous regions of the three alloys heat capacities.

A study of the lattice parameters and the electrical resistivity of the alloys through the 150 to 250°K region might also add to the knowledge of the alloy behavior in the "rubber-plastic" region, and might help to elucidate the mechanisms of the transformation.

A measurement of the heat capacity of an orthorombic phase Au-Cd alloy would perhaps indicate if the "rubber-like" to plastic behavior change is produced by the same mechanism as in the In-Tl system.

Measurement of the mechanical behavior of f.c.c. alloys from 150-300°K is also indicated.

SUMMARY

The heat capacities and thermodynamic functions of the three In-Tl alloys have been determined from 5-300°K. The alloy that transformed from f.c.t. to f.c.c. exhibited the expected deviations from normal lattice behavior for an alloy undergoing a martensitic transformation. All alloys exhibited anomalous rises in their heat capacities at temperature greater than 195°K.

The anomalous rise in the heat capacities of the f.c.t. alloy is believed to correlate to the transition from "rubber-like" to plastic behavior in the alloys. This is the first time such a correlation has been found in any alloy system. This behavior should also be exhibited in the f.c.c. alloys, as the heat capacity in those alloys is similar in behavior to the heat capacity of the f.c.t. alloy, which does exhibit this behavior.

The lack of anomalous behavior below 195°K is possibly attributed to anomalous behavior of the Grüneisen γ in the lower temperature regions.

The general purpose of this investigation was to gain knowledge about the behavior of the system and the correlations thus obtained, and then, possibly suggest ways of altering the alloy properties, so as to be able to design alloy properties for predetermined uses. Knowledge was gained on the behavior of the alloys and if a need existed for "rubber-like"

behavior or for alloys that exhibited heat capacity rises in the 195-240°K region, perhaps an In-Tl alloy could be made to fulfill the specific intensive properties desired. An explanation for the behavior was not found.

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APPENDIX I

Experimental Heat-Capacity Data

Table 7. Experimental heat-capacity data^{a,b} for 34.6-at. % Tl alloy (Joules/mole-°K) (°C = 273.15°K)

$T_{av}(^{\circ}\text{K})$	ΔT	C_p	$T_{av}(^{\circ}\text{K})$	ΔT	C_p
<u>Run 1^c</u>			<u>Run 3</u>		
5.229	0.795	0.435	99.364	7.287	23.748
6.246	1.207	0.661	107.720	9.428	24.037
7.582	1.462	1.085	117.462	10.052	24.327
9.143	1.680	1.731	127.380	9.779	24.626
10.646	1.374	2.479	137.063	9.587	24.863
11.954	1.224	3.314	147.183	10.654	25.057
13.219	1.307	4.135	170.296	11.162	25.480
14.638	1.519	5.068	204.088	10.790	25.923
16.251	1.702	6.070	215.833	12.239	26.458
18.016	1.820	7.169	227.835	11.894	27.588
19.924	1.995	8.326	239.670	11.788	27.756
21.993	2.143	9.517	250.666	10.239	27.405
24.209	2.292	10.823	260.764	10.223	27.292
26.526	2.330	11.934	270.881	10.098	27.769
31.514	2.747	14.147	281.332	10.829	27.819
34.276	2.775	15.192	292.111	10.760	27.964
37.365	3.406	16.200	302.837	10.718	27.992
45.296	4.245	18.327			
49.386	3.935	19.177			
53.201	3.969	19.882			
56.806	3.512	20.421			
			<u>Run 4</u>		
			81.029	4.415	22.804
			96.198	7.309	23.608
			103.441	7.175	23.874
			112.007	9.946	24.155
50.406	4.325	19.413	131.372	7.547	24.697
54.908	4.677	20.120	139.316	8.346	24.903
59.495	4.495	20.814	150.305	13.635	25.141
63.878	4.269	21.362	163.805	13.367	25.350
68.060	4.092	21.791	174.007	7.037	25.534
72.084	3.952	22.102	181.019	6.982	25.648
77.139	6.156	22.515	187.981	6.936	25.740
84.182	7.925	23.030	194.904	6.895	25.809
92.281	8.272	23.445	201.800	6.850	25.928

^aNot corrected for curvature.

^bAt. wt. In = 114.81g; at. wt. Tl = 204.37g; alloy wt. = 399.69g; mol. wt. = 146g.

^cA run is defined as a series of measurements made in one 24-hour period. Runs are numbered chronologically.

Table 7. Continued

$T_{av} (^{\circ}\text{K})$	ΔT	C_p	$T_{av} (^{\circ}\text{K})$	ΔT	C_p
<u>Run 5</u>			<u>Run 7</u>		
211.275	11.622	26.337	168.108	10.389	25.461
222.219	10.509	27.441	177.584	8.560	25.619
233.380	12.023	27.618	183.997	4.252	25.694
245.290	11.945	27.662	191.189	10.139	25.761
256.409	10.298	27.774	198.375	4.197	25.870
267.068	11.046	27.801	203.872	6.694	25.948
277.690	10.234	27.704	207.669	0.861	24.902
288.639	11.717	27.923	213.539	10.878	26.187
300.315	11.689	27.858	220.992	4.123	26.669
			225.041	4.067	27.277
			229.052	4.033	27.609
			235.056	8.033	27.715
			242.261	6.400	27.796
			247.417	3.986	27.747
			253.778	8.740	27.817
			260.126	3.973	27.699
			266.459	8.711	27.773
			275.145	8.705	27.664
			285.359	11.783	27.902
			297.002	11.520	27.916
<u>Run 6</u>			<u>Run 8</u>		
6.088	1.457	0.547			
7.083	1.005	0.788			
8.360	1.599	1.374			
9.690	1.108	1.990			
10.940	1.375	2.682			
12.427	1.604	3.588			
14.019	1.611	4.647			
15.697	1.733	5.456			
17.334	1.782	6.573			
19.168	1.876	7.839	243.992	3.259	27.802
21.106	2.010	9.015	248.470	5.708	27.702
23.235	2.248	10.202	254.994	7.364	27.793
25.553	2.389	11.438	263.159	8.988	27.745
27.901	2.306	12.666	269.675	4.068	27.863
30.350	2.525	13.658	273.712	4.076	27.692
32.949	2.674	14.710	278.988	6.503	27.763
35.818	3.062	15.708	287.479	10.517	27.892
39.144	3.592	16.773	295.134	4.849	27.831
42.867	3.854	17.761	304.778	14.494	27.954
47.001	4.415	18.683			
51.332	4.252	19.535			
56.378	5.842	20.362			
61.642	4.687	21.065			
66.568	5.164	21.629			
73.396	8.495	22.221			

Table 8. Experimental heat-capacity data^{a,b} for 28.9-at. % Tl alloy (Joules/mole-°K) (°C = 273.15°K)

T_{av} (°K)	ΔT	C_p	T_{av} (°K)	ΔT	C_p
<u>Run 1^c</u>			<u>Run 3</u>		
7.464	1.672	1.012	57.182	5.787	20.420
9.182	1.735	1.708	63.147	6.143	21.259
10.883	1.649	2.588	69.727	7.017	21.941
12.573	1.719	3.610	75.095	3.716	22.425
14.359	1.849	4.793	78.764	3.612	22.683
16.307	2.005	5.982	82.328	3.512	23.029
18.552	2.439	7.352	85.801	3.433	23.245
21.272	2.980	8.925	89.201	3.365	23.425
24.407	3.271	10.638	92.534	3.298	23.685
27.861	3.628	12.331	98.788	9.207	23.835
31.617	3.883	13.976			
35.269	3.419	15.404			
38.837	3.708	16.528		<u>Run 4</u>	
42.707	4.030	17.579	106.658	6.498	24.101
46.931	4.419	18.571	114.690	9.563	24.365
51.836	5.387	19.561	123.089	7.249	24.641
57.317	5.578	20.438	131.776	10.118	24.865
63.143	6.073	21.255	141.788	9.904	25.152
			151.606	9.728	25.387
			161.753	10.541	25.611
			172.219	10.385	25.741
			182.564	10.274	25.877
			192.794	10.172	25.995
			202.965	10.086	26.109
			212.631	9.070	26.359
			221.631	8.889	27.167
			230.440	8.759	27.792
			239.175	8.730	27.867
			247.836	8.704	27.845
			256.492	8.628	27.874
			265.084	8.582	27.866
<u>Run 2</u>					
77.664	1.155	22.642			
81.599	6.712	23.040			
89.004	8.097	23.327			
97.310	8.532	23.776			
107.219	11.260	24.127			
117.452	9.205	24.441			
126.539	8.967	24.742			

^aNot corrected for curvature.

^bAt. wt. In = 114.81g; at. wt. Tl = 204.37g; alloy wt. = 352.5g; mol. wt. = 140g.

^cA run is defined as a series of measurements made in one 24-hour period. Runs are numbered chronologically.

Table 8. Continued

$T_{av}(^{\circ}\text{K})$	ΔT	C_p	$T_{av}(^{\circ}\text{K})$	ΔT	C_p
273.642	8.560	27.850	88.080	3.830	23.566
282.162	8.511	27.936	90.720	1.450	23.515
290.631	8.461	28.098	94.674	6.463	23.664
299.911	10.133	28.019			
	<u>Run 5</u>			<u>Run 7</u>	
137.286	10.093	25.033	74.290	3.033	22.288
146.295	7.917	25.257	76.561	1.509	22.540
155.616	10.727	25.398	77.831	1.033	22.644
188.061	10.303	25.953	78.952	1.205	22.662
197.868	9.282	26.904	80.187	1.267	22.775
207.611	10.116	26.198	81.264	0.882	22.948
217.172	8.994	26.967	82.143	0.875	23.060
225.642	7.935	27.843	83.067	0.971	23.026
234.433	9.653	27.895	84.505	1.971	23.112
243.632	8.758	27.796	86.485	2.041	23.290
252.354	8.725	27.833	88.011	1.011	23.568
261.052	8.701	27.823	89.020	1.005	23.426
			90.519	1.991	23.562
			92.009	0.989	23.610
			92.982	0.957	24.800
			94.001	1.079	23.671
			95.615	2.148	23.642
			97.221	1.064	23.775
	<u>Run 6</u>			<u>Run 8</u>	
8.262	1.889	1.313			
10.019	1.605	2.089			
11.441	1.283	2.919			
13.174	2.175	3.988			
15.327	2.137	5.361			
17.567	2.343	6.744	133.901	1.414	24.889
20.169	2.856	8.295	136.624	4.027	25.007
23.175	3.151	10.004	144.573	11.872	25.215
26.338	3.176	11.596			
29.834	3.824	13.222			
33.416	3.339	14.701			
36.881	3.591	15.931	70.856	0.251	22.055
40.728	4.104	17.051	71.158	0.354	22.083
46.486	7.413	18.490	71.570	0.470	22.084
54.688	8.988	20.023	72.098	0.586	22.101
60.766	3.169	21.003	72.682	0.582	22.135
66.231	7.743	21.614	73.265	0.581	22.102
72.304	4.402	22.158	73.844	0.578	22.211
75.774	2.532	22.538	74.422	0.576	22.197
77.615	1.149	22.690	74.997	0.567	22.515
80.215	4.044	22.809	75.565	0.567	22.521
84.199	3.921	23.191	76.131	0.566	22.472
			76.694	0.560	22.662

Table 8. Continued

$T_{av} (^{\circ}\text{K})$	ΔT	C_p	$T_{av} (^{\circ}\text{K})$	ΔT	C_p
77.333	0.716	22.621	94.670	1.275	23.550
78.047	0.711	22.723	95.640	0.778	23.670
78.619	0.426	22.623	96.418	0.775	23.726
79.201	0.705	22.825	97.115	0.618	23.749
79.767	0.422	22.753	97.732	0.619	23.717
			98.476	0.871	23.835
			99.345	0.867	23.914
	<u>Run 10</u>		100.282	1.005	23.979
80.330	0.702	22.746	101.289	1.004	23.887
81.030	0.698	22.848			
81.655	0.554	22.986		<u>Run 11</u>	
82.208	0.551	23.063			
82.760	0.549	23.092	102.350	1.091	23.886
83.377	0.683	23.172	103.437	1.084	24.002
84.069	0.679	23.252	104.518	1.079	24.056
84.740	0.676	23.289	105.596	1.076	24.038
85.417	0.675	23.225	111.025	9.778	24.249
86.092	0.672	23.291	119.479	7.127	24.543
86.466	0.074	23.252	127.034	7.978	24.752
86.540	0.074	23.013	140.691	19.340	25.081
86.614	0.072	23.221	153.197	5.672	25.361
86.763	0.226	23.266	164.910	4.645	25.556
86.989	0.225	23.310	170.000	5.530	25.713
87.215	0.226	23.320	185.553	5.443	25.878
87.440	0.225	23.377	190.985	5.410	26.010
87.665	0.225	23.433	195.952	4.497	25.942
87.889	0.224	23.506	200.897	5.360	26.125
88.656	1.308	23.491	209.279	11.310	27.253
89.540	0.412	23.482	221.196	12.069	27.387
89.951	0.411	23.469	233.118	11.916	27.783
91.120	0.283	23.677	242.023	5.931	27.827
91.405	0.212	23.513	246.678	3.392	27.682
91.652	0.200	23.648	250.902	5.069	27.808
91.858	0.200	23.593	255.115	3.371	27.870
92.058	0.200	23.576	259.318	5.052	27.828
92.259	0.199	23.583	263.522	3.361	27.862
92.459	0.199	23.617	267.713	5.031	27.906
92.658	0.199	23.744	271.480	2.512	27.911
92.857	0.198	23.763	275.662	5.870	27.774
93.056	0.198	23.714	279.842	2.511	27.790
93.256	0.199	23.691	284.005	5.835	27.938
93.454	0.198	23.639	288.986	4.418	28.078
93.653	0.238	23.699	293.121	4.147	28.010
93.872	1.257	23.618	297.670	4.973	27.957

Table 8. Continued

$T_{av} (^{\circ}\text{K})$	ΔT	C_p
<u>Run 12</u>		
48.630	0.140	19.004
49.017	0.633	18.970
53.148	7.630	19.785
59.149	4.373	20.678
64.597	6.534	21.430
70.032	2.099	22.037
72.113	2.065	22.131
73.669	1.043	22.182
74.708	1.032	22.382

Table 9. Experimental heat-capacity data^{a,b} for 18.8-at. % Tl alloy (Joules/mole-°K) (°C = 273.15°K)

T_{av} (°K)	ΔT	C_p	T_{av} (°K)	ΔT	C_p
<u>Run 1^c</u>			18.864	2.569	7.239
6.010	2.768	0.571	21.221	2.140	8.599
8.340	1.878	1.267	23.849	3.117	10.025
10.027	1.570	2.006	26.744	2.674	11.473
11.440	1.313	2.794	29.721	3.282	12.855
14.956	2.067	4.945	33.979	5.234	14.551
17.184	2.395	6.279	38.332	3.474	15.852
			43.109	6.081	17.493
			48.430	4.560	18.651
<u>Run 2</u>			53.236	5.051	19.519
5.554	3.015	0.461	58.396	5.269	20.394
8.139	2.116	1.189	63.500	4.940	21.134
9.990	1.588	2.000			
11.449	1.306	2.788	<u>Run 4</u>		
13.021	1.843	3.716	81.220	8.253	22.774
15.004	2.130	4.939	89.280	7.845	23.303
17.295	2.452	6.307	96.455	6.502	23.593
19.917	2.795	7.860	115.141	12.021	24.350
22.810	2.989	9.471	126.010	9.713	24.693
25.860	3.108	11.051	135.610	9.490	24.992
32.233	2.945	13.927	145.020	9.323	25.183
35.299	3.188	15.069	154.714	10.088	25.392
38.751	3.719	16.171	164.726	9.937	25.584
50.609	3.833	19.131	175.048	10.702	25.770
			185.693	10.583	25.963
<u>Run 3</u>			196.262	10.517	25.974
5.432	2.471	0.599	206.983	10.374	26.414
7.691	2.141	1.026	217.139	10.165	27.195
9.539	1.554	1.781			
10.960	1.265	2.499	<u>Run 5</u>		
12.392	1.597	3.378	239.629	11.660	27.529
14.189	1.926	4.468	251.657	12.425	27.516

^aNot corrected for curvature.

^bAt. wt. In = 114.81g; at. wt. Tl = 204.37g; alloy wt. = 366.5g; mol. wt. = 132g.

^cA run is defined as a series of measurements made in one 24-hour period. Runs are numbered chronologically.

Table 9. Continued

$T_{av}(^{\circ}\text{K})$	ΔT	C_p	$T_{av}(^{\circ}\text{K})$	ΔT	C_p
263.119	11.501	27.557	<u>Run 8</u>		
274.595	11.471	27.693	11.916	2.416	3.061
286.405	12.154	27.815	15.154	2.477	5.026
298.515	12.105	27.856	17.946	3.104	6.688
<u>Run 6</u>			21.273	3.547	8.626
83.749	10.305	22.920	24.497	2.901	10.358
92.711	7.615	23.448	27.771	3.644	11.925
100.717	8.395	23.831	31.164	3.145	13.489
109.986	10.142	24.153	33.815	2.159	14.417
120.454	10.791	24.515	36.998	4.209	15.618
130.559	9.417	24.816	40.535	2.865	16.735
139.956	9.376	25.096	44.463	4.991	17.696
149.718	10.124	25.352	54.206	14.496	19.664
159.769	9.968	25.518	63.376	3.844	21.068
170.129	10.725	25.760	67.741	4.887	21.602
190.940	9.622	26.059	73.662	6.956	22.115
200.987	10.410	26.179	79.900	5.520	22.633
<u>Run 7</u>			87.384	9.447	23.241
211.798	11.049	26.813	96.125	8.032	23.627
223.057	11.684	27.423	105.274	10.270	23.991
234.268	10.795	27.399	152.458	10.025	25.404
245.437	11.564	27.462	162.414	9.878	25.570
256.926	11.507	27.548	172.241	9.760	25.720
268.840	12.260	27.630	182.818	11.394	25.912
280.655	11.394	27.665	193.736	10.406	26.059
292.391	12.116	27.881	203.270	8.593	26.244
304.457	12.047	27.998	214.323	13.475	26.974
			236.804	11.576	27.422
			247.937	10.704	27.422
			259.827	13.103	27.506
			<u>Run 9</u>		
			271.972	11.420	27.641
			282.945	10.548	27.745
			295.061	13.710	27.884

APPENDIX II

Thermodynamic Functions

Table 10. Thermodynamic functions^{a, b} for 34.6-at. % Tl alloy
(Joules/mole-°K) (0°C = 273.15°K)

T(°K)	C _p	S _T ^o	-(H _T ^o -H _o ^o)/T	-(G _T ^o -H _o ^o)/T
6	0.570 ^c	0.357	0.210	0.147
8	1.133	0.590	0.363	0.227
10	2.133	0.943	0.610	0.332
12	3.340	1.437	0.963	0.473
14	4.633	2.067	1.412	0.655
16	5.923	2.770	1.896	0.874
18	7.152	3.539	2.411	1.127
20	8.357	4.354	2.946	1.409
24	10.674	6.087	4.045	2.043
28	12.709	7.890	5.141	2.749
32	14.358	9.699	6.194	3.505
36	15.778	11.473	7.181	4.292
40	17.013	13.201	8.104	5.097
44	18.032	14.872	8.962	5.910
48	18.917	16.480	9.755	6.724
50	19.307	17.260	10.130	7.130
60	20.859	20.926	11.796	9.129
70	21.952	24.228	13.174	11.054
80	22.732	27.213	14.322	12.891
90	23.313	29.925	15.290	14.635
100	23.761	32.405	16.116	16.290
120	24.406	26.798	17.447	19.351
140	24.908	40.599	18.478	22.121
160	25.300	43.951	19.307	24.644
180	25.637	46.951	19.992	26.959
200 ^d	25.893	49.665	20.570	29.096
204	25.966	50.179	20.675	29.504
208	26.131	50.684	20.778	29.907
212	26.401	51.184	20.881	30.304
216	26.806	51.681	20.986	30.695
220	27.251	52.177	21.096	31.081
224	27.518	52.671	21.209	31.462

^aNot curvature corrected.

^bAt. wt. In = 114.81g; at. wt. Tl = 204.37g; alloy wt. = 399.69g; mol. wt. = 146g.

^cExtrapolated to 0°K.

^dValues for 200-240°K region are those of highest smooth curve through the region.

Table 10. Continued

$T(^{\circ}\text{K})$	C_p	S_T°	$-(H_T^{\circ}-H_O^{\circ})/T$	$-(G_T^{\circ}-H_O^{\circ})/T$
228	27.640	53.159	21.321	31.838
232	27.700	53.641	21.430	32.210
236	27.730	54.114	21.537	32.577
240	27.750	54.581	21.640	32.940
242	27.743	54.811	21.691	33.120
244	27.708	55.039	21.740	33.299
246	27.671	55.265	21.789	33.476
248	27.683	55.489	21.836	33.653
250	27.730	55.712	21.883	33.829
252	27.788	55.933	21.930	34.003
254	27.819	56.153	21.976	34.177
256	27.787	56.371	22.021	34.349
258	27.736	56.587	22.066	34.521
260	27.707	56.801	22.109	34.691
262	27.692	57.013	22.152	34.861
264	27.703	57.224	22.194	35.030
266	27.758	57.433	22.236	35.197
268	27.857	57.641	22.277	35.364
270	27.837	57.848	22.318	35.530
272	27.742	58.053	22.359	35.695
274	27.682	58.256	22.398	35.859
276	27.669	58.459	22.436	36.022
278	27.711	58.657	22.474	36.184
280	27.792	58.856	22.511	36.345
282	27.842	59.054	22.549	36.505
284	27.852	59.251	22.586	36.665
286	27.859	59.447	22.623	36.823
288	27.869	59.641	22.660	36.981
290	27.877	59.834	22.696	37.138
292	27.886	60.025	22.731	37.294
294	27.896	60.216	22.766	37.450
296	27.903	60.405	22.801	37.604
298	27.911	60.593	22.835	37.758
300	27.916	60.779	22.869	37.911

Table 11. Thermodynamic functions^{a,b} for 28.9-at. % Tl alloy
(Joules/mole-°K) (0°C = 273.15°K)

T(°K)	C _p	S _T ^o	-(H _T ^o -H ₀ ^o)/T	-(G _T ^o -H ₀ ^o)/T
6	0.544 ^c	0.184	0.136	0.048
8	1.213	0.426	0.316	0.110
10	2.116	0.789	0.581	0.207
12	3.262	1.273	0.930	0.343
14	4.558	1.871	1.354	0.517
16	5.796	2.561	1.833	0.729
18	7.012	3.314	2.340	0.974
20	8.201	4.116	2.868	1.248
24	10.426	5.811	3.945	1.865
28	12.394	7.568	5.014	2.554
32	14.132	9.340	6.048	3.292
36	15.668	11.095	7.034	4.062
40	16.858	12.810	7.959	4.851
44	17.894	14.467	8.816	5.650
48	18.810	16.064	9.612	6.452
50	19.227	16.840	9.988	6.852
60	20.839	20.494	11.668	8.826
70 ^d	21.994	23.801	13.068	10.733
80	22.826	26.795	14.238	12.557
90	23.421	29.520	15.227	14.293
100	23.859	32.011	16.069	15.942
120	24.547	36.424	17.427	18.997
140	25.092	40.249	18.484	21.766
160	25.527	43.630	19.338	24.292
180	25.854	46.656	20.045	26.611
200 ^e	26.082	49.392	20.638	28.755

^aNot curvature corrected.

^bAt. wt. In = 114.81g; at. wt. Tl = 204.37g; alloy wt. = 352.5g; mol. wt. = 140g.

^cExtrapolated to 0°K.

^dValues for 70-100°K region obtained from a smooth curve through the region.

^eValues for 200-236°K region are those of highest smooth curve through the region.

Table 11. Continued

$T(^{\circ}\text{K})$	C_p	S_T°	$-(H_T^{\circ}-H_O^{\circ})/T$	$-(G_T^{\circ}-H_O^{\circ})/T$
204	26.465	49.912	20.747	29.164
208	27.154	50.433	20.865	29.568
212	27.311	50.953	20.986	29.967
216	27.321	51.463	21.103	30.360
220	27.364	51.965	21.216	30.749
224	27.472	52.459	21.327	31.132
228	27.615	52.946	21.436	31.510
232	27.756	53.428	21.544	31.884
236 ^e	27.844	53.903	21.650	32.253
238	27.858	54.138	21.702	32.436
240	27.853	54.371	21.753	32.618
242	27.829	54.602	21.803	32.799
244	27.779	54.831	21.853	32.979
246	27.743	55.058	21.901	33.157
248	27.740	55.282	21.948	33.335
250	27.771	55.505	21.994	33.511
252	27.827	55.727	22.040	33.687
254	27.856	55.947	22.086	33.861
256	27.858	56.165	22.131	34.034
258	27.861	56.382	22.175	34.207
260	27.863	56.597	22.219	34.378
262	27.868	56.811	22.262	34.549
264	27.871	57.023	22.305	34.718
266	27.876	57.233	22.347	34.887
268	27.881	57.442	22.388	35.054
270	27.887	57.649	22.429	35.221
272	27.880	57.855	22.469	35.386
274	27.834	58.059	22.508	35.551
276	27.770	58.261	22.546	35.715
278	27.758	58.462	22.584	35.878
280	27.797	58.661	22.621	36.040
282	27.888	58.859	22.658	36.201
284	27.973	59.056	22.695	36.361
286	28.042	59.253	22.732	36.521
288	28.088	59.448	22.769	36.679
290	28.093	59.643	22.806	36.833
292	28.040	59.836	22.842	36.994
294	27.999	60.027	22.877	37.150
296	27.978	60.217	22.912	37.305
298	27.983	60.405	22.946	37.459
300	28.015	60.592	22.979	37.613

Table 12. Thermodynamic functions^{a,b} for 18.8-at. % Tl alloy
(Joules/mole-°K) (0°C = 273.15°K)

T(°K)	C _p	S _T ^o	-(H _T ^o -H _o ^o)/T	-(G _T ^o -H _o ^o)/T
6	0.572 ^c	0.320	0.201	0.119
8	1.125	0.553	0.356	0.196
10	2.000	0.893	0.593	0.300
12	3.138	1.355	0.920	0.435
14	4.343	1.929	1.323	0.606
16	5.538	2.587	1.775	0.812
18	6.718	3.308	2.259	1.049
20	7.905	4.077	2.764	1.313
24	10.112	5.716	3.808	1.909
28	12.073	7.425	4.850	2.574
32	13.822	9.154	5.865	3.289
36	15.299	10.869	6.833	4.036
40	16.565	12.542	7.739	4.803
44	17.676	14.175	8.593	5.581
48	18.570	15.752	9.389	6.363
50	18.963	16.518	9.764	6.754
60	20.602	20.128	11.441	8.687
70	21.792	23.397	12.838	10.559
80	22.678	26.368	14.016	12.352
90	23.321	29.078	15.016	14.062
100	23.780	31.560	15.870	15.690
120	24.502	35.962	17.251	18.711
140	25.083	39.785	18.330	21.454
160	25.540	43.165	19.204	23.961
180	25.888	46.302	20.029	26.273
190	25.989	47.704	20.340	27.364
196 ^d	26.052	48.513	20.514	27.999
200	26.130	49.040	20.625	28.415
204	26.267	49.559	20.734	28.824
208	26.489	50.071	20.843	29.228
212	26.795	50.578	20.952	29.626

^aNot curvature corrected.

^bAt. wt. In = 114.81g; at. wt. Tl = 204.37g; alloy wt. = 366.5g; mol. wt. = 132g.

^cExtrapolated to 0°K.

^dValues for 196-220°K region are those of highest smooth curve through the region.

Table 12. Continued

$T(^{\circ}\text{K})$	C_p	S_T°	$-(H_T^{\circ}-H_O^{\circ})/T$	$-(G_T^{\circ}-H_O^{\circ})/T$
216	27.094	51.082	21.063	30.019
220	27.301	51.581	21.175	30.406
224	27.411	52.074	21.285	30.789
226	27.426	52.318	21.340	30.978
228	27.429	52.560	21.393	31.167
230	27.431	52.799	21.446	31.354
232	27.433	53.037	21.497	31.540
234	27.439	53.272	21.548	31.724
236	27.442	53.506	21.598	31.908
238	27.449	53.737	21.647	32.090
240	27.452	53.967	21.695	32.272
242	27.460	54.195	21.743	32.452
244	27.466	54.421	21.790	32.631
246	27.473	54.645	21.836	32.809
248	27.480	54.868	21.881	32.986
250	27.489	55.088	21.926	33.162
252	27.499	55.307	21.970	33.337
254	27.509	55.525	22.014	33.511
256	27.520	55.741	22.057	33.684
258	27.532	55.955	22.099	33.856
260	27.547	56.168	22.141	34.026
262	27.559	56.379	22.182	34.196
264	27.574	56.740	22.375	34.366
266	27.589	56.949	22.414	34.535
268	27.604	57.155	22.453	34.703
270	27.621	57.361	22.491	34.870
272	27.638	57.564	22.529	35.036
274	27.654	57.767	22.566	35.201
276	27.673	57.968	22.603	35.365
278	27.692	58.168	22.639	35.529
280	27.713	58.367	22.676	35.691
282	27.732	58.564	22.711	35.853
284	27.753	58.760	22.747	36.013
286	27.772	58.955	22.782	36.173
288	27.791	59.148	22.817	36.332
290	27.814	59.341	22.851	35.490
292	27.835	59.532	22.885	36.647
294	27.854	59.722	22.919	36.803
296	27.877	59.911	22.952	36.959
298	27.899	60.099	22.985	37.114
300	27.919	60.285	23.018	37.267