Letters to the Editor

The Editor does not hold himself responsible for opinions expressed by his correspondents. He cannot undertake to return, or to correspond with the writers of, rejected manuscripts intended for this or any other part of NATURE. *No notice is taken of anonymous communications.*

NOTES ON POINTS IN SOME OF THIS WEEK'S LETTERS APPEAR ON P. 620.

CORRESPONDENTS ARE INVITED TO ATTACH SIMILAR SUMMARIES TO THEIR COMMUNICATIONS.

Transition Temperatures of Superconductive Alloys

THE transition between the normal and the superconductive state of a metal is a phase transition of the second kind, that is, there is no latent heat but a discontinuous jump in the specific heat, as at the λ-point of liquid helium or at the Curie point of a ferromagnetic. At the transition temperature in such phase changes, the entropy of the two phases as well as the free energy is equal. Thus if the entropies of the superconductive and the normal states are plotted as functions of the temperature T, the intersection of these curves determines the transition temperature. In the normal state the entropy is known to depend linearly on T at low temperatures. The entropy of the superconductive state can be determined from the magnetic threshold curve[1] and is found for most superconductors to vary approximately as T^2. There is a fairly well established theory which gives the entropy in the normal state, and we can predict with fair certainty how this will change when small quantities of other metals are added in solid solution. It is the purpose of this letter to show that the change in the normal state which can be roughly calculated is by itself sufficient to account rather satisfactorily for the observed changes in the transition temperature. The conclusion is therefore that the entropy-temperature curve for the superconductive state is not sensitively affected by the addition of small quantities of other metals in solid solution.

The entropy of the normal state for low temperatures is given by

$$S_n = aT,$$

where a, apart from universal constants, depends only on the density of electron states in the metal at the boundary between occupied and unoccupied levels. This quantity is usually denoted in the literature[2] by $N(E_0)$. In the Sommerfeld free electron model, $N(E_0)$ varies as $n^{1/3}$, where n is the number of free electrons per unit volume. In an actual metal it is known that $N(E_0)$ is rather greater than the value given by the Sommerfeld model and in general increases rather more rapidly with n. For the superconductive state the entropy may be represented by

$$S_s = bT^x,$$

where x lies between 2 and 3 and is, in fact, in most cases very close to 2. The variation in the transition temperature T_c due to a variation of a with b remaining constant is given by

$$\frac{\delta a}{a} = \frac{x-1}{T_c}\delta T_c.$$

Using the Sommerfeld model for the normal state, we have therefore

$$\frac{\delta T_c}{\delta n} = \frac{1}{3(x-1)}\frac{T_c}{n}. \qquad (1)$$

In the case of an actual metal, the factor 1/3 is replaced by the number $(n/N(E)^2)\,(dN(E)/dE)_0$ which may differ from 1/3 by a factor of 2 or 3. It is more convenient to use the number of free electrons per atom, n_0, in place of n in equation (1), so that in a real metal n_0 will correspond to the valency and in a solid solution to the weighted average valency.

Solute	Valency	$(dT_c/dc)_0$ exp.	dn/dc	(dT_c/dc) calc.(1)
Solvent metal lead, $T_c = 7{\cdot}26$				
Hg	2	−1·7	−2	−1·2
In	3	−0·8	−1	−0·6
Tl	3	−4·1	−1	−0·6
Bi	5	+7·1	+1	+0·6
Solvent metal thallium, $T_c = 2{\cdot}38$				
Sn	4	+2·7	+1	+0·26
Pb	4	+5·5	+1	+0·26

EUTECTIC ALLOY OF TIN WITH THE FOLLOWING METALS (TRANSITION TEMPERATURE OF PURE TIN, 3·69° K.)

Metal	Valency	Limit of solubility in tin	T_c
Bi	5	12% (atomic)	3·79°K.
Zn	2	1% ,,	3·66
Cd	2	10% ,,	3·62

The accompanying table gives the available relevant experimental data[3]. $(dT_c/dc)_{c=0}$ is the rate of change of the transition temperature with concentration of solute atoms, c, for zero concentration. This quantity can only be obtained roughly from the existing experiments. The fourth column gives the rate of change of electron concentration with concentration of solute atoms, and the fifth the values calculated from equation (1). Apart from changes in electron concentration, the entropy of the normal state is affected by changes in the lattice parameters arising in the formation of the solid solution, and this may in special cases be of importance.

Agreement in order of magnitude between experimental values and those given by (1), and particularly the fact that the transition temperature varies in the same direction as the electron concentration, support the view that the change in transition temperature is brought about largely by the change in the normal state of the metal.

H. JONES.

Royal Society Mond Laboratory,
Cambridge.
Aug. 26.

[1] Gorter, C. J., and Casimir, H., *Physica*, **1**, 305 (1934).
[2] Mott and Jones, "The Theory of Metals and Alloys", Oxford, 1936.
[3] Meissner, W., *Erg. Exakten Nat.*, **11**, 219 (1932).