3.832°K indicates that the sample is somewhat under stress. The width of the transition was 0.028°K. While the thickness of the first set of samples (3830 Å) was less than $2\xi_0=4690$ Å (for tin) the second set of samples was sufficiently thick (6455 Å) so that on the side with the electric field a superconducting layer could have been formed with some of the tin still remaining normal-conducting. If this had happened, it would have led to observations quite similar to those of S.M. If the surface superconducting layer had been much thinner, the first set of samples would have given better accuracy. In neither case was any sign of surface superconductivity detected.

ACKNOWLEDGMENTS

This work was supported by a grant from the National Aeronautics and Space Administration. The U. S. Office of Naval Research supplied the necessary helium gas free of charge. Much of the work was performed by Teofils Turlais.

PHYSICAL REVIEW VOLUME 154, NUMBER 2 10 FEBRUARY 1967

Superconductivity in the Alloy System Indium-Thallium*

M. F. Merriam,† J. Hagen, and H. L. Luo
Department of Physics and the Institute for the Study of Matter,
University of California, San Diego, La Jolla, California

(Received 6 June 1966)

The superconducting transition temperatures of over 75 samples spanning the entire composition range of the indium-thallium alloy system have been measured. The highest T_c measured was about 3.8°K in the bcc phase; the lowest was 2.5°K in the fcc phase. In all phases, T_c decreases with increasing Tl content, the rate of decrease in the tetragonal (indium) phase being, however, much less steep than in the other phases. The Seraphim empirical rule, $\Delta T_c=k_1x+k_2\ln x$, is found not to describe our data in the dilute thallium range. An anomaly in the T_c-versus-composition plot at 4.4 at.% Tl is extremely similar in form to one previously identified in In-Cd as a Brillouin-zone effect. Transition temperature and isothermal magnetization data are used to locate the two-phase region separating the tetragonal and cubic phases; the boundaries of this region are: 30.1 ± 0.4 and 31.7 ± 0.3 at.% Tl at 3.3°K. The existence of such a region indicates that the tetragonal-cubic transformation is first-order, in agreement with the earlier room-temperature calorimetric work of Predel. The transition temperature of bcc Tl was estimated by extrapolation of the bcc alloy data to zero solute concentration; the result was 2.49°K.

I. INTRODUCTION

The alloy system indium-thallium has been the subject of many investigations. This system is popular with physicists and metallurgists interested in the electronic structure of metallic alloys for several reasons. The important reasons are: (1) both In and Tl are reasonably "simple" metals, i.e., their conduction-electron dynamics approach those of free electrons, and (2) they are nomially isoelectronic, each having three electrons per atom available for metallic conduction. Thus, the alloys all have three electrons/atom, independent of composition. The extent to which this is meaningful is not clear, but it certainly is true that thallium as a solute in indium causes a smaller change in almost any physical property than any other solute metal. The system is also convenient to handle experimentally, the metals are available in high purity, solid solubilities are extensive, temperatures are in a convenient range, etc. Not many properties, however, have been measured over the entire composition range except for the basic constitution diagram information,[1] the electrical resistance,[2] and the superconducting transition temperature (T_c).[2]

We undertook this work as one of a series[3–8] of studies of the electronic structure of nontransition metal alloys through measurement of the superconducting transition temperature. This technique in other alloy systems has lead to the discovery of electronic structure effects, e.g., Brillouin zone overlaps[9] and an order-disorder transformation.[10] It has also proved useful in investigating

---

* Supported by the U. S. Air Force Office of Scientific Research.

† Present address: Department of Mineral Technology, University of California, Berkeley, California.

[1] R. W. Meyerhoff and J. F. Smith, Acta Met. **11**, 529 (1963)

[2] W. Meissner, H. Franz, and H. Westerhoff, Ann. Physik **13**, 505 (1932).

[3] M. F. Merriam, M. A. Jensen, and B. R. Coles, Phys. Rev. **130**, 1719 (1963).

[4] M. F. Merriam and M. von Herzen, Phys. Rev. **131**, 637 (1963).

[5] T. Claeson, H. L. Luo, and M. F. Merriam, Phys. Rev. **141**, 412 (1966).

[6] T. Claeson, Phys. Rev. **147**, 340 (1966).

[7] G. Knapp and M. F. Merriam, Phys. Rev. **140**, A528 (1965).

[8] M. F. Merriam, Phys. Rev. **144**, 300 (1966).

[9] M. F. Merriam, Rev. Mod. Phys. **36**, 155 (1964); Phys. Rev. Letters **11**, 321 (1965).

[10] T. Claeson, H. L. Luo, T. R. Anantharaman, and M. F. Merriam, Acta Met. **14**, 285 (1966).

constitution diagrams.[5,10–12] We hoped also to be able to establish the T_c of bcc Tl by extrapolation from the solid solution. (The T_c of this allotrope cannot be measured directly because bcc Tl is unstable below 234°C.) A probable electronic structure effect was found, and the T_c of the bcc allotrope was estimated, though it could not be established with precision. We did obtain reliable transition temperatures over the whole system, extended the phase diagram in one very important area, and learned something about the superconductive behavior of In-Tl as compared to the other indium based systems we have studied previously. A parallel study of the Tl-rich end of the system was undertaken by Luo and Willens, and is reported separately.[13]

The superconducting properties of In-Tl alloys were investigated many years ago by Meissner, Franz, and Westerhoff.[2] They measured the electrical resistivity and superconducting transition temperature (T_c) of 14 alloys covering the binary range. Our work has amounted to verifying, refining, and extending their T_c results, by considering many more alloys in the light of a considerably better known phase diagram. Stout and Guttman[14,15] also investigated these two properties, but only over the composition interval 0–50 at.% Tl. Previous experience[3,4,7,16] in measuring T_c's of indium-based alloys has led us to adopt the criterion that transitions more than 100 mdeg. in width should usually be rejected, as indicative of a strained, inhomogeneous, or otherwise imperfect sample. Consequently, we have excluded those transitions of Stout and Guttman, and of Meissner, Franz, and Westerhoff, which were broader than 100 mdeg. The transition temperatures of Love, Callen, and Nix[17] are not reliable as they were obtained by fitting critical field curves to $H_c=H_0(1-T^2/T_0^2)$ and thus are really fitting parameters rather than experimentally determined primary quantities. Other workers have studied alloys at the In-rich[18,19] and Tl-rich[20] ends of the phase diagram.

The portion of this investigation concerned with the region of the martensitic tetragonal—cubic phase transformation has already been published[21]; consequently that portion of the work will only be summarized here.

II. EXPERIMENTAL DETAILS

Samples were prepared from 99.999% pure indium obtained from the Indium Corporation of America, and thallium of the same stated purity obtained from the American Smelting and Refining Company. Lumps of the pure elements were sealed, after weighing, in quartz tubes with about one-fifth of an atmosphere of helium. They were kept in these tubes, and the tubes remained sealed throughout the melting, annealing, and T_c measurements. Melting was done in a rocking furnace where the samples were mixed in the liquid state by sloshing back and forth in the tube for about 30 min. After rocking, the samples were quick frozen by immersing the tubes in liquid nitrogen. They were then annealed for several weeks or longer at temperatures close to solidus in order to homogenize the alloys. The samples were transferred from the annealing furnace to liquid nitrogen immediately prior to measuring and kept at 77°K or below until after the measurement. This was done in order to improve chances of keeping the samples in a well-defined metallurgical state, that characteristic of the annealing temperature. Annealing times varied with composition. Each sample was annealed as long as was necessary to give a reasonably sharp transition. Often a sample was put back for more annealing after measuring, then remeasured later in the hope (often realized) of obtaining a sharper T_c. Annealing times and temperatures are given in Table I. Almost all samples were annealed for at least a week.

Since the sample tubes were not opened, compositions were taken to be the nominal ones derived from weights of constituents. No chemical analyses were made. Some x-ray phase identification work was done, using the Debye-Scherrer method and an XRD-5 diffractometer. The superconducting transition temperature measurement was made by putting the sample in a coil forming one arm of a conventional bridge circuit. The bridge was driven at a frequency of 1 kc, and the measuring field at the sample was approximately 0.1 G. The bridge unbalance was amplified, detected, fed to an x-y recorder, and plotted against temperature. This technique detects the development of infinite conductivity in the sample. It will indicate a complete superconducting transition when essentially all the sample volume is enclosed by superconducting sheath, even if all the sample is not superconducting (for example, a lead-plated golf ball). A microscopic network of superconducting filaments can make a sample which is more than 99% normal material appear to be completely superconducting to this ac susceptibility test.[22] However this requires pathological metallurgy, and we believe our samples to be well behaved. We have no doubts that our measurement method is accurate and reliable for the indium-based alloy systems.

---

[11] B. R. Coles, M. F. Merriam, and Z. Fisk, J. Less Common Metals **5**, 41 (1963).

[12] T. Claeson and M. F. Merriam, J. Less-Common Metals (to be published).

[13] H. L. Luo and R. H. Willens, following paper, Phys, Rev. **154**, 436 (1966).

[14] J. W. Stout and L. Guttman, Phys. Rev. **88**, 703 (1952).

[15] J. W. Stout and L. Guttman, Phys. Rev. **88**, 713 (1952).

[16] M. F. Merriam and M. A. Jensen, Cryogenics **2**, 301 (1962).

[17] W. F. Love, E. Callen, and F. C. Nix, Phys. Rev. **87**, 844 (1942).

[18] R. A. Connell, Phys. Rev. **129**, 1952 (1963).

[19] G. Chanin, E. A. Lynton, and B. Serin, Phys. Rev. **114**, 719 (1959).

[20] D. J. Quinn and J. I. Budnick, Phys. Rev. **123**, 466 (1961).

[21] H. L. Luo, J. Hagen, and M. F. Merriam, Acta Met. **13**, 1012 (1965).

[22] G. Arrhenius, E. Corenzwit, R. Fitzgerald, T. H. Geballe, D. C. Hamilton, B. A. Holm, G. W. Hull, Jr., and B. T. Matthias, J. Appl. Phys. **35**, 3487 (1964).

TABLE I. Superconducting transition temperatures of indium-thallium alloys.

Composition[a] (at.% Tl)	Annealing temperature (°C)	Annealing time (weeks)	Transition[b] temperature (°K)	Reference[c]
0.0			3.404	C
0.0			3.405	SG
0.045			3.402[d]	CLS
0.081			3.402[d]	CLS
0.153			3.400[d]	CLS
0.307			3.395[d]	CLS
0.529			3.387[d]	CLS
0.6[e]	23	100	3.391–3.386	
0.827			3.381[d]	CLS
1.00	130	8	3.383–3.370	
1.4	"Near melting point"	0.5	3.375	C
1.5[e]	23	100	3.365–3.356	
2.00	130	1	3.330–3.322	
2.50	130	8	3.314–3.303	
3.00	130	8	3.303–3.295	
3.48	130	7	3.300–3.292	
3.52	"Near melting point"	0.5	3.287	C
3.52[e]	140	2	3.309–3.292	
3.98	130	1	3.289–3.281	
4.50	130	8	3.281–3.272	
5.0	23	100	3.300–3.294	
5.04	140–145	1–2	3.319–3.307	SG
5.2	130	3	3.292–3.278	
5.49	130	7	3.272–3.267	
6.00	130	7	3.272–3.267	
6.2	23	100	3.284–3.278	
6.2	"Near melting point"	0.5	3.268	
6.47	130	7	3.281–3.261	
7.00	130	1	3.278–3.267	
7.4	"Near melting point"	0.5	3.26	C
7.38[e]	130	8	3.272–3.267	
7.98	130	8	3.269–3.258	
8.98	130	8	3.267–3.255	
9.95	130	1	3.264–3.255	
10.07	140–145	1–2	3.299–3.284	SG
11.4	"Near melting point"	0.5	3.26	C
11.44[e]	130	8	3.264–3.255	
12.3	"Near melting point"		3.295–3.237	MFW
12.50	130	1	3.255–3.244	
13.0	130	1	3.267–3.261	
14.0	130	1	3.244–3.241	
14.0	23	>12	3.261–3.247	
14.2	130	1	3.249–3.229	
14.45	130	8	3.249–3.232	
14.9	130	3	3.252–3.229	
14.9	23	>12	3.250–3.241	
15.0	140–145	1–2	3.274–3.259	SG
16.0	130	1	3.249–3.238	
16.0	23	>12	3.250–3.238	
17.0	130	1	3.275–3.244	
17.0	23	>12	3.250–3.232	
18.0	130	1	3.270–3.238	
18.0	23	>12	3.272–3.235	
19.9	130	1	3.255–3.229	
20.0	140–145	1–2	3.257–3.225	SG
21.9	130	1	3.252–3.217	
24.3	130	1	3.223–3.184	
25.0	130	1	3.223–3.178	
25.2	130	1	3.223–3.184	
27	"Near melting point"		3.295–3.208	MFW
27.0[e]	130	8	3.238–3.162	
29.0	130	1	3.208–3.162	
30.1	140–145	1–2	3.349–3.289	SG
30.4	130	1	3.267–3.193	
31.0	130	1	3.346–3.330	
31.9	130	1	3.306–3.295	
33.0	130	0.14	3.244–3.235	
34.0	130	0.14	3.193–3.184	
35.0	130	3	3.172–3.150	
36.0	130	0.14	3.081–3.064	
37.5	130	0.14	2.992–2.977	
38.0	130	3	2.760	DK

TABLE I (*continued*)

Composition[a] (at.% Tl)	Annealing temperature (°C)	Annealing time (weeks)	Transition[b] temperature (°K)	Reference[c]
40.0	130	2	2.857–2.818	
42	"Near melting point"		2.705–2.611	MFW
44.7	130	3	2.624–2.590	
45.7	"Near melting point"		2.619–2.548	MFW
46.9	130	1	2.554–2.497	
49.7	130	2	2.510–2.503	
51	"Near melting point"		2.516–2.470	MFW
52.0	130	1	2.566–2.463(broad transition)	
53.9	130	25	3.388–3.003(broad transition)	
55.9	130	5	3.722–3.413(broad transition)	
56.7	"Near melting point"		2.507–2.477	MFW
57	Not recorded		3.309–3.252	
60.2	200	1	3.751–3.413(broad transition)	
62.0	200	1	3.835–3.662(broad transition)	
63	"Near melting point"		3.653–3.575	MFW
64.5	200	1	3.906–3.703(broad transition)	
65.7	130	3	3.853–3.752(broad transition)	
66.6	"Near metling point"		3.620–3.582	MFW
69.0	200	1	3.835–3.789	
70.0	200	1	3.808–3.742	
72	"Near melting point"		3.742–3.676	MFW
73.0	200	1	3.722–3.486(broad transition)	
75.7	200	1	3.555–3.438(broad transition)	
75.7	23	>12	3.600–3.510	
76	"Near melting point"		3.647–3.571	MFW
76.2	Not recorded		3.599–3.462(broad transition)	
77.3	200	1	3.438–3.362	
78.8	200	1	3.486–3.336(broad transition)	
79.8	200	2	3.357–3.317	
82.9	200	1	3.223–3.208	
82.9	23	>12	3.211–3.202	
83.5	'Near melting point"		3.309–3.210	MFW
85.0	200	1	3.127–3.114	
86.0	200	1	3.104–3.088	
87.2	200	1	3.043–3.032	
89.8	200	12	2.933–2.923	
	23	38	2.899–2.878	
92.3	200	3	2.840–2.827	
92.3	23	38	2.796–2.782	
95.2	200	5	2.704–2.694	
95.2	23	43	2.435–2.427	
97.2	200	3	2.596–2.590	
97.2	23	38	2.195–2.185	
			2.185–2.180(two transitions)	
99.9	Not stated		2.391[f]	QB
99.9	Not stated		2.370[f]	QB

[a] Our compositions are nominal, from weights of constituents. Most of the literature values are the result of chemical analysis.

[b] When two temperatures are given, they indicate the beginning and end of the transition. When one temperature is given it usually indicates the midpoint of a resistance transition. Broad transitions (broader than 100 mdeg) have been identified or, in the case of data of previous investigators, omitted.

[c] If no reference is given, the data is that obtained in the present study. Otherwise: CLS—Chanin, Lynton and Serin (Ref. 19); C—Connell (Rev. 18); SG—Stout and Guttman (Ref. 14); MFW—Meissner, Franz, and Westerhoff (Ref. 2); QB—Quinn and Budnick (Ref. 20); DK—Doidge and Kwan [P. R. Doidge and Kwan Sik-Hung, Phys. Letters **12**, 82 (1964)].

[d] Obtained by subtracting the ΔT given by CLS from 3.406°K.

[e] These samples were prepared at the IBM Research Laboratory and kindly donated to us by Dr. C. Chiou. They were chemically analyzed at IBM.

[f] Obtained by adding the ΔT given by QB to 2.360°K.

The sensitivity to superconductivity of our apparatus varied with sample size and conductivity, but typically was such that 2% of the full transition either from superconducting to normal or from normal to superconducting could be detected with signal-to-noise of unity. The temperature resolution was somewhat better at 4.2°K than at 2.4°K, but was never worse than 6 mdeg (0.006°K), and in the critical region (near 3.3°K) was about 2 mdeg.

Temperature was determined by measuring the He^4 vapor pressure with a Wallace and Tierman FA129 absolute pressure gauge, supplemented, when necessary, by a mercury manometer. The 1958 scale[23] was used to derive the absolute temperature from the vapor pressure. A carbon resistor was used to drive the recorder.

III. RESULTS AND DISCUSSION

A. General Features

More than 75 alloys were synthesized and measured; all were superconducting. Transition temperatures

---

[23] F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, Natl. Bur Std. (U.S.) Monograph **10**, 12 (1960); J. Res. Natl. Bur. Std. **64A**, 1 (1960).

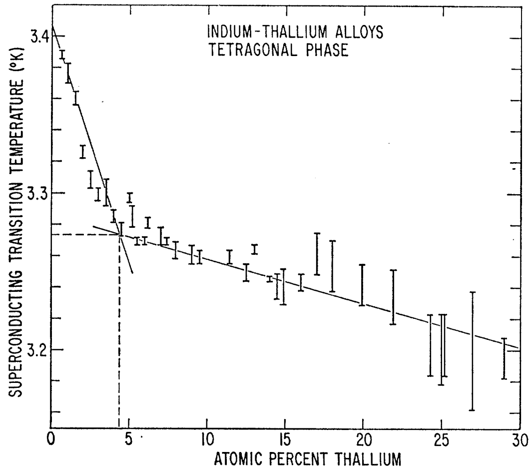

FIG. 1. Superconducting transition temperatures of tetragonal phase indium-thallium alloys annealed at 130°C. The spreads shown indicate total transition widths, and are not to be interpreted as experimental uncertainty. The feature at 4.4% Tl is believed to be a Brillouin-zone overlap effect. The deviation from linearity at about 1.75% Tl is attributed to saturation of the mean-free-path effect (depression of T_c arising from washing out energy-gap anisotropy). The sudden broadening and slight raising of the transitions beginning at 17 at.% Tl is a metallurgical effect discussed in the text.

varied from 3.9 to 2.1°K, a rather narrow range. The narrowness of this range reinforces our previous comments about the electronic similarity of In and Tl. The data, together with those of previous investigators, are collected and summarized in Table I. Portions of the data in this table are shown graphically in the various figures. Within each phase (tetragonal, face-centered cubic, body-centered cubic, and hexagonal) T_c decreases with increasing Tl content, a fact which would lead the empiricist to say that Tl in an In-Tl alloy has fewer effective electrons per atom than In. Svechkarev[24] has pointed out that when the effects of Cd and Tl solutes on the c/a ratio of tetragonal In are compared, Tl acts as if it contributed 2.75 electrons/atom, considering In and Cd to have 3.00 and 2.00, respectively. The number of electrons/atom effective in electronic specific heat is about 12% greater for In than for Tl. If the electronic specific heat is γT, then for In,[25] $\gamma=1.66$ and for Tl,[26] $\gamma=1.47$, in units of millijoules per mole degree.

No detailed comparison of our data with the microscopic theory of T_c has been attempted. In these alloys, the normal-state electronic structure changes with composition are subtle and not unimportant (i.e., for determining T_c the free-electron model is not good enough). The crystal structure is really all we know for these alloys, but even if we were to measure the electronic specific heat at all compositions it is unlikely that this parameter alone would dominate all others and control T_c (as it does, for example, in some transition element alloys). The variation of electron-phonon coupling strength (the "V" in BCS[27]) is presumably not very pronounced in this alloy system, but neither is the variation of T_c. We now consider each portion of the phase diagram in turn.

B. Tetragonal Indium and the Martensitic Transformation

In Fig. 1 we show our data for the tetragonal indium phase. To avoid cluttering the graph, we have not included the data of previous investigators; if the reader desires to make this comparison, all the data are included in Table I. In general, the data of previous investigators have a tendency to be higher than ours; we attribute this to incomplete annealing. The effect of insufficient annealing is always to raise T_c.[4,7,16] Our samples at 5.0, 5.2, 6.2, and 13.0 at.% Tl have high T_c's relative to the rest of the data; we do not know why. We do suspect the T_c's shown for these four samples to be spuriously high, but since we could find no reason for excluding them they are included as part of the data.

The data in the tetragonal phase contain three features which invite interpretation. Looking at Fig. 1 we are immediately struck by the feature at about 5 at.% Tl, where T_c versus x has a drastic change of slope. Another feature, almost as obvious, is the sudden broadening, and slight displacement, of the transitions at 17 at.% Tl and above, compared with those of samples having less Tl. A third feature, somewhat less apparent in Fig. 1, occurs between 1.75 and 2.00 at.% Tl, in the form of a departure from linearity of the T_c versus x plot.

We consider this last anomaly first. In order to see it better, we consider Fig. 2, which contains our data, plus the data of previous investigators, over the range 0–4 at.% Tl. The straight line would appear to be a reasonable representation of the initial decrease in T_c. It fits the data of Chanin, Lynton, and Serin,[19] and also our data up to 1.5 at.% Tl. The data depart markedly from linearity at a Tl concentration between 1.50 and 2.00 at.%.

The initial decrease of T_c with solute concentration in dilute primary solid solutions is virtually the only aspect of the composition dependence of T_c which is understood. Solute scattering effectively makes the energy gap progressively more isotropic (with respect to crystalline direction). Without scattering the electrons in the superconducting state are able to pair themselves in such a way as to take advantage of this energy-gap anisotropy to lower their total energy slightly, thus raising T_c. The initial drop in T_c with increasing solute concentration (usually called the "mean-free-path effect") occurs in a wide range of alloy systems and is the dominant effect at low concentrations of solute (long mean-free

---

[24] I. V. Svechkarev, Zh. Eksperim. i Teor. Fiz. **47**, 960 (1964) [English transl.: Soviet Phys.—JETP **20**, 643 (1965)].

[25] D. K. Finnemore and D. E. Mapother, Phys. Rev. **140**, A512 (1965).

[26] B. J. C. van der Hoeven and P. H. Keesom, Phys. Rev. **135**, A631 (1964).

[27] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

paths). When the solute concentration becomes high enough so that the mean-free path becomes appreciably shorter than the Pippard coherence length in the material the mean-free-path effect saturates out, although it continues to contribute to ΔT_c through a term linear in ρ (or linear in x, when ρ is linear in x). Various other effects come to dominate the change in T_c; these are usually referred to collectively as the "valence effect." Attempts[28–30] have been made to understand the "valence effect" in terms of a correlation with accessible parameters such as valence difference, (whence the name) atomic volume difference, etc., between solvent and solute; these attempts have not been completely successful. The theory of Markowitz and Kadanoff,[31] well summarized by Ginsberg,[28] is a theory of the mean-free-path effect. For the moment we are concerned not with any detailed theory but only with the general idea that the plot of T_c versus x should show some sort of a recognizable turnup or turndown at the point where the valence effect begins to dominate. This feature should be recognizable because (1) it will be the first feature to appear (i.e., there will be no features at lower solute concentration) and (2) it should appear at a mean-free path somewhat shorter (but not a great deal shorter) than the Pippard coherence length of the solvent. The crucial step in identifying the feature at 1.5–2.0 at.% Tl with the changeover from mean-free path dominated to valence dominated behavior then, is to compare the mean-free path, which can be deduced from electrical-resistance measurements, with the coherence length in indium which is 4400 Å, according to Dheer.[32] We now compute the mean-free path from the electrical resistance data of Stout and Guttman.[15]

As pointed out by Chanin, Lynton, and Serin[19] and applied in the previous work on In-Cd alloys,[8] the mean-free path may be obtained from the fact that ρl, the product of resistance ratio and mean-free path, is a constant, independent of scattering, for any given host metal. Thus, for indium-based alloys,

$$1.40\times10^6\rho l=1\,,$$

where l is the mean-free path in centimeters and ρ is the reduced residual resistance ratio, defined by

$$\rho\equiv R_{4.2}/(R_{273}-R_{4.2})\,.$$

The constant in the equation for ρl depends only on the properties of the solvent (indium), in essence on the average Fermi velocity. This quantity may be obtained from a high-frequency surface impedance measurement; we have used the data of Dheer.[32] The measurements of Stout and Guttman give $\Delta\rho/\Delta x=0.0205/\text{at.\%}$ Tl. We are thus led to a mean-free path of

$$l=3.5\times10^{-5}/x\,,$$

where l is in centimeters and x in at.% Tl. This gives $l=7000$ Å at 0.5 at.% Tl, 3500 Å at 1.0 at.% Tl, 2330 Å at 1.5 at.% Tl, and 1750 Å at 2.0 at.% Tl. The mean-free path is equal to the coherence length of 4400 Å at about 0.8 at.% Tl, and is about half this value or a little less when the departure from linearity of the initial T_c depression begins to show up. We would *a priori* have expected the effect to appear at a mean-free path of 3000–3500 Å, rather than 2000. However, considering the uncertainties in estimating mean-free path and coherence length, and the approximations in the theory, we regard the agreement as satisfactory and the identification of the anomaly at 1.5–2.0 at.% Tl as reasonably firm.

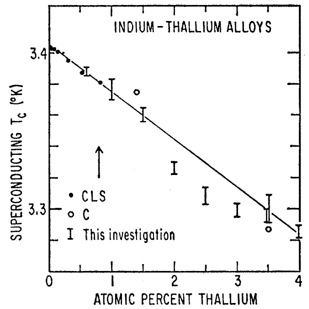

FIG. 2. Superconducting transition temperature as a function of composition for dilute In-Tl alloys in the indium primary solid solution. The arrow marks the composition at which the mean-free path equals the coherence length, as discussed in the text. The departure from linearity in the T_c plot between 1.5 and 2.0 at.% Tl presumably reflects the appearance of effects on T_c other than reduction of energy-gap anisotropy by scattering, which causes the initial depression. Spreads shown are total transition widths, determined principally by sample metallurgy, and not measurement errors. Previous workers: CLS—Chanin, Lynton and Serin (Ref. 19), C—Connell (Ref. 18).

Before discussing the other two features of Fig. 1, we compare our low-concentration data with the expected theoretical form. Markowitz and Kadanoff, in making up their theory, were guided by an empirical rule proposed by Seraphim, Chiou and Quinn,[33] according to which it is empirically true in a number of primary solid solutions that $\Delta T_c=k_1x+k_2x\ln x$ or, in our case, where ρ is linear in x,

$$\Delta T_c=k_1'\rho+k_2'\rho\ln\rho\,. \tag{1}$$

The k's are constants, x is mole fraction (or at.%) solute, and ρ is the reduced residual resistance ratio defined previously. This apparently successful empirical rule was part of the background for the theory, which does in fact yield the above formula for ΔT_c, with a microscopic interpretation of the constants. In particular, it yields

$$\begin{aligned}\Delta T_c&=A\rho+B\rho\ln\rho\,,\\ A&=\lambda^i\gamma K^i+\langle a^2\rangle T_c[-0.36+0.078\ln(\lambda^i\gamma)]\,,\\ B&=0.078\langle a^2\rangle T_c\lambda^i\gamma\,,\end{aligned}\tag{2}$$

---

[28] D. M. Ginsberg, Phys. Rev. **136**, A1167 (1964).

[29] R. I. Gayley, Phys. Letters **13**, 278 (1964).

[30] D. M. Ginsberg, Phys. Rev. **138**, A1409 (1965).

[31] D. Markowitz and L. P. Kadanoff, Phys. Rev. **131**, 563 (1963).

[32] P. N. Dheer, Proc. Roy. Soc. (London) **A260**, 333 (1961).

[33] D. P. Seraphim, C. Chiou, and D. J. Quinn, Acta Met. **9**, 861 (1961).

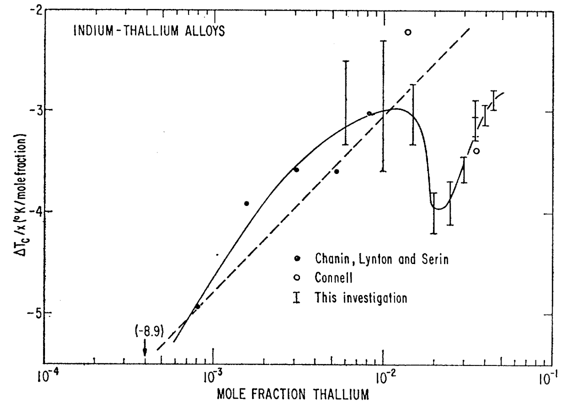

FIG. 3. Seraphim plot to test the relation $\Delta T_c = k_1x + k_2x\ln x$. The dashed line is drawn from the constants for this alloy system given by Seraphim *et al.* (Ref. 33). The data at the higher concentrations are obviously not described by any straight line. The other workers whose data are included are: Chanin, Lynton, Serin (Ref. 19) and Connell (Ref. 18). Spreads shown are total transition widths, not measurement errors.

in the notation of Ginsberg,[28] where $\langle a^2 \rangle$ is the anisotropy parameter, γ is a constant dependent only on the solvent metal, and λ^i and K^i are constants dependent on both solvent and solute (but independent of concentration). The constants are microscopically interpreted in terms of various relaxation times and the electronic structure of the host metal. The second term in Eq. (2) always dominates for sufficiently small ρ and insures the initial decrease of ΔT_c. Although the theory is for the mean-free-path effect part of the shift in T_c, any valence effect terms which are linear in solute concentration can of course be absorbed into Eq. (2) with a new value of the constant A.

In an earlier paper dealing with In-Cd alloys[8] it was found that the Seraphim empirical rule did not describe the data—i.e., a plot of $\Delta T_c/x$ versus $\ln x$ was not linear, as it should be if Eq. (1) above is correct. We have made such a plot for the In-Tl data (Fig. 3), and it is obviously far from linear. We therefore feel very little confidence in the general validity of Eq. (1), or Eq. (2), believing that the data originally used to justify them were too limited in range. The implications of our data for the general validity of the Markowitz-Kadanoff theory are less clear. Equation (2) results from a specialization of the theory in an attempt to display Eq. (1), and perhaps only this specialization is inappropriate and not the entire theory. The whole question of the composition dependence of T_c in dilute alloy systems is in need of further clarification. It is our conviction that further experiments would be more informative than additional theoretical work at this time.

Turning now to the sudden change in slope shown in Fig. 1, we are reminded of a feature very similar in appearance which showed up in the In-Cd data at 2 at.% Cd. In Fig. 4 we compare the two cases, plotting one above the other, with the abscissas scaled so that the kinks lie directly beneath each other. The morphological resemblance of the two features is striking.

On the basis of the striking similarity in form, we argue that the two features must arise from similar origins. This amounts to claiming that the In-Tl feature is a Brillouin zone effect, since the origin of the In-Cd kink is well established, by independent evidence (see Ref. 8) as a Brillouin zone effect.

The term "Brillouin zone effect" in this context means an effect caused by the presence of energy discontinuities in k space which must be crossed by an expanding or contracting Fermi surface. The feature in In-Cd was interpreted as corresponding to the filling of the last of the 1st zone holes as the Fermi surface expands through the stability range of the tetragonal indium structure (2.95 to 3.10 electrons per atom). What we mean when we talk about the Fermi surface expanding or contracting in In-Tl alloys, which are nominally isoelectronic, is not completely clear. However, we do wish to call attention to the two experimental facts mentioned earlier—the fact that adding Tl to In decreases T_c, as does Cd (whereas Sn and Pb increases it) and also decreases c/a (measured at room temperature) as does Cd (again, Sn and Pb increase it). A number representing the "effective electrons per atom" for Tl dissolved in In, may be obtained by comparing the magnitude of the effects caused by Tl solute with those caused by Cd solute, and assigning 3.00 and 2.00 electrons per atom to In and Cd, respectively. The results of doing this are: 2.55 from the critical concentration for the Brillouin zone effect; 2.81 from $\Delta T_c/\Delta x$ on the high solute side of the kink, 2.49 from $\Delta T_c/\Delta x$ on the low solute side of the kink; 2.75 from $\text{M}(c/a)/Gx$, according to Svechkarev.[24] We

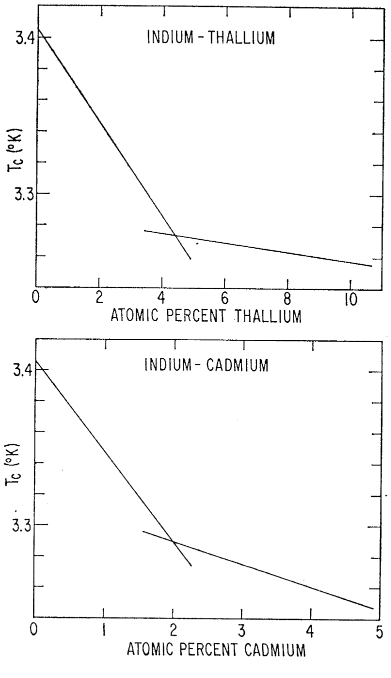

FIG. 4. Comparison of the T_c anomaly in In-Tl with that in In-Cd. The abscissas of the two graphs have been scaled so that the kinks fall at the same horizontal position. The identification of the In-Cd kink as arising from Fermi surface-Brilloun zone interaction is well established (Ref. 9). On the basis of the similar appearance of the two anomalies we propose the In-Tl kink arises from the same cause.

intend to continue work directed experimentally defining the "effective number of electrons per atom" or "effective valence" more quantitatively for Tl, by working with ternary alloys, and fundamentally toward understanding the meaning of the concept "effective electrons per atom" and the limits of its usefulness. We are well aware that this is a very primitive sort of concept; however, we doubt that anyone is at present in a position to use the microscopic theory of superconductivity and realistic electronic distributions for In, Tl and Cd to predict with confidence the variation of T_c in In-Tl alloys, knowing its variation in In-Cd and knowing the trend of the axial ratio in these two alloy systems. This we can do (admittedly after the fact) with the electrons per atom concept.

Consider now the third feature in the tetragonal phase T_c data, the broadening and shift of T_c which sets in at 17 at.% Tl. This arises from the tetragonal-cubic phase transformation (Fig. 5). The samples affected are those which are cubic at the annealing temperature (130°C) and tetragonal at the superconducting transition temperature. Our samples are polycrystalline, and are cooled abruptly from the annealing temperature to 77°K and then to 4.2°K. Since the martensitic transformation requires a change in the external dimensions of each grain, and since each grain is in intimate contact with, and strained by, its neighboring grains, it is clear that the transformation will result in strains in the crystallites. It is well established[4,16] that the superconducting transition is very sensitive to strain, and that the effect of strain is always to raise and broaden the transition. Thus, even though the martensitic transformation goes smoothly and reversibly to completion, it leaves a record in the form of strain in the crystallites. Superconductivity is the only phenomenon known to us which is sensitive enough to read this record. We point this out as an example of the application of superconductivity to physical metallurgy.

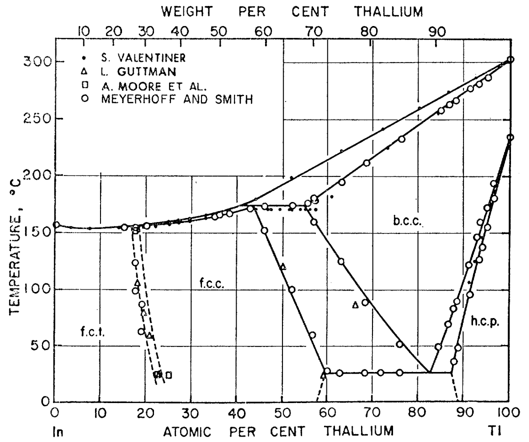

FIG. 5. Phase diagram of the In-Tl binary alloy system, taken from the work of Meyerhoff and Smith (Ref. 1). The limit of the hcp phase is at 87.5 at.% Tl, the eutectoid composition is 82.5 at.% Tl and the eutectoid temperature is 29.9°C. The hcp-bcc transformation in pure Tl occurs at about 234°C.

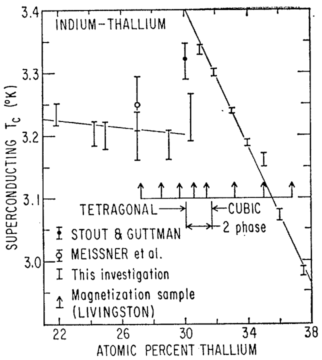

FIG. 6. Superconducting transition temperature as a function of composition for some In-Tl alloys in the neighborhood of the tetragonal-cubic transformation. The spreads indicate total transition widths, rather than experimental errors. The compositions of Livingston's magnetization curves (Fig. 7) are indicated. The phase boundaries have been located using the magnetization and T_c data, as discussed in the text.

C. Martensitic Phase Transformation

The tetragonal–cubic-phase transformation in In-Tl has been considered by many workers,[1,15,21,34–38] and has thereby taken on something of the flavor of a "classical" problem. As a consequence of superconductivity measurements and other recent studies we feel the thermodynamic aspects, at least, of this transformation are now understood.

The mapping of the martensitic phase transformation to 3°K was an application of superconductivity to metallurgy—in this case phase diagram determination. We have already reported[21] the details of that work, which was accomplished partly by conventional x-ray diffraction methods. The essential result of the superconductivity part of that study was the fact that the transition does in fact take place even at liquid-helium temperatures, and that the Tl concentration at which the transformation line in the phase diagram crosses the 3°K isotherm can be quite well determined from a plot of T_c versus x. Figure 6 is such a plot.

The phase transition stands out even more strikingly in the magnetization data than in the T_c plot. The magnetization measurements were all made at the General Electric Research Laboratory (Schenectady, New York) by Dr. J. D. Livingston, who has kindly communicated the results to us for inclusion in this paper. The samples were not the same as those used for the T_c measurements. The magnetization data are contained in Fig. 7 and in Table II. Note the dramatically larger magnetization hysteresis and trapped flux, and the general gross distortion of the form of the magnetization curves, in the two samples at 30.6 and 31.4 at.% Tl. The effects in these two samples strongly suggest a two phase micro-

---

[34] P. W. Anderson and E. I. Blount, Phys. Rev. Letters **14**, 217 (1965).

[35] G. V. Raynor and J. Graham, Trans. Faraday Soc. **54**, 161 (1958).

[36] A. Moore, J. Graham, G. K. Williamson, and G. V. Raynor, Acta Met. 3, 579 (1955).

[37] G. V. Raynor in *Theory of Alloy Phases* (American Society for Metals, Cleveland, 1956), p. 321.

[38] B. Predel, Z. Metallkunde **55**, 117 (1964).

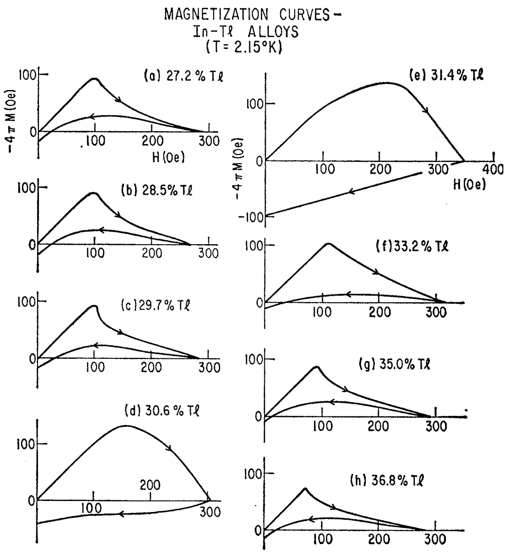

FIG. 7. Magnetization curves for eight In-Tl samples, taken by Dr. J. D. Livingston of the General Electric Research Laboratory. We are indebted to Dr. Livingston for sending us these data.

structure. In our earlier tentative interpretation[21] of the T_c data we mentioned, as an alternative to the two-phase region, the possibility that the intermediate-temperature transitions at 30.4 and 31.0 at.% Tl arose from single-phase tetragonal samples which were severely strained. In view of the magnetization curves, this possibility becomes very unlikely, and we will therefore abandon it. Visual inspection of the magnetization curves of Fig. 7 leads to the conclusion that the first three samples (27.2, 28.5, and 29.7 at.% Tl) are single-phase tetragonal, the next two (30.6 and 31.4% Tl) are two phase with substantial amounts of each phase, the next (33.2% Tl) is predominately cubic, but with a trace of tetragonal remaining, and the last two (35.0 and 36.8% Tl) are cubic, single phase. The H_{c2} values (Table II) are all consistent with this except the value for the 29.7% Tl sample which we might expect to be lower instead of higher than the preceding (28.5%) sample. Overlooking this, and considering also the T_c data of Fig. 6, we are led to place the limit of the tetragonal phase (at 3.3°K) at 30.1±0.4 at.% Tl. The position of the limit of the cubic phase would be placed a little above 33.2% from the magnetization data alone. However, it is very difficult to reconcile such a high number with the T_c data, according to which the phase boundary must be below 32%, since the T_c for this sample is sharp and has the proper value to be consistent with the composition dependence of the cubic phase. We therefore locate the limit of the cubic phase (at 3.3°K) at 31.7±0.3 at.% Tl. The width of the two-phase region at 3.3°K is thus 1.6 at.%. The (slightly) nonideal magnetization curve for the 33.2 at.% Tl sample thus remains unexplained, but could arise from a number of experimental causes, such as internal strains.

TABLE II. Upper critical fields of In-Tl alloys at 2.15°K.[a]

At.% Tl	H_{c2}(Oe)[b]
27.2	290
28.5	275
29.7	285
30.6	310
31.4	350
33.2	320
35.0	295
36.8	280

[a] These data were taken by Dr. J. D. Livingston of the General Electric Research Laboratory.

[b] Estimated experimental uncertainty: ±7 Oe.

Establishing the existence of a two-phase region at the superconducting transition temperature is a matter of some importance, since it has been proposed that the In-Tl transformation is a phase transition of the second order, in which case no equilibrium two-phase region could exist. A first-order phase transition, on the other hand, implies a two-phase region. The superconductivity data, then, particularly the magnetization data, support the view that the transition is first order. This is in concordance with the recent room temperature calorimetric result of Predel,[38] who measured a latent heat for this transformation. (A second-order phase transition has no latent heat, only a discontinuity in specific heat.)

The enthalpy of transformation measured by Predel for the transformation in In-Tl was about 0.5 cal/mole, or 2.2×10^{-5} eV/atom, which is an extremely small value. There is still enough thermal energy available at T_c, however, to make this transformation go (kT at 3°K is 2.6×10^{-4} eV).

Predel also measured the volume change on transformation, which is $\Delta V_{\text{In-Tl}}=2.6\times10^{-3}$ cm^3/mole, the cubic phase being denser. The T_c increase on passing to the cubic phase (T_c increasing with decreasing volume), is thus consistent with the trend of T_c within each phase (T_c decreases with increasing Tl content; volume per atom increases[1] with increasing Tl content). However, this correlation of T_c with volume per atom cannot be very fundamental; it does not work for In-Cd, where volume per atom decreases with increasing Cd content and T_c decreases too. The jump in T_c at the phase transformation has the same sign as for In-Tl, and the ΔV does also,[38] but the magnitudes do not scale.

The preceding paragraph illustrates again the point that T_c in the nontransition metals is not correlated with any ready accessible crystallographic or electronic property. If any generally valid correlation is to be found it will have to be with some characteristic of the electronic structure.

D. Face-Centered and Body-Centered Cubic Phases

The transition temperature data for these phases is shown mainly in Fig. 8. In the fcc phase T_c decreases rapidly and uniformly with increasing thallium concentration. The transitions are sharp. We do not understand why the composition dependence of T_c in the fcc phase is so very much steeper than in the tetragonal phase (see Fig. 6.) The same situation was found previously in In-Cd and In-Hg, though with the opposite sense in this last case. Presumably it is a reflection of a close similarity in electronic structure between the two alloy systems. The parameters affecting T_c, according to the well-known BCS formula

$$T_c = 1.15\Theta_D e^{-1/N_0V},$$

are Θ_D, N_0, and V, of which only Θ_D and N_0 are independently measurable. The Debye temperature, Θ_D, in In-Tl at least,[39] is not a particularly strong function of composition in the fcc phase, and furthermore increases with increasing thallium concentration, whereas T_c decreases. No measurements of specific heat, from which the density of states N_0 could be obtained, have, to our knowledge, been carried out in either the fcc or the concentrated tetragonal alloys. Specific-heat measurements could tell us, perhaps, if the density of states varies much more rapidly with composition in the cubic phase than in the tetragonal. If it does this might help us to understand the electronic-structure situation which is responsible for the tetragonal distortion; if it does not then presumably the T_c variation is coming from variation in the electron-phonon coupling parameter V. Like Θ_D, V shifts when the phonon-energy distribution shifts. A change in V can be very effective in changing T_c because of the exponential dependence. If the difference in the behavior of T_c in tetragonal and cubic phases does arise from this source it might be possible to learn something about the way the fundamental crystalline parameters enter into V. The difference between the two phases from the standpoint of ordinary crystallographic and physical parameters is not large, whereas the difference in superconducting behavior (especially in In-Cd) is substantial. The similarity in superconducting behavior between In-Cd and In-Tl is all the more interesting because the two alloy systems differ in so many ways—solute-solvent mass difference, solute-solvent charge difference, even the sign of the trend with composition of volume per atom.[1,40] An understanding of this question in In-Tl would be a major step toward understanding the variation of T_c in superconducting alloys generally.

The fcc phase ends, according to our T_c data, at about 52 at.% Tl, whereas the phase diagram of Meyerhoff and Smith (Fig. 5) locates the intersection of the 130°C (our annealing temperature) isotherm and the fcc boundary at about 48 at.% Tl. Possibly the phase diagram is wrong, but we think it more likely that our samples (and the 51% Tl sample of Meissner, Franz, and Westerhoff) between 48 and 52% Tl were actually two phase (bcc and fcc) at the annealing temperature and converted to fcc on quenching. A 52% Tl sample lies in the fcc phase field below about 100°C.

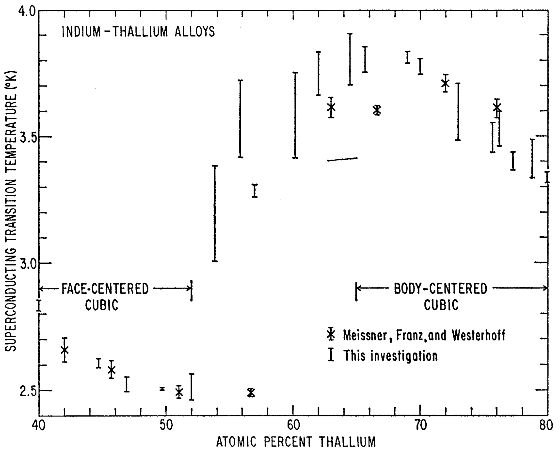

FIG. 8. Superconducting transition temperatures for indium-thallium alloys in the composition range 40–80 at.% Tl. Samples in this range are face-centered cubic, body-centered cubic, or two phase. The spreads shown represent total transition widths and are not measurement errors. Samples having less than 57 at.% Tl were annealed at 130°C, those with higher Tl at 200°C.

The samples between 52 and 66 at.% Tl have broad transitions (the transitions of Meissner, Franz, and Westerhoff are much narrower than ours, but this is attributable to their measurement technique). These samples are presumably all two phase and strained, since the conditions of quenching neither completely prevented the partial transformation of bcc to fcc nor allowed it to go to completion. Above 60 at.% Tl, of course, a completely equilibrated sample would be two phase, fcc+hcp, below the eutectoid temperature (29.9°C), but we think it unlikely that any of our samples contain hexagonal phase. Presumably they are all ill-defined conglomerates of fcc+bcc with unknown microstructure and unknown ratios of the two phases. The situation for the 60.2, 62.0, and 64.5 at.% Tl samples is further confused by an experimental blunder; these were annealed at 200°C, at which temperature, according to Fig. 5, they were above solidus. The 200°C isotherm crosses the solidus line at about 65% Tl.

The bcc samples show, in general, sharp transitions decreasing rather rapidly with increasing Tl content. Virtually all the bcc T_c's are higher than those of any other phase; evidently this structure is quite favorable for superconductivity. The bcc phase also has the highest electrical resistance,[2] indicating, perhaps, that a stronger electron-phonon coupling is responsible for the higher T_c's.

We have attempted to use the T_c's of the bcc alloys to estimate T_c for bcc Tl, as we will now describe.

E. Body-Centered Cubic Phase and Transition Temperature of bcc Tl

Thallium metal is known to exist in three different crystal structures, hexagonal, body-centered cubic, and

---

[39] D. B. Novotny and J. F. Smith, Acta Met. 13, 881 (1965).

[40] W. B. Pearson, *Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon Press, New York, 1958), p. 481.

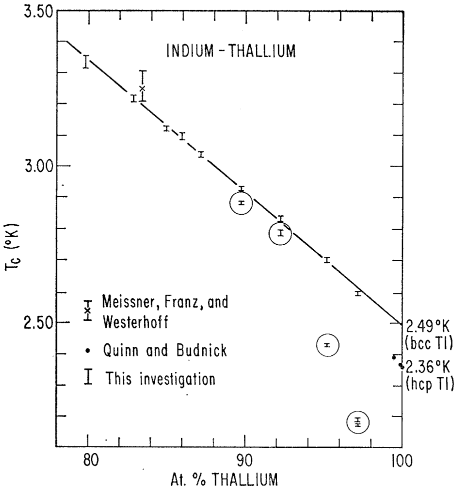

FIG. 9. Superconducting transition temperatures for In-Tl alloys spanning the hexagonal and most of the bcc phase. The T_c of bcc Tl, which is unstable at low temperatures, has been estimated by extrapolation. The transitions shown are those of samples equilibrated at 200°C and quenched into liquid nitrogen just before measurement, except for the four circled transitions which are of samples annealed at room temperature as described in the text. The cross ($-X-$) is taken from the paper of Meissner *et al.* (Ref. 2). The solid circles are the data of Quinn and Budnick (Ref. 20).

face-centered cubic. The stable form at atmospheric pressure is hexagonal below 234°C and bcc above that temperature. The fcc form of pure thallium is stable only at high pressure[1]; scattered observations[41,42] of fcc patterns at atmospheric pressure, if correct, presumably arise from stabilization by minor amounts of contaminant. Such stabilization is consistent with the fact, deduced from elastic constant measurements,[39] that fcc Tl is not absolutely unstable at atmospheric pressure, only less stable than the hexagonal form. (By contrast fcc indium is unstable absolutely.)

Occurrence of a superconducting element in more than one allotropic form is not common in the periodic system. Comparisons of the superconducting properties of different allotropic forms have been made however, for Hg, La, Bi, Ga, and U. Consequently, it is of some interest to attempt to determine the superconducting transition temperatures of the cubic forms of thallium, in order to compare them with each other, and with the hexagonal form. The T_c of the fcc allotrope has recently been determined by Gey[43] to be 1.45°K at 35 kbar. At this same pressure the T_c of the hcp phase (ordinary thallium) is reduced to 1.95°K, from its atmospheric pressure value of 2.34°K. The fcc phase is not retained, even metastably, at pressures below about 25 kbar, but a T_c for (hypothetical) fcc at atmospheric pressure may be obtained by extrapolation, and is useful for comparison with atmospheric pressure data on the other allotropes. Such an extrapolation of Gey's data indicates a T_c of about 1.7°K for fcc at atmospheric pressure.

The body-centered phase cannot, unfortunately, be retained in the pure element by rapid quenching from the solid or liquid state, even at extremely rapid quenching rates.[13,44,45] Furthermore, it cannot be made stable at low temperatures by the application of pressure. Two possibilities come to mind for getting an estimate of T_c of bcc Tl. One is to attempt to prepare metastable bcc Tl at low temperature by some exotic method, such as epitaxial growth of a crystal from the vapor on a suitable bcc substrate; the other is to extrapolate Tl rich alloy T_c's to vanishing solute concentration. We have used this extrapolation method with indium solute. In a related but distinct investigation utilizing splat cooling, Luo and Willens[13] (LW) have made the same extrapolation. The two different experimental approaches both give a T_c for bcc Tl which is higher, but not a great deal higher, than that for the hexagonal form.

Our results with bulk samples annealed to equilibrium at 200°C, and quenched into liquid nitrogen immediately prior to measurement are shown in Fig. 9. The phase diagram (Fig. 5) indicates that samples at 200°C are bcc to a concentration of 95 at.% Tl or higher. The smooth variation of T_c with composition, and the sharp transitions, together with the known phase diagram, lead us to believe that the data of Fig. 9 is indeed characteristic of the bcc phase, and thus that 2.49°K is a reasonable estimate of T_c for bcc thallium.

The crucial question here is whether or not we have successfully quenched in the bcc phase in the alloys of Fig. 1. We have made no low-temperature x-ray examination of the samples after quenching; this would have been experimentally difficult. It would have been easier experimentally to embed a thermocouple in the sample and observe the bcc $\rightarrow$ hcp transformation or absence thereof, during quenching, by differential thermal analysis, but we did not do this either. Our argument for retention of the bcc phase depends on the indirect evidence from the superconductivity data. The data of Fig. 9 do not reflect the eutectoid at 82.5 at.% Tl, or the limit of the hcp phase at 87.5 at.% Tl. If transformation to the hcp phase on quenching were taking place we would expect broad transitions in all samples and especially at Tl contents below 87.5 at.%, and a composition-independent T_c over most of the interval 82.5 to 87.5 at.% Tl. We would also be surprised if the bcc $\rightarrow$ hcp transformation were taking place at our cooling rates (400–500°C/min), in view of the fact that Meyerhoff and Smith,[1] using much smaller rates, reported the transformation to be sluggish.

We also annealed some samples at room temperature for a long time (many months) to see if T_c changed. (The bcc phase should not be present at room tempera-

---

[41] S. Sekito, Z. Kristallogr. **A74**, 189 (1930).

[42] A. Schneider and G. Heymer, Z. Anorg. Chem. **286**, 118 (1956).

[43] W. Gey, Solid State Comm. **4**, 403 (1966).

[44] E. I. Abaulina and N. V. Zavaritskii, Zh. Eksperim. i Teor. Fiz. **28**, 230 (1955) [English transl.: Soviet Phys.—JETP **1**, 184 (1955)].

[45] P. Duwez, Trans. AIME **191**, 765 (1951).

ture—the eutectoid temperature is 29.9°C.) The transitions for these four samples, which should all be in the hexagonal phase, are shown circled in Fig. 9. They all fall below the values for the 200°C annealed samples. This supports our contention that quenching from 200°C effectively retained the bcc phase, and that the T_c's lying along the straight line in Fig. 9 are *not* characteristic of the hexagonal phase. On the other hand, the actual values of the T_c's measured for two of the samples, 95.2 and 98.6 at.% Tl, after room-temperature annealing, are disturbingly low, and difficult to understand. The 98.6 at.% Tl sample, in particular, is far too low to be consistent with the known T_c of pure Tl and its very dilute solutions with In.[20] Furthermore, the transition is double, indicating the existence of two phases. This suggests additional complexity in the phase diagram near the Tl-rich end, at or below room temperature. The compound $HgIn_2$ in the Hg-In system was discovered in just this way, by noting a few anomalous superconducting transition temperatures.[12] Alternatively, the phase diagram of Fig. 5 could be complete with respect to ordinary crystallographic transformation, but a pronounced perturbation in the electronic structure could be occurring at a few percent indium.

The approach of LW[13] is to use the "splat cooling" technique originally developed by Duwez. When In-Tl alloys were quenched from the liquid state to 77°K at rates of the order of 10^6 °K/sec, the bcc phase appeared in alloys from 95 to 55 at.% Tl. In the center of this composition interval, from 83 to 65 at.% Tl, the sample was pure bcc. Extrapolation from this region to pure Tl yielded a T_c of about 3.0°K, somewhat higher than our result for the bulk samples. One might expect a higher value for the "splat cooled" samples, because of strains, but the T_c's were not lowered appreciably by annealing at 60°C. Higher T_c's could also result from compositional inhomogeneity, and the annealing treatment given might not have been sufficient to eliminate this.

The experiment of Luo and Willens has the advantage that the samples were x rayed, and the phase positively identified, just prior to measurement, and in some cases following measurement as well. It has the disadvantage that the correspondence with the phase diagram of Fig. 5 is uncertain because of the method of sample preparation. Both the T_c and the x-ray data of Luo and Willens do, however, reflect the eutectoid feature of the phase diagram, showing a break at the eutectoid composition. This tends to support their identification with the phase diagram, and makes it more difficult to argue against their extrapolation to bcc Tl.

There is no apparent correlation of the superconducting transition temperature for hcp, bcc, and fcc Tl with the thermodynamic free-energy differences between the various forms, as discussed, for example, by Kaufman.[46] This leads to the not very surprising conclusion that the stability of the various allotropic forms is not controlled by the conduction-electron distribution alone. If it were, we might expect to find the phase with the lowest normal-state free energy (i.e., the most stable) having the lowest T_c, the next most stable having the next lowest T_c, etc.

F. Hexagonal Phase

As discussed in the preceding section, the situation with regard to the transition temperatures characteristic of the hexagonal phase is one of great confusion. All that is really clear is that they decrease with increasing Tl content, and lie between 2.3 and 3.5°K. The confusion may reside in the phase diagram, or in the method of preparation of samples for the T_c measurement, or elsewhere. Further investigation is clearly needed.

ACKNOWLEDGMENTS

We are indebted to Dr. J. D. Livingston of the General Electric Research Laboratory (Schenectady) for providing magnetization curves and H_{c2} data. We also thank Dr. C. Chiou of the IBM Research Laboratory who provided some of the indium rich samples as described in Table I, Dr Meyerhoff and Dr. Smith for permission to reproduce Fig. 5, and Professor G. Arrhenius for help and advice with the x-ray work.

---

[46] L. Kaufman, Acta Met. **9**, 896 (1961).