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Superconducting Transition Temperatures of Dilute Indium-Based Alloys*

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An anomalous dependence of superconducting transition temperature on solute concentration in very dilute *InCd*, *InHg*, and *InTl* alloys reported previously has been confirmed in a series of measurements on these and other In-based alloy systems. Systematics of the anomalous behavior are discussed. In particular, the divalence of both Cd and Hg in trivalent In suggests that solute electropositivity is a possible origin of the anomaly, and points to an effective electropositivity of Tl in In.

Recently Gubser, Mapother, and Connelly¹ reported results of superconducting critical temperature measurements in dilute *InTl* alloys. They found an anomalous decrease in critical temperature T_c for low Tl concentrations which was believed to be unique to the *InTl* system. The purpose of the present work is to point out that similar anomalous behavior has also been observed in *InHg*² and *InCd*,³ and to discuss systematic features of the three anomalous systems which, to the authors' knowledge, have not been previously noted. In addition, results of a comprehensive program of T_c measurements in binary In-based alloys are presented which confirm the results of previous work,¹⁻⁸ and which, in particular, indicate anomalous behavior in *InTl*, *InHg*, and *InCd*. To within experimental error no alloy systems other than these three exhibit an anomaly; the electropositivity of the latter two solutes with respect to In is therefore a possible source of the anomalous behavior.⁴

Measurements were made on powdered (325-mesh) 99.999%-pure indium and alloy samples of Ga, Hg, Sn, Pb, Cd, and Tl in In which have been described by Anderson *et al.*⁹ and by Thatcher and Hewitt.¹⁰ A bulk sample of pure In was also studied. Superconducting transitions were determined by a standard ac (210 Hz) measurement of the self-inductance of a coil around the sample. Temperatures were determined by measuring the He⁴ bath vapor pres-

sure with a mercury manometer and converting to temperature by means of the 1958 He⁴ scale of temperature.¹¹ Hydrostatic pressure difference, manometer temperature, and gravity corrections were made.¹¹ Transition widths (10-90%) were typically 6 mK; data from samples with widths greater than 20 mK were discarded.

Transition temperatures as measured for the powdered alloy samples do not differ to within experimental error from reported results for bulk samples.¹⁻⁸ For pure powdered indium we find a transition temperature 4 mK below that of a bulk sample. This depression can be attributed to boundary scattering effects¹²; although an exact evaluation is difficult due to the distribution of particle sizes and shapes in the powder, the decrease is of the expected order of magnitude. The transition temperature of pure In is therefore taken to be that of the bulk sample, measured to be 3.403 ± 0.004 K.

Figure 1 gives the results of our measurements and those of other workers^{1-3,5} for the *InCd*, *InHg*, *InPb*, and *InTl* systems. (No anomaly was observed in the *InSn* system, and data from the *InGa* system showed too much scatter to be considered reliable.) Conversion from solute concentration to residual resistivity ratio ρ , defined by

$$\rho = R_{4.2 \text{ K}} / (R_{273 \text{ K}} - R_{4.2 \text{ K}}), \quad (1)$$

was made by means of data given by Refs. 1-3 and

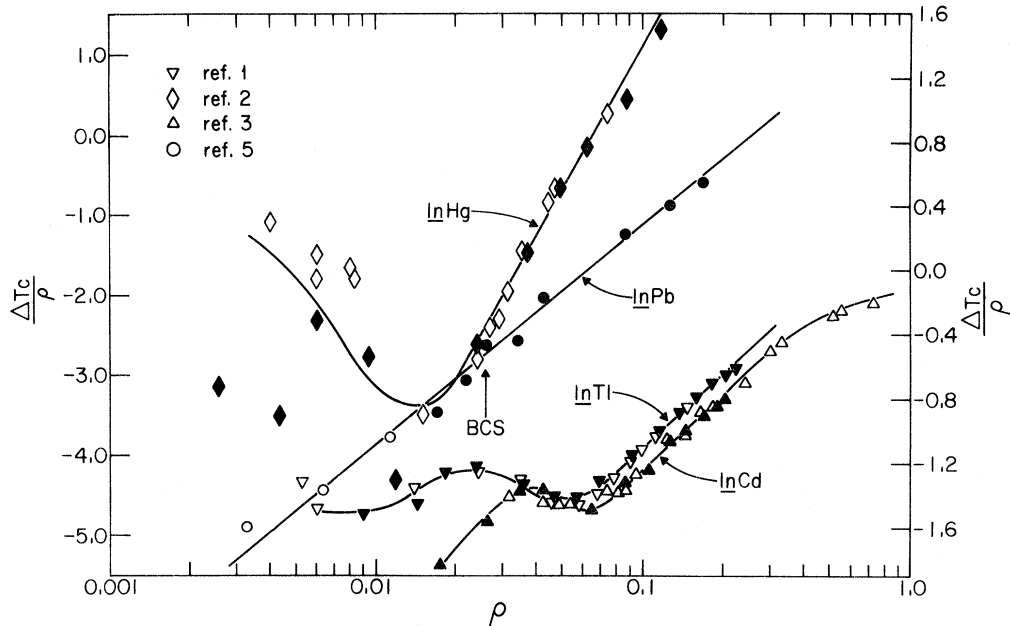


FIG. 1. Dependence of the superconducting transition temperature on residual resistivity ratio in several In-based dilute alloys. Closed experimental points indicate the present work. Open points give results of previous work reported in the indicated references. The right-hand ordinate gives the scale for the Cd, Pb, and Tl data. The left-hand ordinate refers to the Hg data. The quantities ρ and $\Delta T_c/\rho$ are defined in the text. The arrow indicates the value of ρ which corresponds to a mean free path equal to the BCS coherence length. The *InHg*, *InCd*, and *InTl* systems are anomalous, whereas *InPb* (and *InSn*, not shown) behave normally.

5.

Seraphim, Chiou, and Quinn⁶ first proposed the formula

$$\Delta T_c(\rho) = T_c(\rho) - T_c(0) = A\rho + B\rho \ln\rho \quad (2)$$

as an empirical rule for the dependence of T_c on residual resistivity ratio. Markowitz and Kadanoff¹⁵ (MK) subsequently confirmed the validity of Eq. (2) over a wide range of ρ from a microscopic theory of impurity scattering and its effect on energy-gap anisotropy and other properties of the superconducting state. MK pointed out that the second term in Eq. (2) describes the effect of conduction-electron mean free path, whereas both mean-free-path and "valence" effects contribute to the first term.¹⁴ For sufficiently small ρ the second term should dominate. The nonlinearity in the experimental $\Delta T_c/\rho$ -vs- $\ln\rho$ plot of Fig. 1 for Hg, Cd, and Tl solutes constitutes the anomalous behavior. For these alloys normal behavior is found only above a critical value of the resistivity ratio.¹⁵ (Anomalies observed at high solute concentrations in the *InSn* and *InPb* systems by Merriam¹⁶ and others^{17,18} are outside the dilute region considered here.)

It is suggestive that for all three anomalous systems the critical resistivity corresponds to a mean free path approximately equal to the BCS coherence length, as might be the case if the MK theory applied

only to essentially "dirty" alloys. However, critical-field measurements in *InTl* made by Gubser *et al.*¹ reveal a discrepancy between experiment and the energy-gap anisotropy theory of Clem¹⁹ even for the high-resistivity region in which $\Delta T_c/\rho$ is linear in $\ln\rho$.

In Fig. 1 the slopes for *InPb* and the high-resistivity region of *InCd* and *InTl* are all approximately equal, as the MK theory suggests. But for *InHg* the slope is very different than for any other In-based alloy which has been investigated, with *InGa* remaining an indeterminate case as discussed above.

Merriam and co-workers^{3,4} observed the anomaly in *InCd* and *InTl*, and attributed it to interaction between the Fermi surface and a Brillouin-zone boundary. Both Cd and Hg are electropositive with respect to *InTl* if the anomaly is ascribed to this electropositivity via Brillouin-zone or other effects its presence in *InTl* argues that Tl, although nominally isoelectronic with In, is acting in an electropositive way as well. There is some independent evidence for this effect, based on phase-shift calculations¹⁰ and the sign of the first term of Eq. (2) for *InTl*.⁴

Note added in proof. Further confirmation is furnished by the similarity between *InTl* and *InCd* in the dependence of the c/a ratio⁴ and the nuclear-quadrupole-coupling constant¹⁰ on solute concentration.

We conclude, then, that the superconducting state of dilute electropositive-solvent In-based alloys is generally poorly described by a model in which only the effect of impurity scattering on energy-gap anisotropy is treated *ab initio*. The breakdown is most noticeable in (but not limited to) samples

with low residual resistivity. The fact that no anomaly is found for electronegative-solvent alloys indicates that a mean-free-path effect is not involved.

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Comments on the Dielectric Function of Toigo and Woodruff*

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The approximation to the electron-gas dielectric function recently proposed by Toigo and Woodruff is examined and found to differ from the known Hartree-Fock result in the limit of zero frequency and large wave number. It is shown that Toigo and Woodruff erred in evaluating this limit; the correct expression for it is obtained and two incorrect conclusions drawn from the erroneous result are corrected.

In two recent papers,^{1,2} Toigo and Woodruff (to be referred to as TW) have described a method of calculation of the polarizability $\alpha(k, \omega) = 1 - 1/\epsilon \times (k, \omega)$ of the electron gas. Their method is based on decoupling the equation of motion of the double-time retarded commutator of density fluctuations. In their approximation, the irreducible polarization function $Q(k, \omega)$, which determines the dielectric function by $\epsilon(k, \omega) = 1 + Q(k, \omega)$, was found to be of the form

$$Q(k, \omega) = Q_0(k, \omega) / [1 - P_0(k, \omega)], \quad (1)$$

where $Q_0(k, \omega)$ corresponds to the well-known Lind-

hard screening function.³ Restricting present attention to the static (zero-frequency, $\omega = 0$) limit of their approximation, $P_0(k, 0)$ was given by¹

$$P_0(k, 0) = - \frac{3\alpha r_s}{8\pi^3 k^2} \int d^3p d^3p' (\theta_{\vec{p}+\vec{k}}^\zeta - \theta_{\vec{p}}^\zeta) (\theta_{\vec{p}+\vec{k}}^\zeta - \theta_{\vec{p}'}^\zeta) \\ \times \frac{1}{(\vec{p} - \vec{p}')^2} \left[1 - \left(\frac{2\vec{k} \cdot \vec{p} + k^2}{2\vec{k} \cdot \vec{p} + k^2} \right) \right] \quad (2)$$

in the standard notation.

In the limit of small wave number, TW showed¹

$$P_0(k, 0) \rightarrow \alpha r_s / \pi \text{ as } k \rightarrow 0, \quad (3)$$