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Vortex phase transition with decoupling of the adjacent layers in the organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br

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The temperature dependence of the local magnetic induction measured by using a miniature Hall probe shows a tiny step at a field-dependent temperature in the titled compound. This result implies that there exists a first-order phase transition in the vortex system in this organic superconductor as reported in high-T_c cuprates. The height of the step is of the order of 10 mG, from which the entropy change at the transition is estimated to be about 0.1 (k_B/vortex)/layer. The measurements of the Josephson plasma resonance reveal that the interlayer phase coherence abruptly changes across the transition line, indicating the decoupling of the adjacent layers. [S0163-1829(98)51310-0]

Owing to large thermal fluctuations and the effect of layered structures, the H-T phase diagram of the mixed state of high-T_c superconductors (HTSC) is drastically different from that of the conventional superconductors. In particular, it is widely accepted that the vortex lattice in HTSC melts into the vortex liquid at a first-order phase transition well below the mean-field upper critical field.[1–5] The equilibrium magnetization measurements in $Bi_2Sr_2CaCu_2O_{8+y}$ (Refs. 1 and 2) and $YBa_2Cu_3O_{7-\delta}$ (Refs. 3 and 4) have revealed that the density of vortices discontinuously decreases upon cooling at the thermodynamic phase transition like freezing water. The calorimetric measurement in untwinned $YBa_2Cu_3O_{7-\delta}$ (Ref. 5) clearly indicates that the transition is first order. The nature of the transition, however, is not yet fully understood. One of the unresolved questions is whether or not the decoupling—the loss of coherence between the layers—takes place at the melting transition. To date experiments on this issue are controversial.[6–9] For example, two papers reporting flux transformer-type measurements in $Bi_2Sr_2CaCu_2O_{8+y}$ have drawn the contradictory conclusions.[8,9] It should be noted, however, that in such experiments only the coherence of vortices between top and bottom faces of the entire crystal can be evaluated instead of the coherence between the adjacent layers.

Microscopic information on the phase coherence between the adjacent layers can be obtained experimentally by using the Josephson plasma resonance (JPR) as a probe.[10–13] The resonance occurs when the plasma frequency ω_p of the superconducting carriers across the Josephson-coupled layers coincides with the measurement frequency. In the mixed state, ω_p^2 is proportional to the interlayer phase coherence $\langle \cos \phi_{n,n+1} \rangle$, where $\phi_{n,n+1}$ is the gauge-invariant phase difference between the layers n and $n+1$, and $\langle \cdots \rangle$ denotes thermal and disorder averaging.[14] Quite recently, Matsuda *et al.*[12] have found that $\langle \cos \phi_{n,n+1} \rangle$ shows different temperature dependence between well above and below the melting transition line in $Bi_2Sr_2CaCu_2O_{8+y}$. However, whether or not the loss of the interlayer coherence occurs at the transition line is still unclear.

The κ-type BEDT-TTF superconducting salts, where BEDT-TTF is bisethylenedithio-tetrathiafulvalene, have the layered structure consisting of superconducting and insulating sheets, similar to HTSC. Consequently, these superconductors have similar characteristic superconducting properties including the intrinsic Josephson effect[15–18] and the mixed-state properties.[19] This similarity suggests the existence of the vortex phase transition in the organic layered superconductors as observed in HTSC. Because the temperature scale is much lower in organic materials, the thermal fluctuations are expected to be small compared to HTSC. Thus, the comparison between the high-T_c and organic superconductors can give important clues as to the nature of vortex phase transitions.

In this paper, we report on the measurements of the local field in the layered organic superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br by using a Hall probe. A vortex phase transition with a step of local magnetic induction, which is similar to the melting transition in HTSC,[2] was observed. The complementary measurements of the Josephson plasma resonance revealed that the phase coherence between the adjacent layers decreases more than a factor of 5 on crossing the transition with increasing field. The results strongly suggest the existence of the first-order transition with decoupling of the layers in the vortex state of this organic superconductor.

The miniature Hall probe has been known to be a powerful tool for the local measurements of magnetic induction B of a superconductor.[20,2] We used a two-dimensional electron gas Hall probe with active area of $30\times 30\ \mu m^2$,[21] on which a κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br crystal with a T_c of 11.3 K was put directly with a tiny dot of grease. In this study, the field is applied perpendicular to the superconducting layers, and the temperature dependence of the perpendicular component of B was measured in the field-cooling or field-warming conditions at a typical rate of 30 to 70 mK/min. Owing to the decrease of thermal noise at low temperatures, the use of a high-precision ac resistance bridge to detect Hall signals, and the high stability of applied field H by the persistent mode of a superconducting magnet, we obtained a high resolution of $\delta B/H \simeq 1-5$ ppm at $H \leq 10.5$ kOe.

For the measurements of the JPR, we used the microwave cavity perturbation technique.[13] Three Cu cavities operating

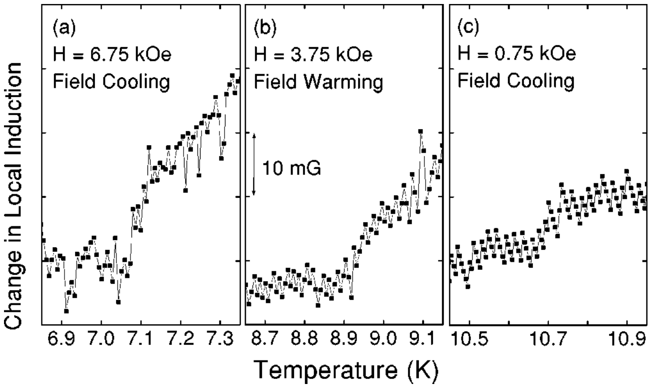

FIG. 1. Typical Hall-probe results of the change in the local induction B as a function of temperature at constant fields of 6.75 kOe (a), 3.75 kOe (b), and 0.75 kOe (c) applied perpendicular to the superconducting layers in a single crystal of κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. A linear background temperature dependence was subtracted to emphasize the tiny step at the phase transition of vortex system. Solid lines are guides for the eye.

at 24, 41, and 56 GHz were used to measure the microwave loss of the sample as a function of the applied field H in the configuration with the microwave electric field perpendicular to the layers. We used the same crystal in both the Hall-probe and the microwave measurements. We also determined the irreversibility line of the crystal by magnetization hysteresis measurements using a commercial superconducting quantum interference device (SQUID) magnetometer with a criterion of the critical current density $J_c = 20$ A/cm^2.

Figure 1 shows typical results of the Hall-probe measurements. A clear step in local B was observed by sweeping temperature at constant fields. These results indicate that the first-order phase transition in vortex systems exists in this organic superconductor. The density of vortices discontinuously increases on crossing the transition with increasing temperature as observed in HTSC.[1–4] In addition, the slope of $B(T)$ changes at the transition; dB/dT is greater above the transition. Such a change in the slope is quite consistent with the results in HTSC,[4] suggesting that the underlying mechanisms of the transition in both the organic and cuprate superconductors are similar. From these results we infer that at the transition the vortex lattice melts into the vortex liquid in this organic superconductor.

The phase transition line $H_{step}(T)$ is plotted in Fig. 2(a).[22] Its temperature dependence is also similar to the results of HTSC;[2] the overall feature can be fitted by the predictions of both the melting transition $H_m(T) = H_{m0}(1 - T/T_c)^\alpha$ with $\alpha \leqslant 2$ (Ref. 23) and the decoupling transition $H_d(T) = H_{d0}(T_c - T)/T$ (Refs. 24 and 25) with $H_{d0} = \alpha_d \Phi_0^3/[16\pi^2 \lambda_\perp^2(0) k_B T_c d]$. Here $\alpha_d = (\pi e)^{-1} \simeq 0.12$ (Ref. 25) is a universal constant, $d = 15$ Å is the interlayer spacing, Φ_0 is the flux quantum, and $\lambda_\perp(T)$ is the out-of-plane penetration depth. The fitting to the decoupling scenario is shown by the solid curve in Fig. 2(a) as an example. In this fitting, however, there is a clear deviation above about 10.3 K, contrary to the case in HTSC.[2,7] This deviation is partly because of the finite width of the transition ~ 1 K, which may modify the temperature dependence of the penetration depth near T_c. From this fitting we obtained $\lambda_\perp(0) \simeq 17$ μm, the value of which will be discussed later.

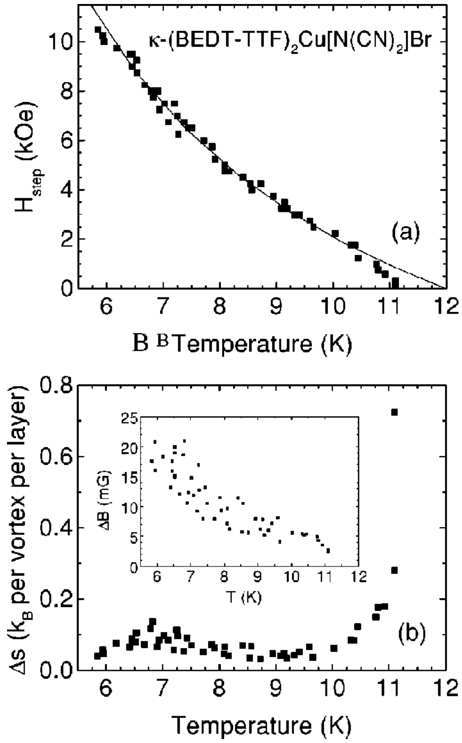

FIG. 2. (a) First-order phase transition line determined by the step in local B in κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. The solid curve is a fit to a prediction of the decoupling transition; $(T_c - T)/T$ dependence. (b) Temperature dependence of the entropy change per vortex per layer at the transition extracted from the height of the step $\Delta B(T)$ (inset).

The height of the step, ΔB, is of the order of 10 mG [see the inset of Fig. 2(b)], which is more than one order of magnitude smaller than that in HTSC.[2,4] By using the Clasius-Clapeyron relation, the entropy change at the transition per vortex per superconducting layer is estimated by $\Delta s \simeq -(d\Phi_0/4\pi)(\Delta B/B_{step})(dH_{step}/dT)$.[2] The obtained result of $\Delta s(T)$ is shown in Fig. 2(b). The magnitude of entropy change is about $0.1k_B$ per vortex per layer at temperatures below 10 K, which is comparable to that of HTSC. The value of Δs in $YBa_2Cu_3O_{7-\delta}$ (Ref. 5) is reported to be about $0.4k_B$, which is somewhat larger than our result. However, it is also reported in HTSC (Ref. 21) that Δs is quite sensitive to the disorder of the sample; in the disorder-induced sample the entropy change becomes small or the melting transition disappears.

Above 10 K close to T_c, Δs increases rapidly with temperature, which is quite similar to the results in $Bi_2Sr_2CaCu_2O_{8+y}$ (Ref. 2) and can be explained neither by the melting nor the decoupling theories. However, this divergent dependence near T_c is mainly due to the large magnitude of $(1/B_{step})(dH_{step}/dT)$, which may be explained by the finite superconducting transition width discussed above.

Next let us turn to the results of the Josephson plasma resonance. The plasma frequency is related to the interlayer phase coherence by[14]

$$\omega_p^2(H,T) = (8\pi^2 cd/\epsilon_0 \Phi_0) J_0(T) \langle \cos \phi_{n,n+1} \rangle (H,T). \tag{1}$$

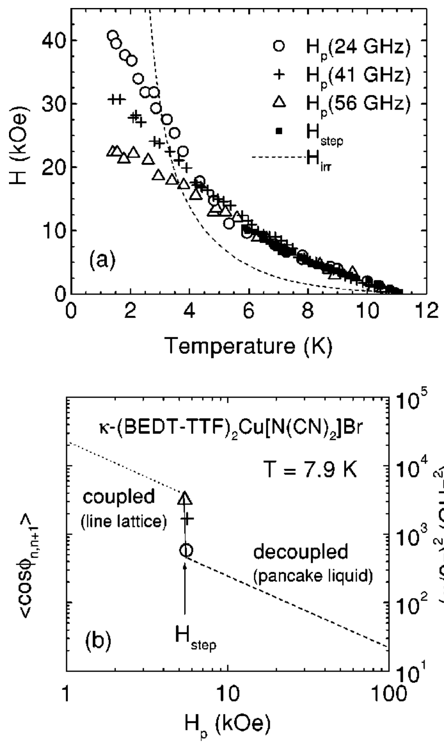

FIG. 3. (a) Temperature dependence of the resonance field H_p of Josephson plasma measured using three microwave cavities. Also shown are the transition line $H_{step}(T)$ [the same data as Fig. 2(a)] and the irreversibility line $H_{irr}(T)$ determined by using a SQUID magnetometer. Note that the frequency-independent H_p coincides with the transition line at high temperatures. (b) A plot of the interlayer phase coherence $\langle \cos\phi_{n,n+1}\rangle$, which is proportional to the square of the plasma frequency ω_p^2, as a function of applied field at a constant temperature. Contrary to the power-law dependence $\omega_p^2 \propto H^{-\mu}$ expected in both the coupled linelike vortex lattice (dotted line) and the decoupled pancakelike vortex liquid (dashed line), the frequency-independent H_p at the transition indicates a sudden change of the phase coherence between the layers.

Here ϵ_0 is the high-frequency dielectric constant, and the parameter $J_0(T)=c\Phi_0/8\pi^2 d\lambda_\perp^2(T)$ characterizes the Josephson interlayer coupling at zero field. In the microwave cavity experiments, however, the resonance was measured by sweeping the field H to change $\langle \cos \phi_{n,n+1}\rangle$ at constant frequencies. In Fig. 3(a), the resonance field H_p defined as the field at which the microwave loss has a peak is plotted as a function of temperature. We have checked from experiments on the polarization dependence that this resonance is due to the Josephson plasma excited perpendicular to the layer. The resonance is seen only when the microwave electric field E_ω is perpendicular to the layer but is absent when the magnetic field H_ω is perpendicular to the layer, which is consistent with the reported results.[11,13] At low temperatures, H_p decreases with increasing frequency. Such an anticyclotronic behavior of the resonance is also consistent with the previous reports of the JPR in $Bi_2Sr_2CaCu_2O_{8+y}$ (Refs. 10–12) and κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.[13] Above about 5 K, however, the resonance field $H_p(T)$ is independent of frequency, and surprisingly it follows exactly the same line as the transition line $H_{step}(T)$ determined in the same crystal by the Hall-probe measurements. In Fig. 3(b) we plot ω_p^2, which is proportional to the interlayer phase coherence $\langle \cos \phi_{n,n+1}\rangle$ [see Eq. (1)], as a function of field at a constant temperature (7.9 K). The measured three points show an almost vertical line, which indicates the coherence between the adjacent layers changes abruptly at the transition. In both the vortex solid and the decoupled pancake vortex states, the power-law dependence $\omega_p^2 \propto H^{-\mu}$ with μ close to unity is predicted[14,26] as represented by the dotted and dashed lines, respectively. In $Bi_2Sr_2CaCu_2O_{8+y}$ (Refs. 10–12) and κ-(BEDT-TTF)$_2$Cu(NCS)$_2$,[13] the power-law behavior with exponent $\mu \simeq 0.7-0.9$ was observed in the vortex liquid state. Contrary to this behavior, the observed frequency-independent resonance is direct evidence for the loss of interlayer coherence at the first-order transition line. The coincidence of the field H_p, where the phase coherence changes, with the step in the local field suggests that the melting and decoupling take place at the same time. Because of the limited frequency range, we cannot exactly determine how much coherence is lost at the transition. Our measurements at three frequencies, however, demonstrate that the change in the interlayer coherence is more than a factor of 5 at the transition. Since the transition line depends on the material parameter such as anisotropy, we have not found similar decoupling transition in the Cu(NCS)$_2$ salt[13] within our microwave frequency window.

At 24 GHz, the temperature dependence of H_p above about 6 K still follows the transition line, and above 3 K (above the irreversibility line) it can be fitted[27] by a theoretical prediction[26] assuming almost decoupled vortices; $\omega_p^2 = 2\pi f d J_0^2(T)\Phi_0/\epsilon_0 k_B T H$, where f is a dimensionless function of order unity with weak temperature dependence. Therefore, this result implies that at frequencies just below 24 GHz the resonance field follows a power-law dependence $\omega_p^2 \propto H^{-\mu}$ as observed in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.[13] If we assume $f=1$ and $\epsilon_0=25$ in the fitting, we obtain $\lambda_\perp(0)\simeq 95$ μm,[27] which is considerably longer than the obtained value (17 μm) in the fitting to a decoupling transition theory. Similar discrepancies can be seen in the case of HTSC. In the optimally doped $Bi_2Sr_2CaCu_2O_{8+y}$, for example, a fitting of the transition line to the decoupling theory gave $\lambda_\perp(0)\simeq 28$ μm,[2] while an estimation from the fitting of the plasma resonance was $\lambda_\perp(0)\simeq 102$ μm.[12] If we consider the approximations used in these theories, the difference would not be a serious problem. However, this discrepancy may be due to the in-plane correlations of pancake vortices, which are not taken into consideration in the JPR theory with decoupled vortices.[26] This effect may be responsible for the smaller exponent μ [0.7–0.9 (Refs. 10–13)] in the liquid state than the expected value (unity) in the above theory, which results in an overestimation of $\lambda_\perp(0)$.

Next we comment on the frequency dependence near the transition line in $Bi_2Sr_2CaCu_2O_{8+y}$. Matsuda *et al.*[12] reported that $H_p(T)$ at 80 GHz below the transition line shows different temperature dependence from that at 55 GHz above the transition. Although not stated, the frequency dependence seems to change near the melting transition line, consistent with our results. At fields higher than the transition line, 45 and 55 GHz data show the power-law dependence $\omega_p^2 \propto H^{-\mu}$ with $\mu = 0.7-0.9$. Below the melting line, 80 GHz data no longer follow the power-law dependence especially above the irreversibility line. This frequency dependence suggests that $\langle \cos \phi_{n,n+1} \rangle$ changes near the melting line in $Bi_2Sr_2CaCu_2O_{8+y}$. However, the resonance field still shows a small frequency dependence at these two frequencies. This suggests that the change in the interlayer coherence at the transition, if present, is smaller than a factor of 2 in $Bi_2Sr_2CaCu_2O_{8+y}$. The difference of the magnitude of this change between the high-T_c and organic superconductors may be due to the difference of the thermal fluctuations. This point will be a promising subject for the future studies in understanding the nature of the vortex system in layered superconductors.

Concurrent with our work, Fruchter *et al.*[28] have observed a step in magnetization in the sample having lower irreversibility field and they assigned it to be the melting transition. Our transition line is somewhat above their assigned line, and both lines are different from the line where the transport data by Kwok *et al.*[29] show zero resistivity. Although the origins of such sample dependence of the transition line (or the anisotropy) remain to be clarified, we note that our two experiments in a given sample provide clear evidence for the first-order decoupling transition.

In conclusion, we have found the existence of the first-order transition line in the vortex system of the organic layered superconductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. The temperature dependence of the magnetic induction shows characteristic features similar to HTSC. The entropy change at the transition is estimated to be about 0.1 (k_B/vortex)/layer. One of our important findings is that the interlayer phase coherence probed by the JPR shows a sudden change at the transition line, which is indicative of the decoupling of the adjacent layers in this organic superconductor.

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