CRITICAL PHENOMENA IN SHEATH SUPERCONDUCTIVITY OF Nb*

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Very close to the superconducting transition temperature, the ratio of the critical magnetic field for surface superconductivity to the upper critical field for the vortex state, H_{c3}/H_{c2}, falls far below the Saint James–de Gennes factor of 1.7.

One of the many triumphs of the Ginsburg-Landau[1] approach to the theory of superconductivity has been the discovery by Saint James and de Gennes[2] that superconductivity could nucleate at a vacuum-metal interface for a magnetic field, H_{c3}, which is 1.7 times higher than the upper critical field for the vortex state, H_{c2}. This surface sheath shows the usual properties associated with superconductivity,[3] but it differs from the Meissner or vortex state in that the superconducting characteristics appear only within a coherence distance, ξ, of the vacuum-metal interface. A remarkable number of experiments have confirmed the ratio of H_{c3}/H_{c2} to be about 1.7 and many of the small deviations from this value have been explained theoretically.[4,5]

Despite this strong confirmation, the Ginsburg-Landau theory of superconductivity is a molecular-field approach, and there must be a temperature region very close to the critical temperature T_c in which thermal fluctuations invalidate the uniform field approximation.[6] Hence close to T_c one might expect significant deviations from the theory. For bulk superconductivity[7] this range appears to be much less than 10^{-3} K, but for surface superconductivity there might be a broader range because the total free-energy difference between the superconducting and normal phases is smaller. Only the surface region of the sample contributes to the free-energy change so the total free-energy difference might be many orders of magnitude smaller. Thermal fluctuations may be rather important in this situation.

In this paper we present evidence for critical phenomena in the phase transition from sheath superconductivity to normal state. Data are presented for the ratio of H_{c3}/H_{c2} for pure Nb over the entire temperature range above 4.2 K with special emphasis on the region very close to T_c. Deviations from the Saint James–de Gennes[2] and Ebneth-Tewordt[8] theories are interpreted as a breakdown of the molecular field approximation.

Experimental aspects of these measurements differ from earlier work only in that the ac susceptibility was measured rather than the bulk magnetization. The sample preparation, sample dimensions, cryostat, and germanium resistance thermometers were the same as those previously reported.[9] Both the in-phase and out-of-phase components of the susceptibility, χ' and χ'', were determined for cylindrical samples with both the steady magnetic field and the 33-Hz measuring field parallel to the axis of the sample. The bulk resistivity ratio for these samples was greater than 500 so the bulk coherence distance is much smaller than the electron mean free path. It would be a mistake, however, to try to infer the electronic mean free path in the region of the surface from such bulk measurements. The surface condition might be quite different from the bulk.

For all temperatures, the magnetic field dependence of χ' was similar to the two runs shown in Fig. 1. Note that the abscissa has been normalized by H_{c2} to emphasize the ratios H_{c1}/H_{c2} and H_{c3}/H_{c2}. At H_{c1} there is a rather broad dip in χ' as the vortex state begins to form. At H_{c2} there is a very sharp spike which has a width which is less than $10^{-2}H_{c2}$. Identification of this spike with H_{c2} and identification of the minimum of the broad dip with H_{c1} give good agreement with the bulk magnetization values.[9] The ratio of H_{c1}/H_{c2} increases monotonically from 0.50 at

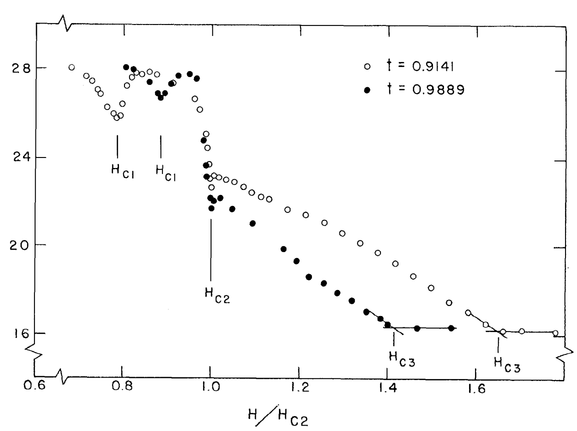

FIG. 1. Differential susceptibility of Nb as a function of applied field for two different temperatures.

4.2 K to 0.90 at T_c in agreement with earlier work.[9]

At fields slightly above H_{c2}, χ' is about halfway between the full superconducting and the normal-state value. As the field increases, χ' approaches the normal-state value with a nearly linear field dependence. The rounding at H_{c3} is never more than 5% of H_{c2}. The general shape of the transitions is the same for all temperatures and the important changes are reflected in the ratios H_{c1}/H_{c2} and H_{c3}/H_{c2}.

Below 8 K the measurements of H_{c3}/H_{c2} are in good agreement with the Ginsburg-Landau theory. It decreases monotonically from 1.85 at 4.2 K to 1.73 at 8 K in good agreement with the experiments of Webb.[5] Broadly speaking they also confirm the theoretical treatments of this problem by Ebneth and Tewordt[8] and by Hu and Korenman.[10]

Above 8 K and especially above 9 K, there are very large deviations from the theory. H_{c3}/H_{c2} plunges below the theoretical value of 1.695 and seems to approach 1.00 as T goes to T_c. As shown in Fig. 2, the data begin to drop away from the Ebneth-Tewordt (dashed line of Fig. 2) linear behavior at a reduced temperature, $t=T/T_c$, of about 0.85; and at $t=0.99$ the magnetic field range of sheath superconductivity has dropped by a factor of 2.

These are enormous changes, far outside experimental error. As shown in Fig. 1, the depression of H_{c3}/H_{c2} is 10 times as big as the precision in defining H_{c3} and H_{c2}. In addition,

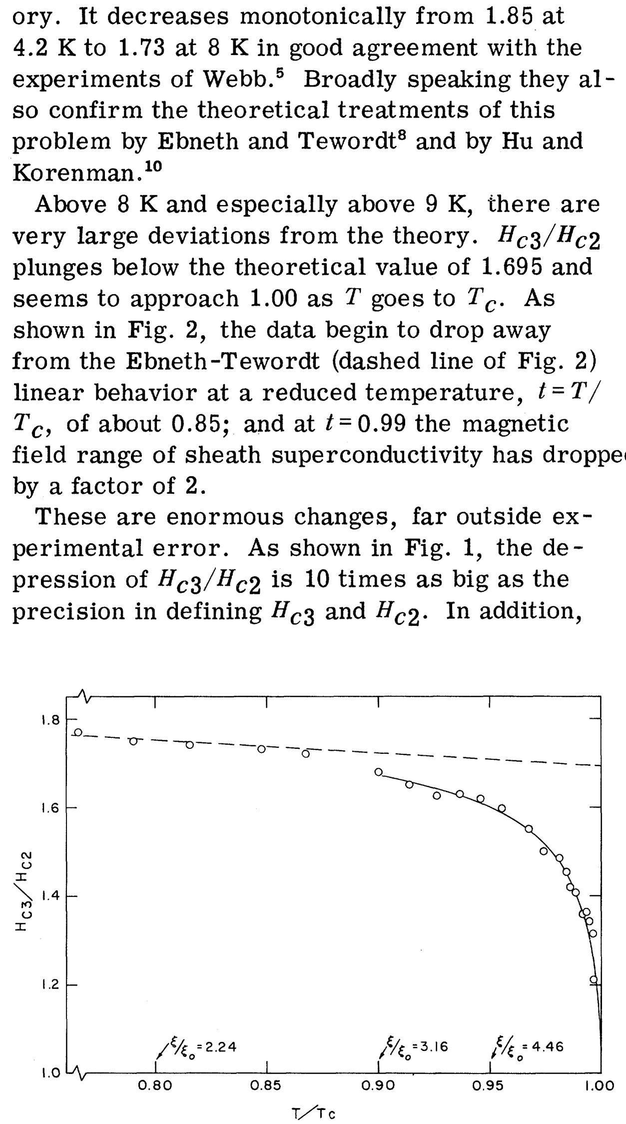

FIG. 2. The temperature dependence of H_{c3}/H_{c2} near T_c. The dashed line would be expected if the Ginsburg-Landau theory applies. The solid line is a fit with an equation of the form $\delta h=\alpha e^{-\beta\xi_0/\xi}$ where α and β are constants.

errors which might arise from the amplitude of the measuring field are negligible as long as the measuring field is 10^3 times smaller than H_{c2}. To check for errors due to misalignment of the magnetic field relative to the sample surface, the orientation of the field was systematically varied by applying a small field perpendicular to the main field. χ' was then mapped for the solid angle within 2 deg of the main field direction. The magnitude of χ' was sensitive to field direction but the values of H_{c3} and H_{c2} did not change within experimental error. This result was to be expected for these small angles from earlier measurements of the angular dependence at lower temperatures.[3,4] As a further check on the validity of these results, two different Nb samples have been studied in this temperature range and they both show the same behavior.

At present there is no theory to describe these results so it may be helpful to discuss some of the relevant parameters. Deviations from the molecular-field theories begin at temperatures where the coherence distance ξ, and the penetration depth λ, are rapidly increasing. For example the ratio of ξ to its value ξ_0 at $T=0$ increases from 2.2 to 4.5 in the range from $t=0.80$ to $t=0.95$ as shown in Fig. 2. In this region the extent of the superconducting wave function becomes large and the available free energy is spread over a correspondingly larger volume. This effect then would cause the free-energy density to vary as ξ^{-1}. Within the Ginsburg-Landau theory $\xi=\xi_0\epsilon^{-1/2}$, where $\epsilon=(T_c-T)/T_c$, so one might expect the free energy per unit volume to be proportional to $\epsilon^{+1/2}$. If, in addition, the probability that the a region of the surface fluctuates into the normal state is exponential in the free-energy difference per unit volume, then deviations from the molecular-field model, δh, would be of the form

$$\delta h=\alpha e^{-\beta\sqrt{\epsilon}}, \qquad (1)$$

where α and β are constants. In terms of our data, δh is taken to be the difference between the dashed line of Fig. 2 which is expected from molecular field theory and the measured value of H_{c3}/H_{c2}. A least-squares fit of Eq. (1) to our data above $t=0.9$ gives $\delta h=0.686e^{-8.20\sqrt{\epsilon}}$. This expression, shown by the solid line of Fig. 2, fits the data rather well and interestingly enough it extrapolates to very close to $H_{c3}/H_{c2}=1$ at T_c. The difference between $\alpha=0.686$ and $\alpha=0.695$ is easily within experimental error. All the reasoning leading to Eq. (1) may not be correct, or may not apply, but the fact remains that this expression describes the data better than any other simple expression we can find.

The data can also be fitted with the usual critical-phenomenon expression

$$\ln\epsilon = \ln a + b\,\delta h, \qquad (2)$$

where a and b are constants. This type of analysis gives $a = 0.15$ and $b = 8.9$. The fit with Eq. (2) is not quite as good as Eq. (1) at small values of ϵ but it is certainly not to be ruled out.

There is no doubt that these samples show large deviations from the Saint James–de Gennes[2] or Ebneth-Tewordt[8] theories very close to T_c. In view of the great success of these theories at lower temperatures it seems most likely to us that the deviations are caused by critical phenomena[11] but, of course, this is not the only possible conclusion. The task now is to investigate the generality of the effect.

J. R. Clem, S. H. Liu, and C. A. Swenson have made important contributions to this work.

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JAHN-TELLER EFFECT IN THE Γ EXCITON OF LiBr

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A previously unobserved splitting of the lowest exciton of LiBr is attributed to the exciton-phonon interaction in terms of a dynamical Jahn-Teller effect.

In this Letter we report on the optical properties of LiBr in the region of the lowest Γ-exciton peak, which appears as a doublet. Somewhat similar results have been obtained also for NaBr and NaI, but we confine the discussion to LiBr, because in the latter the splitting is better resolved. The data are shown in Fig. 1, which reports the imaginary part of the dielectric constant and the near-normal-incidence reflectivity at 55°K of a LiBr single crystal, cleaved in vacuum (about 5×10^{-7} Torr); the peak is clearly split into two components with a separation of 0.055 eV for ϵ_2 and 0.047 for R.

The features of the band structure which are relevant for the present experiment consist of a valence band associated essentially to the p states of the halogen ions, with a maximum at Γ_{15} split by spin-orbit interaction (Γ_6- and Γ_8-); the conduction-band minimum is at Γ_1 and the lowest exciton is associated to the $\Gamma_8- \to \Gamma_1$ edge. The experimental results in the literature are consistent with this picture,[1] but it appears that this purely electronic scheme is not sufficient to explain the structure shown in Fig. 1.

The spin-orbit splitting of the alkali bromides is about 0.5 eV and the binding energy is nearly the same[2]; these energies, confirmed also by two-photon absorption measurements,[3] are an order of magnitude higher than that of the observed splitting, and clearly rule out the attribution of the high-energy component of Fig. 1 to spin-orbit interaction, or to the envelope of the $n \geq 2$ members of the Wannier series. Furthermore, from the examination of the band structure calculations on the bromides,[4] on the basis of the magnitude involved and of the general trend of the energy bands, one can reject transitions either to other conduction-band minima, or from valence-band points other than Γ_8-. On the other hand, longitudinal-transverse splitting of the exciton, recently proposed,[5] seems hard to be supported in our case, since longitudinal ex-