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The Magnetic Properties of Superconducting Alloys of Indium and Thallium*

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Magnetization curves for spherical samples of a series of alloys in the solid solution range of thallium in indium have been measured as a function of temperature and composition, and critical field curves have been obtained. These alloys show a fairly strong Meissner effect, and the breadth of the transition region increases for increasing thallium content. Alloys of high thallium content were found to have magnetic properties strongly sensitive to mechanical shock while in the intermediate state.

I. INTRODUCTION

SUPERCONDUCTIVITY of alloys of the In-Tl system has been studied by Meissner, Franz, and Westerhoff[1] who made measurements of the resistivity as a function of temperature, and by Stout and Guttman[2] who have reported on the Meissner effect in these alloys. The purpose of the present investigation was to study the magnetic properties of superconducting solid solution alloys, for which the system In-Tl is rather convenient. The results of previous workers[3,4] have shown that thallium is soluble at room temperature in indium up to concentrations around 60 atomic percent thallium. Alloys with compositions ranging approximately from 15 to 25 atomic percent thallium can exist in two phases, a face-centered cubic structure stable at high temperatures, and a face-centered tetragonal structure stable at low temperatures. The transformation is a diffusionless one and is accompanied by a splitting up of an original crystal into a lamellar structure typical of the martersitic transformation in low carbon iron-carbon alloys.[4,5]

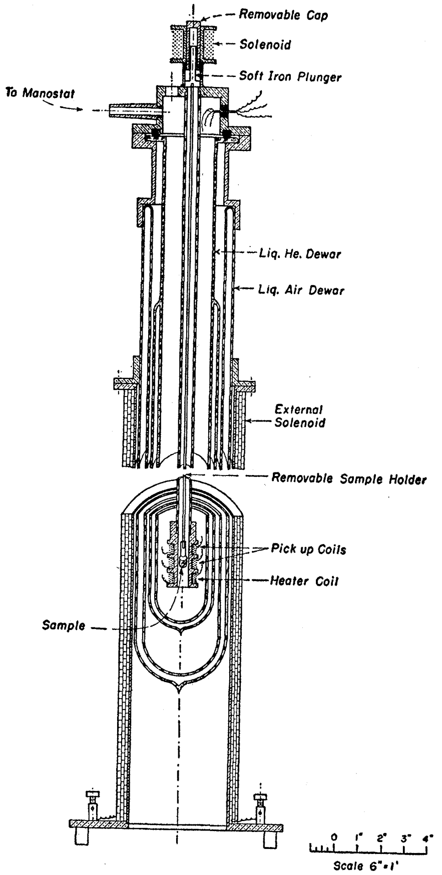

FIG. 1. Schematic diagram of measuring apparatus.

II. EXPERIMENTAL TECHNIQUE

1. Preparation of Samples

The indium used was obtained from the Idium Corporation of America and the thallium from the American Smelting and Refining Company. In both cases, the purity was given as 99.98 percent. The two components were weighed out carefully on an analytical balance and melted together in a closed graphite crucible over a Bunsen burner. The liquid metal was shaken vigorously to homogenize the melt and was then rapidly cooled by putting the crucible in running water. The resulting slug was placed in a graphite mold, remelted, and lowered through a single crystal vacuum furnace. The mold was made in two halves and shaped so that $\frac{1}{4}$-inch diameter spherical specimens could be obtained. The samples were kept in an annealing oven at 135°C for periods ranging from one day to several weeks. To check for homogeneity of

TABLE I. Results of chemical and analyses to check homogeneity of samples.

Atomic % Tl nominal value	Atomic % Tl from chemical analysis Sample No. 1	Sample No. 2
5	5.24	5.27
10	sample ruined	9.96
17	16.92	16.97
25	24.99	25.01
30	28.46	28.49
37	36.52	36.67

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[1] Meissner, Franz, and Westerhoff, Ann. Physik 13, 505 (1932).

[2] J. W. Stout and L. Guttman, Phys. Rev. 79, 396 (1950).

[3] S. Valentiner, Z. Metallkunde 32, 244 (1940).

[4] L. Guttman, Trans. Am. Inst. Mining Met. Engrs. 188, 1472 (1950).

[5] Bowles, Barrett, and Guttman, Trans. Am. Inst. Mining Met. Engrs. 188, 1478 (1950).

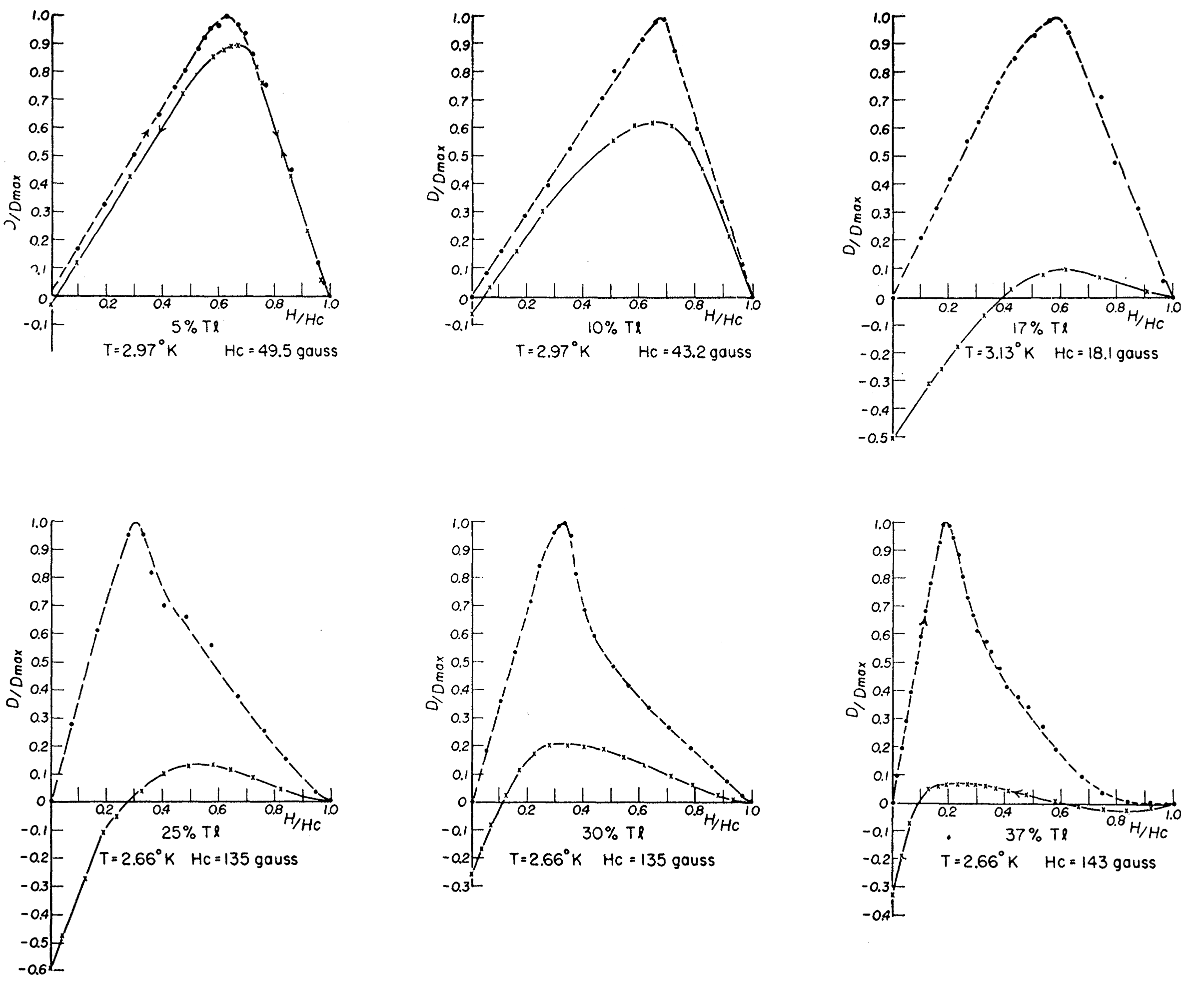

FIG. 2. Typical magnetization curves for a series of indium-thallium alloys.

composition, the spheres were cut in half transversely along the axis of growth after the measurements had been made and each half separately analyzed for its thallium content by a titration method due to Beale and co-workers.[6] The results are given in Table I. It can be seen from this table that segregation in these alloys is negligible.

2. Measuring Apparatus

The method of measurement is that originally used by Schoenberg.[7] A schematic diagram of the apparatus is shown in Fig. 1. The spherical sample is mounted at the end of a long glass tube and is placed at the center of the lower of a set of two identical pick-up coils, each consisting of 1000 turns of No. 40 Formex-coated copper wire. These coils are wound in opposition and connected in series. When the sample acquires a magnetic moment in the field of the external solenoid and is displaced sharply to the center of the other coil, the net flux change produces a ballistic throw of an external galvanameter proportional to its magnetic moment. The sample is displaced by the action of a solenoid on a soft iron plunger attached to the top of the glass rod. Samples can be exchanged during a single run by removing the top cap and pulling out the glass tube. The two pick-up coils are mounted on a Bakelite form attached to another larger glass tube. This tube has holes in its sides at frequent intervals in order to avoid the oscillations of the helium gas which occur in a closed tube terminated in a liquid helium bath. At the very bottom of the apparatus is placed a heater coil to produce thermal equilibrium in the bath. The pressure over the bath was maintained constant to 0.1 mm by means of a Cartesian manostat obtained from The Emil Greiner Company of New York. The pressure was measured with a Wallace and Tiernan absolute manometer.

III. EXPERIMENTAL RESULTS

A set of typical magnetization curves is shown in Fig. 2 for concentrations of Tl up to 37 atomic percent.

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[6] Beale, Hutchison, and Chandlee, Ind. Eng. Chem., Anal. Edition **13**, 240 (1941).

[7] D. Shoenberg, Proc. Roy. Soc. (London) **A175**, 49 (1940).

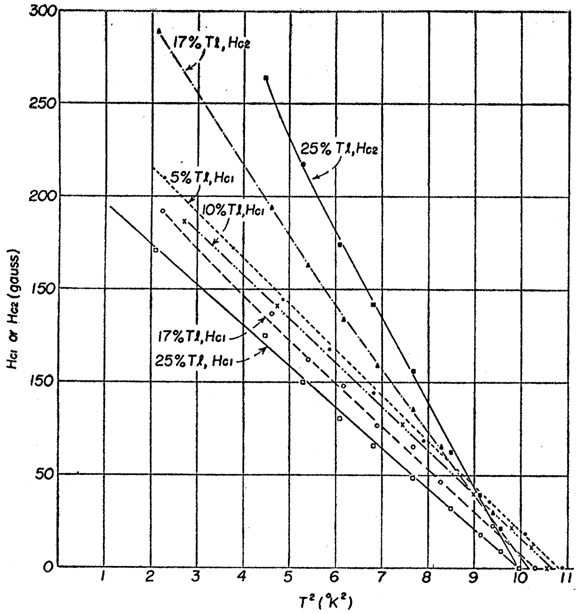

FIG. 3. Critical magnetic field curves for a series of indium-thallium alloys.

For purposes of comparison, the data have been plotted in "reduced" form, i.e., the ratio of the galvanometer deflection to the maximum deflection occurring for any field ($D/D_{\max}$), which is proportional to the diamagnetic moment of the sample, is plotted against H/H_c, where H_c is taken to be the field at which superconductivity is completely destroyed. For a sample showing a perfect Meissner effect, this curve would increase linearly to a value of 1 at $H/H_c=\frac{2}{3}$ and decrease linearly to 0 at $H/H_c=1$ for both increasing and decreasing fields. Except for a small amount of frozen-in flux, this is seen to be the case for the 5 and 10 percent samples. However, an increasing breadth of transition is observed in the samples of higher Tl content. The abnormally large frozen-in flux in the 17 and 25 atomic percent samples is attributed to the presence of a polycrystalline structure caused by the cubic-to-tetragonal structure transformation that occurs in these two alloys.

The effect of grain structure on the magnetic properties was tested in a 10 atomic percent sample that was measured as a single crystal and then cold worked drastically to produce a polycrystalline specimen. It was found that the polycrystalline specimen showed about twice as much frozen-in flux as the single crystal, the breadth of transition remaining the same. It was also found that various heat treatments produced no appreciable difference in the superconductive properties of these alloys at low temperatures, i.e., a sample showed the same behavior whether it had been annealed for long or short periods of time, quenched or slowly cooled to room temperature. Of course, the possibility remains that there might be some influence due to the manner in which the sample is cooled to liquid helium temperatures. In these experiments, measurements were made on samples that were quenched from room temperature to liquid helium temperatures by lowering them rapidly into the bath.

By taking magnetization curves at different temperatures, critical field data have been obtained for a number of samples. In an alloy with an appreciable breadth of transition, one cannot define a unique critical field, since field penetration takes place over too large an interval. Consequently, in Fig. 3 we plot the field at which penetration starts (H_{c1}), as well as that at which it is complete (H_{c2}), against T^2 for four different concentrations of Tl. These two fields are the same for the 5 and 10 atomic percent samples, but differ considerably for the 17 and 25 atomic percent samples. It can be seen from the figure that both of these fields can be represented fairly closely by a parabolic variation with temperature. The slope of the straight line obtained is the same for each sample for the field at which penetration begins. In Table II are shown the values of the parameters H_0 and T_c which describe the variation of the two critical fields with temperature by means of the relation $H_c=H_0[1-(T^2/T_c^2)]$.

For the 5 and 10 atomic percent samples, which show a well-defined critical field and high reversibility in their magnetic transitions, it is possible to apply the thermodynamics of the pure superconducting state. The thermodynamic properties as determined from the critical field curves differ very little from those of pure indium. For example, the electronic specific heat coefficient γ is found to be 3.72×10^{-4} cal/mole deg² for the 5 percent Tl specimen and 3.67×10^{-4} cal/mole deg² for the 10 percent Tl specimen. These must be considered to be the same within the validity of the parabolic law. This result is to be expected since indium and thallium have the same valence, and consequently, the number of valence electrons remains unchanged as the concentration of thallium is increased. The only effects to be expected are those of a secondary nature such as variation of the lattice constant. The application of thermodynamics to the 17 and 25 atomic percent Tl samples is more doubtful because of the breadth of transition and lack of reversibility. However, by assuming that H_{c1} represents the true equilibrium field, the calculated electronic specific heat coefficients are 3.38×10^{-4} and 2.78×10^{-4} cal/mole deg², respectively, for the 17 and 25 atomic percent samples.

An interesting, but at the same time disturbing, aspect of the magnetic properties of these alloys was

TABLE II. Critical field data for indium-thallium alloys.

Atomic % Tl	H_{01}	H_{02}	T_c
5	263	263	3.30
10	257	257	3.25
17	242	390	3.21
25	216	500	3.16

brought about by the technique of measurement. It was found that, in those alloys that exhibit strong irreversibility and broad transitions, the magnetic moment is very sensitive to mechanical disturbances. Each measurement involved some mechanical jarring of the sample when it was displaced sharply. Figure 4 shows how this mechanical effect changes the magnetization curve for a 37 percent Tl specimen. The solid curve gives the galvanometer deflection as a function of applied field when only a single reading was taken. The dashed curve shows the "equilibrium" reading after the specimen has been displaced a number of times, i.e., the diamagnetic moment decreases with successive displacements in the intermediate state until a value is reached, after which it remains essentially constant with further jarring. It can be seen that the over-all effect of jarring the sample is to reduce the field at which penetration begins and to decrease the frozen-in flux by a considerable amount. Thus, you can get an apparently stronger Meissner effect by waiting for "mechanical" equilibrium to take place. No such effect as this was found in pure indium and only to a very small extent in the 5 and 10 atomic percent Tl specimens. This result cannot be attributed to time effects, since the magnetic moment remains constant for periods up to 30 minutes provided the sample has not been disturbed mechanically. It serves to emphasize the fact that a true state of thermodynamic equilibrium is difficult to achieve in alloys. Thus, it is difficult to make positive statements about the "fundamental" behavior of these alloys. Our data on magnetization curves and critical fields were taken by minimizing the mechanical influence on the specimens.

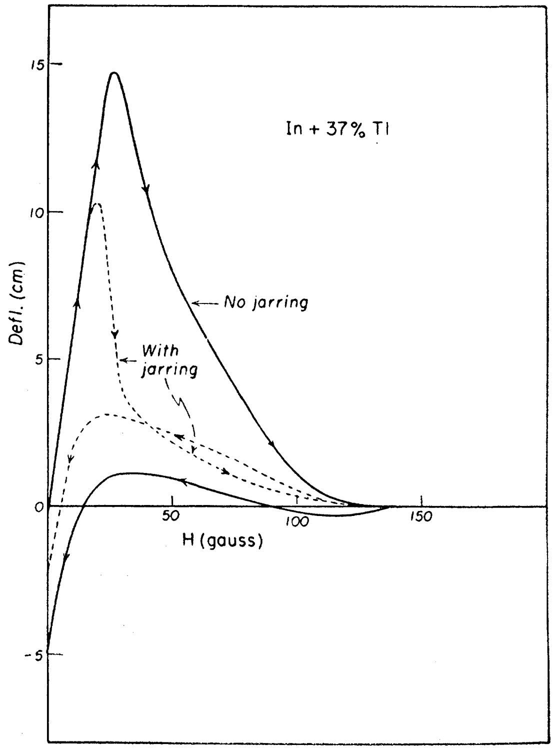

FIG. 4. Magnetization curves showing the effect of mechanical jarring on a 37 atomic percent thallium sample.

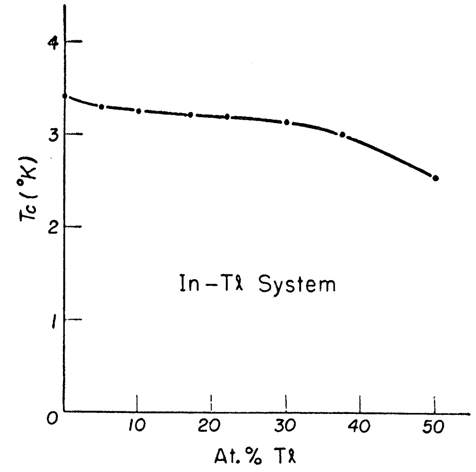

FIG. 5. Transition temperatures as a function of atomic percent of thallium.

Transition temperatures were obtained for these alloys by measuring the temperature at which the first appreciable signs of diamagnetism occurred in a low field (2 gauss). The results are shown in Fig. 5. They are in essential agreement with the resistivity measurements of Meissner, Franz, and Westerhoff.[1]

IV. CONCLUSIONS

The results of these measurements show that homogeneous solid solution alloys of In-Tl approach the behavior of a pure metal more closely than has previously been found in other alloy systems. However, significant differences remain, the most important of which is the broad transition. It can be argued thermodynamically that a solid solution should either separate into its pure constituents or go over into an ordered structure at the absolute zero of temperature. The tendency to do either of these might set up microscopic strains within the material, which could cause the broadening effect actually observed in the superconductive transition. Another possible explanation is that these strains are produced in the lattice by the introduction of the larger thallium atoms. An x-ray investigation of these alloys at liquid helium temperatures is being undertaken in order to gain more insight into their structure at the temperature at which the measurements were taken. The existence of a mechanical effect further emphasizes the lack of thermodynamic equilibrium in these alloys.

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