SURFACE SUPERCONDUCTIVITY IN TYPE I AND TYPE II SUPERCONDUCTORS*

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Saint-James and de Gennes[1] have shown theoretically that a surface superconducting layer with a critical field H_{c3} can exist above the bulk critical field H_c when the external field is parallel to the sample surface. They find that $H_{c3} = 2.39\kappa H_c$ where κ is the Ginzburg-Landau parameter. For type II superconductors ($\kappa > 1/\sqrt{2}$) this relation becomes $H_{c3} = 1.69 H_{c2}$. Experimental evidence[2-6] has confirmed the existence of a surface critical field H_{c3} above H_{c2}, for type II superconductors. For values of κ between $1/\sqrt{2}$ and $1/2.39$, surface critical fields are predicted for type I superconductors, although observation of H_{c3} in type I materials has not yet been reported. We have measured the real and imaginary parts (χ' and χ'') of the ac susceptibility in type I and type II superconductors in both parallel and perpendicular dc magnetic fields. This technique yields much sharper transitions in H_{c3} than have been reported and permits demonstration of the existence of surface effects in superconductors with H_{c3} barely above H_c. In a lead alloy containing only 0.1% Bi we find that H_{c3} is slightly above H_c. This alloy shows a reversible type I magnetization curve. In pure Pb, H_{c3} was not detectable and the paramagnetic ac susceptibility characteristic of the intermediate state[7] in type I superconductors was observed. Because of high sensitivity in determining H_{c3} in dilute Pb-Bi alloys, κ for pure Pb could be determined by extrapolating the κ vs concentration curves to zero concentration.

The complex ac susceptibility was measured with an electronic mutual inductance bridge[8] at 18, 35, and 100 cps and with an axial field on the sample of about 0.04 oersteds. The samples used were cylinders with a diameter of 0.06 inch and 0.5 inch long. The real part of the ac susceptibility, χ', is a measure of the diamagnetism caused by the induced ac currents. A superconducting surface layer will make the sample appear completely diamagnetic in this measurement. The imaginary part of the ac susceptibility, χ'', is a measure of the power loss in the sample. In superconducting transitions, under certain conditions, the ac losses can exceed those in a normal material, leading to peaks in χ'' vs field[9] or temperature.[9,10] It can be shown that a peak in the power loss will occur in a superconducting sheath at sufficiently low frequencies.

The magnetization curves and χ' in a longitudinal magnetic field are shown in Fig. 1 for Pb and 0.1% Bi in Pb together with χ'' for the 0.1% Bi in Pb sample. Neither sample showed flux trapping although some slight hysteresis near H_c was observed in the alloy sample. It can be seen that in pure Pb, χ' shows the differential paramagnetic effect[7] characteristic of the intermediate state in ideal type I superconductors. χ' in longitudinal fields for 0.1% Bi in Pb clearly shows a transition above H_c. When the sample was placed in a field perpendicular to the axis, the ac susceptibility characteristic of the intermediate state was observed.[7]

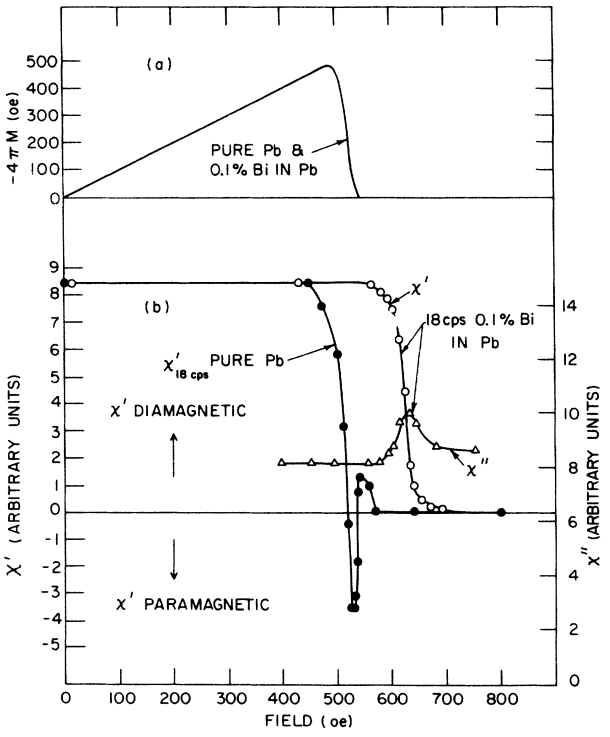

FIG. 1. (a) Magnetization curve at 4.2°K for Pb and 0.1% Bi in Pb. Curves are the same for both samples within experimental error. (b) Real part of the susceptibility, χ', for pure Pb and 0.1% Bi in Pb and imaginary part, χ'', for 0.1% Bi in Pb. χ'' is plotted to the same scale as χ' and magnitudes can be compared. $T = 4.2$°K.

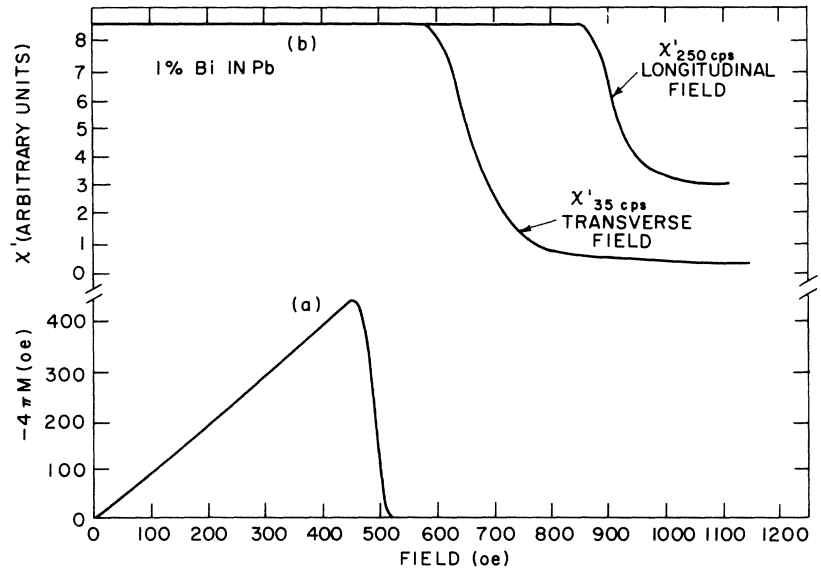

FIG. 2. (a) Magnetization curve at 4.2°K for 1% Bi in Pb. (b) χ' for 1% Bi in Pb in perpendicular and parallel fields at 4.2°K.

The interpretation of the susceptibility measurements in a transverse field for cylindrical samples is complicated by the fact that different regions of the surface are at different angles to the dc field. It has been found experimentally that H_{C3} is a monotonic function of angle between surface and field.[3] The angle effect together with the different magnet geometry that had to be used to obtain transverse fields made it difficult to discern whether there was any superconductivity above H_C in the transverse case in 0.1% Bi in Pb. However, in the case of 1% Bi in Pb, shown in Fig. 2, it can be seen that the χ' transition in the transverse field case occurs at lower fields than the transition in the axial field case. Above H_C the regions of the cylindrical sample normal to the field should not be superconducting. These regions would interrupt the superconducting surface sheath along the path of the circulating ac currents. Hence, if only surface superconductivity were present the ac transition should occur at H_C. Since the magnetization curve precludes any bulk effect, the ac transition in the transverse case must be due to some superconducting network of negligible volume that does not exist on the surface.

In annealed samples we have observed sharp χ'' peaks (see Fig. 1). In cold-worked samples the χ'' peak broadens and appears to develop structure, indicating that the shape of the χ'' peak is a sensitive method of studying details of the H_{C3} transition.

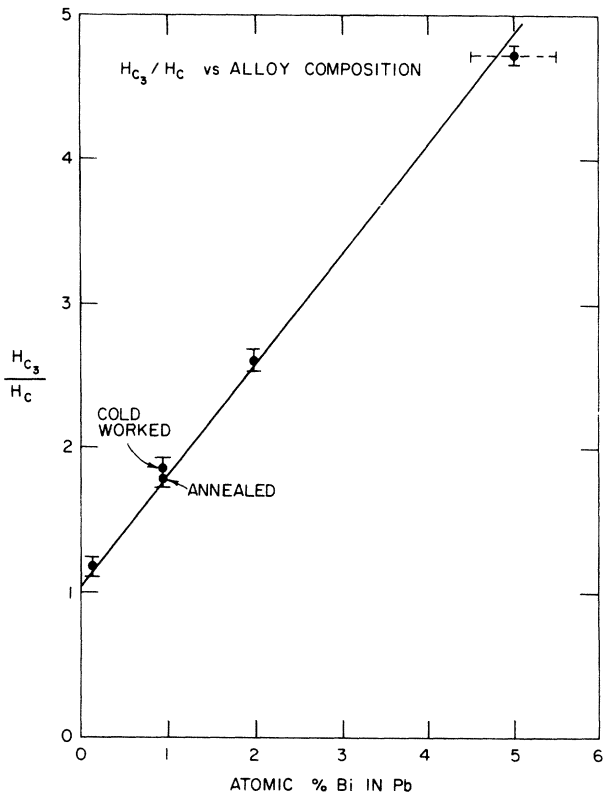

FIG. 3. H_{C3}/H_C vs atomic % Bi in Pb at 4.2°K. The horizontal uncertainty bar for the 5% composition indicates the maximum range in composition in bar from which sample was taken. The analysis for this sample is still not available.

In Fig. 3 we have plotted H_{c3}/H_c at 4.2°K against alloy concentration, where H_c is the critical field of pure Pb and H_{c3} is identified with with the sharp transition in χ' and χ''. The observed curve is approximately linear over the concentration range studied. Linearity is expected if κ varies linearly with concentration, and if $H_{c3} = C\kappa H_c$. For a slab in a parallel field, Saint-James and de Gennes[1] find that the constant C is 2.39. From the ratio of H_{c3}/H_{c2} for type II superconductors in an axial field we have found that the constant C appears to be about 10% above 2.39. Similar results were found in Pb-In alloys by Gygax, Olsen, and Kropschot.[4] Extrapolation of κ's deduced from Fig. 3 to zero Bi concentration yields a value of κ for pure Pb of 0.38 ± 0.05. Although H_{c3}/H_c for zero concentration appears to lie slightly above unity the difference does not exceed experimental error and the value of unity was used in calculating κ.

We have also made some preliminary measurements in triply zone-refined, single-crystal Ta which demonstrates that H_{c3} can exist in a pure material as well as an alloy. At about 1.8°K a type I magnetization curve and an H_{c3} significantly above H_c was found. In our Ta sample, a value of about 0.5 was found for κ.

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ITINERANT ELECTRON FERROMAGNETISM IN $ZrZn_2$ †

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In this Letter we describe the direct observation, by polarized neutron scattering, of a large degree of nonlocalization of the zirconium spin density in ferromagnetic $ZrZn_2$. Comparison with free-atom $4d$ electron configurations would suggest that the ferromagnetism of this compound is attributable in significant measure to the conduction band, so that some sort of itinerant electron model is clearly required to explain it.

$ZrZn_2$, which is a cubic Laves phase (structure type $C15$), was reported to be ferromagnetic by Matthias and Bozorth,[1] who remarked upon the unusual fact that neither of the constituent atoms of this intermetallic compound is strongly paramagnetic. An earlier unpolarized neutron diffraction study by Abrahams[2] was inconclusive in establishing the presence of a moment, because of its smallness ($\mu = 0.18\ \mu_B$/molecule) relative to the nuclear scattering. Olsen[3] was unable to detect an anomaly in the electrical resistivity of $ZrZn_2$ at its ferromagnetic transition (~35°K) and attributed this to a lack of ordered local moments. This suggestion is borne out by the measurements reported here.

The polarized neutron method, since it retains the interference between nuclear and magnetic scattering, is ideal for measuring very small magnetic structure factors accurately. One obtains, by reversing the incident neutron polarization, the polarization ratio R_{hkl} for each Bragg reflection

$$R_{hkl} = \frac{(1+\gamma)^2}{(1-\gamma)^2}$$

where $\gamma = F_{\text{magnetic}}/F_{\text{nuclear}}$. R, which for $\gamma \ll 1$ is linear in γ, can be measured to any desired statistical precision. The present mea-