Meissner Effect in Superconducting Alloys of Indium and Thallium

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THE magnetic properties associated with the superconductivity of solid solutions containing 5, 10, 15, and 20 atomic percent thallium in indium have been investigated. The samples were cylindrical rods, 0.6 cm diameter and 15 cm long, grown from the melt in a single crystal furnace. The etched surface of the crystals showed some twin markings, due presumably to slight deformation, and a very small volume or recrystallized material near these markings. The bulk of each specimen, however, was of a single crystallographic orientation. The composition of each sample was determined by chemical analysis of pieces cut from its ends. The 5 and 10 percent samples were uniform in composition within the accuracy of the analysis (0.2 percent of the thallium content). The 15 percent sample varied from 14.91 to 15.26 atom percent Tl and the 20 percent sample from 19.36 to 20.45. The samples were mounted in a helium cryostat in a longitudinal magnetic field uniform to 1.5 percent over the length of the specimens. The change in magnetic induction produced by interruption of the magnet current was measured by small coils wound around the equator of each sample and connected to a ballistic galvanometer.

We have found the behavior of these specimens to resemble much more that of pure metals than has been found previously[1] for alloys. In particular, most of the magnetic flux is expelled on decreasing the magnetic field below a critical value (Meissner effect). If the critical field is taken as that at which penetration begins for increasing field strength, then for all of the samples and for temperatures between 1.3 and 3.2°K the trapped flux remaining in zero applied field varied between 15 and 20 percent of that corresponding to complete penetration at the critical field. The initial penetration of flux into the sample upon isothermal application of a magnetic field occurred sharply for all samples. For the 5 and 10 percent specimens the penetration was complete within a two percent range of field strength, but occurred more gradually for the 15 and 20 percent samples. At the lowest temperature and for the 20 percent sample a field of nearly double that at which flux penetration began was needed before it was complete. The transition temperatures extrapolated to zero magnetic field strength agree fairly well with those determined from resistance measurements by Meissner, Franz, and Westerhoff.[2] Shoenberg[3] has shown that the compound Au_2Bi when properly prepared has superconducting properties resembling those of a pure metal and has suggested that the usual behavior of alloys is due to secondary causes, such as inhomogeneities. Our measurements support this idea but show further that the inhomogeneity on an atomic scale which is present in a disordered solid solution, and which drastically changes the resistance of the normal metal at low temperatures,[2] is apparently not responsible for the anomalous magnetic behavior that has previously been found in alloys.

[1] K. Mendelssohn, Rep. Prog. Phys. **10**, 358 (1946). D. Shoenberg, *Superconductivity* (Cambridge University Press, London, 1938), Chapter VI.

[2] Meissner, Franz, and Westerhoff, Ann. d. Physik **13**, 505 (1932).

[3] D. Shoenberg, Nature **142**, 874 (1938).

Alternating Current Conduction in Ice

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THE a.c. conductivity of any dielectric which exhibits anomalous dispersion due to a polarization of a single relaxation time increases monotonically with frequency and approaches a limit which we shall call σ_p. This quantity may be described as the *polarization conductivity* or *local conductivity* of the dielectric; it is a property of the polarizable structures which determine the dielectric constant.[1]

The writer has obtained data on the conductivity of ice which show that σ_p is given by

$$\sigma_p = 631 e^{-11500/RT}\ (\text{ohm}\cdot\text{cm})^{-1} \tag{1}$$

in the interval (0, −35°C); R is the gas constant, T the absolute temperature. (The full expression, to be given later, has two terms.)

Pauling's theory of the residual entropy of ice, based on the assumption that each hydrogen nucleus has available at all temperatures two equivalent sites, is in good agreement with experiment.[2] Therefore we discuss Eq. (1) in terms of a model consistent with Pauling's model for ice, by assuming that the elementary polarizable structure in ice is a proton moving back and forth on the line between two adjacent oxygen atoms O_1 and O_2. We assume that the proton traverses a distance d and crosses an activation energy barrier of height w in moving from a site 0.99A from O_1 to a site 0.99A from O_2. An expression for σ_p can be derived for this model of the elementary polarization process by assuming that the probability that the proton has at least the energy w is given by an equilibrium calculation similar to that for the equilibrium between a solid and its vapor, and that while the proton has the energy w it is effectively moving as a gas particle in a one-dimensional box of length d with the average velocity of a Maxwell distribution. This motion is "biased" by the applied field E, and the resultant current is

$$i = ne[(2\pi mkT)^{\frac{1}{2}}/h] d e^{-w/kT} (kT/2\pi m)^{\frac{1}{2}} 2 \sinh(Eed/2kT), \tag{2}$$

where m is the mass of the proton, k is Boltzmann's constant, h is Planck's constant, e is the charge on the proton, and n is the number of protons per cc. If in Eq. (2) we take $\sinh x \cong x$ and change from e.s.u. to $(\text{ohm}\cdot\text{cm})^{-1}$ and from w in ergs per molecule to W in cal./mole, we obtain

$$\sigma_p = (9\times 10^{11} h)^{-1} n e^2 d^2 \exp(-W/RT) (\text{ohm}\cdot\text{cm})^{-1}. \tag{3}$$

From Eqs. (1) and (3) we have

$$ne^2 d^2 (9\times 10^{11} h)^{-1} = 631\ (\text{ohm}\cdot\text{cm})^{-1} \tag{4}$$

and taking $n = 2\times 3.06\times 10^{22}$, $e = 4.8\times 10^{-10}$, $h = 6.55\times 10^{-27}$, we get $d = 1.6\times 10^{-8}$ cm. Pauling gives as the separation of the two equivalent sites of the hydrogen nucleus 0.78A. Taking d to be the average value of the projection in the field direction of randomly directed vectors 0.78A in length, we obtain 0.39×10^{-8} cm as the number with which the value $d = 1.6\times 10^{-8}$ cm calculated above should agree.

The assumption in this model that the proton does not have vibrational energy when it is occupying its proper site 0.99A from an oxygen atom is a simplification based in part on the following consideration. There is an infra-red absorption for ice at $\lambda = 4.7\mu$ which is distinguished from the other bands by the fact that it does not appear in water vapor.[3] This suggests that it is associated with the presence of the hydrogen bond between H_2O molecules in ice. If we attribute it to vibration of the proton when it is bound in its proper site 0.99A from an O atom, the corresponding partition function should be represented in the model. But putting the frequency corresponding to $\lambda = 4.7\mu$ into the expression for the partition function of an harmonic oscillator gives approximately unity at temperatures below 0°C. Consequently, this vibrational frequency will not appear in the model. It is assumed also that vibrations normal to the path direction of the proton in the activated state can be neglected.

The activation energy (W) derived from (1) has the value 11.5 kcal./mole, or 0.50 ev. It is approximately equal to the heat of sublimation of ice (11.8 kcal./mole at 0°K). If we assume that W is due to the breaking of two hydrogen bonds per molecule, the energy of the hydrogen bond in ice comes out as 5.75 kcal./mole, or 0.25 ev. This is a determination of the energy of a chemical bond by means of radiofrequency measurements of dispersion: it agrees with the value 5.8±0.2 kcal./mole given by Fox and Martin as