known in molecular spectra.[15]) For Xe the energy gain due to molecular formation in the excited state has been estimated by Mulliken[16] to be 0.5 to 1.0 eV. The total binding energy of the metastable exciton in Xe, measured relative to its parent interband edges, is about 1.5 eV. It appears that about half the binding energy can be ascribed to Jahn-Teller formation of the molecular ion.

A complete analysis of the spectra[1,2] for Na, K, Rb, and Cs compounded with Cl, Br, and I as well as the spectra of Kr and Xe[3] will be given elsewhere.[17] I am grateful to S. Rice, M. H. Cohen, and R. Mulliken for stimulating discussions of the self-trapped exciton.

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*Work supported in part by the National Science Foundation.

†Alfred P. Sloan Fellow.

[1]J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. 116, 1099 (1959).

[2]H. R. Philipp and H. Ehrenreich, Phys. Rev. 131, 2016 (1963).

[3]G. Baldini, Phys. Rev. 128, 1562 (1962).

[4]J. C. Phillips, Phys. Rev. 125, 1931 (1962); 133, A452 (1964).

[5]J. C. Phillips, J. Phys. Chem. Solids 11, 226 (1959).

[6]M. H. Cohen and V. Heine, Phys. Rev. 122, 1821 (1961).

[7]A. W. Overhauser, Phys. Rev. 101, 1702 (1956).

[8]R. S. Knox and N. Inchauspé, Phys. Rev. 116, 1093 (1959).

[9]R. Hilsch and R. W. Pohl, Z. Physik 59, 812 (1930).

[10]J. C. Phillips, Phys. Rev. Letters 10, 329 (1963).

[11]M. Cardona and G. Harbeke, Phys. Rev. Letters 8, 90 (1962).

[12]E. A. Taft and H. R. Philipp, J. Phys. Chem. Solids 3, 1 (1959).

[13]D. L. Dexter, Nuovo Cimento, Suppl. 7, 252 (1958).

[14]T. G. Castner and W. Känzig, J. Phys. Chem. Solids 3, 178 (1957).

[15]G. Herzberg, Spectra of Diatomic Molecules (D. Van Nostrand and Company, Inc., Princeton, New Jersey, 1950), p. 394.

[16]R. S. Mulliken, quoted in O. Schnepp and K. Dressler, J. Chem. Phys. 33, 54 (1960); also (private communication).

[17]J. C. Phillips (to be published).

RESISTIVE TRANSITIONS AND SURFACE EFFECTS IN TYPE-II SUPERCONDUCTORS

C. F. Hempstead and Y. B. Kim
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received 23 December 1963)

We have been using sheet samples of type-II superconductors to investigate resistive transitions in the mixed state. When the external magnetic field is applied parallel to the sample surface, superconductivity in these materials persists far beyond Abrikosov's upper critical field H_{c2}. Recently, Saint-James and de Gennes[1] have shown by solving the Gor'kov-Landau equations with physical boundary conditions, that in parallel fields nucleation to a superconducting sheath will occur at the field $H_{c3} = 1.695 H_{c2}$. In this Letter we report our experimental results relevant to this theoretical calculation.

Measurements of longitudinal voltages (along the direction of J) on a well-annealed Nb-Ta sample are shown in Fig. 1. The external field H is provided by a Varian magnet rotatable around the vertical axis. When H is aligned parallel to the sample surface, a sharp transition takes place at $H = H_{c2}$, but partial superconductivity persists far beyond H_{c2}.[2] The angular dependence of the resistance is so sensitive that the $\theta = 0$ orientation is usually determined by measuring voltages as a function of θ with H set slightly above H_{c2}. For this particular sample orientation, J is parallel to the rolling direction (RD) of the sample and H becomes parallel to J at $\theta = 0$. Measurements have been made for $J \perp$ RD and/or $J \perp H$ at $\theta = 0$ to establish that the observed phenomenon is essentially a surface effect. Because of this, the resistance above H_{c2} depends strongly on the measuring currents, as is shown by plotting R/R_N for various currents at the $\theta = 0$ orientation. As the current is decreased, the spike at H_{c2} diminishes in height and the return to the normal resistivity takes place more gradually. This behavior is very similar to the remanent superconductivity observed in Ta wires (type-I superconductor) by Seraphim and Connell[3] and by Budnick.[4] The residual superconductivity beyond H_{c2} has been observed in Nb wires by Autler, Rosenblum, and Gooen[5] and in Pb-In wires by Druyvesteyn,

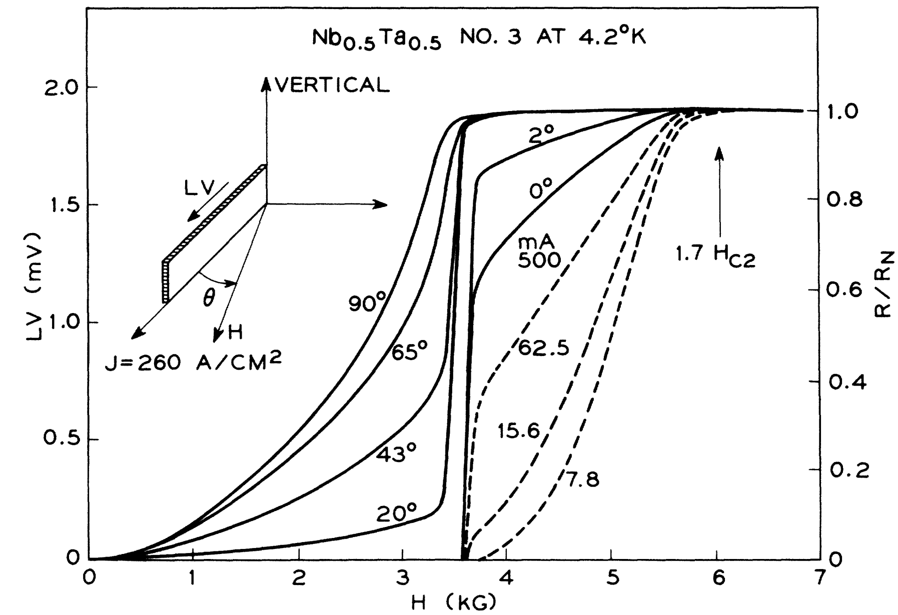

FIG. 1. Resistive transitions observed in Nb-Ta sheet. The sample is 1.5 cm × 0.25 cm and 7.6×10^{-3} cm thick. The solid curves are the voltage readings taken at a fixed current ($I = 500$ mA; $J = 260$ A/cm^2) and for different θ's. The dashed curves are the voltage readings (reduced to R/R_N) taken at $\theta = 0°$ and for different measuring currents. At 4.2°K, $H_{c2} = 3.55$ kG for this sample. The theoretical value of $H_{c3} = 1.7H_{c2}$ is indicated by the arrow.

Van Ooijen, and Berben.[6] The latter authors introduced the notation H_{c3}. The present investigation, however, establishes that this phenomenon is basically a surface effect.

In the theoretical calculation of Saint-James and de Gennes, the Ginzburg-Landau equation for the wave function Ψ is solved in the presence of a plane boundary between the superconductor and an insulator. For H parallel to the surface so that $A_x = A_z = 0$, $A_y = Hx$, the boundary condition

$$\{[-i\hbar\partial/\partial x - (2e/c)A_x]\Psi\}_{x=0} = 0,$$

$$\text{or } [\partial\Psi/\partial x]_{x=0} = 0 \qquad (1)$$

allows a solution whose eigenvalue is lower than the usual Abrikosov solution at $H = H_{c2}$. As a consequence, for $H_{c2} < H < H_{c3} = 1.695H_{c2}$, there will be a superconducting sheath near the sample surface. For H perpendicular to the surface, the solution reduces to that of Abrikosov and no remanent superconductivity is expected beyond H_{c2}. These conclusions are well supported by the experimental results shown in Fig. 1. The experimental determination of H_{c3} is, however, somewhat uncertain because R/R_N approaches unity very gradually. If we take as H_{c3} that field at which $R/R_N = 0.99$, we obtain $H_{c3}/H_{c2} = 1.52$ for $J = 260$ A/cm^2, the largest current shown in Fig. 1. The value of H_{c3}/H_{c2} gradually increases for decreasing current and reaches 1.71 for $J = 4.06$ A/cm^2. Although the value of H_{c3}/H_{c2} varies slightly from one sample to another depending on the amount of residual defects, it is found to be insensitive to the temperature down to $T/T_c \simeq 0.2$ for both Nb-Ta and Pb-In alloys. This is to be expected since the theoretical ratio H_{c3}/H_{c2} is temperature independent. There are some doubts, however, whether the Ginzburg-Landau equation itself is valid at low temperatures. We also observe that H_{c3} is much less sensitive to the angle θ than is the resistive behavior itself.

The boundary condition (1) is applicable only when the superconductor is bounded by an insulator, and the theory anticipates quite a different result if the surface is coated with a normal metal. To check this point, we measured several Pb-In samples, some with copper coating on the surface, and others without. In Fig. 2 we show typical data representing the two cases. Clearly, the copper coating does not affect H_{c2} but reduces H_{c3} significantly. For the copper-coated Pb-In, the parallel resistances of copper and Pb-In are measured experimentally. Since R_N for Pb-In and the resistance of the copper (which is essentially independent of H at such low field strengths) are known, the resistance of the Pb-In alone can readily be calculated at any field. This refinement, however, hardly changes the value H_{c3}/H_{c2}

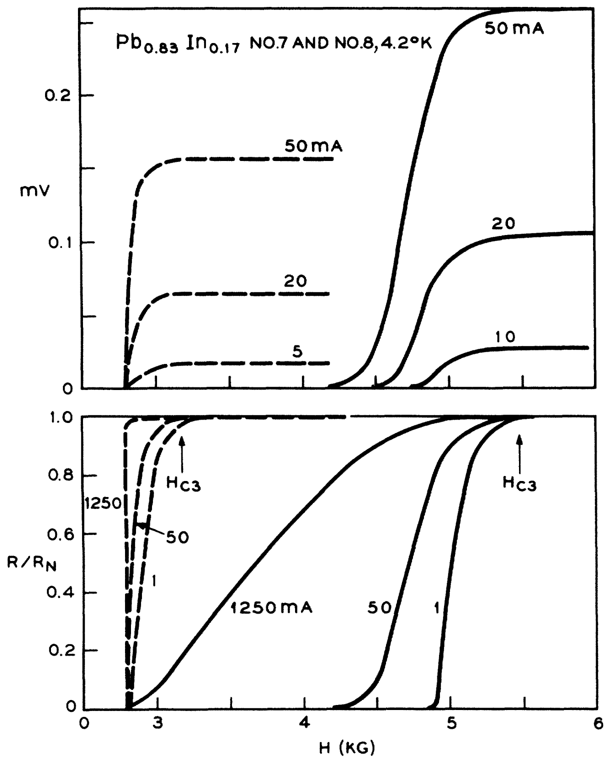

FIG. 2. Resistive transitions observed in Pb-In sheets. $\theta = 0°$ for all measurements. The solid curves were obtained with a Pb-In sheet (1.5 cm $\times$0.25 cm and 11×10^{-3} cm thick). $H_{c2} = 2.8$ kG and $H_{c3} = 5.5$ kG $= 1.96 H_{c2}$ for this sample. This high value of H_{c3} is probably due to residual defects in the sample. The dashed curves were obtained with another Pb-In sheet, identical to the previous, but coated with copper of 1.2×10^{-4} cm thick. No change in H_{c2} for this sample, but H_{c3} is lowered to 3.18 kG.

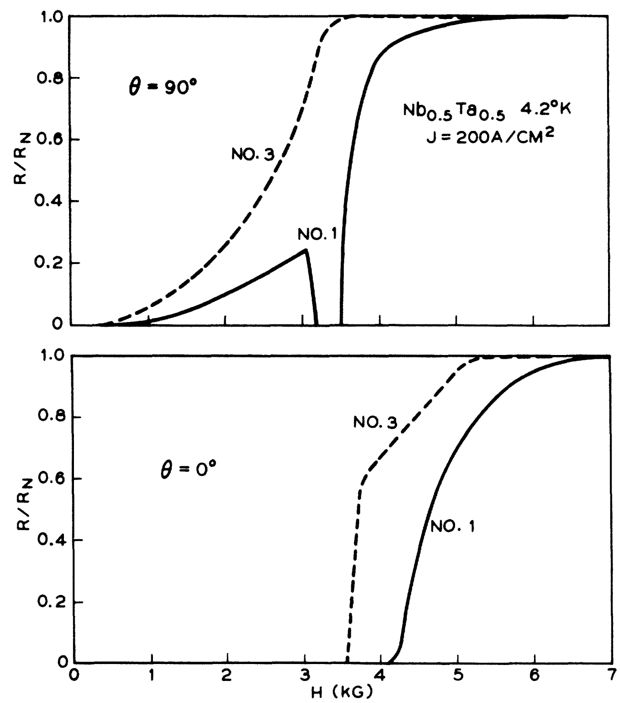

FIG. 3. Resistive transitions observed in Nb-Ta sheets. Sheet No. 3 is the same sample as shown in Fig. 1. Sheet No. 1 is identical to No. 3, but no annealing was applied to this sample.

$= 1.15$ already obtained. This ratio remains unchanged down to $T/T_c \simeq 0.2$. Samples coated with other normal metals are now being investigated.

Our measurements on defect-loaded samples will be mentioned briefly here. By defects, we simply mean flaws of various sorts present in the crystal structrue of a metal. Defects, in general, do not affect the H_{c2} value of a specimen. As the amount of defects increases, however, H_{c3} tends to shift toward higher fields and the distinction between the parallel and perpendicular field orientations becomes less significant. To illustrate this tendency in the Nb-Ta sample of Fig. 1, which is about as defect-free as we could make it by simple annealing, we show in Fig. 3 the resistive behavior of a cold-rolled Nb-Ta sample. For the perpendicular field orientation the peak effect (or the resistance drop) takes place near H_{c2}, but in the parallel field orientation H_{c2} is no longer identifiable and superconductivity persists up to much higher fields. This trend is in the proper direction if defects are assumed to participate in the nucleation process, as has been suggested by Saint-James and de Gennes. This idea of nucleation by defects is quite attractive in that remanent superconductivity beyond the critical fields (H_c for type-I and H_{c2} for type-II superconductors) need not rely on the filament model originating from the Mendelssohn sponge, for which no basic theory has yet been provided.

The resistive behavior below H_{c2} can be adequately explained in terms of the flux-flow process[7] caused by the Lorentz force $\vec{\alpha} = \vec{J} \times \vec{H}$. For the data of Fig. 1 the Lorentz force is proportional to $H \sin\theta$, and at a given voltage level we do observe $H \sin\theta$ to be the same (see Table I). In the flux-flow state, each flux line experiences the Lorentz force $F = J\varphi_0/c$ per unit length and attains an equilibrium velocity

$$v = \eta F = (\eta\varphi_0/c)J, \tag{2}$$

where φ_0 is the flux unit $hc/2e$ and $\eta(H, T)$ is the inverse of a viscosity coefficient. This flow of

Table I. Values of Lorentz force parameter. The values of H and $H\sin\theta$, in kG, are shown for $V=0.1$ and 0.5 mV of Fig. 1.

	$V=0.1$ mV		$V=0.5$ mV	
θ	H	$H\sin\theta$	H	$H\sin\theta$
90°	0.80	0.80	1.94	1.94
65°	0.84	0.76	2.15	1.94
43°	1.17	0.80	2.84	1.94
20°	2.34	0.80	⋯	⋯

flux lines induces an emf

$$V=Hv/c=(\eta\varphi_0/c^2)JH, \tag{3}$$

which is linear in $\alpha=JH$. Because of the field dependence of η, V is not linear under the H variation (see Fig. 1). When J is varied at a fixed H, however, we do observe a linear dependence of V on J as expected from (3). At very small values of α the sample exhibits the flux-creep behavior, probably because of flux pinning by residual defects. Further studies are under way to determine if the resitive behavior between H_{c2} and H_{c3} can be explained by the superconducting sheath model.

We are indebted to A. R. Strnad for his collaboration in the experiments and to R. Epworth and J. Hasiak for their technical assistance. We are grateful to P. W. Anderson for his helpful discussions.

[1]D. Saint-James and P. G. de Gennes, Phys. Letters 7, 306 (1963).

[2]The values of H_{c2} obtained by resistance measurements are in agreement with those from magnetization measurements.

[3]D. P. Seraphim and R. A. Connell, Phys. Rev. 116, 606 (1959).

[4]J. I. Budnick, Phys. Rev. 119, 1578 (1960).

[5]S. H. Autler, E. S. Rosenblum, and K. H. Gooen, Phys. Rev. Letters 9, 489 (1962).

[6]W. F. Druyvesteyn, D. J. Van Ooijen, and T. J. Berben, Rev. Mod. Phys. 36, 58 (1964).

[7]Y. B. Kim, C. F. Hempstead, and A. R. Strnad, Phys. Rev. 131, 2486 (1963). More details on flux flow and flux creep are given in the papers by the present authors and by P. W. Anderson and Y. B. Kim, Rev. Mod. Phys. 36, 39 (1964).

EXPERIMENTAL EVIDENCE FOR A NEW SUPERCONDUCTING PHASE NUCLEATION FIELD IN TYPE-II SUPERCONDUCTORS*

W. J. Tomasch
Atomics International Division of North American Aviation, Incorporated, Canoga Park, California

and

A. S. Joseph
North American Aviation Science Center, Canoga Park, California
(Received 24 December 1963)

Utilizing a null-deflection torque magnetometer,[1,2] we have studied remnant superconductivity in thick films (4-10 μ) and bulk foils (51-127 μ) of Pb-Tl alloys in the field interval H_{c2} to $1.7\times H_{c2}$, where H_{c2} is the bulk upper critical field.[3] Measurements were made over the range 1.1-4.2°K on well-annealed homogeneous specimens of composition 4.2-10.0 at. % Tl. Our technique defines two critical fields H_l (longitudinal) and H_t (transverse) which mark, respectively, the cessation of superconductivity with the field applied parallel and perpendicular to the plane of the specimen. Numerically H_t correlates well with H_{c2}, the latter being deduced from the data of Bon Mardion, Goodman, and Lacaze.[4] Our results show that the ratio Hl/Ht is essentially constant, independent of composition, thickness, and temperature, hence implying a basic effect rather than one caused by specimen defects of various types. Recently Saint-James and de Gennes[5] have independently advanced a theory which predicts a new superconducting phase nucleation limit $H_{c3}>H_{c2}$ when H is applied parallel to the plane of a superconductor-vacuum interface. Furthermore, H_{c3}/H_{c2} is a calculable constant which they have evaluated numerically. Our observed values of H_l/H_t are in remarkable agreement with their theoretical value. The results of earlier tunneling studies[6] which prompted the present investigation are believed