luminescence has also been observed from the rough metal surfaces. The mechanism leading to such luminescence is not yet understood.

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Search for Vortex Unbinding in Two-Dimensional Superconductors

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The Kosterlitz-Thouless theory applied to two-dimensional superconducting films suggests that vortex unbinding can explain their gradual resistive transitions. An experiment which directly probes the dynamics of unbinding is reported. The results indicate that, if vortex unbinding does occur in our superconducting films, the dynamic theory overestimates the relaxation time by almost two orders of magnitude.

PACS numbers: 74.40.+k, 64.60.Cn, 73.60.Ka

Phase transitions in two-dimensional (2D) systems are important because of their marginal dimensionality and have received considerable attention recently.[1] The Kosterlitz-Thouless (KT) prediction of a dislocation unbinding transition has been discussed in several systems including vortex unbinding in superconductors.[2-4] Experimentally, 2D superconducting systems are particularly interesting because of the ease with which one can make measurements.[5-7] Unfortunately, the subtle effects of the KT transition are difficult to distinguish unambiguously from effects due to inhomogeneity, and since the very thin samples used are known to be inhomogeneous,[7] direct evidence of vortex unbinding is necessary.

The dynamics of vortex unbinding provides such a characteristic fingerprint. However, experimental results reported in this Letter show no evidence for vortex unbinding in samples whose homogeneity is unquestionably improved over that of others.[6,7] These negative results will be discussed within the context of theoretical models.

The KT theory applied to superconductors[2-4]

predicts that bound vortex pairs will dissociate into free vortices above the transition temperature T_{KT} and give rise to resistance due to flux flow. As T increases above T_{KT}, so does the areal number density of free vortices n_f, and a dynamic equilibrium is established between the bound vortex pairs and the free vortices. The resistance per square $R_\square$, is given by[4] $2\pi R_\square^N n_f \times \xi^2(T)$, where $\xi(T)$ is the temperature-dependent Ginzburg-Landau (GL) coherence length referred to the superconducting transition temperature T_{c0}, and $R_\square^N$ is the normal-state resistance per square. Since $\xi(T)$ varies relatively slowly for $T - T_{KT} \ll T_{c0} - T_{KT}$, $R_\square^N$ effectively measures n_f.

A nonequilibrium excess population δn_f will decay by binary recombination into pairs at a rate proportional to n_f, as in the case of quasiparticles and Cooper pairs in ordinary superconductors,[8] providing $\delta n_f \ll n_f$. The free vortices move by diffusion with a flux flow mobility μ, and the time to diffuse a distance b is given by $b^2/\mu kT$. Because of their finite size, the distance through which free vortices must diffuse before recombination is less than their average spacing, $(n_f)^{-1/2}$, and so the calculated[4] recombination time τ is $(8\pi\mu kTn_f)^{-1}$. By using the theoretical expression[9] for $\mu = (2e^2/\pi\hbar^2)\xi^2(T)R_\square^N$, the recombination time can be written as $\tau(\mathrm{ns})T(\mathrm{K})R_\square(\Omega/\mathrm{sq}) = 12.6$. Note that the strong temperature dependence of $R_\square$ (see Fig. 1) dominates the temperature dependence of τ, and that ξ^2 cancels out in the final expression for τ. For typical samples of granular aluminum (gAl), $T \sim T_{KT} \sim 2$ K, so that a resistance of 1 $\Omega/\square$ results in an experimentally measurable time of about 6 ns.

In the experiment, δn_f is created by a light pulse, and the resulting $\delta R_\square(T, t)$ is measured as a voltage pulse with the current held constant. If $\delta R_\square \ll R_\square$, the measured decay time τ is predicted to be inversely proportional to $R_\square(T)$ or $n_f(T)$.

A GaAs injection laser provides the light pulse which is coupled to the sample with fiber optics to reduce pickup.[10] Signal averaging results in an experimental resolution of ~1 μV and 2 ns. The voltage resolution is important because the linear region of the current-voltage characteristics $I(V)$, at temperatures for which τ is long enough to measure, is of order 1 μA. Therefore, resistances of several ohms are required to keep $\delta R_\square \ll R_\square(T)$, and samples containing many squares are necessary in order to also have sufficient time resolution. Samples are made by photoetching a meander path containing about 50 squares.

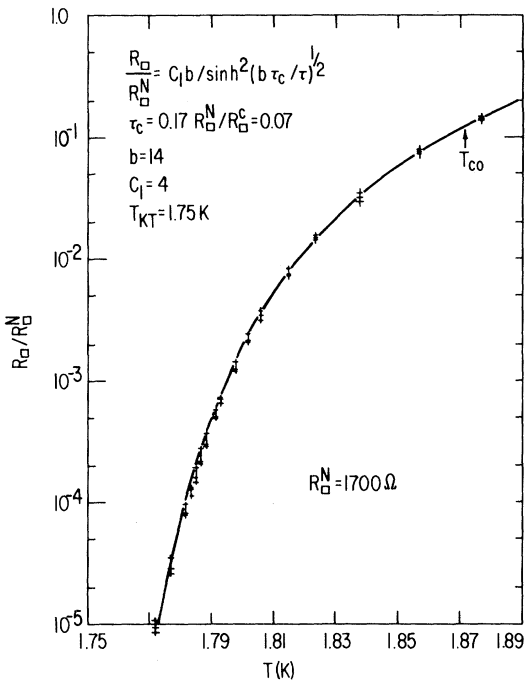

FIG. 1. The resistive transition of a sample of granular aluminum on freshly cleaved mica. The data are for four separate sections of a meander path and agree within 30% at reduced resistances of 10^{-5}. The solid curve is the theoretical dependence (Ref. 4) for the parameters shown (see text).

The legs of the path are 250 μm wide and the pattern is contained on a 2-mm^2 square to provide uniform illumination from the fiber optics. The ambient magnetic field was reduced to a few milligauss by a graded triple Mu-metal shield, which is degaussed before each helium transfer.

Sample homogeneity is crucial to this experiment, and all attempts to make gAl on glass substrates failed.[7] However, freshly cleaved mica substrates provided very homogeneous samples (thickness 150 ± 30 Å) in which the resistive transitions of four sections of the meander path (shown in Fig. 1) are within 30% at a reduced resistance of 10^{-5}. Although this data, and others on mica, can be fitted by the KT prediction,[4] there are three adjustable parameters which cannot be determined independently. With use of the theoretical expression[2] relating T_{c0}/T_{KT} to $R_\square^N$, the parameters which should be universal vary by at least a factor of 3 for gAl films and up to a factor of 10 for NbN films on sapphire substrates. Therefore, the fit is of dubious value.

The decay times measured for these very homogeneous samples do not show the strong variation with temperature predicted by the dynamic theo-

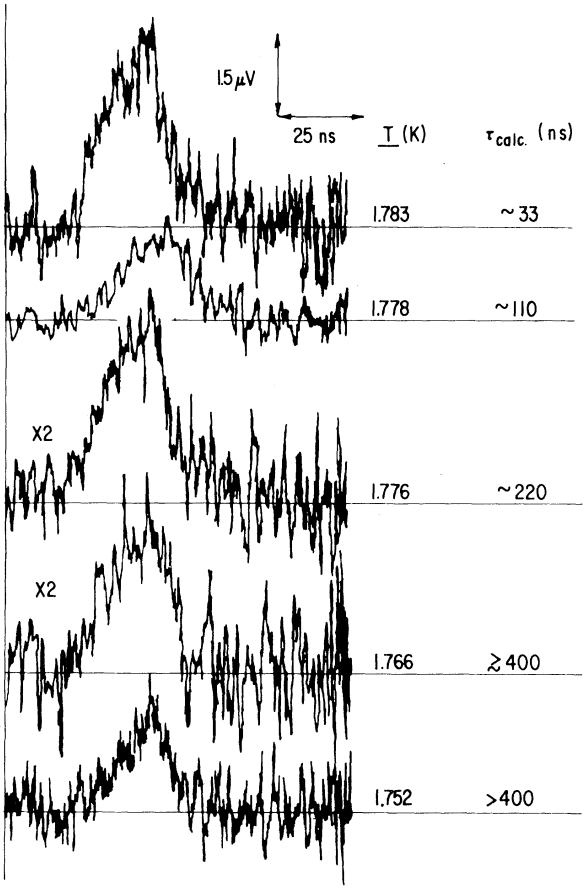

FIG. 2. The response of the voltage across the sample of Fig. 1 at a constant current bias. The 25-ns light pulse begins at the same time as the voltage increase. The temperatures and theoretical decay times (Ref. 4) are also shown.

ry, but rather are independent of temperature (or $R_\square$). A particular set of results are shown in Fig. 2 in which the measured τ is always 10–12 ns whereas the predicted values exceed 400 ns. Presumably what is measured is the thermal time constant of the boundary between the film and helium, since one calculates about 6 ns for this time if the substrate is ignored. Care was exercised to ensure that (a) the light-pulse amplitude was small so that $\delta R_\square < 0.25 R_\square$; (b) the $I(V)$ was linear at the bias point; (c) all temperatures were measured from well above to below T_{KT}; and (d) pulse lengths were long enough for the free vortices to move more than their mean separation by flux flow.

This last point is particularly important. If the free vortices created by the laser do not move sufficiently far from each other during the pulse, they may recombine more quickly than the theoretical prediction. This could occur if the laser pulse is too short or if there exists a large number of pinning sites. Since pinned vortices do not move, they play no role in the measured signal, and it is only necessary to ensure that each free vortice moves by flux flow a distance equal to the average free vortex spacing at that temperature. Then they should be uncorrelated and the above calculation is valid. If the flux flow velocity is determined by using the measured value for μ (see below), then the longest time to become uncorrelated is about 1 μs (corresponding to the longest expected decay time). This time is even shorter if the theoretical expression[9] for μ is used, or for shorter decay times. However, experiments using pulses up to 3 μs long showed the same decay time as with the shorter pulses shown in Fig. 2. In addition, the voltage pulse was constant during the longer pulses, verifying that a steady-state nonequilibrium was achieved.

The conclusion of these experiments is that, if vortex unbinding does occur, then the dynamic theory[4] overestimates the relaxation time by almost two orders of magnitude. This is hard to imagine because of the simplicity of that calculation. Use of the theoretical value of μ could be questioned; however, direct determination of μ for our samples on mica indicate that it is about an order of magnitude *smaller* than the theoretical estimate.[9] This implies an even *longer predicted* recombination time, unless the source of the discrepancy is in $\xi(T)$ which cancels out in the final expression for τ. The dc flux flow resistance, R_{ff}, shown in Fig. 3, is linear in H and displays the correct divergence of μ, due to $\xi^2(T)$, right up to the temperature at which the broad resistive transition begins. These results extrapolate to a T_{c0} corresponding to a reduced resistance of 0.5; however, for the sample shown in Fig. 1, the extrapolation was to a lower reduced resistance. Hebard and Fiory[11] report a divergent μ for gAl on glass which extrapolates to the beginning of the broad resistive transition.

It is also possible that the simple dynamic theory outlined above is inadequate: For example, interactions of free vortices with bound vortices are neglected. If the density of bound vortices n_b exceeds n_f, then recombination may correspond to establishing a new set of pair correlations, thus avoiding free-vortex diffusion over large distances (~10 μm) with the resultant long τ. However, because of the short recorrelation time implied by this experiment, the concept of

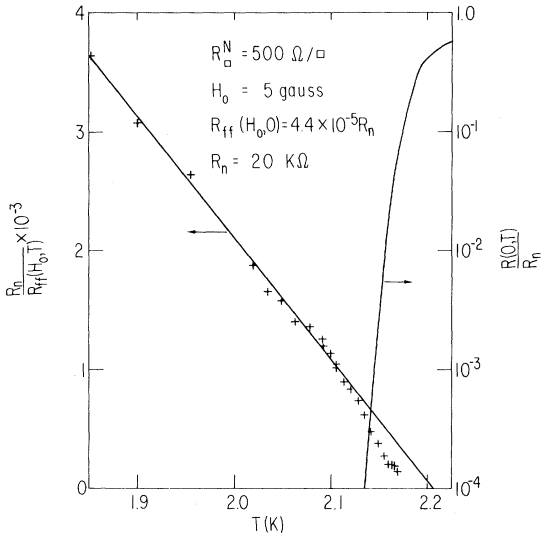

FIG. 3. The reciprocal of the flux flow resistance as a function of temperature, showing the expected linear dependence extrapolating to T_{c0}. The flux flow mobility μ is derived from this data, and is about an order of magnitude smaller than the value given by (Ref. 9) theory.

bound pairs unaffected by flux flow must be modified. "Bound" vortices would contribute to the flux flow voltage by reorientation and/or polarization followed by recorrelation. The resistive transition would *not* be related to vortex *unbinding* through $n_f(T)$, but would also strongly depend on $n_b(T)$. Current theories do not account for dynamic bound-pair–free-vortex interactions. Another proposed explanation involves recombination of free vortices with a high density n_p of pinned, but unbound, antivortices. However, our measured values of μ and τ would imply $n_p \gtrsim 1000 n_f$ at $T \sim 1.772$ K. In this case, the resistive transition would certainly be dominated by *depinning* and not unbinding. Finally, recent noise measurements[12] indicate that the mean free path of unpaired vortices is 2–8 μm, independent of T. This result is in conflict with either of the above explanations based on fast interactions with bound pairs or strong pinning.

A more likely conclusion of this experiment, in our opinion, is that vortex unbinding is not responsible for the resistive transition. Recently the authors have shown[7] that the dependence of T_c on the normal-state resistance $R_\square^N$ is in much better agreement with a Josephson-coupling model of *independent* junctions rather than with the KT theory. A collection of Josephson junctions reduces to an x-y model (and hence might be expected to show KT unbinding) only for an array of sufficiently uniform junctions. Because of the high sensitivity of junction resistance to intergrain oxide thickness, this is unlikely even for our samples, which are very homogeneous on a much larger length scale.

Returning to the unbinding model, agreement of the frequency dependence with the dynamic theory[6,11] is used as evidence for the KT unbinding transition in gAl films on glass substrates. However, it is pointed out in Ref. 7 that this frequency dependence can be understood qualitatively by the measured[13] frequency dependence of the loss of phase coherence across a discrete Josephson junction.

In summary, direct experiments such as the above must be performed on better, well-characterized samples before the existence of vortex unbinding can be definitely concluded in 2D superconducting films.

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Rotationally Inelastic Gas-Surface Scattering Investigated by Laser-Induced Fluorescence

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Variations of the rotational energy distributions of NO molecules scattered at a Pt(111) surface have been determined by means of laser-induced fluorescence. Scattering of a rotationally cold (32 K) supersonic molecular beam at a NO-covered surface results in full rotational accommodation due to trapping/desorption. No Boltzmann distribution of the rotational energies is observed if the molecules are directly (specularly) scattered at a graphitic overlayer.

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A complete description of the dynamics of the interactions between gaseous molecules and solid surfaces includes the transition probabilities between the various quantum states. Measurements of angular and velocity distributions in molecular-beam experiments provide this kind of information with respect to the translational motion. These techniques could also be used to identify indirectly variations of the rotational state in scattering of H_2 at surfaces of ionic crystals.[1-3]

Separation of energy accommodation coefficients into contributions arising from translational and internal excitations[4] provides another qualitative approach to this problem.[5-7] What would be needed, of course, is an analysis of the population of the internal (vibrational plus rotational) states of the molecules before striking and after leaving the surface. To our knowledge, so far only the second part of this task has been tackled in two studies applying the technique of electron-beam–induced fluorescence[8]: Ramesh and Marsden determined the rotational accommodation coefficient for N_2 on various metal surfaces,[6] and Thorman, Anderson, and Bernasek[9] reported on the vibrational-energy distributions of N_2 molecules formed by recombination of N atoms at an Fe surface. Whereas this technique has so far been restricted to N_2 molecules, the method of laser-induced fluorescence (LIF)[10] offers a much wider range of applications and has also recently been successfully used to study rotationally inelastic scattering in homogeneous gas phase.[11,12] We report here on the first application of this technique concerning the determination of the variation of internal-energy distribution in gas/solid scattering. The sensitivity in the present configuration allows detection of less than 10^7 molecules per cubic centimeter per state.

The experimental arrangement is reproduced schematically in Fig. 1. A supersonic beam of NO molecules is formed in a bakable beam-gen-

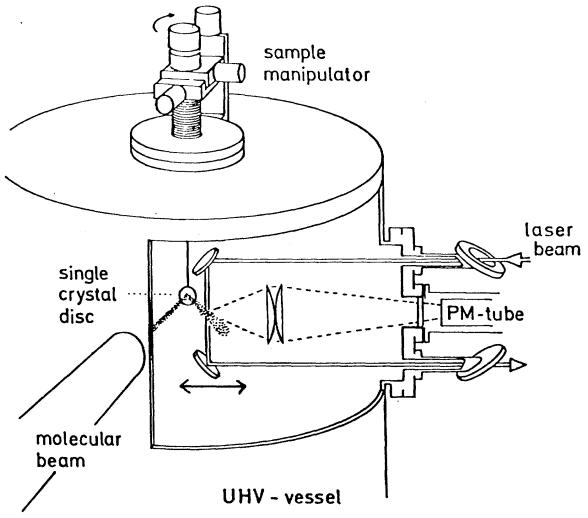

FIG. 1. Experimental arrangement (schematic).

