Study of the Superconducting Transition Temperature in Dilute Thallium Solid Solutions*

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The superconducting transition temperature, T_c, has been measured for dilute solid solutions of indium, bismuth, and lead in thallium. The transition temperature is found to increase in all cases thus exhibiting a behavior opposite to that observed by Serin, Lynton, and co-workers in their studies of solid solutions of tin, indium, and aluminum. Some loss in residual impurity scattering which occurs upon annealing suggests the migration of solute atoms to grain boundaries in the dilute alloys.

INTRODUCTION

STUDIES of the superconducting transition temperature of dilute solid solutions of tin, indium, and aluminum which have been made by Serin, Lynton, and co-workers,[1] Show an initial linear decrease in the transition temperature T_c. This initial decrease is a function solely of the normal state electronic mean free path and is independent of the specific impurity added over this limited range. A similar dependence of T_c on residual resistivity has been observed in studies of tantalum by Budnick[2] and by Seraphim[3] *et al.* It was felt that this sort of behavior would be found for all superconductors at least in the initial limit of very long mean free paths. As more impurity is added, the transition temperature is found to depend on the specific solute atom concerned.

In the investigation of the system In-Ga[1] in which small amounts of gallium were added to indium, no initial decrease in T_c was noted: on the contrary, a gradual increase was observed. Chanin, Lynton, and Serin attributed this to one or more of the following, first, the relatively low scattering cross section of gallium in indium, second, the smaller ionic radius of gallium, or third, to a metallurgical problem in the preparation of these dilute solid solutions. As to the first however, they noted that thallium in indium was almost as poor a scatterer as gallium whereas thallium produced a large depression in the transition temperature of indium.

A study of the dilute solid solutions of indium in thallium was begun since indium bears in a general way, the same relationship to thallium as does gallium to indium, i.e., both solutes have smaller ionic radii than the solvent atoms, the same valence, and approximately the same relative masses. Our results show that indium produces relatively small changes in the residual resistivity of dilute solutions of indium in thallium and does in fact cause an initial increase in T_c. However, small additions of lead, bismuth, and tin to thallium were also found to raise the transition temperature.

PREPARATION OF SAMPLES

Thallium of 99.999% purity, obtained from the American Smelting and Refining Company, was used as the solvent material to which small quantities of very high purity solute metals were added. The samples were melted in quartz tubes since molten thallium leaches sodium from ordinary glass. The constituents were melted in a vacuum of approximately 1×10^{-6} mm Hg, sealed in a tube, and mechanically mixed in the molten state for about 20 min. From this bulk we prepared, *in vacuo*, slowly cooled coarse grained polycrystals, and extruded finer grained polycrystals.

In our initial experiments the melt was quenched after mixing, extruded and then annealed. This procedure was followed in order to minimize segregation effects which occur in slowly cooled samples which are not zone leveled. Later reference will be made to the results on the extruded samples. The coarse grained samples were vacuum cast into quartz tubes then cooled over a period of about one hour and subsequently annealed.

EXPERIMENTAL APPARATUS AND PROCEDURE

Measurements of the residual resistivity ratio, $\rho=R_{4.2°K}/(R_{295°K}-R_{4.2°K})$, were made with a Rubicon six-dial potentiometer. Care was taken to ensure good voltage contacts since the surface of the sample is readily attacked and corroded by the ambient atmosphere.

Helium-temperature measurements were made in a conventional glass Dewar as described in Fig. 1 with an overwound solenoid providing a longitudinal field. Values of T_c were obtained by extrapolation to zero field of the critical field curve measured in the region of the transition temperature. The critical field was determined by measuring as a function of magnetic field the change in magnetic induction of a sample when an applied magnetic field is removed.

A sensitive galvanometer, operated ballistically, was used to observe the changes in induction with applied field. Three samples were mounted in the sample holder during a run so that differences in critical field and

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[1] E. A. Lynton, B. Serin, and M. Zucker, J. Phys. Chem. Solids **3**, 165 (1957); and G. Chanin, E. A. Lynton, and B. Serin, Phys. Rev. **114**, 719 (1959).
[2] J. I. Budnick, Phys. Rev. **119**, 1578 (1960).
[3] D. P. Seraphim, D. T. Novick, and J. I. Budnick, Acta. Met. (to be published).

critical temperature could be measured relative to a standard sample which remained from run to run. Corrections for hydrostatic pressure differences were made in the conventional manner. This procedure did not introduce large errors since during the course of measurements at one temperature point, no large change in liquid level or behavior of the bath occurred.

EXPERIMENTAL RESULTS

Samples of thallium were prepared with various atom percents of indium, lead, and bismuth. Figure 2 shows the effect of impurity on the residual resistivity of thallium. The difference in slopes is a measure of the relative scattering cross sections of the various solutes. For the pure thallium a rough run of resistance versus temperature was made below 4.2°K and revealed the presence of thermal scattering at these temperatures, which further indicates the high purity of the starting material used in these experiments. Prolonged annealing at high temperatures (240°C) of dilute In-Tl samples apparently causes some migration of the impurity to the grain boundaries. After a prolonged anneal of a fine grained polycrystal sample the resistance ratio would approach that for pure thallium. A spectrographic examination, however, revealed the original concentration of indium present in the volume of sample analyzed. Our first measurements of T_c were made on extruded samples which were not annealed at elevated temperatures, and which probably contained large amounts of

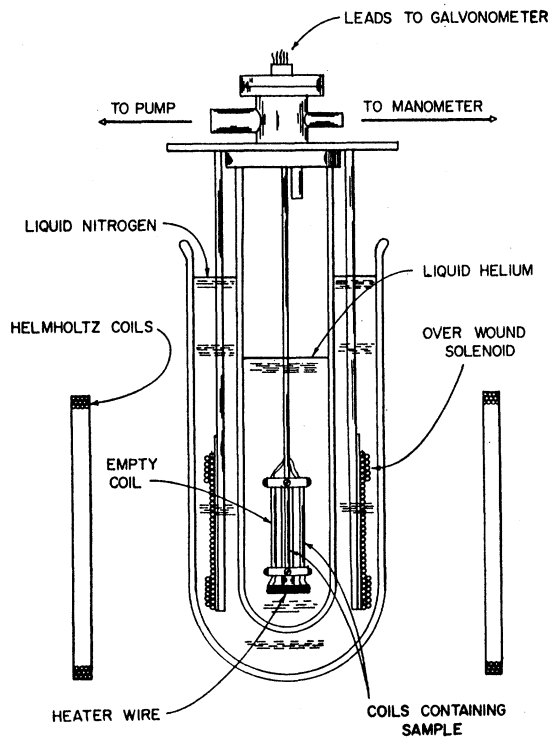

FIG. 1. Schematic diagram of experimental apparatus.

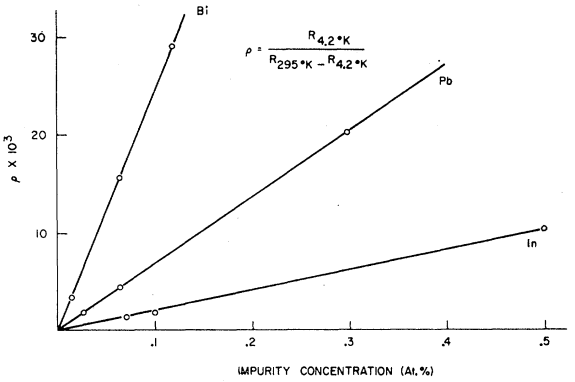

FIG. 2. The variation in resistance ratio ρ is shown for various solute concentrations in thallium. The linearity with composition suggests a region of single-phase material with regular changes in mean free path.

dislocations and vacancies. This loss of impurity scattering upon high temperature anneal was found also for lead and bismuth but for the same annealing conditions was much reduced due to the higher masses of these solutes. Higher concentrations of In-Tl also failed to exhibit any large change in their resistance ratios with annealing, indicating that the grain boundaries saturate at approximately 0.1 atomic percent of impurity.

In order to reduce this clustering of impurities at grain boundaries and to reduce the number of vacancies and dislocations present, coarse grained polycrystal samples were prepared by slow cooling from the melt. These specimens were similar in behavior to the unannealed extruded samples, thus indicating the relatively small combined effects of dislocations and vacancies in these measurements. The segregation introduced by our slow cooling techniques did not broaden the magnetic transitions which we investigated but would certainly have had a pronounced effect on resistive transition measurements.

All specimens here reported were found to have sharp transitions, one percent or less in width, and were found to have parallel critical field curves in the neighborhood of T_c. This we feel is a good assurance that these alloys were well-behaved superconductors. It is well to note here that thallium undergoes a martensitic transformation from a bcc to hcp structure at 234°C. This may in fact be changed or altered by impurities and indeed seemed to have some bearing on the results we obtained when various quantities of tin were added to thallium. No complete investigation was made of this system and we here merely report our observations. The tin-thallium melts were found to contract upon solidification, enabling them to be easily removed from the quartz tubes in which they were cast. This is in complete contrast to the other alloys, where it was necessary to etch the quartz tubes from the samples. Low-temperature flux measurements on the tin-thallium

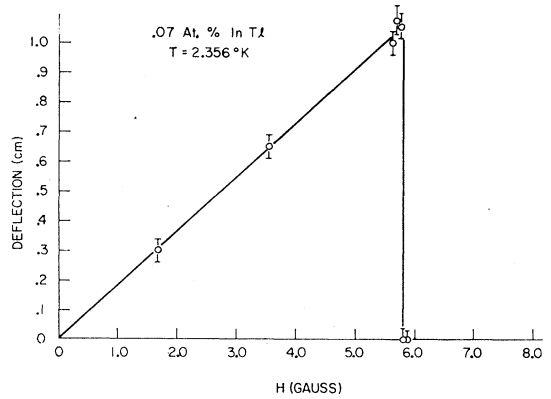

FIG. 3. The relative magnetization is plotted versus field in order to determine the critical field.

specimens indicated broad superconducting transitions while x-ray studies at room temperature gave evidence of the presence of a phase mixture, the new phase having lines which fit those reported by Sekito[4] whose work was later questioned by Pearson.[5] Due to the uncertainties in the metallurgy, a detailed study of the tin-thallium system has not been carried out but the measurements of the variation of T_c with composition are in general agreement with the other thallium alloys studied.

Figure 3 shows a representative flux transition in a magnetic field for solutes other than tin, in thallium, while Fig. 4 shows the temperature dependence of the critical field for several samples containing various amounts of indium added to thallium. Close to the transition temperature the samples all show similar behavior as indicated by the same slope of H_c vs T. In Fig. 4 is also seen the steady upward shift of T_c upon alloying as compared to the standard pure thallium sample.

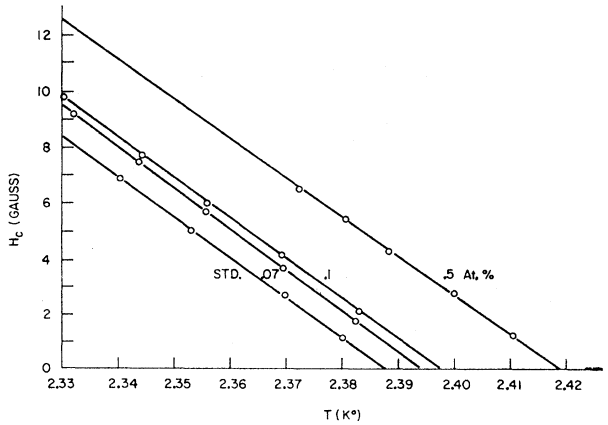

FIG. 4. The critical field of some InTl solid solutions is plotted versus T for temperatures close to T_c. The critical field curves are similar for the impure samples, while T_c is found to increase with addition of impurity.

[4] S. Sekito, Z. Krist, **A74**, 189 (1930).
[5] W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon Press, New York, 1958).

The results of our transition temperature determinations as a function of resistance ratio are given in Fig. 5. Note that these samples are all cast samples. For the extruded samples of indium in thallium, which were not annealed, the results are similar in that only positive changes in T_c were observed. No depression of T_c was found in the region of ρ investigated even though the annealed starting material had a ρ of about 3×10^{-3} and showed appreciable thermal scattering below 4.2°K.

Annealing caused a decrease in T_c of 2 to 3 millidegrees in both the pure and very dilute samples. The corresponding decrease in ρ on anneal was of the order of 10 to 15%. The annealing process most probably removed physical defects from the materials which could act as electron scatterers thus giving rise to the decrease in ρ. This observed lowering of T_c, upon anneal is just what is to be expected in *thallium* solid solutions and is of opposite sign to what is found in tin, indium, and aluminum.

Our estimated uncertainty in T_c determinations is ~0.002°K which uncertainty occurred in the reproducibility of our standard from run to run.

CONCLUSIONS

We therefore conclude from our observations, that in rather dilute solid solutions of thallium we see a positive shift in T_c as shown in Fig. 5 which initially is strongly dependent on the specific impurity added. This is in strong contrast to the initial systematic depression in T_c for tin, indium, aluminum, and tantalum which seems solely dependent on the electronic mean free path. The solid solutions we have examined are well behaved in their superconducting properties thus making it possible to look for some fundamental interpretation of these results. The explicit effect on T_c of impurities located at grain boundaries seems to

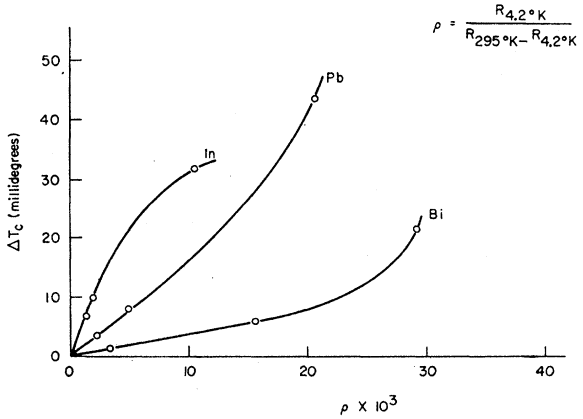

FIG. 5. The difference in transition temperature ΔT_c between the standard sample and the solid solution is plotted versus the resistance ratio which is proportional to the reciprocal mean free path.

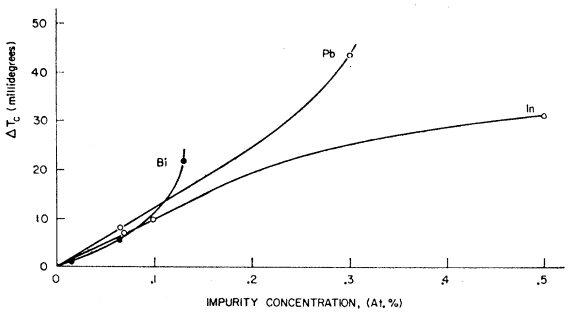

FIG. 6. The shift in transition temperature ΔT_c is plotted versus the atomic concentration of impurity added to the thallium.

be small in absolute magnitude but no detailed study of this effect is contained in this work.

Figure 6 shows the shift in T_c plotted as a function of impurity concentration for various solutes. The similarity in the initial slopes is surprising when the large difference in scattering cross section per impurity atom of the different materials is considered. This is of course also contrary to what would be expected if a mean free path effect were the prime determinant of T_c in this region.

We have neglected any anisotropy effects in our studies of the correlation in T_c with residual resistivity and feel that this is justified in view of the polycrystalline samples we used and also in the fact that the resistivity varied monotonically with the atomic percent impurity added.

The pressure dependence of the critical field for thallium is just opposite to that for other superconductors[6] at least in the limit of small strain. In addition, the length change[7] in going through the superconducting transition was found to be of opposite sign to that found for tin and lead. There may be some fundamental reason for these differences of behavior which also explains our results and which may be solely applicable to thallium.

Thallium, mercury and lead are all similar on an atomic criterion, i.e., having incomplete f shells surround by a closed s shell and in their metallic form all have quite low Debye temperatures. It is felt that studies of impurity effects in very dilute solid solutions of lead and mercury might help to understand the present results. Recent work of Anderson[8] seems to show that an initial depression in T_c should always be expected in going from the pure material (very long mean free path) to the impure case. We are able to present no explanation for our results on the basis of a fundamental theory of superconductivity but only point out the need for a detailed explanation of the effects of impurities on T_c for real metals.

Note added in proof. Recent work of Chiou, Quinn, and Seraphim,[9] which provides an analytical expression to fit the experimental observations on impurity effects in tin, indium, and aluminum solid solutions, does not seem to fit our results for thallium-rich solid solutions.

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[6] L. D. Jennings and C. A. Swenson, Phys. Rev. **112**, 31 (1958).
[7] G. D. Cody, Phys. Rev. **111**, 1078 (1958).
[8] P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).
[9] C. Chiou, D. Quinn, and D. Seraphim, Bull. Am. Phys. Soc. **6**, 122 (1961).