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Shubnikov–de Haas effect in the quantum vortex liquid state of the organic superconductor \( \kappa\)-\((\text{BEDT-TTF})_2\text{Cu(NCS)}_2\)

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We report the Shubnikov–de Haas (SdH) oscillations observed in the vortex liquid state of the quasi-two-dimensional organic superconductor \( \kappa\)-(BEDT-TTF)_2Cu(NCS)_2, where BEDT-TTF denotes bis(ethylene-dithio)tetrathiafulvalene. The SdH oscillations can be observed down to about 5 T at 0.5 K, where the flux flow resistivity becomes as small as about 30% of the normal-state value. Below the upper critical field \( H_{c2} \) of about 7 T, the additional damping of the SdH oscillation amplitude appears, as well as that of the de Haas–van Alphen (dHvA) oscillations, with respect to the normal-state one that is described with the standard Lifshitz-Kosevich formula. The magnitude of the additional damping near \( H_{c2} \) is the same with that observed in the dHvA oscillations and well explained by the theoretical predictions in consideration of fluctuations in the thermal vortex liquid state. In the quantum fluctuation region at lower temperature, however, only the SdH effect shows the stronger damping than that of the dHvA oscillations. The different magnetic-field dependence of the additional damping of the oscillation amplitude between the SdH and dHvA effects is discussed in connection with the effect of the transport current on the short-range order of vortices in the quantum vortex slush state, which appear in the quantum vortex liquid region.

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I. INTRODUCTION

After the report of the magnetic quantum oscillations in the superconducting state of \( 2\text{H-NbSe}_2 \) more than quarter century ago,\(^1\) the oscillations of the magnetization, de Haas–van Alphen (dHvA) effect, in the vortex state seem to be confirmed experimentally for a variety of the type-II superconductors in the last decade.\(^2\) Common experimental result of the dHvA oscillations in the superconducting state is that the additional damping of the oscillation amplitude appears below the upper critical field \( H_{c2} \) with respect to the normal-state damping. The additional damping has been discussed in several ways theoretically.\(^3\) The questions in those discussions are summarized as follows:\(^3\) (1) if the superconducting gap \( \Delta_0 \) exists in the vortex state just below \( H_{c2} \), it would have drastically damped the oscillations at low temperatures by a factor of \( \exp(-\Delta_0/k_B T) \), (2) the inhomogeneous field distribution due to the flux lattice would broaden the Landau levels, and (3) the inhomogeneity in the superconducting order parameter associated with the vortex lattice leads to inhomogeneous broadening of the Landau levels in the quasiparticle spectrum near the Fermi surface. Thus the oscillations include basically rich information on the quasiparticle in magnetic fields and also the vortex matter properties.\(^4\)

The Shubnikov–de Haas (SdH) oscillations in the superconducting state are very difficult to be observed because the finite resistivity is needed inevitable. Then it can appear in the quite limited field-temperature region where the long-range translational order of the vortices is lost. Quasi-two-dimensional (Q2D) organic superconductors are good candidates for the observation of the SdH effect in the vortex state because large fluctuations induce the wide vortex liquid region.\(^5,6\) At low temperature below 1 K, the quantum vortex liquid (QVL) is realized in \( \kappa\)-(BEDT-TTF)_2Cu(NCS)_2 (\( T_c \) = 10 K) due to the large quantum fluctuation instead of the thermal one,\(^7,8\) where BEDT-TTF denotes bis(ethylene-dithio)tetrathiafulvalene. In the QVL region, the finite resistivity is expected to remain even below \( H_{c2}(T=0) \). Recently the transport properties in the QVL region have been examined in detail, and the finite resistivity has been confirmed.\(^9\)

In this paper, we report the SdH oscillations observed in the QVL region of the Q2D organic superconductor \( \kappa\)-(BEDT-TTF)_2Cu(NCS)_2. An additional damping of the oscillation amplitude appears on both the SdH and dHvA effects around \( H_{c2} \), which may come from the superconducting fluctuation. At lower temperature in the QVL region, however, the stronger damping is observed only on the SdH effect. The different magnetic-field dependence of the additional damping of the oscillation amplitude between the SdH and dHvA effects is discussed in connection with the effect of the transport current on the short-range order of vortices in the quantum vortex slush state\(^5\) in the QVL region.

II. EXPERIMENT

High quality single crystals of \( \kappa\)-(BEDT-TTF)_2Cu(NCS)_2 were grown by an electrochemical oxidation method. The magnetic torque measurements were performed by using precision capacitance torquemeter. The in-plane and the out-of-plane resistivities were measured along the \( b \) and \( a^* \) axes, respectively, by means of a conventional ac or dc four-terminal method. The electrical terminals were made of evaporated gold films, and gold wires (10 \( \mu \)m) were glued onto the films with gold or silver paint. The contact resistance was about 10 \( \Omega \) for each contact at room temperature, but it became less than 1 \( \Omega \) at low temperature where the experiments were carried out. The torquemeter and the samples for the resistivity measurements were fixed to the single-axis rotation holder which can change the sample direction with respect to the magnetic field with the accuracy of 0.05°. The holder with the samples was cooled slowly from room temperature to 4.2 K in 48 h and specially slow cooling rate was used between 50 and 75 K in order to
activity is found in the QVL region. Such nonlinearity is not
noted only here that a weak nonlinear behavior of the resis-
torque region \( H \) amplitude of the dHvA oscillations. The reversible magnetic
properties in the QVL region has been already reported. 9 It is
expected to be the QVL region. The finite resistivity appears in
the QVL region even at \( T \approx 0 \). The detail of the transport
changes a little with the current density because of the weak
flux flow resistivity in the QVL region, however,
irreversible and reversible regions are separated at \( H_{irr} \approx 3 \) T [Fig. 1(b)], and the dHvA oscilla-
tions with one fundamental frequency of \( F_\alpha = 599 \pm 2 \) T are observed in both the normal and superconducting states. The quality of the sample used in this study seems to be better than that in the previous work 7 judging from the large amplitude of the dHvA oscillations. The reversible magnetic torque region \( (H_{irr} \approx 3 \text{T} < H < H_{c2} \approx 7 \text{T}) \) below 1 K is ex-
pected to be the QVL region. The finite resistivity appears in
the QVL region even at \( T \approx 0 \). The detail of the transport
properties in the QVL region has been already reported. 9 It is
noted only here that a weak nonlinear behavior of the resist-
vity is found in the QVL region. Such nonlinearity is not
avoid the disorder of the terminal ethylene group of the
BEDT-TTF molecules. 10 The holder was directly immersed
in liquid \( ^3 \)He of the refrigerator that was combined with a
15-T superconducting magnet at the High Magnetic Field
Laboratory for Superconducting Materials (HFLSM), IMR,
Tohoku University. The results presented in this paper were
obtained on three samples: No. 1 for the magnetic torque,
and No. 2 and No. 3 for the resistivity measurements from
different batches. We found that two other samples for the
magnetic torque and the resistivity measurements gave quali-
atively similar results that were not presented in this paper.

III. RESULTS AND DISCUSSION

Figure 1 shows the magnetic torque curves of the sample
No. 1 at \( T = 0.52 \) K. The overall features are the same with
the previous report; 7 the irreversible and reversible regions
are separated at \( H_{irr} \approx 3 \) T [Fig. 1(b)], and the dHvA oscilla-
tions with one fundamental frequency of \( F_\alpha = 599 \pm 2 \) T are observed in both the normal and superconducting states. The quality of the sample used in this study seems to be better than that in the previous work 7 judging from the large amplitude of the dHvA oscillations. The reversible magnetic torque region \( (H_{irr} \approx 3 \text{T} < H < H_{c2} \approx 7 \text{T}) \) below 1 K is ex-
pected to be the QVL region. The finite resistivity appears in
the QVL region even at \( T \approx 0 \). The detail of the transport
properties in the QVL region has been already reported. 9 It is
noted only here that a weak nonlinear behavior of the resist-
vity is found in the QVL region. Such nonlinearity is not
observed in the thermal vortex liquid (TVL) region above 1
K. The concept of the quantum vortex slush has been pro-
posed for the nonlinear behavior below 1 K. The vortex slush
with only the short-range order of vortices has been found in
the high-\( T_c \) oxides. 11–13 The effect of the quantum vortex
slush and the TVL states on the dHvA and SdH effects will
be discussed latter.

Figure 2 shows the magnetic-field dependence of the re-
istivity in the sample No. 2 at \( T = 0.52 \) K. The in-plane \( (\rho_b) \)
and the out-of-plane \( (\rho_a) \) resistivities are measured in one
single crystal along the \( b \) and \( a^* \) axes, respectively. The magnitude of the magnetic-field dependence of the resistivity
and the resistivity onset corresponding to \( H_{irr} \) are not influ-
enced by the applied current density in both configurations.
The flux flow resistivity in the QVL region, however,
changes a little with the current density because of the weak
non-linear resistance. 9 The two curves in this figure are mea-
sured using the current density (current) of \( J = 0.16 \) A/cm\(^2\)
\( (I = 100 \) \( \mu \) A) for \( \rho_b \) and 1.6 mA/cm\(^2\) \( (10 \) \( \mu \) A) for \( \rho_a \),
respectively. The SdH oscillations with the frequency of \( (599 \pm 2) \) T are clearly observed. The oscillations come from the
\( \alpha \) orbit centered at the \( Z \) point of the first Brillouin zone
depicted in the upper left inset. In higher magnetic fields, the
magnetic breakdown orbit \( \beta \), consisting of the \( \alpha \) and opened
\( \gamma \) orbits, has been observed in both the SdH and dHvA oscilla-
tions. 14,15 We, however, restrict ourselves to the single-band
model for the following analysis and discussion on the
SdH and dHvA effects because the magnetic field used in the
present study is smaller than the magnetic breakdown
field. 14,15 The amplitude of the SdH oscillation on \( \rho_b \) is much
larger than that on \( \rho_b \), although the magnitude of the magnetic-field dependence of the resistivity is almost the same with two configurations. The reason is not known at present but the similar tendency is commonly seen in the
Q2D organic conductors. 16

In order to look at the SdH oscillations in low magnetic-
field region, \( \Delta \sigma/\sigma_n \) is shown in the lower right inset of Fig. 2. Here, \( \Delta \sigma \) is the oscillatory part of the conductivity obtained by subtracting the nonoscillatory part of the conductivity, and \( \sigma_n (= \rho_n^{-1}) \) is the normal conductivity which is the same with the nonoscillatory part of the conductivity in the normal state. In the vortex state below about 7 T, the SdH oscillations come from the normal (quasiparticle) component of the total conductivity which includes additional nonequilibrium superconducting component due to the vortex pinning. The normal (quasiparticle) part of the conductivity roughly corresponds to the flux flow conductivity. Then the normal resistivity \( \rho_n (= \sigma_n^{-1}) \) in the vortex state is assumed to be extrapolated smoothly from the normal state into the vortex state toward \( \rho = 0 \) at \( H = 0 \). The dotted line in Fig. 2 shows the normal (quasiparticle) resistivity \( \rho_n (= \sigma_n^{-1}) \) in the normal (vortex) state. The line is obtained as almost linear in the vortex state and passing through the middle of the SdH oscillations in the normal state. In intermediate region around 7 T, two lines are connected smoothly by the simple second-order polynomial function. The SdH oscillation is persisting down to about 5 T where the resistivity is about 30% of the normal-state value \((\sim 1.5 \Omega \text{cm}) \) at 7 T. In the other sample No. 3 the oscillations can be seen in lower magnetic field of about 4.5 T, which are shown in Fig. 4. This is the first unambiguous observation of the SdH oscillations in the flux flow resistance of the well characterized superconductor. Similar SdH effect in the superconducting state is shown in Ref. 17. But it did not show the additional amplitude damping in both the SdH and dHvA oscillations in the superconducting state. It may be necessary to consider the smaller \( H_{c2} \) value reported by another group\(^{18} \) than the value expected in Ref. 17.

The additional damping of the SdH and dHvA oscillation amplitude in the vortex state is demonstrated in Fig. 3. The oscillation amplitude \( \Delta \tau \) and \( \Delta \sigma/\sigma_n \) for the dHvA and SdH effects are shown by the circles in Figs. 3(a) and 3(b), respectively. In the normal state above about 7 T, both oscillation amplitudes are well described by the standard Lifshitz-Kosevich (LK) formula.\(^{19} \) The amplitude \( A_{\text{LK}} \) of the first harmonics of the oscillations in the single band is given by \( A_{\text{LK}} \approx 2 \hbar \pi k_F R_D R_S \), where the temperature factor \( R_T = (\lambda m c T / 2 m_0) \), the Dingle factor \( R_D = \exp(-\lambda m c T / 2 m_0) \), and the spin factor \( R_S = \cos(\pi m c T / 2 m_0) \). Here, \( \lambda = 2 \pi^2 k_F / \hbar = 14.69 \text{ T/K} \), \( m_0 \), \( m_\pi \), and \( m_0 \) are the band, cyclotron effective, and free-electron masses, and \( T_D \) is the Dingle temperature related to the scattering rate \( \tau_0 \) with \( T_D = \hbar / 2 \pi k_B \). The power \( n \) of \( H \) depends on the measured quantity and the dimensionality. For the SdH and the torque-dHvA amplitude (\( \Delta \sigma/\sigma_n \) and \( \Delta \tau \)) in the 3D (2D) case, \( n \) is 3/2 (1). The fittings in both cases are very good with \( m_\pi = 3.5 m_0 \) and \( T_D = 0.26 \pm 0.05 \text{ K} \) (0.17 \pm 0.03 K) for the dHvA and 0.24 \pm 0.05 K (0.16 \pm 0.03 K) for the SdH effects in the 3D (2D) case.\(^{21} \) The 2D formula, however, is adopted for the latter analysis because the quantized Landau-level spacing in the present magnetic-field region is considered to be fairly larger than the interlayer transfer integral of this Q2D organic superconductor.\(^{22} \)

Below about 7 T the amplitude starts to deviate smoothly downward from \( A_{\text{LK}} \) in both the dHvA and SdH effects. This indicates the additional amplitude damping in the vortex state, which has been reported so far on the dHvA effect in \( \kappa-(\text{BEDT-TTF})_2 \text{Cu(NCS)}_2 \).\(^{7,20,23,24} \) The origin of such smooth damping has been discussed on the basis of the model of the quasiparticle scattering by the random vortex lattice with the large superconducting (vortex) fluctuation around the mean field \( H_{c2} \).\(^{2,3,24} \) In the approach by Maniv et al.,\(^{3} \) the additional damping term \( R_{\text{SC}} \) as being multiplied to \( A_{\text{LK}} \) is \( R_{\text{SC}} = \exp(-\pi^2/2 \lambda^2) \), where \( n_F = E_F / \hbar \omega_c \), \( \omega_c = eH / m_\pi c \), \( E_F \) is the Fermi energy, and \( \langle |\Delta|^2 \rangle \) is the mean square of the superconducting order parameter averaged over space coordinates. The tilde above \( \Delta \) indicates that energy is measured in units of \( \hbar \omega_c \). This expression is very similar to the Maki-Stephan-type mean-field approach.\(^{24,25} \) In a simple analytic expression derived by Maniv et al.,\(^{3} \) \( \langle |\Delta|^2 \rangle \) is given by \( (|\Delta|^2) = (alpha/beta)(1 + |exp(-x^2/2)|/2 \sqrt{pi} exp(-y^2/2)) \), where \( alpha = (1/2 \hbar \omega_c ln(\sqrt{\beta}/\hbar / \omega_c)) \) and \( beta = 1.38 n_F / \omega_c \). Ito et al.\(^{20} \) and Clayton et al.\(^{24} \) have used an approximated interpolation formula for the mean square of the gap function, \( \langle |\Delta|^2 \rangle = \sqrt{(\Delta(0))^2(1 - H/H_{c2})^2 + alpha(T)^2 + (Delta(0))^2(1 - H/H_{c2})^2} \), where \( alpha(T) \) is a temperature-dependent parameter to scale the fluctuations. Both calculations of \( R_{\text{SC}} \) are shown in Fig. 3(c) by using the same mean field \( H_{c2} = 4.8 \text{ T} \). The results on \( R_{\text{SC}} \) are fairly in good agreement with each other.

The dotted curves in Figs. 3(a) and 3(b) show the expected magnetic-field dependence of the oscillation ampli-
tude taking $R_{\text{SC}}$ into account. The dHvA effect is well represented in these fluctuation approaches as has been reported.\textsuperscript{3,20,24} In the SdH effect, the experimental results follow well $A_{2D}^2R_{\text{SC}}$ near $H_{c2} \approx 7$ T as well as the dHvA effect. A stronger damping, however, appears below about 6.5 T in only the SdH effect.

We discuss the stronger damping in the vortex state observed only in the SdH effect in connection with the quantum vortex slush state at low temperature. In the QVL region the finite resistance appears in the vortex liquid state between the melting $H_{c2}$ or irreversible field $H_{c1}$ and $H_{c2}$ even at $T=0$. In the case of less or no quantum fluctuation, the zero resistance should appear just below $H_{c2}$ and $H_{m}(T)$ or $H_{m}(T)$ coincides with $H_{c2}(T)$ at $T=0$. The former QVL region has been actually found in $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ as a demonstration of the importance of the quantum fluctuations in this material.\textsuperscript{7,8} Recently, two vortex liquid regions have been found at low temperature.\textsuperscript{9} The low-resistivity state with nonlinear current response below about 1 K has been distinguished from the high-resistivity state at higher temperature. A steep drop of the resistivity around $T_L \approx 1$ K separates the vortex liquid state into these two regions. The schematic phase diagram is shown in the inset of Fig. 5. The short-range order of vortices has been expected to exist in the former low-resistivity state referred to as the quantum vortex slush state because these features in the low-resistivity state are phenomenologically similar to the observations explained by the vortex slush concept with the short-range order of vortices in the high-$T_c$ oxides.\textsuperscript{11-13} The latter high-resistivity state has been considered as the TVL state where no translational long-range order of vortices is formed.

Since the additional damping of the oscillation amplitude in the vortex state is explained to be sensitive to the local phase modulation of the superconducting order parameter,\textsuperscript{3} some kind of perturbation on the vortices, for example, applying the transport current in the SdH measurements, is expected to influence the phase coherence. It is noted that both the dHvA and SdH oscillations in this experiment are measured in the quantum vortex slush region. In the case of such measurements in the TVL state, the additional damping in the vortex state is expected to be the same in the dHvA and SdH effects because the TVL does not have any order of vortices. Thus neither the presence of the transport current in the measurements of the SdH effect nor the absence of current in the dHvA effect alters any phase coherence. On the other hand, the SdH effect in the quantum vortex slush state may be affected by moving vortices because of applying the transport current. It may disturb such coherence of the vortices and quasiparticles. Nonobservation of stronger oscillation amplitude damping in the dHvA effect with basically no transport current demonstrates the influence of the moving vortices by the current in the quantum vortex slush state.

Besides applying transport current, the effect of moving vortices on the damping of the dHvA oscillations has been seen in the superconducting state of $2H$-NbSe$_2$.\textsuperscript{27} The damping of the oscillations depended on the history of reciprocal partial sweeps of the external magnetic field in the hysteretic region where the pinning strength was changing. For explaining the observations, Maniv \textit{et al.} have suggested that the motion of vortices, depending on the pinning strength, influences the magnitude of the damping of the oscillations.\textsuperscript{3}

In order to see the difference of the damping in the quantum vortex slush and the TVL regions, we tried to compare the SdH oscillations at higher temperatures. Figure 4 shows the SdH oscillations at higher temperatures in the sample No. 3. The SdH oscillations in the vortex state are clearly seen down to about 4.5 T at 0.43 K. The sample No. 3 seems to have better quality to observe the SdH oscillations in lower magnetic field than that in the sample No. 2 presented in Fig. 1.

The magnetic-field dependence of the observed SdH oscillation amplitude scaled by $A_{2D}^2$ in the normal state is shown in Fig. 5. The value of $(\Delta \sigma/\sigma_n)/A_{2D}^2$ corresponds to the additional damping in the vortex state. The additional damping starts smoothly around $H_{c2} \approx 7$ T. The magnitude of the additional damping becomes larger in higher temperatures near $H_{c2}$. It is naturally understood by the fluctuations. The lower inset shows calculations of the additional damping factor $R_{\text{SC}}$ proposed by Ito \textit{et al.}\textsuperscript{20} and Clayton \textit{et al.}\textsuperscript{24} The fluctuation parameter $\alpha$ is expected to take a larger value in higher temperature. This has been actually confirmed in the dHvA experiments on the same material by Clayton \textit{et al.}\textsuperscript{24} The $\alpha$ value has changed almost continuously from 0.13 at 0.03 K to 0.32 (meV)$^2$ at 0.44 K. It is noted that the $R_{\text{SC}}$ curves calculated with $\alpha$ or corresponding temperature are continuously shifting to a smaller value, and do not cross each other. The present SdH oscillation damping near $H_{c2}$ is in agreement with the theoretical calculations. But the oscillation amplitude at 0.43 K shows stronger additional damping in low magnetic field than others measured at high temperature. This stronger damping observed at 0.43 K is considered to be due to the moving vortices in the quantum vortex slush state as discussed above.

It is expected that the similar stronger damping may appear below about 5.5 and 5 T at 0.76 and 0.88 K, respectively, where the boundary between the quantum vortex slush
The SdH oscillation amplitude at 0.88 K, however, does not show the clear stronger damping given in Ref. 9. The SdH oscillation amplitude at 0.76 and separates QVS from TVL. The detail on the phase diagram is given in Ref. 9. The additional damping factor proposed from TVL. The detail on the phase diagram is given in Ref. 9. Each curve from top to bottom is calculated with $\alpha=0.10$, 0.15, 0.20, 0.25, and 0.30 (meV)$^2$.

The SdH oscillations near $H_c$ are well described by the model on the superconducting (vortex) fluctuations as well as those observed in the dHvA effect. In only the SdH effect, the stronger damping appears in the quantum vortex slush region. The stronger damping may reflect the perturbation of a phase coherence of vortices and quasiparticles in the quantum vortex slush state with the short-range order of vortices due to their movement by the transport current.

**IV. SUMMARY**

We observed the SdH oscillations on the flux flow resistivity in the vortex state of the Q2D organic superconductor $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$. The additional damping of the SdH oscillation amplitude near $H_c$ is well described by the model on the superconducting (vortex) fluctuations as well as those observed in the dHvA effect. In only the SdH effect, the stronger damping appears in the quantum vortex slush region. The stronger damping may reflect the perturbation of a phase coherence of vortices and quasiparticles in the quantum vortex slush state with the short-range order of vortices due to their movement by the transport current.

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3. T. Maniv, V. Zhuravlev, I. Vagner, and P. Wyder, Rev. Mod. Phys. 73, 867 (2001), and references therein.
21 In the calculation of $T_D$’s the effective mass ($m_e = 3.5m_0$) determined from the temperature dependence of the dHvA and SdH amplitude is used. In the strict sense the band mass should be used. By using $m_b = 1.2m_0$ as the mass obtained from the cyclotron resonance [S. Hill et al., Synth. Met. 56, 2566 (1993)], each $T_D$ shows a value 2.9 times as much.