PARALLEL AND PERPENDICULAR MAGNETIC TRANSITIONS OF SUPERCONDUCTING FILMS AND FOILS OF LEAD

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The perpendicular and parallel magnetic transitions for pure Pb films and foils have been determined from transverse magnetization and ac susceptibility measurements as a function of thickness (400 Å to 35 μ) and temperature (1.4 to 4.2°K). The research was undertaken for several reasons. The first was to examine the validity of the Tinkham–de Gennes–St. James (TGS)[1,2] theory of the transition in thin films. While measurements on thin Sn and In films[3,4] are in surprisingly good agreement with the theory, there is considerable uncertainty concerning both the upper limit of film thickness for which the theory can be applied and whether it is restricted to "dirty" films. The second reason was to determine the transverse critical field ($H_\perp$) over a sufficient range of thicknesses to overlap both the TGS region where flux vortices dominate the transition and the Davies region where macroscopic domains of positive energy dominate.[5,6] Published data[3,5] on Sn indicate that $H_\perp$ does not vary smoothly between these two thickness domains. Finally, it appeared important to search for resistance at the magnetic transition ($M=0$). Published data[7,1] for Sn suggest that the resistive transition occurs at fields about twice that of the magnetic transition.

Several important conclusions can be drawn from the data for lead at 4.2°K; qualitatively similar conclusions can be inferred at lower temperatures:

(1) Lead films from 500 Å to 10 kÅ are in excellent agreement with TGS for both perpendicular ($H_\perp$) and parallel ($H_\parallel$) magnetic transitions. For example, for films in the range 3 to 10 kÅ, $H_\parallel/H_\perp \approx 1.7$ as predicted by TGS for a film of type-I material. It is noteworthy that the results show that the TGS theory is in agreement with experiment, for these pure films, up to thicknesses of the order of $10\xi_0$ at 4.2°K ($\gtrsim 50\xi_0$ at 1.4°K), where ξ_0 is the bulk coherence distance.

(2) For films and foils thicker than 10 kÅ, the transverse magnetization exhibits a reversible tail that is absent below this thickness. A critical thickness for the transition to an intermediatelike state prior to $H_\perp$ has not previously been reported. The behavior of $H_\perp$ for $d > 10$ kÅ at 4.2°K can be explained satisfactorily by the theory of the effect of positive surface energies on the free energy of a thin superconductor in the intermediate state. For Pb, $H_\perp$ in the Davies region approaches $H_\perp$ in the TGS region smoothly, as expected, but not observed for Sn.[3,5] Thick foils approach bulk specimens where $H_\perp \approx H_c$, and $H_\parallel/H_\perp \approx 1.1$.[8]

(3) For films from 1.2 to 10 kÅ, the dc resistive transition in parallel and perpendicular fields is about a factor of 2 higher than the respective magnetic transitions. However, ac susceptibility measurements show that the films have a finite resistivity at $H_\perp$ and $H_\parallel$. The effective resistivity, derived from the susceptibility, is considerably smaller than that of the normal state and is believed to be related to a flux-flow mechanism.

Lead was chosen for the initial investigation, chiefly for the ease of sample preparation, and the availability of data on $\kappa(T)$ (the Ginzburg-Landau parameter) for bulk lead.[8] The film samples were obtained by evaporation on a room-temperature glass substrate (Corning 7059) at a pressure of 8×10^{-7} mm Hg, and a rate of 50 Å/sec. The samples were $\frac{7}{16}$-in. diameter disks. The circumference was scraped to remove the penumbra. Measurements of the normal resistivity of the films indicate a bulk mean free path (l) of 40 kÅ and $\rho l = 1.5\times10^{-11}$ Ω cm^2. Foils were rolled from 6-9's pure lead. For a 16-μ foil, the resistivity ratio, $\rho(300)/\rho(4.2)$, was 1600. Magnetization measurements were made conventionally[9] with a galvanometer–galvanometer-amplifier combination which had a sensitivity of 1.6×10^{-4} G cm^3/mm. The susceptibility of the specimen was determined from the ac impedance of a split coil about $\frac{1}{2}$ in. in diameter, through which the specimen was inserted. The impedance was determined by an Anderson bridge from 100 to 10 000 cps. At 1000 cps, the coil had an inductance of about 150 mH and an ac resistance of about 50 Ω.

Figure 1 shows transverse magnetization data for a 10- and a 12-kÅ film at 4.2°K. The reversible region near the transition field ($M=0$) observed for the 12-kÅ film was observed for

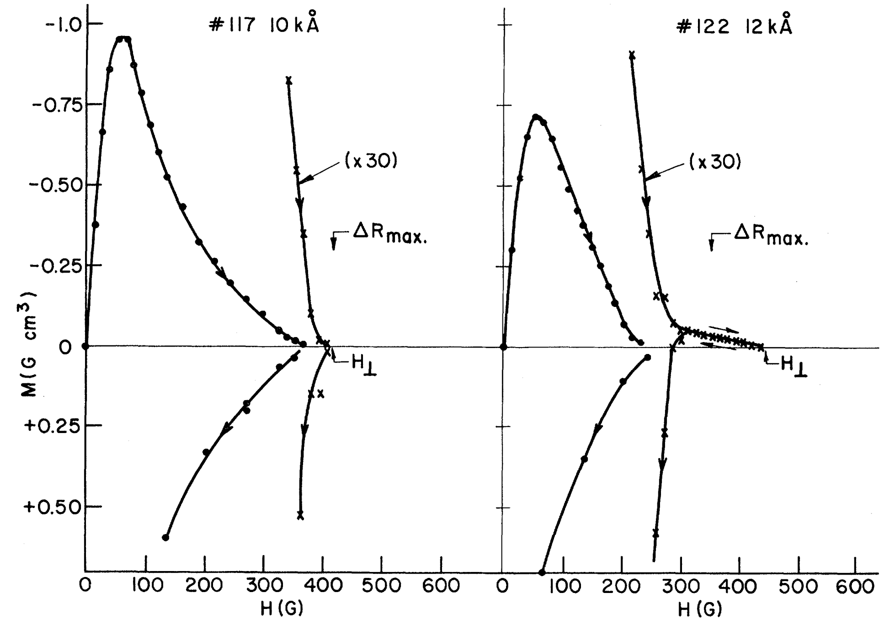

FIG. 1. Magnetization curves in a transverse field for two films ($d = 10$ kÅ and $d = 12$ kÅ) at 4.2°K. $H_\perp$ denotes the magnetic transition field ($M = 0$); $\Delta R_{\max}$ denotes the position of the peak in power absorption.

all samples thicker than this value. Figure 2 shows the change in inductance (ΔL) and resistance (ΔR) of the specimen coil at 1000 cps for films with $d = 2$ and 10 kÅ as a function of perpendicular and parallel dc field. The ac field was of the order of 0.01 G. For all samples below 10 kÅ, the peak in power absorption in a perpendicular dc field ($\Delta R_{\max} \approx 25\ \Omega$ at 1000 cps) occurred, within experimental accuracy, at the point where $M = 0$. For $d \geq 12$ kÅ, the peak occurred in the reversible tail (Fig. 1). In a parallel dc field, the peak is within 10% of the transition field measured by Lock[10] by magnetization ($M = 0$) on films of lead from 2 to 8 kÅ. In the present paper, the value of the parallel field for which this peak occurs is identified with $H_\parallel$.

The correlation of the peak in the imaginary susceptibility (χ'') with the transition fields $H_\parallel$ and $H_\perp$ in the TGS region is experimentally important since χ'' is considerably easier to measure than M and experimentally shows no field hysteresis. We believe that the peak is related to an intrinsic power absorption in the specimen, and not due to magnetic hysteresis,[11] for the following reasons. First, for $d < 10$ kÅ, the magnitude of the peak is independent of sample thickness, depends on the cube of the radius not its volume, and has almost the same value in parallel and perpendicular fields. Second, for $d > 10$ kÅ, the peak occurs where M is reversible ($M \neq 0$) and is of the same magnitude as for the lower thickness. Finally, the magnitude of the peak is about 20 times larger than the maximum loss expected from magnetic hysteresis in the TGS region.

These considerations imply that the peak arises from the variation of an effective sample resistivity from zero in the superconducting state to some fraction of its normal value. Due to demagnetizing effects the maximum power absorption per cycle in thin specimens should occur when the skin depth (δ) is of the order of magnitude of the thickness (d). This conclusion has been checked on foils in the range 6 to 16 μ in the normal state (in this case, the frequency, not the field is varied). For the Davies region, where the transition to the normal state is presumably spread out over a wide field region, one expects the position of the peak, and indeed its existence, to depend on thickness and frequency and this has been observed. In the TGS region, the rise in resistance through the critical coupling region ($\delta/d \approx 1$) occurs over a very narrow field range, the peak occurs where $M = 0$, and its position

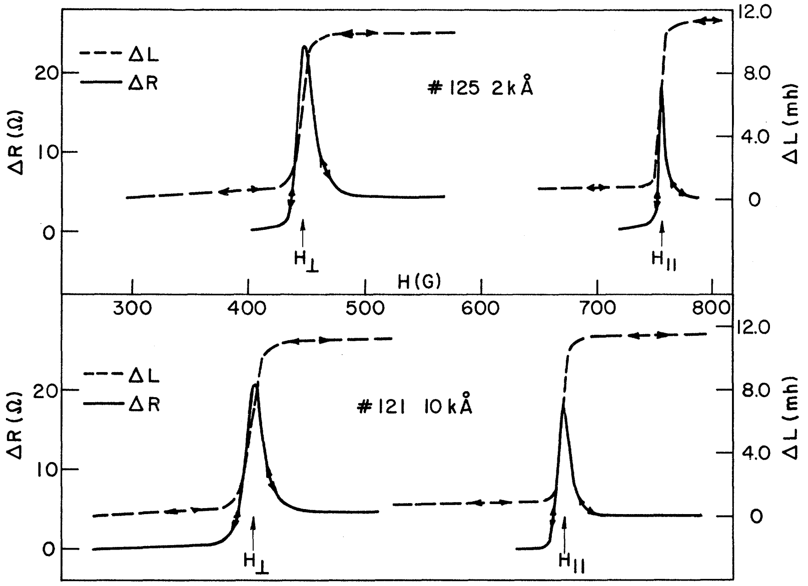

FIG. 2. Changes in the real (ΔL) and imaginary susceptibility (ΔR) of two films ($d = 2$ kÅ and $d = 10$ kÅ) in perpendicular and parallel fields at 4.2°K.

is independent of frequency. It is important to note that the peaks in the power absorption per cycle that occur at $H_\perp$ and $H_{\parallel}$ in the TGS region, in the reversible tail for the Davies region, and in the normal state (as a function of frequency) are of the same magnitude and are within 20 to 30% of what one would estimate from an eddy-current calculation taking into account the field distortion due to demagnetization effects ($\Delta R_{\rm max} \approx 0.3\Delta L_{\rm max}\omega$).

In the absence of an exact calculation of eddy-current absorption in thin films we have measured $\Delta R/f$ as a function of frequency (f) for normal foils of Pb, 6 and 16 μ in thickness. Empirically, the maximum loss per cycle occurs at $d/\delta = 0.1$ where $\delta^{-1} = 2\pi(f/10^9\rho)^{1/2}$. The present results in the TGS region are thus interpreted in terms of a rapid field variation of resistance with field at $H_\perp$ from $\rho = 0$ through the value of ρ that gives optimum coupling $d/\delta \approx 0.1$. Consistent with this view is the fact that we have observed peaks of the same magnitude for Sn and In at $H_\perp$ and $H_{\parallel}$.

At present, it is difficult to understand the effective resistivity observed at $H_\perp$ in the TGS region, in detail. Simple substitution in the above formula for a 6-kÅ film at 1000 cps leads to $\rho \approx 3 \times 10^{-11}$ Ω cm at the peak absorption. This value of resistivity is so small that it is presumably due to flux flow rather than conventional scattering.[12] However, with sufficient sensitivity, such a flux-flow resistivity may be observable in dc measurements. The advantage of ac susceptibility over dc determinations of resistivity is, of course, its high sensitivity for very low ρ values.

Figure 3(a) shows the perpendicular transition fields ($H_\perp$) defined by $M = 0$. The curve labeled T in Fig. 3(a) is a best fit to the data for $d < 10$ kÅ and is given (d in Å) by

$$H_\perp = \sqrt{2}H_c(0.50)[1 + (260/d)]. \tag{1}$$

If we interpret the coefficient of $\sqrt{2}H_c$ as $\kappa(4.2°\mathrm{K})$ (from TGS), we note that it is about 4% larger than that measured for bulk lead.[8] Similar analysis at 1.4°K leads to $\kappa(1.4°\mathrm{K}) = 0.63$ with the coefficient of $1/d$ given by ≈200 Å. This value of $\kappa(1.4°\mathrm{K})$ should be compared to $\kappa(1.4) = 0.56$ for bulk lead.[8] The thickness dependence of $H_\perp$ given by the above equation can be interpreted as arising from the thickness dependence of the penetration depth λ. A reasonable form for the thickness dependence of the penetration depth is $\lambda = \lambda_\infty[1 + (\lambda_L{}^2\xi_0/\lambda_\infty{}^2 L)]^{1/2}$ where λ_∞ is the bulk penetration depth, λ_L is the London penetration depth, and L is an effective mean

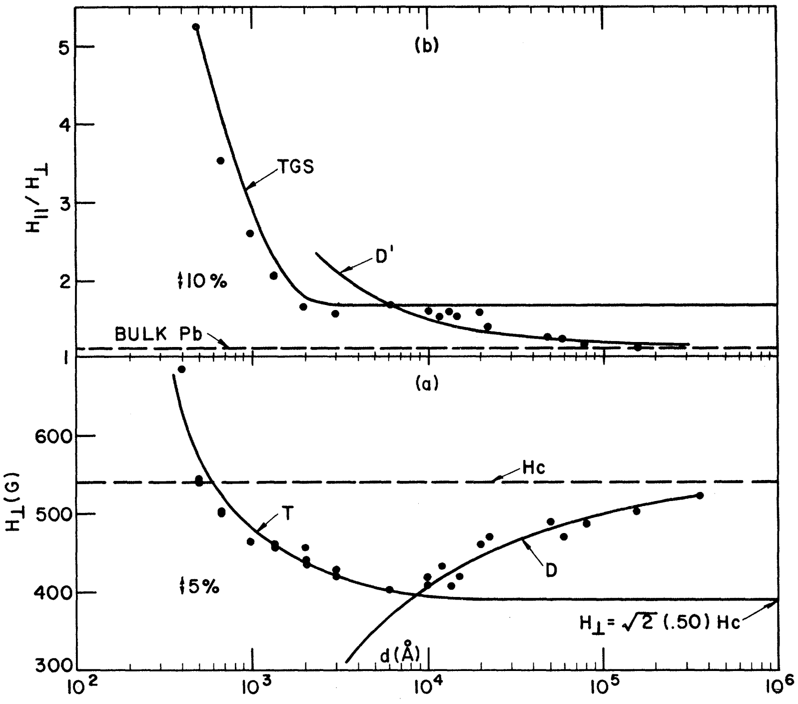

FIG. 3. (a) $H_\perp$ as a function of thickness at 4.2°K. The smooth curves are theoretical fits to the data points. (b) $H_\parallel/H_\perp$ as a function of thickness at 4.2°K. The curve labeled TGS is a function only of the measured $H_\perp$ and the thickness d. The curve labeled D' is based on $H_\perp$ and the assumption that $H_\parallel = H_{c3}$.

free path.[13] From Eq. (1) we obtain $\lambda_\infty(4.2) = 470$ Å and $L \approx 2d$, since for Pb, $\lambda_L(4.2) \approx 390$ Å and $\xi_0 \approx 800$ Å.[14] From the two-fluid model, $\lambda_\infty(0) = 440$ Å, in fair agreement with $\lambda_\infty(0) = 390$ Å quoted in the literature.[10] Furthermore, the thickness dependence of L agrees with the estimate $L \approx 8d/3$, obtained from thin-film surface scattering.[15]

Figure 3(b) shows the ratio of $H_\parallel$ (from susceptibility) to $H_\perp$ (from magnetization and susceptibility) as a function of d. The curve labeled TGS is derived from that theory, from the measured $H_\perp$, and from the thickness d. Changes in d of the order of 10% would be sufficient to bring the points to the line. The curve saturates to a value $H_\parallel/H_\perp = 1.695$ at about 3 kÅ which implies $\xi(4.2°\mathrm{K}) = 1100$ Å and $\xi(0) = \xi_0 \approx 780$ Å.

The curve labeled D in Fig. 3(a) is derived from fairly crude calculations of the effect of positive surface energy on the free energy of the intermediate state of a thin specimen in a perpendicular field. It is of the form $(H_\perp/H_c) = [1-(C\Delta/d)^{1/2}]$, where Δ is the surface-energy parameter and the constant C, depending on the details of the model, varies from 0.8 to 2.0. The plotted curve leads to $C\Delta \approx 630$ Å. The magnitude of Δ, within this uncertainty, is quite reasonable since with $\lambda = 470$ Å, $\kappa = 0.50$, one obtains from Bardeen[16] $\Delta = 660$ Å. Curve D' in Fig. 3(b) is calculated from the above expression for $H_\perp$ and the bulk value at 4.2°K of H_{c3} where it is assumed $H_\parallel = H_{c3}$.

It is interesting to note that the critical d for the intersection of the Davies region and the TGS region varies as $\Delta(1-2\kappa)^{-2}$. Thus, if 10 kÅ is the intersection at 4.2°K, 50 kÅ should be the intersection at 1.5°K. We observe $\gtrsim 50$ kÅ.

The present paper shows that for clean lead films and foils, current theories of thin-film magnetic transitions are in remarkable agreement with experiment over a wide range of thicknesses. It appears that some of the previous discrepancies were associated with the reliance on low-sensitivity dc measurements in the thin-film region for the determination of $H_\perp$. In addition to the data presented, the present paper describes a technique that permits rapid and convenient measurement of $H_\parallel$ and $H_\perp$ over the entire range of thickness in the TGS region and with no hysteresis. Uncertainties remain as to the nature of the resistivity observed at $H_\perp$ and $H_{\parallel}$, and whether the present excellent agreement with TGS for temperatures below T_c is restricted to nearly local superconductors such as lead.

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DIELECTRIC SUSCEPTIBILITY OF ION IMPURITY SYSTEMS AT LOW TEMPERATURES*

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Considerable interest has been aroused in the electrocaloric effect in ion impurity systems, mainly alkali halides doped with Li^+, OH^-, CN^-, and NO_2^-.[1-6] At the same time, the details of motion of impurity species located at lattice vacancies have been investigated, in particular in the case of CN^-, utilizing a variety of calorimetric and spectroscopic techniques.[7] A particularly striking system, and apparently the only one for which extensive measurement of dielectric properties has been carried out, is OH^- in KCl.[3,4] This system shows a low-temperature peak in dielectric susceptibility as a function of temperature, which has been qualitatively interpreted as indicative of a transition to an ordered state,[4,8] reminiscent of the behavior of the magnetic susceptibility in an antiferromagnet. In this picture, the peak in dielectric susceptibility is interpreted as an electric Néel point, account being taken of the dilute and random character of the assembly of impurity species.

It is the object of this note to point out that careful consideration of the data reported in Ref. 3 forces one to a rather different interpretation of the situation in OH^- than that mentioned above, and, in so doing, offers the opportunity to extract considerable information about impurity motional states in systems like OH^- from dielectric data. Our conclusion is that the peak in dielectric susceptibility in OH^- is, in essence, a single-particle effect modified and shifted by interactions, but not equivalent to a Néel point. Empirical justification for this assertion is given in Fig. 1, a plot of the temperature at which the dielectric susceptibility maximum occurs versus the concentration (data of Ref. 3). The extrapolation to zero C is guided by the consideration that any model based on the notion of interactions as responsible for the occurrence of a maximum must give an expansion for $T_{\max}$ as a function of C of the form $T_{\max}(C) = T_{\max}(0) + aC^2 + \cdots$. The slope of the curve must therefore vanish at $C = 0$, as shown. The intercept of the curve is found to be at about 0.26°K, and