B. R. Coles*

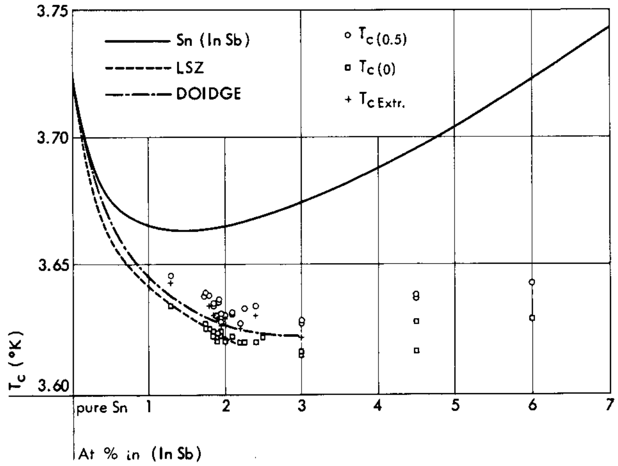
Effects of Electron Concentration and Mean Free Path on the Superconducting Behaviour of Alloys

Abstract: A brief review is given of the superconducting behaviour of solid-solution alloys. Intermetallic compounds are not considered but some reference is made to secondary solid solutions. Two topics are discussed: some factors affecting the transition temperature, and the role played by surface energy between normal and superconducting regions.

The scope of this discussion is restricted to solid-solution alloys, either primary substitutional solid solutions of one metal in another, or secondary solids where appreciable range of solid solution is found in an intermediate phase of a crystal structure (normally a simple one) different from that of the component metals.

In heavily alloyed materials ($> 5\%$ solute) we are in the region of strong scattering or the "dirty superconductor" region, and the mean-free-path changes as a function of composition in this region are not very significant. There is a great deal of evidence that, in the absence of localized magnetic moments, changes in composition produce their principal effect on T_c through their effect on $n(E)$, the density of electron states at the Fermi surface. Much of this evidence is due to the work of Matthias,[1] while recently Blaugher, Taylor and Hulm[2] have produced related evidence for body-centred-cubic transition metal alloys. There is a striking correlation in some systems between the behaviour of T_c and that of other properties strongly dependent on $n(E)$. Thus the Ti-Mo system shows the disappearance of superconductivity in the composition range where both the magnetic susceptibility and the hydrogen absorption have fallen to a low value.[3] On close examination, however, certain disparities are apparent. As emphasized by Pippard, the fall of T_c to zero in some such systems (Nb-Mo) is more rapid than one would calculate from the BCS expression using experimental values of $n(E)$, and a more rapid variation than that $n(E)$ would indicate is also found in other regions of the long periods. It is noteworthy that such evidence is drawn from transition metals and in some of these, at least, the isotope effect seems to be absent. If some interaction other than the phonon-electron one plays a part here, it may well be that the energy term outside the exponential in the T_c expression will depend on the electronic structure more strongly than does the Debye temperature. It may also be significant that at the ends of the transition groups, where the d-bands are narrowing rapidly and the overlaps of

Figure 1 **Transition temperatures of Sn-In and Sn-(InSb) specimens.**



---

* Imperial College, London.

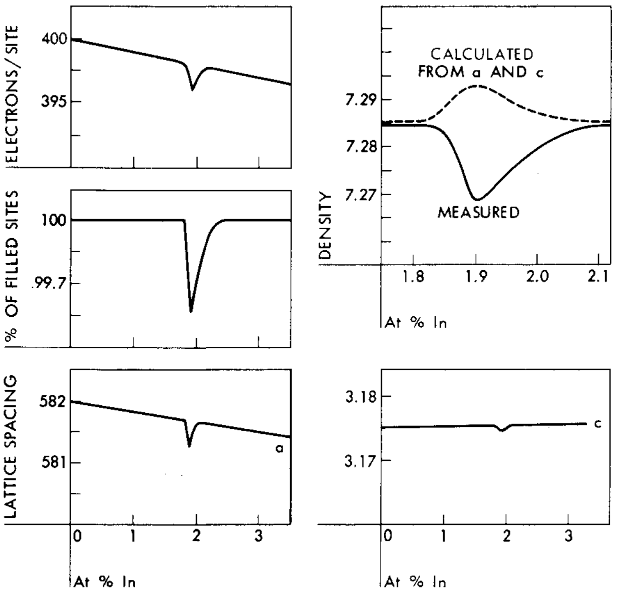


Figure 2 **Structural anomalies reported for Sn-rich Sn-In solid solutions.**

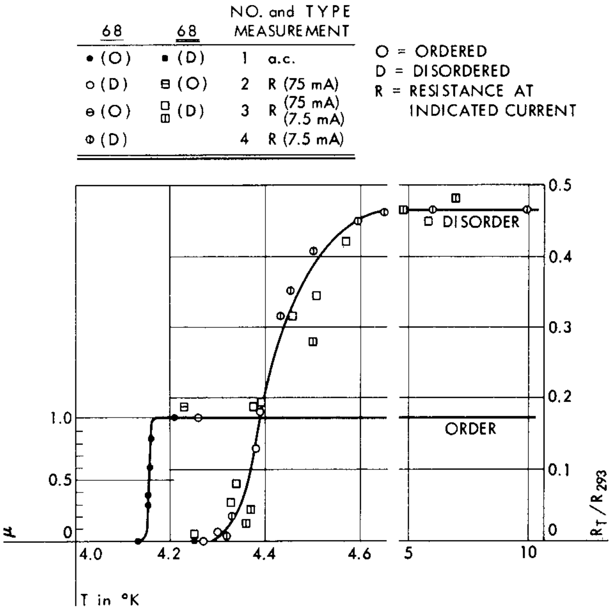


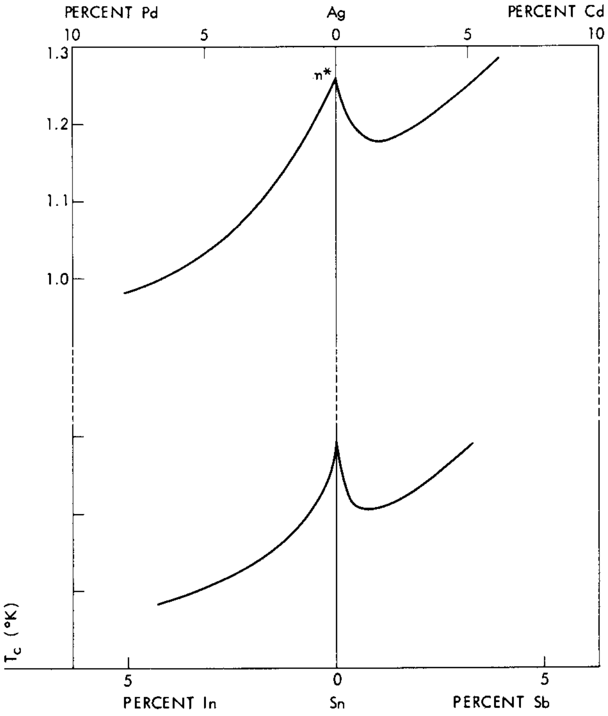
Figure 3 **Effect on T_c brought about by ordering of fcc secondary solid solution.** *Data for specimen of 26 Bi-74 Tl.*

d-functions on neighboring atoms are decreasing, the marked rise in *n*(*E*) with electron concentration is not marked by the reappearance of superconductivity.

It would be of the greatest interest to have more information on both the electronic structures and superconducting behaviour in alloys of nontransition metals. Complete solid solubility in such systems does not occur, but there are wide secondary solid solutions in some lead alloys and we are beginning to study these. We have found finite changes of T_c with composition in more concentrated Sn-(InSb) alloys (upper curve in Fig. 1), where changes in electronic structure should be absent and mean-free-path effects unimportant. Striking effects[4] in the structures of Sn-In solid solutions (Fig. 2) which have been ascribed to Brillouin zone effects do not seem to be reflected, however, in T_c (lower points in Fig. 1). Furthermore the ordering (probably in a Cu_3Au structure) of the fcc secondary solid solution of the Tl-Bi alloys seems to produce only a small change in T_c (see Fig. 3). Details of work on these alloys will be published shortly.

The effects of mean free path in *dilute* solid solutions have been established by the work of Lynton, Serin, Zucker, and Chanin[5,6], and it appears to be widely accepted that this is associated with the smearing out of anisotropy in the energy gap. It is amusing to compare (Fig. 4) the qualitative effects of indium and antimony on T_c of tin with those of palladium and cadmium on the effective number of conduction electrons given by Hall-effect measurements on dilute alloys of silver. These elements stand in the same relation to silver as In and Sb do to tin and probably[7,8]

Figure 4 **Effects of In and Sb on T_c of Sn compared qualitatively with effects of Pd and Cd on effective number of conduction electrons in Ag.**



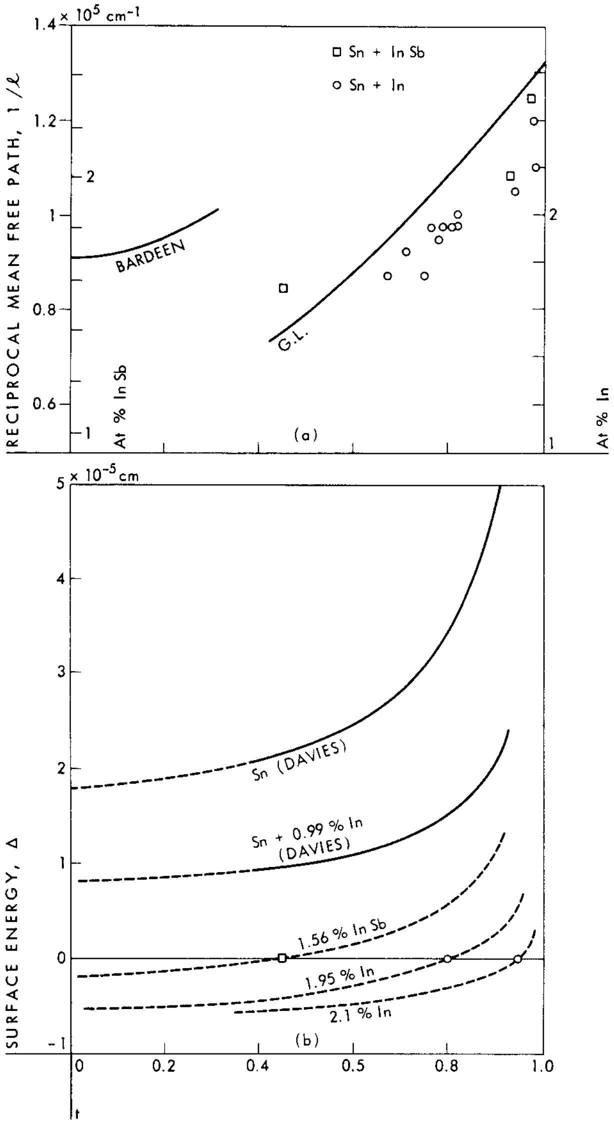


Figure 5 **(a) Reciprocal mean free path vs reduced temperature for Sn-In and Sn-InSb; (b) surface energies Δ of tin and tin alloys vs temperature, showing a mean free path dependence of the reduced temperature below which Δ is negative.**

produce their initial effects by the introduction of isotropic relaxation times.

As yet there is no clear evidence as to whether or not there is a dilute alloy mean-free-path effect in transition-metal superconductors.

There are a number of indications that an important mean-free-path effect in dilute tin alloys is the reduction and eventual change of sign of the surface energy (Δ) between normal and superconducting phases. Dr. Goodman has discussed the effect of such a change in Δ in rendering thermodynamically stable an intermediate state. Dr. S. Wipf of Imperial College has recently produced striking evidence of effects of this sort and of a mean-free-path dependence of the reduced temperature below which Δ is negative (points on axis of lower part of Fig. 5). The reciprocal mean free path is plotted against these temperatures for Sn-In and Sn-(InSb) in the upper part of Fig. 5, together with values derived from the Ginsburg-Landau theory[9] (right-hand curve). The derivation uses the empirical dependence of penetration depth on mean free path and temperature, and Gor'kov's substitution[10] of $2e$ for e. Details of this work will be published shortly.

Acknowledgement

The writer's thanks are due to Dr. Wipf for permission to reproduce some of his unpublished results in this paper; Figs. 1, 3 and 5 are taken from his Ph.D. dissertation.

References

1. B. T. Matthias, *Revs. Modern Phys.* **33**, 4 (1961).
2. Blaugher, Taylor and Hulm, this issue, p.116
3. Jones, Pessall and McQuillan, *Phil. Mag.* **6**, 455 (1961).
4. J. A. Lee and G. V. Raynor, *Proc. Phys. Soc.* (*London*) **B67**, 737 (1954).
5. Lynton, Serin and Zucker, *J. Phys. Chem. Solids* **3**, 165 (1957).
6. Chanin, Lynton and Serin, *Phys. Rev.* **114**, 719 (1959).
7. B. R. Coles, *Phys. Rev.* **101**, 1254 (1956).
8. J. R. A. Cooper and S. Raimes, *Phil. Mag.* **4**, 145 (1959).
9. V. L. Ginsburg and L. D. Landau, *J. Exptl. Theoret. Phys.* (U.S.S.R.) **20**, 1064 (1950).
10. L. P. Gor'kov, *J. Exptl. Theoret. Phys.* (U.S.S.R.) **36**, 1918 (1959). [Translation: *Soviet Phys.-JETP* **9**, 1364 (1959)].

Received July 15, 1961