Meissner Effect in Superconducting Alloys of Indium and Thallium

J. W. STOUT AND LESTER GUTTMAN
Institute for the Study of Metals, University of Chicago, Chicago, Illinois
May 29, 1950

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$_2$Bi 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.

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Alternating Current Conduction in Ice

E. J. MURPHY
Bell Telephone Laboratories, Murray Hill, New Jersey
May 25, 1950

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

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

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

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

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 (ohm·cm)$^{-1}$ and from w in ergs per molecule to W in cal./mole, we obtain

$$\sigma_p = (9 \times 10^{11} h)^{-1} ne^2 d^2 \exp(-W/RT)(\text{ohm·cm})^{-1}. \quad (3)$$

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

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

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$_2$O 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

the energy of the hydrogen bond derived from the heat of sublimation.[4,5]

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An Attempt to Detect Thermal Energy Positrons*

LEON MADANSKY AND FRANCO RASETTI
Johns Hopkins University, Baltimore, Maryland
May 25, 1950

IT has been assumed that positrons diffuse through a solid during their lifetime.[1] It was considered worth investigating whether they would diffuse through and out of various materials. The number, n_s, of positrons of thermal energies diffusing out of a unit surface per unit time can be estimated as follows. The "average diffusion length" L is expressed by the formula $L = (\frac{1}{3}\lambda v \tau)^{\frac{1}{2}}$, where λ is the mean free path for elastic collisions, v the average thermal velocity, and τ the mean life. Assuming λ to be of the order of 10^{-8} cm, τ of the order[1] of 10^{-9} sec., the average diffusion length in a heavy metal would be of the order of $6 \cdot 10^{-6}$ cm. This means that the number of thermal positrons diffusing out of a metal should be of the order of the number of positrons stopped in a layer $6 \cdot 10^{-6}$ cm thick. This number may be compared with the number, n_f, of fast positrons emitted by the same material, assuming the radioactive atoms to be uniformly distributed. Fast positrons emerge from a layer of thickness equal to the range, or rather, in view of the continuous energy spectrum, of the order of the reciprocal of the absorption coefficient.

An experiment was attempted using as sources copper foils of initial activity of the order of 10 to 30 mC. The absorption coefficient of the positrons of Cu^{64} in copper may be taken[2] as 30 cm^3/g, hence fast positrons emerge from a layer 0.032 g/cm^2 or 0.0038 cm thick. Then the ratio n_s/n_f should be of the order of $5 \cdot 10^{-3}$.

In order to detect a small fraction of thermal energy positrons above the larger background of fast positrons, the following arrangement was used. The positron source was mounted at one end of an evacuated tube, containing, at a distance of 80 cm from the source, a thin aluminum foil kept at a negative potential and acting as positron collector. A pair of scintillation counters, placed opposite the collector and at 180° from each other, detected the positrons falling on the collector by means of coincidences between the two quanta of the annihilation radiation. The collector subtended approximately 5×10^{-5} of the total solid angle from the source, hence it absorbed less than that fraction of the fast positrons emerging from the copper foil. To increase the efficiency of collection of slow positrons, the tube was placed in an axial magnetic field of the order of 100 gauss. The tube, including a grid placed at 1 cm from the source, was at zero potential, and the source was either at +150 or −150 volts. Under these conditions with a positive source potential we expect the collector to capture most of the emerging thermal energy positrons, whereas none would reach the collector when the source is at a negative potential. From this calculation we might expect the effect of the thermal energy positrons, given by the difference in the numbers of counts with positive and negative source potentials, to be as much as 100 times greater than the fast positron background. Even allowing for a margin of error in the estimate of the mean life and mean free path, there should still be a considerable effect.

No difference in the number of counts exceeding the statistical error (about five percent) was observed. In order to avoid the possible unfavorable effect of the oxide layer on the copper surface, clean surfaces of various materials were used. A thin platinum foil heated at 1450°C in order to eliminate surface layers of adsorbed gases and other impurities gave negative results. No effect was observed with potassium evaporated in vacuum. Finally, assuming that positrons might diffuse in a liquid but not in a solid, we tried a thin, liquid layer of gallium evaporated in vacuum, and also obtained a negative result. No effect was observed with insulating layers of glass, mica, celluloid, and octoil.

In all these experiments the annihilation radiation from fast positrons reaching the collector was readily detectable, giving 20 to 100 counts per minute. The number of counts was almost doubled when the magnetic field was turned on, owing to partial focusing of the low energy portion of the positron spectrum. However, the effect was totally insensitive to the polarity of the source potential, showing that it was not due to positrons with energies of less than 150 ev.

In order to be certain that failure to observe the effect was not due to improper arrangement of the electric and magnetic fields, insufficiently good vacuum, or other imperfect experimental conditions, the identical arrangement was tested with electrons by coating the above-mentioned platinum foil with emitting oxides. With the filament at −150 volt, we immediately recorded large currents on the collector, even with much weaker magnetic fields than had been used in the previous experiments, showing the high efficiency of our focusing arrangement.

The conclusion is that thermal energy positrons do not appear to diffuse out of solids or liquids. Possible reasons are: (1) positrons do not diffuse through a crystal lattice, but are trapped in potential minima and annihilate before moving appreciable distances; (2) positrons diffuse through the lattice but are trapped at the surface; and (3) positronium is formed, and even if it should diffuse out of the material, it would not be detected in these experiments.

We wish to thank Dr. T. H. Berlin for stimulating discussions.

* This document is based on work performed for the AEC.
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Nuclear Magnetic Resonance in Metallic Hydrides

MARTIN A. GARSTENS
Electricity Division, Naval Research Laboratory, Washington, D. C.
May 29, 1950

THE method of nuclear magnetic resonance has been applied to the determination of the resonance absorption line widths at room temperature in some of the metal hydrides. The latter range in structure from true compounds to absorption mixtures, interstitial compounds, and solid solutions. It is frequently difficult to decide, in the cases of certain hydrides, which of these structures is present, especially since the same hydride may have different structures depending on the concentration of hydrogen present. Thus, palladium hydride is thought to exist as two immiscible solid solutions approaching a true compound as the concentration of hydrogen is increased.[1] As the concentration of hydrogen increases, tantalum is believed to go from a body-centered cubic phase to a hexagonal phase and back again to a body-centered cubic phase.[1] In some of these it is difficult to make out whether the hydrogen atoms or molecules wander freely through the metal lattice or cluster about certain fixed positions. A clue as to these possibilities is offered by observations of the nuclear magnetic absorption line widths due to proton resonance.

The experimental apparatus was similar to that of Bloembergen, Purcell, and Pound[2] except for the use of a twin T radiofrequency bridge. A phase-sensitive detector of about 1-cycle band width was used, since the resonance signals were too weak to be observed directly on an oscilloscope.

The spread between the maximum and minimum slopes of the absorption lines, as indicated on the output meter of the lock-in amplifier, was taken as a measure of the line width. The resonances