Quantum liquid of vortices in the quasi-two-dimensional organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

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(Received 25 November 1997)

We present magnetic torque measurements on the quasi-two-dimensional organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ at low temperature $T/T_c \simeq 0.01$. The irreversible field $H_{\rm irr}$ lies far below the upper critical field H_{c2} even at $T \simeq 0$. In the magnetic field region, $H_{\rm irr} \leqslant H \leqslant H_{c2}$, a vortex liquid state exists even at $T \simeq 0$, resulting from the quantum fluctuations instead of the contribution of the thermal one at higher temperature. This finding is explained as the quantum vortex liquid state driven by the quantum fluctuations from the different theoretical models. In the liquid state, de Haas–van Alphen oscillations are observed, and H_{c2} is defined by the appearance of the additional damping on the oscillation amplitude. [S0163-1829(98)11017-2]

Vortices in the layered superconductor (i.e., high-T_c superconducting oxide, organic superconductor) have strong thermal fluctuations, which have been extensively studied experimentally and theoretically.[1]

The material parameters of the superconductors, implying their short coherence length and large anisotropy of the effective mass, enhance the importance of the fluctuation effect on the phenomena such as the vortex melting or the giant creep.[2] At low enough temperatures, vortices are also expected to be affected by quantum fluctuations. The observation of a strong magnetic relaxation at very low temperature has demonstrated the quantum effects. The importance of quantum fluctuations on the melting of the vortex lattice has been studied in the high-T_c oxide superconductors.[1,3–8] The favorable material parameters for the experimental observation of a quantum melting transition involve a large normal-state resistivity, a moderate upper critical field $H_{c2}(0)$ at zero temperature, and a small length scale s for the fluctuations (i.e., short coherence length or short layer separation). The BEDT-TTF molecule based organic superconductors are good candidates for the observation of this effect. In this paper, we show that a quantum vortex liquid state appears on the organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, where BEDT-TTF denotes bis(ethylenedithio)tetrathiafulvalene. The liquid state is observed widely below $H_{c2}(T)$ even at a very low temperature $T/T_c \simeq 0.01$, which has been predicted by some theories[3–7] and simulations using quantum Monte Carlo techniques.[8] The de Haas–van Alphen (dHvA) oscillation is also observed in the quantum vortex liquid state with shorter scattering time than that in the normal state.

There have been several studies on the vortex states of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. The anisotropy of the effective mass $\gamma \equiv \sqrt{m_\perp/m_\parallel}$ was estimated to be $\sim$ 200.[9,10] A dimensional crossover phenomenon between the three-dimensional (3D)-flux-line-lattice and the 2D-vortex pancake structures was observed around the crossover field B_{2D} ($\sim$0.01 T) as the second peak effect on the magnetization[11] and was confirmed by muon spin rotation measurements,[12] which revealed the change of the internal field distribution. Josephson plasma mode was observed in the microwave surface resistance below T_c.[13] These observations resemble some of the high-T_c compounds such as $Bi_2Sr_2CaCu_2O_8$. A moderate $H_{c2}(0)$ ($\simeq$6 T) in the magnetic field normal to the two-dimensional plane can be exceeded by using standard superconducting magnets. This implies that the organic superconductors have a good potential for general studies on the vortex matter.

High-quality single crystals of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ were grown by an electrochemical oxidation method. The crystals have platelet shape, and the weight of a piece of the crystal used in the present study was 0.85 mg for sample 1 and 0.79 mg for sample 2. Magnetic torque measurements were performed by using a precision capacitance torque meter. The torque meter had an improved thermal contact to the sample in comparison with the previous one.[14] The capacitance was measured by the auto precision capacitance bridge (Andeen-Hagerling, AH2500A). The torque meter with sample was cooled down to 0.46 K (sample 1) and 0.12 K (sample 2) during the sweep of the magnetic field by using ^{3}He and ^{3}He-^{4}He dilution refrigerator, respectively. Temperature was monitored by a calibrated ruthenium-oxide thermometer.

Figure 1(a) shows the magnetic torque curves for sample 2 at various temperatures below 1 K. The sample is tilted about $\theta = 1°$, where θ is the angle between the magnetic field and a direction normal to the b-c plane. The torque curves show the hysteresis against the up and down sweep of the

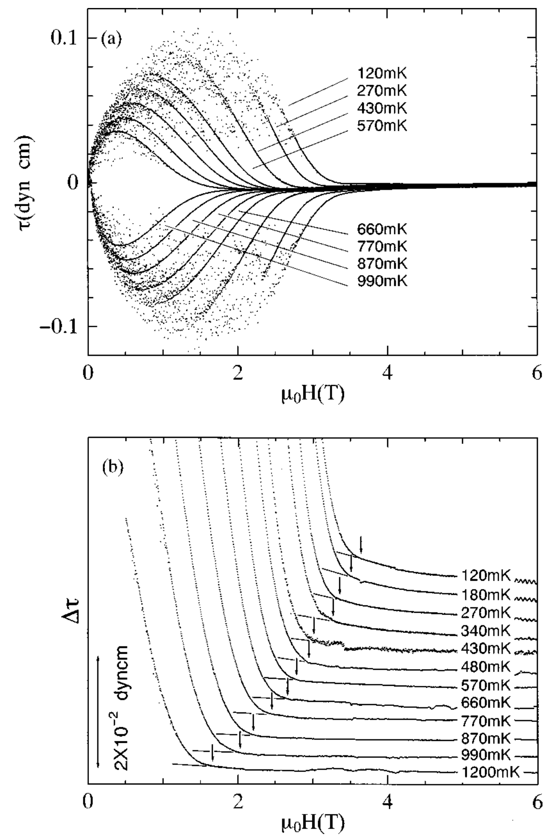

FIG. 1. (a) Magnetic torque curves of the sample 2 below 1 K in the magnetic-field direction $\theta = 1°$. (b) Amplitude of the hysteresis, $\Delta\tau \equiv \tau$ (down sweep)$- \tau$ (up sweep), as a function of the magnetic field. The curves are shifted by 4×10^{-3} dyn cm each. The irreversible field H_{irr} is indicated by the arrows.

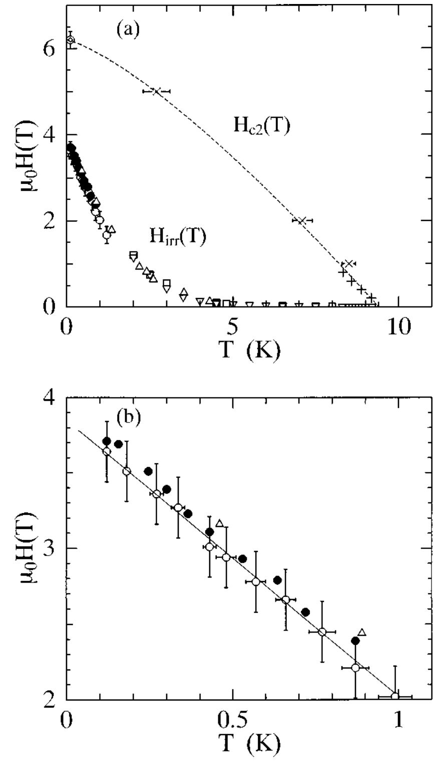

FIG. 2. Temperature dependence of the irreversible field H_{irr} and the upper critical field H_{c2}, (a) the whole *H-T* diagram, (b) the expanded view in the low-temperature region. The symbols are referred to in the text. The dashed curve and the solid straight line are guides for the eye.

magnetic field. It is noted that the torque becomes zero at $H=0$, where the remanent magnetization remains still finite, simply because the torque is expressed as $\tau = \boldsymbol{M} \times \boldsymbol{H}$. The amplitude of the hysteresis becomes large with decreasing the temperature, and the irreversible field H_{irr} simultaneously shifts to larger magnetic field. A remarkable large scattering of the magnetic torque appears in the irreversible part of the curves below about 500 mK. The instability is not due to the extrinsic origin of the torque meter we used. The same type of the torque meters have not shown such instability even in detecting larger magnitude of the torque at higher magnetic field or larger tilt angle.[14] The scattering always occurs inside the envelope curve of the torque. It means that the torque acts on the sample toward the stable direction. Thus the scattering may result from the flux jumps in the sample, which have a tendency to take place effectively at low temperature. This phenomenon at low temperature may have a close relation to the quantum creep of the vortices,[2] but the detail has not been investigated yet.

Let us return to the field region around H_{irr}. First, no visible discontinuity of the magnetic torque is observed around H_{irr}, which will remind us of a first-order phase transition such as the vortex melting. There are recent findings of a discontinuous step of the magnetization in the similar type of the organic superconductor, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br,[15] which is concluded to be an evidence of the vortex melting. No direct experimental observation on the present organic superconductor suggesting the melting phenomena has been reported yet. The reason is not clear, but it may relate to different material parameters in these two compounds. The anisotropy γ of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ is about two times larger than that of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br,[16] and the mean-free path of the former, indicating the quality of the sample, is almost one order longer than that of the latter.[17]

The irreversible field H_{irr} is determined by the onset of the increase of a quantity $\Delta\tau \equiv \tau$ (down-sweep)$- \tau$ (up-sweep), as indicated in Fig. 1(b). The criterion for the onset is about 1% of the maximum amplitude of the hysteresis. This definition has an ambiguity to some extent, but it does not exceed the error bar of ± 0.2 T, which is shown in the following phase diagram.

Figures 2(a) and 2(b) show the irreversible field H_{irr} and the mean field upper critical field H_{c2} as a function of temperature. The meaning of the symbols are following: the open squares and the reverse triangles for the superconducting quantum interference device (SQUID) data in Ref. 18 and Ref. 11, the triangles for the torque data on the sample 1 at $\theta = 4°$, and the open and filled circles for the data on the sample 2 at $\theta = 1°$ and 5°, respectively. The crosses and the plus are determined by the fluctuation analysis on the magnetization using a scaling-low[18] and by taking the mean-field value of the specific-heat measurements.[19] The point of the double circle is determined by the dHvA effect described later. The present H_{irr} values above 2 K are in good agreement with the previous SQUID measurements. The temperature dependence of H_{irr} below 1 K is almost linear in T, which is evidenced in Fig. 2(b) in the expanded linear scale.

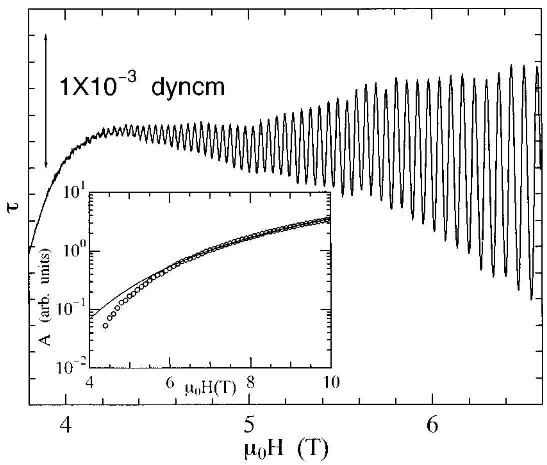

FIG. 3. de Haas–van Alphen oscillation in the normal state above 6 T and in the vortex state below 6 T. The inset shows the magnetic-field dependence of the oscillation amplitude. The clear deviation from the Lifshitz-Kosevich formula (solid curve) is seen below 6 T, which results from the additional scattering for the quasiparticle in the vortex state.

Neither saturation nor further upturn is seen down to the lowest temperature 0.12 K. This T-linear dependence is much different from either a power law $H_{\rm irr}\propto(1-T/T_c)^n$ with $n\sim 2$ in the 3D vortex line lattice region below the crossover field B_{2D}, or an exponential of $1/T$ like $H_{\rm irr}\propto\exp(a/T)$ in the 2D vortex pancake region above B_{2D},[11] both of which are based on the Lindemann-type melting scenario driven by the thermal fluctuations. The observed T-linear dependence is connected smoothly to the exponential dependence in the 2D vortex pancake region.[11] At lower temperature, the quantum vortex fluctuation should become dominant in place of the thermal one. Therefore, the downward shift of $H_{\rm irr}$ from $H_{\rm irr}\propto\exp(a/T)$ to $H_{\rm irr}\propto T$ at low temperature is considered to be a demonstration of the influence of the quantum vortex fluctuation. In addition, it must be noted that the extrapolation of the T-linear dependence to lower temperature points to the field 3.8 T at $T=0$. This means that a finite vortex liquid state exists between $H_{c2}(0)$ and $H_{\rm irr}(0)$ even at $T=0$. In order to confirm this point, it is important to show how to define H_{c2} at the lowest temperature, indicated as the double circle in Fig. 2(a).

Figure 3 shows the dHvA oscillations on the magnetic torque curve of sample 2 ($\theta=1°$) at 0.12 K. Clear oscillations are visible above about 4 T. The dHvA frequency of 597 ± 2 T is in very good agreement with previous reports.[20] The effective mass m^* obtained by a fit of the temperature dependence of the dHvA oscillation to the Lifshitz-Kosevich (LK) formula[21] is $(3.5\pm0.2)m_e$ at 6.2 T and higher magnetic fields, and $(3.5\pm0.4)m_e$ at 4.4 T. Within the experimental error, no magnetic field dependence of the effective mass is observed. The dHvA oscillation in the vortex state is known to have an additional damping of the oscillation amplitude as compared to the normal state.[22–25] The mechanism is still unclear and controversially discussed by some theories.[26–29] The inset of Fig. 3 shows the field dependence of the dHvA oscillation amplitude. The solid line is a fit curve of the LK formula with the effective mass of $3.5m_e$ to the high magnetic-field region. The fit is good above 6 T. The Dingle temperature $T_D\simeq 0.28$ K obtained there is in agreement with the reported one in the normal state.[20,25] A downward deviation from the fit curve is clearly seen below 6 T. This behavior is similar to a common feature observed in the vortex state of the 2D (Refs. 22 and 25) as well for the 3D superconductors.[23,24] The deviation starts at H_{c2} although the origin of the additional damping as is due to the quasiparticle scattering is not clear. Thus H_{c2} at the lowest temperature 0.12 K is determined as 6 T, which is indicated by the double circle in Fig. 2(a), where the normal-state LK formula starts to deviate from the measured dHvA oscillation amplitude.

At higher temperatures, H_{c2} values are not determined by this way because the dHvA oscillations are not observed in low enough magnetic fields than the H_{c2} points expected. Further discussion of the damping effect is beyond the scope of this paper.

Let us return to the quantum vortex liquid phenomenon. Several theoretical works have already reported on the quantum melting and the quantum liquid of vortices.[3–8] Blatter and Ivlev[3] have examined the influence of quantum fluctuations at finite temperature to investigate the quantum statistical mechanics of the vortex system. They estimated the shift in the melting curve using a Lindemann criterion.

Blatter *et al.*[4] have also shown that a first-order melting at low temperature occurs below H_{c2}, resulting in a quantum liquid state. Ikeda[5] has independently shown a similar quantum liquid state on the basis of the time-dependent Ginzburg-Landau theory with quantum fluctuations. Chudnovsky[6] has studied a hypothetical 2D quantum liquid state at $T=0$. Onogi and Doniach[8] have calculated the melting field by using quantum Monte Carlo simulation technique. Their results show the quantum vortex state at $T=0$ and a numerical evidence for the fractional quantum Hall state in the resulting liquid state. Rozhkov and Stroud[7] have estimated the conditions for quantum melting of a 2D vortex lattice at $T=0$.

Here, we try to evaluate the melting field at $T=0$ on the basis of the above theories. A first-order melting field B_m at $T=0$ in the 2D system by Blatter *et al.*[4] takes place at $B_m=H_{c2}[1-1.2\exp(-\pi^3c_L^2R_Q/4R_\square)]$, where c_L is the Lindemann number, $R_Q\equiv\hbar/e^2\simeq 4.1$ kΩ the quantum resistance, and $R_\square$ the sheet resistance. Choosing $H_{c2}=6$ T, $C_L=0.2$, and $R_\square\simeq 1$ kΩ ($\rho_n\simeq 0.2$ mΩ cm and $s\simeq 15$ Å),[30] $B_m\simeq 4$ T is obtained, and is close to the observed $H_{\rm irr}(0)$ although the parameters used here are very rough.

The approach by Rozhkov and Stroud[7] leads to a different relation, $B_m/B_{c2}=B_0/(B_0+B_{c2})$, where $B_0=\beta m_pc^2s\Phi_0/4\pi\lambda(0)^2q^2$, m_p is the pair mass ($\sim 2m_e$), q the pair charge ($\sim 2e$), c the light velocity, Φ_0 the flux quantum, $\lambda(0)$ the penetration length at $T=0$ and β ($\simeq 0.1$) the numerical melting condition parameter. Using the value $\beta=0.1$, $s=15$ Å, and $\lambda(0)=6400$ Å,[31] we find $B_0\simeq 11$ T and therefore, $B_m/B_{c2}\sim 0.65$. The evaluation by Ikeda[5] is not easy to compare with the experimental results applying the real material parameters. Considering the Ginzburg-Landau number, $\varepsilon_G^2\equiv 16\pi^2k_BT_{c0}\lambda(0)/\Phi_0s\simeq 0.04$, using the present material parameters for the 2D case to its calculation, however, $H_m(0)/H_{c2}(0)$ tends to be in a range of 0.5–0.7. Although Chudnovsky[6] does not show a numerical formula for the difference between H_m (or $H_{\rm irr}$) and H_{c2}, he points out the possibility that $H_{\rm irr}$ exists well below H_{c2} at

$T=0$. Thus our experimental finding for the finite quantum vortex liquid state at $T\simeq 0$ is explained well by different theoretical ways.

An important question, however, still remains. Our magnetic torque measurements do not detect the melting transition, but the irreversible field. The transition between the solid and liquid states is strongly influenced by the quality of the sample (i.e., degree and the type of the pinning), and also by the magnitude of the magnetic field. The magnetization step, resulting from the first-order vortex melting observed in $Bi_2Sr_2CaCu_2O_8$ (Ref. 32) disappears in the high magnetic field above about the dimensional crossover field B_{2D} and the transition is believed to become a second-order-like one. There is no clear explanation for changing the nature of the transition.

In the present material, there has been no evidence for the first-order melting transition even in low magnetic field. Therefore, we cannot conclude $H_{irr}\equiv H_m$ in our measurements, but it may be possible to consider that H_m lies near by H_{irr}. Even so, the result of the finite quantum vortex liquid state at $T=0$ is not altered.

Finally, the T dependence of H_{irr} persists down to the lowest temperature $T/T_c\simeq 0.01$. A T-independent portion is expected at low enough temperature.[5,8] In order to explain the temperature dependence in the pure quantum fluctuation region, we need to make an experiment at still lower temperatures.

In conclusion, we have presented that the irreversible field H_{irr} of the quasi-two-dimensional organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ lies far from H_{c2} even at low temperature $T/T_c\simeq 0.01$. The quantum vortex liquid state exists in $H_{irr}\leqslant H\leqslant H_{c2}$, which is driven mainly by the quantum fluctuations. The value $H_{irr}(0)/H_{c2}(0)\simeq 0.65$ is explained by the different theoretical ways using the material parameters. Further investigation is required to make the pure quantum fluctuation effect clear at lower temperature.

The authors would like to thank M. Kartsovnik, N. Kobayashi, and T. Nishizaki for their useful discussions. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

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