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Superconductivity and Electronic Structure in the Alloy System Lead-Thallium*

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The superconducting transition temperatures of Pb-Tl alloys covering the entire composition range have been determined. The T_c's of the alloys are in general intermediate between those of Pb and Tl, except for samples in the concentration range 75–85 at.% Tl, for which the T_c's are lower. Two other features, a continuous change of slope of T_c versus composition, and a small peak structure in T_c, occur at about the 50 at.% composition. These features, which occur in the fcc (Pb) phase, might arise from a Brillouin-zone effect of the Merriam type. If the model for the Fermi surface in lead proposed by Anderson and Gold (based upon their de Haas–van Alphen data and using the orthogonalized plane-wave method) is employed, such an effect would be expected at the composition observed. On the other hand, an order-disorder transformation might contribute to the observed effects. A speculation regarding a connection between the electronic structure effect and a possible ordering process is made. Superconductivity behavior suggests an extension of the Pb solid solution, in a limited temperature interval, to higher Tl concentrations than those in the accepted phase diagram. The terminal solid solubility of Tl in Pb is found to be 88±2 at.% at 25 and at 295°C. The solubility of Pb in α-Tl is 2.5±1 at.% at 25°C; in β-Tl it is 5±1 at.% at 295°C. The T_c's of a few Bi-Tl samples were also measured. Structure, similar to that at $Pb_{0.50}Tl_{0.50}$, appeared in the T_c curve at $Bi_{0.15}Tl_{0.85}$.

INTRODUCTION

NUMEROUS investigations of the superconducting transition temperature T_c of metallic alloys and compounds have been made.[1,2] Detailed studies of the composition dependence of T_c in a binary alloy system can give a wealth of information. Use of superconductivity measurements in phase-diagram determinations is well established.[3–5] Moreover, it is known that curves of transition temperature versus composition within a solid solution can show features corresponding to discontinuous changes in the electronic structure of the alloy.[5–7] In particular, changes in the slope of T_c-versus-composition curves in indium alloys have been attributed by Merriam to Brillouin-zone–Fermi-surface interactions.

The Fermi surface is distorted from the free-electron spherical surface by interactions with the Brillouin zones; the distortion is largest when the surface is in the vicinity of a zone. As the electron density is increased through alloying, the Fermi surface expands and at certain critical alloy compositions, e.g., where it first encounters a new Brillouin-zone face, the dynamics of the electrons on parts of the Fermi surface can be strongly affected. The electron density of states N_0 is dependent upon the free area (i.e., that part not in contact with zone boundaries), and the curvature of the Fermi surface. Hence dN_0/dx (x=composition) can change discontinuously at critical compositions.

Solid solutions and intermediate phases extending over large composition ranges are not too common in nontransition-metal alloy systems. In the Pb-Tl system, however, the face-centered-cubic Pb solid solution extends to about 85 at.% Tl.[8] Changes in the electronic properties, including the superconducting transition temperature, from electronic-structure effects as discussed above might be expected to occur within this large homogeneity range.

From electrode-potential measurements and a discontinuous change of slope in the curve of lattice constant versus composition at 54.6 at.% Tl, Ölander[9] concluded that an ordered phase starts to form at 54.6 at.% Tl and extends to higher Tl content. He proposed that the perfectly ordered arrangement of the phase would conform to the formula $PbTl_7$. Later precision lattice-parameter determinations by Tang and Pauling[10] did not confirm the discontinuous change of slope at 54.6 at.% Tl. Other discontinuities in the variation of the lattice constant versus composition led them to suggest, however, that the ordered structures $PbTl_3$ and $PbTl_7$ exist.

The effect of ordering upon superconductivity has been studied in the Cd-Hg system.[11] It was shown that a substantial decrease in the superconducting transition temperature could be obtained in samples with large ordered domains. If ordering in the Pb-Tl system occurs it might be possible to observe its effect upon the superconducting transition temperature, without having to go to He^3 or adiabatic demagnetization techniques.

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† On leave from Chalmers University of Technology, Gothenburg, Sweden.

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The T_c's of some Pb-Tl samples were measured several years ago by Meissner *et al.*[12] Their data indicate a gradual change of slope in T_c versus composition at 60–65 at.% Tl. Recently, T_c as well as magnetization curves and residual resistivities for Pb-Tl samples have been determined by Bon Mardion *et al.*,[13] mainly on Pb-rich samples. Neither set of measurements is extensive enough to allow definite conclusions regarding possible Brillouin-zone or ordering effects.

This study was undertaken to investigate in more detail the possibility of Brillouin-zone or ordering effects on T_c in this alloy system. It was also expected that the superconductivity measurements would give an improved estimate of the positions of the phase boundaries.

EXPERIMENTAL TECHNIQUE

The lead and thallium used were nominally at least 99.999% pure; both metals were obtained from ASARCO. The thallium was cleaned and cut under an argon or a carbon dioxide atmosphere to prevent oxidation. The weighed samples were sealed off under a reduced pressure of helium in quartz tubes, and were heated to above their melting points in a rocking furnace from 3 to 4 h. After being thoroughly mixed, the (liquid) samples were slowly cooled to room temperature. As the liquidus and solidus curves are not as close together in the concentration range 75–95 at.% Tl as they are at other compositions, samples in this range were also quenched from the molten state into ice water or liquid nitrogen. All samples were then annealed at 295°C for 3 to 5 weeks. Annealed samples were quenched into ice water quickly followed by a quench into liquid nitrogen just prior to superconductivity measurements. In order to check the possibility of forming a new phase by slow cooling, the samples, after the first measurements, were reheated to 295°C and then slowly cooled off to 25°C; the cooling procedure lasted 1 week. Following 2 weeks' further annealing at room temperature, several samples were remeasured.

The superconducting transitions were observed with an impedance bridge that compared the inductance of a coil containing the sample with that of a similar, but empty, coil. The bridge operated at 160 cps and produced an ac magnetic field at the sample of less than 1 G. Both coils were either immersed in liquid helium or held in the cold vapor above it. To secure equilibrium above 4.2°K, the coils and the samples were enclosed in a thick-wall copper can. Below 4.2°K the temperature was determined by measuring the vapor pressure of He^4 and using the 1958 He^4 scale.[14] Above 4.2°K the temperature was measured with the aid of a germanium resistor calibrated at several helium and hydrogen temperatures and at the superconducting transition temperature of pure lead (7.19°K). Transition temperatures were measured both during cooling and warming of the samples, and an average was taken. Generally the hysteresis was very small.

Below 4.2°K, the absolute error in the temperature determination was estimated to be ± 0.01°K; the relative uncertainty did not exceed 0.005°K. Above 4.2°K the same errors were of the order of ± 0.1 and 0.02°K, respectively.

RESULTS AND DISCUSSION

The superconducting transition temperature as a function of composition for samples annealed at 295 and 25°C is listed in Table I and plotted in Fig. 1. The transitions are usually rather sharp. The spreads shown on the graph are transition widths, not errors. Some samples exhibited two transitions which are shown connected in the figure by a vertical dashed line.

An increase in T_c and the transition width as a result of rapidly solidifying an inhomogeneous sample has often been observed.[11,15] The effect anneals out after an

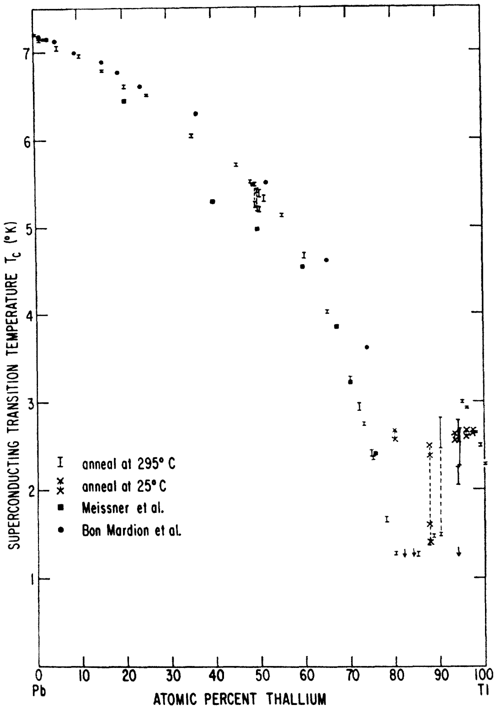

FIG. 1. Superconducting transition temperatures in the Pb-Tl system. Transition widths are plotted. Some samples show two transitions; these are connected in the figure by a vertical dashed line. An arrow indicates that the alloy is not superconducting above 1.25°K. Samples are annealed at 295 and 25°C. Midpoint transition temperatures taken from Refs. 12 and 13 are also included. Note the sharp dip in T_c at 80–85 at.% Tl, the structure at 50 at.%, and the various T_c's of 96 at.% Tl samples.

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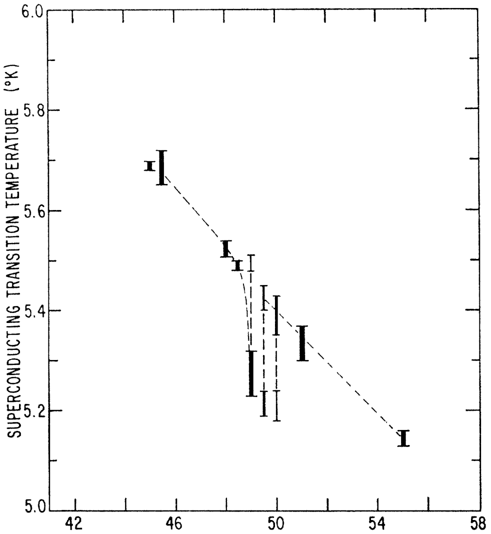

FIG. 2. T_c in the vicinity of $Pb_{0.5}Tl_{0.5}$. The temperature widths of the transitions are plotted. Note that the width of the line representing the transition roughly measures the amount of the sample becoming superconducting. Double transitions are connected by a vertical dashed line.

annealing time dependent upon the annealing temperature and its proximity to the solidus temperature. Here, no change in either the transition temperature or the transition width was observed by prolonged annealing after the initial annealing, an observation which is taken as an indication of the homogeneity of the samples.

Considering first the fcc (Pb) primary solid solution we notice, from Fig. 1, that something is happening at about the 50 at.% composition. The T_c data in the vicinity of the 50:50 composition are plotted in Fig. 2. Double transitions are observed in three cases as the Pb concentration passes through 50 at.%. Subject to certain assumptions, the amount of the sample becoming superconducting is roughly measured by the size of the unbalance signal from the bridge (Fig. 3). The width of the line representing the transition in Fig. 2 is used to display this information. Note that the higher temperature transition is at first the stronger one, but that the lower temperature transition grows stronger with decreasing Tl concentration and becomes predominant until only a single, sharp transition appears.

Besides the mentioned structure, other notable features of the results in the fcc Pb solid solution are the gradual change of slope in the curve of T_c versus composition at about 50 at.%, and the large dip in T_c versus composition close to the boundary of the Pb solid solution. These features may be explained by a Brillouin-zone–Fermi-surface interaction using the model for the Fermi surface of Pb proposed by Anderson and Gold.[16]

Several theoretical methods to calculate the band structure of pure elements exist.[17] Although the translational periodicity of a crystal is broken by alloying, there is some theoretical justification of the extension of band theory to alloys.[18–20] Such applications to alloys have often been very fruitful.[21–24] The fact that Pb and Tl are neighbors in the periodic system contributes to the justification of the extension of the model for Pb to alloys, which will be made here.

The first Brillouin zone for a face centered cubic lattice is drawn in Fig. 4. Conventional symbols for symmetry points and axes are used.[25] There is good evidence[26–29] that a qualitatively correct picture of the electronic structure of many elements can be obtained by employing a free- (or nearly free) electron model.[30] If we assume that Pb has four valence electrons and construct the Fermi sphere in reciprocal space, we find a completely filled first Brillouin zone and a partially filled second zone. A multiply connected Fermi surface

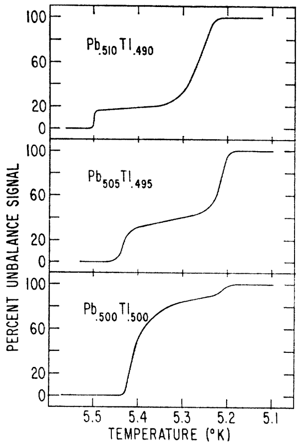

FIG. 3. The unbalance signal displaying the superconducting transition of the 49.0, 49.5, and 50.0 at.% Tl samples. A decreasing temperature scale is used. Note the difference in signal size between the two phases at the three compositions.

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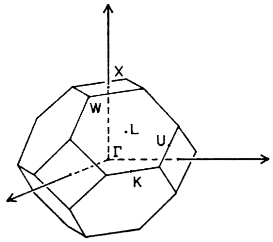

FIG. 4. The first Brillouin zone for a fcc lattice.

with arms along the edges of the hexagonal faces (the "limbs" are thickest around K and U) exists in the third zone, while small electron pockets exist near the points W in the fourth zone. For a figure, see Ref. 26.

Anderson and Gold[16] (A-G) instead used the orthogonalized plane-wave (OPW) method.[17] Four orthogonalized plane waves and a spin-orbit coupling correction were employed. The Fermi energy, two pseudopotential parameters, and the spin-orbit coupling strength were chosen to give orbits that agreed with measured de Haas-van Alphen oscillations. It was shown that the Fermi energy in lead falls below the calculated minimum energy value that the electrons in the fourth zone would have. (This is in agreement with de Haas-van Alphen[16,26] and cyclotron resonance[29,31] data which indicate that no fourth-zone electrons are present in lead. This result is not too surprising as the fourth zone angles in rather sharply towards the center of the zones at the symmetry points W, and so contains little volume near these points. Since few electrons are involved, only a small distortion of the free-electron Fermi sphere is necessary in order to accommodate these in a lower zone, and this will be energetically more favorable than requiring the electrons to jump across an energy gap into the fourth zone.)

By keeping the pseudopotential and spin-orbit coupling parameters constant and varying the Fermi energy, A-G computed the different constant-energy surfaces. The density of states versus energy could then be calculated from the derivatives of these surfaces. The qualitative result is shown in Fig. 5. A sharp rise in the density of states occurs when electrons start to penetrate into the third zone at an energy of 0.641 Ry. A maximum is reached at 0.663 Ry at which energy the several portions of the third-zone Fermi surface make contact at the symmetry points W and form a multiply connected structure. The Fermi energy was fitted to be 0.718 Ry. The free-electron density of states is shown as a dotted line in the figure.

By alloying, it is possible to vary the electron concentration per atom and hence the Fermi energy. Let us assume Pb to have four free valence electrons (an assumption which A-G showed was valid, although there exists a large energy separation between the two 6s and the two 6p electrons). Figure 5 indicates that the free-electron density of states is not, on the average, too bad an approximation for a more realistic picture, at least for energies just below the Fermi energy of Pb. If we use the free-electron-model relationships $E_F \alpha k_F{}^2$ and $k_F \alpha Z^{1/3}$ (where k_F and E_F are Fermi momentum and energy, respectively, Z = number of valence electrons per atom), together with energy values above, then we can calculate that the peak in the density of states will be reached at an electron concentration per atom of about $4\times(0.663/0.718)^{3/2}\approx 3.55$. If Tl is now assumed to possess three valence electrons, about 55 at.% Pb is needed before this is accomplished.

Since we know that the superconducting transition temperature depends strongly on the electron density of states at the Fermi level,[32] we might expect to obtain a structure in T_c corresponding to the details in the theoretical density of states shown in Fig. 5. One might expect T_c to show a peak corresponding to the peak in the density of states. However, if the third-zone electrons were less strongly coupled to the phonon system than the average, they could screen and hence reduce the net electron-phonon interaction and cause a lower T_c. In the transition metals, we know that a high density of states depresses V_{ph}.[32] Therefore, it is difficult, at this stage, to predict the detailed behavior of T_c in the vicinity of the sharp peak in the theoretical density of states curve. Furthermore, we know that the electron-phonon coupling is stronger in Pb than in Tl. Consequently, we will expect the feature in T_c at 3.5 electrons/atom to show up as only a small structure of some kind, superimposed on a continuous increase with increasing electron/atom ratio.

Returning to the superconducting data we see that this is what was observed. A sharp rise in T_c versus composition occurs. Figures 2 and 3 show clearly a structure occurring in the vicinity of the 50:50 composition. That a small two-phase region appears instead of a sharp peak or dip might be explained by small sample inhomogeneities. A discontinuity in T_c versus

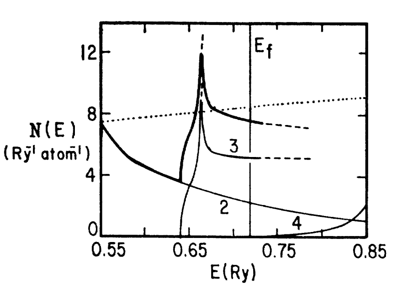

FIG. 5. The electronic density of states versus energy for Pb in the neighborhood of the Fermi energy as calculated in Ref. 16. An OPW method with parameters chosen to fit de Haas-van Alphen oscillations was utilized to obtain the curve. Individual contributions from the second, third and fourth bands as well as the resulting density of states curve are shown. The free-electron density of states is indicated by the dotted line.

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[31] R. T. Mina and M. S. Khaikin, Zh. Eksperim. i Teor. Fiz. **45**, 1304 (1953) [English transl.: Soviet Phys.—JETP **18**, 896 (1964)].

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composition and a small two-phase region has been observed in connection with a proposed Brillouin zone effect in the Hg-In system.[5] However, the transition curves in that report did not show the same peak structure as here. Furthermore, the crystallographic situation is somewhat less clear.[33]

That the sharp rise and the structure occur at a slightly different composition and with a smaller magnitude than the calculated one is not at all surprising. The Fermi-surface model is proposed for pure lead. Here alloys are used, which will lead to considerable deviations even if a rigid-band model is employed and the potentials due to the Tl atoms are assumed to be very similar to those of the Pb atoms. A pronounced smearing of the sharp peak is most probable.

Marked changes in the slope of lattice parameter versus composition have been found in Li-Mg alloys[23] and in several dilute Mg solid solutions.[34] It has been suggested that these changes are caused by stresses due to the Brillouin-zone–Fermi-surface interactions which might be expected at these compositions.[20] In the Pb-Tl system, a discontinuity in the slope of lattice parameter versus composition was early attributed to an ordering tendency.[9] The discontinuity was later discarded by Tang and Pauling.[10] A plot of their results indicated, however, that the rate of decrease in lattice parameter with increasing Tl content does seem to change, though not discontinuously, at about 50 at.%. If true, this would be another indication of a Brillouin-zone–Fermi-surface interaction in Pb-Tl.

A further indication of an electronic structure effect is given by measurements of the T_c's of a few Bi-Tl samples. The interesting electron concentration range (i.e., around $e/a = 3.5$) exists in an fcc phase of the Bi-Tl system.[8] If we assign five valence electrons to Bi, the effect present at the 50:50 composition in the Pb-Tl system should appear at about 25% Bi in Tl. The experimental result is given in Fig. 6. As can be seen, there is a marked change in slope of T_c versus composition at about 85 at.% Tl, or 3.30 electrons/atom, which is close enough to 3.50 to constitute reasonable agreement. Hence the Brillouin-zone–Fermi-surface interaction seems to exist both in the Pb-Tl and the Bi-Tl fcc phases at an electron concentration per atom of about 3.5. Unfortunately, no extensive determination of lattice parameter versus composition exists for the fcc Bi-Tl phase. The four measurements by Ölander[35] indicate, though, that a change of slope in the lattice-constant-versus-composition curve occurs at about the interesting composition.

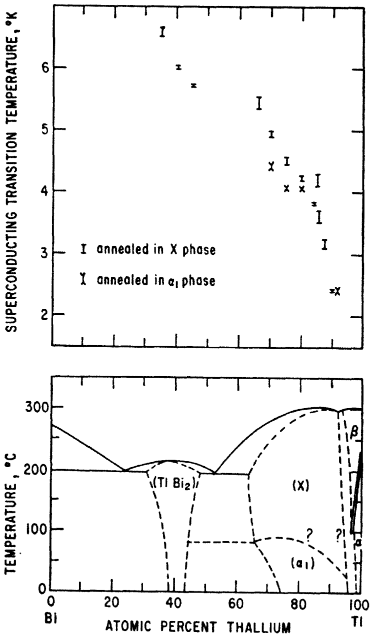

FIG. 6. Phase diagram (mainly from Ref. 8) and superconducting transition temperatures in the Bi-Tl system. Transition widths are plotted for samples annealed in the X and α_1 phases. Note the break in slope and the peak structure at 85 at.% Tl.

The In-Pb system also possesses a fcc phase at the critical electron concentration. The superconducting data of Meissner *et al.*[36] seem to indicate that the curve of T_c-versus-Pb concentration, after an initial sharp increase flattens out at about 40–50 at.% Pb (again the electron concentration of about 3.5). A more detailed study of that system is in progress.

The effect on T_c of proposed Brillouin-zone–Fermi-surface interactions has previously been extensively studied by Merriam in the In-Pb,[6] In-Sn,[6] and Cd-In[7] systems. This is the first time, however, that it has been possible to calculate the composition of an observed Brillouin-zone effect starting with an existing, detailed theoretical model based on experimental measurements of the electronic structure of a pure element.

In spite of the agreement between the observed and calculated composition, the possibility that the T_c anomaly arises from ordering cannot be completely ruled out. Establishing the existence of ordering by observing superlattice lines in x-ray diffraction is not practical in Pb-Tl or Bi-Tl, since the scattering powers of these elements are nearly the same. A small peak in the curve of conductivity versus composition[37] found at the Tl end of the Pb solid solution and the curvature of that curve close to the ordering composition support (weakly) the superlattice proposal of Ölander[9] that, for a Tl content larger than 55 at.%, the atoms sought to arrange themselves in an ordered array corresponding to the formula $PbTl_7$.

The steep fall of T_c with increasing Tl content in the Pb-Tl system could now alternatively be explained by this suggested ordering tendency, if the T_c of the ordered phase is depressed here. It is observed that the largest depression occurs close to the suggested ordering composition. In the Cd-Hg system, it has previously been

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shown[11] that the superconducting transition temperature is substantially depressed in well-ordered samples compared to disordered ones. It was argued that the T_c was lowered either by a smaller electron-phonon coupling, also indicated by the lower resistivity of the ordered phase, or by a change in the density of states by the subdivision of the Brillouin zones, which results from the superlattice formation.

However, the peak structure at the 50% composition cannot easily be understood in detail by hypothesizing an order-disorder transformation. The explanation in terms of a Brillouin-zone effect is regarded to be the more likely (or at least the predominant) one.

The T_c's of a number of samples annealed at both 295 and 25°C were measured, in order to investigate if the annealing temperature has any effect upon T_c. Such an effect would be expected, for example, if the critical temperature for a possible ordering process happened to lie between the two annealing temperatures. X-ray and conductivity measurements, which indicated an ordering, were made at room temperature. Only in one case, however, was any effect detected for samples in the region 0–90 at.% Tl. The T_c of a sample containing 80 at.% Tl annealed at 25°C was raised 1.5°K compared to the T_c of the same sample annealed at 295°C. However, no change was found in several other samples of similar composition. In the Cd-Hg system the superconducting transition of the ordered phase was often shielded by the higher transition temperature of the disordered phase that existed in the walls in between antiphase, or out-of-step domains.[11] However, this could not be the case here, as an eventually formed ordered phase with a higher T_c than the disordered phase cannot be shielded. The single result may be due to an experimental mistake (such as a sudden rise in annealing temperature during the slow-cooling procedure) in the sample preparation.

As no difference in T_c was seen between samples annealed at 295°C (which is not far from the solidus temperature) and at room temperature, it is concluded that if the suggested ordering occurs at all, it takes place at all temperatures up to the solidus temperature.

That the possible ordering terminates at about the same composition as the third-zone states are first occupied might lead to the speculation that there is a connection between the two phenomena. As Fig. 5 shows, the density of electron states in the fcc phase is rather low before the Fermi surface reaches the third Brillouin zone. When electrons are added, with increasing Pb concentration, they have to occupy higher energy states. The total free energy might be lowered if an ordering through its partition of the Brillouin zones could increase the density of states towards its free-electron value and hence make a larger number of lower energy states available.

In the Cd-Hg system, it was also noted that the radius of the free-electron Fermi sphere exceeds the distance from the center to the 011 plane of the first Brillouin zone by only about 2%.[11] In the Bi-Tl system we have already noted a possible Brillouin-zone interaction at an electron concentration of about 3.5. A phase transformation[38,39] occurs in the fcc phase ranging from 65 to 95 at.% Tl in the temperature interval 90–30°C, as can be seen from Fig. 6.[8] It has been suggested that this transformation is an order-disorder phenomenon,[40] where the truly ordered phase has the composition $BiTl_3$. The decrease in T_c for an ordered sample of 74 at.% Tl composition, as measured by Wipf (reported by Coles)[40] agrees with the decrease reported here (Fig. 6).

No evidence (besides the 80 at.% Tl sample discussed above) was found for the occurrence of order corresponding to the formula $PbTl_3$ as suggested by Tang and Pauling.[10]

It might be argued that the structure at the 50 at.% composition could be caused by a compound or an ordered structure conforming to PbTl. However, no abnormalities have been discovered in thermal analysis,[41,42] resistivity measurements,[37] or precision lattice-parameter determinations[9,10] which could indicate the formation of such a compound or ordered phase. Furthermore, due to the theory of space groups, only the ordered structures AB_3 and AB_7 are compatible with the assumption that the atoms are completely ordered and occupy with cubic symmetry the A1 points.[10] A small lattice distortion caused by ordering at the 1:1 composition (cf. AuCu) would probably have been detected in the precision lattice-constant measurements.

From Fig. 1 is seen that the limit of the fcc Pb solid solution is about 88±2 at.% Tl at 25 and 295°C; the boundaries of the Tl solid solutions seem to be 5±1 at.% Pb for the bcc β phase at 295°C and 2.5±1 at.% Pb for the hcp α phase at 25°C.

It is impossible to retain the bcc structure in pure Tl by rapid quenching.[43] The only way then to obtain the T_c of bcc Tl is by extrapolation from a solid solution. As it is difficult to retain the bcc structure in quenched samples with low Pb content, we disregard the T_c of quenched bcc samples of Pb content lower than 4%. The T_c of β-Tl, obtained by extrapolation to zero Pb content of the remaining bcc samples, appears to be slightly higher than the T_c of the hcp α-Tl. This is in agreement with the conclusion of Hagen *et al.*[44] from a similar (more reliable) extrapolation in In-Tl.

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TABLE I. Transition temperatures of annealed Pb-Tl alloys. Note that in a few cases different samples of the same composition have been investigated. When a bracket is present this indicates that the sample has been measured at different temperatures.

Composition (at.% Tl)	Annealing temperature (°C)	Superconducting transition (upper and lower limits in °K)
0	295	7.22–7.19
1.0	295	7.15–7.13
2.0	295	7.17–7.15
5.0	295	7.08–7.03
10.0	295	6.98–6.94
15.0	295	6.81–6.78
20.0	295	6.63–6.59
25.0	295	6.52–6.50
	25	6.53–6.50
35.0	295	6.07–6.03
45.0	295	5.70–5.68
48.0	295	5.54–5.51
48.5	295	5.50–5.48
49.0	295	5.51–5.48 5.32–5.23 [a]
49.5	295	5.45–5.40 5.24–5.19 [a]
	25	5.41–5.36 5.25–5.19 [a]
50.0	295	5.43–5.35 5.24–5.18 [a]
	25	5.43–5.18
51.0	295	5.37–5.30
55.1	295	5.16–5.13
60.0	295	4.71–4.65
	25	4.77–4.73
65.0	295	4.06–4.02
70.0	295	3.31–3.24
72.0	295	3.00–2.92
73.0	295	2.78–2.75
74.7	295	2.47–2.39
75.0	295	2.39–2.37
	25	2.39–2.36
75.1	295	2.43–2.33
	25	2.64–2.51 2.38–2.35 [a]
78.0	295	1.71–1.65
	25	1.70–1.63
80.0	295	1.31–1.25
	25	1.31–1.25
80.0	295	1.29–1.26
	25	2.68–2.58
80.1	295	1.34–1.27
	25	1.31–1.25
82.0	295	<1.24
	25	<1.24
84.0	295	<1.24
	25	<1.25
84.9	295	1.29–1.24
87.5	295	1.44–1.39
	25	2.51–2.39 1.62–1.41 [a]
88.5	295	1.51–1.47
	25	1.50–1.46
90.0	295	2.83–2.98 1.52–1.49 [a]
93.9	295	2.80–2.55
93.9	295	1.97–1.96
94.0	295	<1.25
	25	2.68–2.62
	295	2.70–2.28
	25	2.68–2.61
	295	2.27–2.06
94.0	295	2.45–2.32
94.0	295	2.29–2.23
94.9	295	3.02–3.00
96.0	295	2.95–2.93
	25	2.68–2.61
98.0	295	2.67–2.66
	25	2.68–2.64
99.0	295	2.53–2.50
	25	2.56–2.51
100.0	295	2.36–2.34

[a] Two transitions were found in this sample.

No "mean-free-path effect," i.e., the initial depression of T_c with increasing solute concentration due to the averaging out of gap anisotropies, is apparent. This agrees with earlier observations,[45,46] that impurities of valence higher than that of Tl raise T_c.

A question is raised by the behavior of 94 at.% Tl samples. As can be seen from Table I, the T_c for this composition ranges from about 2.8 to below 1.25°K for samples annealed at 295°C. This is not what is expected for a sample containing two phases; i.e., a large amount of one phase with a higher T_c and a small amount of a second phase with a much lower T_c. One would expect a broadened transition close to the higher T_c or at a T_c slightly lowered by a proximity effect. Here, however, in one case it was possible to get no superconducting transition at all above 1.25°K for a sample of 94 at.% Tl quenched from 295°C.

This leads to the suspicion that the phase diagram shown in Fig. 7 is not quite correct. (That diagram is mainly based upon the compilation by Hansen[8] supplemented by the findings of this investigation.) The low T_c of the sample mentioned suggests that the fcc phase, which has a low T_c as discussed above, could, in a certain temperature interval, extend to much higher Tl compositions than those shown in the phase diagram.

Sekito[47] concluded from x-ray investigations on Tl and Tl alloys containing Bi, Pb (5–10%), Sb, and Sn, that the β phase of Tl was fcc. His (metastable?) samples were all quenched from the molten state into ice water and the determined value of the lattice parameter agrees very well with the value found from an extrapolation to pure Tl of the data for the fcc Pb-Tl phase in Ref. 10. The lattice spacings determined for different temperatures by Schneider and Heymer[48] indicate that these authors found the β phase to have the fcc structure too.

This is in contrast to the accepted view that β-Tl is

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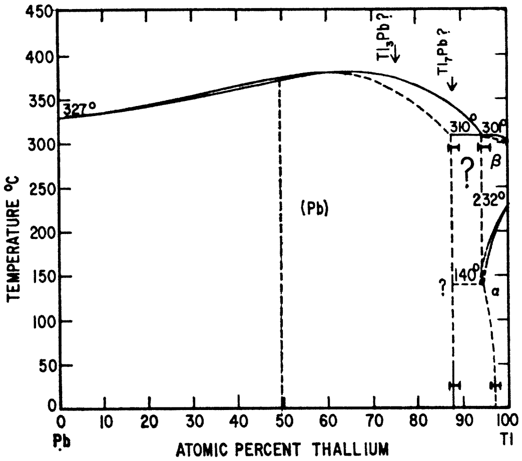

FIG. 7. Phase diagram of the Pb–Tl system. This is based on the work reported in Ref. 8, supplemented by superconductivity measurements as indicated by the bars. The vertical dashed line at the 50 at.% Tl composition results from an electronic structure effect proposed here.

bcc.[43,49,50] A high-pressure fcc Tl phase exists for applied pressures larger than 37 kbar,[51] however. The energy difference between the various forms of Tl is small.[52,53] It is possible to nucleate an unstable crystalline form from the melt, if the interfacial energy between the liquid and the unstable form is less than corresponding interfacial energy between the liquid and the stable form.[53] Such a situation is found in the Fe-Ni system.[54] As the free energies of the various forms do not differ very much, small pressures (much less the 37 kbar) might extend the fcc phase in the Pb-Tl system towards the Tl side.

The structure dependence of T_c has been discussed by Matthias and co-workers.[2] From experiences with La and Os-Ir solid solutions, they suggest that the fcc phase would be more favorable to superconductivity than the hcp phase. (Note, however, that both cases are for transition metals.) A recent investigation of the non-transition-metal system Hg-Mg showed no structure dependence of T_c.[55] In the Pb-Tl (and Bi-Tl) system it seems that the T_c of the fcc phase is lower than the T_c's of the bcc and hcp phases. This indicates that it is impossible to say from symmetry considerations alone if one structure will be more favorable to superconductivity than another. The relative positions of Fermi surface and Brillouin zones, which determine the electronic density of states, have to be taken into consideration. (On the other hand, it is, of course, true that the electronic configuration often is almost the same for many compounds of the same structure. In that case a prediction regarding the expected T_c may very well be valid.)

The phase boundaries determined in this study are incorporated in the phase diagram (Fig. 7). A vertical line at the 50 at.% composition is also added; this represents the proposed electronic structure change there. The observation by Ölander that there was a rather sharp partition in oxidation rate at this composition between rapidly oxidizing Tl-rich samples and more resistant Pb-rich specimens also supports the drawing of the line.

CONCLUSIONS

The most notable features of the superconducting transition temperature versus composition curve are the change of slope and the structure at the 50 at.% composition, and the large dip at 80–85 at.% Tl in Pb. These features could be explained as a Brillouin-zone effect of the Merriam type, when the detailed model for the Fermi surface of Pb introduced by Anderson and Gold was applied. This model is based upon de Haas–van Alphen results. It is gratifying to note that the model seems to work well for alloys too. The low T_c region and the change of slope might also be explained by ordering conforming to $PbTl_7$, but the electronic structure effect seems to be the more probable (or at least predominant) cause. However, the change in the density of states, and hence in the electronic contribution to the free energy, by the superlattice formation suggests a connection between the Fermi-surface–Brillouin-zone effect and the ordering process, if the latter really is present in the Pb-Tl system.

The behavior of 94 at.% Tl samples leads to the speculation that the fcc Pb solid solution, in a limited temperature interval, extends further to the Tl-rich side than presumed in the accepted phase diagram. Some other refinements of the phase diagram of Pb-Tl have been determined by this investigation.

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Mössbauer Study of Kr^{83} in the Compound KrF_2†

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The compound KrF_2 has been studied by use of the techniques of Mössbauer spectroscopy. The results are that (a) the interaction energy is $e^2qQ_g=130\pm4$ mm/sec$=960\pm30$ mHz, (b) the ratio of the nuclear quadrupole moment of the excited state to that of the ground state is $R=Q_e/Q_g=1.70\pm0.02$, and (c) the isomer shift referred to atomic krypton is 1.50 ± 0.10 mm/sec. These results are interpreted as supporting the infrared, Raman, and NMR results which other groups had previously obtained for this compound and as confirming the earlier conclusions reached with the analogous compound XeF_2. The quadrupole moment of the first excited state of Kr^{83} is found to be 0.459 ± 0.006 b, and the fractional decrease in charge radius between the first excited state and the ground state is approximately 4×10^{-4}.

INTRODUCTION

SINCE the discovery of noble-gas compounds some three years ago,[1] many efforts have been made to clarify the various chemical structures. The simplest of these compounds are XeF_2, XeF_4, and KrF_2. Up to now, the two Xe compounds have been experimentally investigated by infrared, Raman, NMR, ultraviolet, and Mössbauer spectroscopy and by thermodynamic measurements, chemical analyses, and x-ray crystallography. These studies combine to show that XeF_2 is a linear molecule and that XeF_4 is a square coplanar one with the Xe in the center; the solids can be oversimplified as merely molecular crystals consisting of these lines or planes. For KrF_2, despite its somewhat weaker bonding, most of the above techniques except Mössbauer spectroscopy have also been used. A purpose of the present investigation was to use Mössbauer spectroscopy to help confirm that KrF_2 is indeed closely analogous to XeF_2.

Another purpose was to find the quadrupole moment of the first excited state of Kr^{83}. It has been known for several years that this nucleus is suitable for Mössbauer investigation.[2] The high spins of the first excited state ($\frac{7}{2}+$) and ground state ($\frac{9}{2}+$) assured that if a hyperfine split pattern could be observed, it would be of sufficient complexity to allow the extraction of both the magnitude and the sign of the quadrupole-interaction constant, as well as the ratio $R=Q_e/Q_g$ of the nuclear quadrupole moments in the first excited state and ground state. The long half-life[3] (147 nsec) of the nuclear state indicates that the resolution ought to be relatively good. Therefore, if a large enough electric field gradient could be applied to this nucleus, the extraction of the quadrupole moment should be relatively straightforward. However, before the discovery of the rare-gas compounds, no environment was known with an electrical asymmetry adequate for this purpose. The successful Mössbauer effect measurements[4] on Xe clearly suggest that either KrF_2 or KrF_4 (if it exists) would be suitable compounds.

DESCRIPTION OF EXPERIMENT

Basically the experiment was a straightforward Mössbauer transmission measurement. The equipment used was the conventional "loudspeaker" drive coupled to a velocity transducer; the output velocity was slaved via a feedback loop to a reference signal derived from the address of the regularly stepped multichannel analyzer used to store the counts. One new feature was the use of an "up-down" address scalar which allowed the use of all 400 channels, as opposed to the normal method which requires that the analyzer store two separate spectra—each of only 200 channels.

The unusual features of the experiment derive mainly from the source and absorber which we discuss in turn. Figure 1 shows a simplified decay scheme for Kr^{83}. A significant feature to notice is the low energy (9.3 keV) of the pertinent γ ray; many experimental difficulties arise from the necessity of keeping adequate transmission for this soft radiation. A simple method for creating a source is to bombard Kr^{82} with thermal neutrons to generate 1.9-h Kr^{83*}, and then to freeze this into krypton ice in a thin-walled container. This has three disadvantages: (a) it is not easy to control the location and thickness of the source since the freezing temperature (116.6°K) is comparable to the temperature of the liquid nitrogen; (b) the measurement must be interrupted in just a few hours to replace the aged source; and (c) the counting rates are not high since only 0.2 mCi of Kr^{83*} is created per milligram of krypton bombarded for $\frac{1}{2}$ h in a slow-neutron flux of 2×10^{13} neutrons cm^{-2} sec^{-1} and the amount of material bombarded is limited by resonant self-absorption (for

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