PHYSICAL REVIEW VOLUME 154, NUMBER 2 10 FEBRUARY 1967

Superconducting Transitions in Body-Centered Cubic Thallium-Indium Alloys

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(Received 6 June 1966)

The superconducting transition temperature and the lattice parameter of the body-centered cubic phase in the In-Tl system are reported. The transition temperature of bcc-Tl is extrapolated to be 3.0±0.1°K. The linear thermal-expansion coefficient of the bcc alloys is computed to be 29×10^{-6}/°K between 77 and 300°K independent of composition.

THE phase diagram of the In-Tl system has been well established.[1,2] Across the phase diagram, the system consists of four phase fields with wide ranges of stability: (i) the face-centered tetragonal In-rich solid solution; (ii) the face-centered cubic (fcc) phase which is definitely related to the high-pressure form of Tl[2]; (iii) the body-centered cubic (bcc) phase which is the high-temperature form of Tl but stabilized by alloying with In; and (iv) the hexagonal close-packed (hcp) phase of the low-temperature form of Tl.

According to the early measurements of Meissner *et al.*,[3] In-Tl alloys of various compositions were all found to be superconducting. Their transition temperatures (T_c) as a function of composition varied in a continuous manner except in the two-phase field between the fcc and the bcc phases where the transition temperature showed a discontinuity of about 1.2°K. Recently a small discontinuity of ~0.1°K on the T_c-versus-composition curve was located near 30 at.% Tl. This anomaly was associated with the tetragonal-cubic transformation at low temperatures.[4]

Since In and Tl have the same number of valence electrons, it is of interest to investigate the effect the crystal structure has on superconductivity. The bcc form of Tl is stabilized down to room temperature by alloying with In. By rapid quenching from the melt the stabilization of the bcc phase is extended. The variation of T_c with In content provides information about the superconductivity of pure Tl in its bcc allotropic form which can not be retained by quenching.

Alloys were prepared from elements of 99.99% purity by induction-melting in alumina or quartz crucibles under a hydrogen atmosphere. Based on the weight losses during melting, the actual compositions of the alloys were estimated to be within ±0.5% of the nominal compositions.

The fast-quenching technique has been described previously.[5] The method consists of ejecting about 100 mg of molten alloy onto a cold target by pressurized helium flow. Because of the relatively low liquidus of the In-Tl system, the target, a 0.01-in.-thick light sand-blasted copper strip, was kept at liquid-nitrogen temperature to prevent any annealing occurring at room temperature. All subsequent experiments were performed without removal of the quenched foil from the copper substrate and without raising the temperature of the sample above the liquid-nitrogen boiling point, except for the annealing investigation. Annealings were performed by letting the sample temperature rise to room temperature or 70°C, in vacuum or in an inert atmosphere.

The crystal structures of the alloys were studied using a low-temperature specimen holder, designed to fit a General Electric XRD unit. The apparatus is equipped with adjusting screws to align the specimen with respect to the x-ray beam and the counter tube. The specimen on substrate is firmly clamped mechanically to a solid copper block which is cooled directly by cryogenic liquids. The specimen is kept in a vacuum and faces a semicylindrical beryllium window of 0.01 in. thick through which the x-ray beam passes. The apparatus has been used down to liquid-hydrogen temperature[4] without difficulty. Lattice parameters were determined at room temperature and at liquid-nitrogen temperature for specimens with single bcc phase, using Cu $K\alpha$ radiation. $\text{Cos}^2\theta$ was used for the extrapolation function.

The superconducting transitions were detected by placing the sample between two coils wound with 200 turns of No. 36 wire with the dimensions of $\frac{1}{8}$-in. I.D. by $\frac{1}{4}$-in. O.D. and $\frac{1}{16}$ in. wide. The coils were spaced $\frac{1}{16}$ in. apart. One coil was connected to an oscillator

* Work supported by the U. S. Atomic Energy Commission and in part by the U. S. Air Force Office of Scientific Research.
† Work supported by the U. S. Atomic Energy Commission.

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TABLE I. Phases in In-Tl alloys and corresponding transition temperatures.

Composition at.% Tl	As quenched Phases[b]	As quenched T_c°K[c]	After annealing[a] Phases	After annealing[a] T_c°K
95	vw. bcc+vs. hcp	2.67∼2.71	hcp	
90	w. bcc+s. hcp	2.93∼3.02	hcp	2.92∼2.97
88	w. bcc+s. hcp	2.98∼3.03	vw. bcc+vs. hcp	
86	m. bcc+m. hcp	3.07∼3.22	w. bcc+s. hcp	
84.5	s. bcc+w. hcp	3.11∼3.18	m. bcc+m. hcp	
83	bcc	3.45∼3.52	bcc	3.36∼3.45
80	bcc	3.46∼3.50	bcc	3.41∼3.48
78	bcc	3.53∼3.56	bcc	3.44∼3.52
75	bcc	3.62∼3.64	bcc	3.60∼3.64
72.5	bcc	3.73∼3.76	vs. bcc+vw. fcc	3.64∼3.68
70	bcc	3.80∼3.83	s. bcc+w. fcc	3.51∼3.57
65	bcc	3.89∼3.95	m. bcc+m. fcc	3.51∼3.66[d]
62	vs. bcc+vvw. fcc	3.91∼4.01[d]	vw. bcc+vs. fcc	2.53∼2.63[d]
60	vs. bcc+vw. fcc	3.94∼4.11[d]	fcc	2.49∼2.52
58	m. bcc+m. fcc	3.87∼4.09[d]	fcc	2.47∼2.49
55	vw. bcc+vs. fcc	Broad transition	fcc	2.46∼2.48
Pure Tl	hcp	2.34∼2.39		

[a] Two annealing procedures were used. (i) Room temperature (26±2°C) for more than 200 h. (ii) 70°C for 10 h. The second procedure always resulted in sharper transitions.
[b] vw. (very weak), w. (weak), m. (medium), s. (strong), and vs. (very strong) indicate the relative x-ray intensities as estimated by the strongest diffraction lines of corresponding phases.
[c] The widths of the transition cover the onset and the completion of at least two independent measurements.
[d] A few samples at these compositions showed very smeared transitions.

while the voltage on the other coil was measured with a phase-sensitive detector. The peak ac field between the coils was never greater than 1.5 G. The superconducting transitions were independent of frequency between 200 and 2000 cps. The temperature was measured by a carbon thermometer, adjacent to the specimen, calibrated against the 1958 He^4 vapor-pressure scale.[6] The calibration was checked, and corrected if needed, every time the assembly was cooled from room temperature. The performance of the apparatus was checked by measuring the T_c's of pure indium and tin. The results were 3.396±0.004 and 3.722±0.007°K, respectively, in good agreement with the previously published values of 3.408°K and 3.722°K.[7]

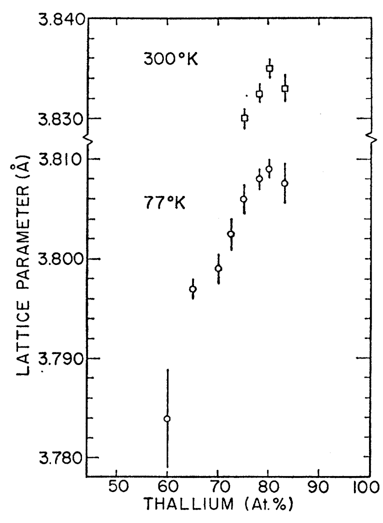

FIG. 1. Lattice-parameter variation of single-phase bcc In-Tl alloys at room temperature and at liquid-nitrogen temperature.

[6] H. von Dijk, M. Durieux, J. R. Clement, and J. K. Logan, U. S. Natl. Bur. Std., Monograph 10, Part 2 (1960).
[7] R. W. Shaw, D. E. Mapother, and D. C. Hopkins, Phys. Rev. **120**, 88 (1960).

The variation of the lattice parameter of the bcc solid solution with concentration is shown in Fig. 1. The alloys containing less than 60 at.% Tl and more than 83 at.% Tl were always two phases. Upon heating to room temperature for a day, only the alloys with a composition between 75 at.% and 83 at.% Tl remained single-phase. For other compositions, the bcc structure decomposed into two phases (i.e., bcc and fcc). The slight deviation from the previously reported 3.828 A for a single-phase bcc alloy containing 74.9 at.% Tl[8] is likely due to the differences in impurity content. From the lattice parameter data, the linear thermal-expansion coefficient of the bcc phase was computed to be 29×10^{-6}/°K.

The results of the measurements of the superconducting transition are summarized in Table I and are

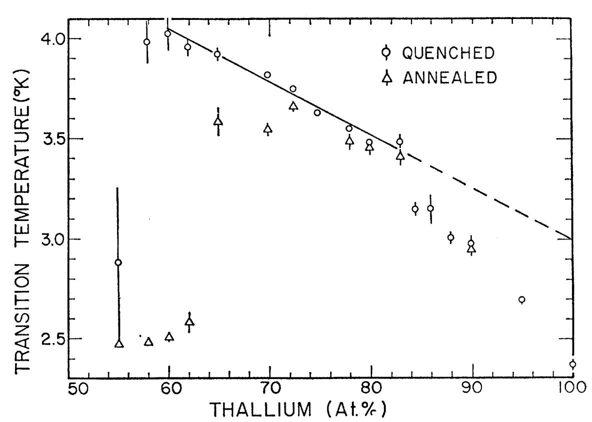

FIG. 2. Superconducting transition temperatures of bcc In-Tl alloys. As quenched alloys are of single phase between 65∼83 at.% Tl; however, after annealing, the single-phase region reduces to 75∼83 at.% Tl.

[8] L. Guttman, J. Metals **2**, 1472 (1950).

shown in Fig. 2. The breadth of the transition (i.e., when the shielding between the two coils by the superconducting foil is at least 90% complete) is indicated by the length of the vertical lines. On each side of the single-phase bcc region there is an abrupt change in the transition temperature. The highest transition temperature (4.12°K) occurs at 60 at.% Ti, where normally the equilibrium structure is fcc with $T_c=2.50$°K. This transition temperature of 4.12°K is higher than any of the equilibrium alloys which occur across the phase diagram, including pure indium.

Several interesting points can be observed from the present study. (1) With the present rate of quenching estimated at the order of several million degrees per second,[9] the bcc to hcp transformation of pure Tl could not be suppressed. This is indicative of the diffusionless nature of the transformation. When In is added, this transformation is gradually retarded, but the full retention of the bcc structure is achieved only when the In concentration reaches the eutectoidal composition of ∼17 at.%. The abrupt change in T_c near 83 at.% Tl is definitely associated with the presence of the hcp phase. (2) The fact that the presence of the hcp phase lowers the T_c's certainly indicates that the bcc form of Tl would have higher T_c than the hcp form if the former could be retained. By linearly extrapolating the T_c versus composition curve to zero In content, the T_c of bcc Tl is estimated to be 3.0 ± 0.1°K (Fig. 2). (3) Undoubtedly the bcc-fcc transformation induces a 1.2°K difference in T_c. Thus, in the In-Tl system, the bcc phase has the highest T_c among the three most common crystal structures occurred in metals (e.g., bcc, fcc, and hcp). However, the T_c's of the fcc and hcp phases can not be compared directly.

The authors are indebted to Professor P. Duwez for his encouragement and to John McCoy for assistance in experiments.

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PHYSICAL REVIEW VOLUME 154, NUMBER 2 10 FEBRUARY 1967

Magnetic Properties of Some Rare-Earth Alloys at High Pressures

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(Received 22 August 1966)

The Néel and Curie temperatures of some alloys of the heavy rare-earth metals with each other and with yttrium have been measured as functions of pressure up to ∼85 kbar. The initial slopes (dT/dP) are approximately proportional to the average de Gennes function $(\sum_i c_i(g_i-1)^2J_i(J_i+1))$. In the molecular field approximation with a first-order correction for the anisotropy energy, the change in the exchange interaction with lattice parameter is given by $k^{-1}dJ(\mathbf{Q})/da=(42\pm6)$°K/Å. It is suggested that this is caused mainly by a change in the generalized conduction-electron susceptibility with pressure. A polymorphic transition from a hexagonal-close-packed structure to a Sm-type structure is found with increasing pressure in many of these alloys, and the Sm-type phase has two ordering temperatures. The higher ordering temperature of the Sm-type phase is 10% lower than that of the hcp phase, and the two ordering temperatures in the Sm-type phase differ by 17%.

In the pressure range from 1 bar to 100 kbar, both volume changes of ∼15% and polymorphic transitions occur in the heavy rare-earth metals. Their magnetic properties change appreciably under these conditions, and the present study completes a survey of the effect of pressure of the Néel and Curie temperatures above 77°K of rare-earth metals and of alloys of the heavy rare earths with each other and with Y. Previous papers include: (1) The elements Gd, Tb, Dy, and Ho,[1] (2) Eu and EuO,[2] and (3) a preliminary report on the Tb-Y alloys.[3] In all of the metals and alloys studied, the magnetic ordering temperatures decrease with increasing pressure and, therefore, the magnetic energies are positive functions of volume. The trend in crystal structures observed in the rare-earth metals with decreasing atomic number is also observed with increasing pressure,[4,5] and many of the heavy rare-earth metals transform from the hexagonal close-packed structure (hcp) to the Sm-type structure with increasing pressure. In the latter structure the initial susceptibility suggests that two independent ordering temperatures exist and that ferromagnetism does not occur above 77°K.

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