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Kyoto University
Magnetic field and temperature phase diagram of the pressurized organic superconductor $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br in the field parallel to the conducting plane

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The upper critical field $H_{c2}$ of the layered organic superconductor $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br has been studied with emphasis on the field direction parallel to the conducting plane. Application of hydrostatic pressure changes the shape of the $H_{c2}(T)$ diagram, removing a notable curvature observed at ambient pressure in the high-temperature region and giving almost linear dependence. The change is ascribed to the dominance of the orbital pair-breaking effect under pressure as opposed to the Pauli paramagnetic limiting of $H_{c2}$ at ambient pressure. An abrupt change by pressure of the slope of the $H_{c2}(T)$ curve in a temperature range near $T_c$ is ascribed to the phase change in the material due to the ordering of the ethylene fragments of the BEDT-TTF molecules.

I. INTRODUCTION

The upper critical field $H_{c2}$ of the quasi-two-dimensional organic superconductors under a magnetic field applied parallel to the superconducting plane ($H_{c2}$) has attracted notable attention recently. The reason for this is the unusually large values, observed in experiments on a number of salts, markedly exceeding the Pauli (P) paramagnetic limit, $H_{P}^{\text{BCS}}$, based on the weak-coupling BCS theory. For example, for $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br (Ref. 4) (hereafter referred to as Br salt), having the highest superconducting transition temperature ($T_c$) of 11.6 K among this class of materials at ambient pressure, the $H_{c2}$ increases very rapidly immediately below $T_c$, with the slope reaching 14 T/K$^{5,6}$ so that $H_{c2}$ reaches $H_{P}^{\text{BCS}}$ already near 10 K, or at approximately 0.8$T_c$. In accordance with this high value, a notable curvature, represented well by $(1-T/T_c)^{1/2}$, is observed in the $H_{c2}(T)$ near $T_c$, suggesting that the $H_{c2}$ is determined by the Pauli paramagnetic effect. The measurement using a high magnetic field$^8$ showed that the $H_{c2}(T)$ in Br salt tends to saturate below 4 K, to a value about two times larger than $H_{P}^{\text{BCS}}$.

By contrast, a sister salt $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$] (abbreviated as NCS salt below), having very similar parameters of the superconducting state, shows a nonsaturating $H_{c2}(T)$ with somewhat upturned behavior on cooling toward very low temperatures. It gives the value of $H_{c2}$ notably exceeding $H_{P}^{\text{BCS}}$. The origin of the difference between Br salt and NCS salt is not clear and it stimulates further studies on this subject.

In this paper we report the $H_{c2}(T)$ of Br salt under hydrostatic pressures in comparison with that at ambient pressure. The decrease of $H_{c2}$ connected to the decrease in $T_c$ by pressure allows to cover the whole magnetic field $H$ versus temperature $T$ domain of the superconducting phase. We found, however, that the $H_{c2}(T)$ loses the tendency of $(1-T/T_c)^{1/2}$ dependence by pressure and becomes almost $T$ linear in the high-temperature region ($T\geq T_c/2$), while the absolute value of $H_{c2}$ in the 0 K limit decreases. We ascribe this change to the dominance of the orbital pair-breaking effect under pressure as opposed to the Pauli paramagnetic limiting of $H_{c2}$ at ambient pressure.

II. EXPERIMENT

The crystals were prepared by a standard electrochemical method. The samples, with typical dimensions of 0.5×0.5×0.1 mm$^3$, were pressurized using a Be-Cu clamp pressure cell. A cylindrical cell with an inner space of 2 mm in diameter and 7 mm in length was filled with Daphne oil 7373 as a pressure medium. The pressure $P$ at low temperatures was estimated from the reported pressure dependence of $T_c$, measured under gas pressure.$^{13,14}$ The cell was set into a mechanical double axis rotator$^{15}$ enabling orientation with the angle resolution of 0.01°. The rotator was inserted into a top-loading$^3$ He cryostat combined with a superconducting 19 T solenoid.

$H_{c2}$ was determined from measurements of the interplane resistance $R$, either from $T$ sweep at fixed $H$ or from $H$ sweep at a fixed $T$. From the position of the inflection point of $R$($T$) or $R$($H$) dependence, $H_{c2}(T)$ was evaluated by finding the maximum of either $dR/dT$ or $dR/dH$, respectively. This method of determination of $H_{c2}(T)$ was justified by the comparison of the specific-heat and the resistive measurements.
carried out simultaneously at ambient pressure under parallel magnetic fields. The transition to the superconducting state under pressure was studied also in the absence of a strong static magnetic field by the ac susceptibility measurement in comparison to the resistive measurement. It is reasonable to take the uncertainty of $T_c$ and $H_c^2$ determinations as $\pm 10\%$, ascribable to the broadness of the transition.

The orientation of the field with respect to the superconducting plane was made by measuring $R$ on field inclination to the conducting plane, characterized by a polar angle $\theta$. The angular resolution of this determination was estimated as $0.2^\circ$. The position of the field within the plane was set by eye to be parallel to the $a$ axis with the accuracy of about $10^\circ$. The in-plane anisotropy of $H_c^2$ with respect to the azimuthal angle $\phi$ of the field within the plane was found to be less than $5\%$.  

It is known that the $T_c$ of Br salt is sensitive to the cooling cycle. At ambient pressure, it is important to cool samples slowly from 90 to 60 K. Although the corresponding sensitivity was not reported for a pressurized sample, we adopted the slow cooling procedure ($\sim 0.1$ K/min) in a 60 to 90 K range even with a pressure cell.

III. RESULTS

The temperature dependence of $H_c^2$ at various pressures is shown in Fig. 1, and the data at ambient pressure are reproduced from Ref. 8. For the pressurized samples the $H_c^2(T)$ increases almost linearly with the temperature decrease in the high-temperature side ($T > T_c/2$), except the proximity to $T_c$ at $H = 0$ where the dimensional crossover can appear. This is in contrast to the results obtained at ambient pressure, in which case $H_c^2(T)$ can be fitted with $(1 - T/T_c)^{1/2}$.

The pressure dependence of the slope $dH_c^2/dT$ near $T_c$ is displayed in Fig. 2, where the pressure is represented by $T_c$ in zero field. In this case, we determined the slope excluding the behavior in the very proximity to $T_c$, since the $H_c^2$ is varied in relation to the dimensional crossover caused by the rapid temperature dependence of the coherence length near $T_c$. It can be seen that the slope decreases dramatically on the initial pressure increase, but then shows moderate change. The behavior shows that some transformation of the superconducting state is taking place under a pressure less than 1 kbar, which can be related to the drastic difference of the $H_c^2$ shape in Fig. 1.

Important information about the mechanism responsible for $H_c^2$ can be obtained from the dependence on the field inclination angle $\theta$ from the plane. The respective curves, obtained at 0.3 K for different pressure values, are shown in Fig. 3. When $H_c^2$ is determined by the orbital effect, the effect of the inclination is different for cases of an aniso-
tropic three-dimensional (3D) superconductor and a two-dimensional (2D) superconductor. In the 3D case, the angle dependence can be fitted by an effective-mass formula, represented as

\[
\left[ \frac{H_{c2}(\theta) \sin \theta}{H_{c2}} \right]^2 + \left[ \frac{H_{c2}(\theta) \cos \theta}{H_{c2}} \right]^2 = 1, \quad (3.1)
\]

where \( H_{c2} \) is obtained in the field applied perpendicular to the plane. The characteristic feature of this relation is gradual variation of \( H_{c2} \) near the parallel field direction. In the 2D case, a dependence is described by a formula \(^19\) giving a cusp in \( H_{c2}(\theta) \) near the in-plane field orientation. Since no cusp is seen in our data obtained under pressure, we fitted the experimental results with the formula (3.1), as shown in Fig. 3. The data are normalized with \( H_{c2} \). The parameters determined for various pressure values are listed in Table I. This \( H_{c2}(\theta) \) dependence is in contrast with the reported results on NCS salt at ambient pressure, showing a notable cusp as typical for the 2D superconductor.\(^9\) Worth noting is that the coherence length in the in-plane direction (\( \xi_\perp \)) notably increases with pressure, while that in the interplane direction (\( \xi_\parallel \)) increases only weakly.

### IV. DISCUSSION

#### A. Temperature dependence of \( H_{c2} \)

In order to demonstrate the change in the shape of \( H_{c2}(T) \) on pressure application, we show it on the dimensionless scale, \( H_{c2}/H_p^{\text{BCS}} \) versus \( T/T_c \), as shown in Fig. 4. Here \( H_p^{\text{BCS}} = \Delta_0/(\sqrt{2} g \mu_B) \), \( \Delta_0 = 2 \alpha T_c \) is the superconducting gap with \( \alpha = 1.76 \) in the weak-coupling BCS model, \( g \) is the electron \( g \) factor, and \( \mu_B \) is the Bohr magneton. Assuming \( g = 2 \), we get \( H_p^{\text{BCS}} = 1.84 T_c \), with \( H_p^{\text{BCS}} \) and \( T_c \) in tesla and Kelvin units, respectively. At ambient pressure the \( H_{c2} \) exhibits the temperature dependence characteristic of the Pauli paramagnetic pair-breaking effect, dominating due to the weakness of the orbital magnetic effect. That is, the influence of the magnetic field on the electron orbital motion is depressed when the field is applied exactly parallel to the superconducting plane, due to the weak interplane electron transfer.

In the Ginzburg-Landau (GL) model, the \( H_{c2} \) is inversely proportional to the product \( \xi_\perp \xi_\parallel \) and, in conjunction with

### TABLE I. Parameters of the superconducting state for pressurized \( \kappa-(\text{BEDT-TTF})_2 \text{Cu}[\text{N(CN)}_2] \text{Br} \).

<table>
<thead>
<tr>
<th>( T_c/(K)/P(\text{kbar}) ) ( a )</th>
<th>( \mu_0 H_{c2,0} ) (T)</th>
<th>( \mu_0 H_{c2,1} ) (T)</th>
<th>( \xi_{0,0} ) (nm)</th>
<th>( \xi_{0,1} ) (nm)</th>
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</thead>
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<td>2.4/2.4</td>
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<td>4.4</td>
<td>1.9</td>
<td>38</td>
</tr>
<tr>
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<td>0.9</td>
<td>9.4</td>
<td>1.8</td>
<td>19</td>
</tr>
<tr>
<td>6.3/1.5</td>
<td>1.7</td>
<td>14</td>
<td>1.7</td>
<td>14</td>
</tr>
<tr>
<td>11.3/1 bar</td>
<td>0.4 (^b)</td>
<td>3.7 (^b)</td>
<td>0.6 (^c)</td>
<td>2.3</td>
</tr>
</tbody>
</table>

\(^a\)Reference 13.  
\(^b\)Reference 5.  
\(^c\)Reference 20.

\( H_{c2} \) normalized with \( H_p^{\text{BCS}} \) versus the dimensionless temperature \( T/T_c \). The broken line represents the temperature dependence expected for Pauli limiting, represented by \( (1 - T/T_c)^{\frac{1}{2}} \).

\( H_{c2} \sim 1/\xi_0^2 \), it allows to evaluate \( \xi_{0,0} \) and \( \xi_{0,1} \), assuming that \( \xi_{0,0} \) is isotropic within the plane. Table I shows the reported values of the coherence lengths determined in this way at ambient pressure,\(^5,20,21\) and the values determined from the inclination dependence at 0.3 K under pressure in this work. An abrupt change in the pressure dependence is found for both \( \xi_{0,0} \) and \( \xi_{0,1} \), with the pressure boundary lying in the region less than 1 kbar.

In Fig. 5 we compare the effect of pressure on the temperature dependence of the interplane resistance \( R \) and in-plane resistance \( R_\parallel \). The data for \( R_\parallel \) are in reasonable agreement with previous reports.\(^13\) Both \( R_\parallel \) and \( R \) notably decrease with pressure, indicating the increase of the in-plane and interplane transfer integrals. The resistance maximum, due to ethylene ordering,\(^18\) seen at ambient pressure for both in-plane directions, is completely suppressed at 1.5 kbar. In the pressure range between these two \( P \) values, anomalies in pressure dependence of \( T_c \) (Ref. 22) and of ultrasonic attenuation\(^23\) were reported, indicating phase transition in the low-pressure region. The transition can be

**FIG. 4.** \( H_{c2} \) normalized with \( H_p^{\text{BCS}} \) versus the dimensionless temperature \( T/T_c \). The broken line represents the temperature dependence expected for Pauli limiting, represented by \( (1 - T/T_c)^{\frac{1}{2}} \).

**FIG. 5.** Temperature dependence of the interplane (a) and inplane (b) resistances for \( P = 0 \) kbar and \( P = 1.5 \) kbar.
ascribed to the change in the arrangement of the ethylene fragment in the outer rings of BEDT-TTF molecules. At ambient pressure the state of ordering is influenced by the cooling procedure and the disorder cannot be completely removed down to low temperatures at any cooling rate. A similar phenomenon in relation to the disorder in the arrangement of the ethylene groups has a strong effect on $T_c$ of $\beta-(\text{BEDT-TTF})_2\text{I}_3$. Recently we proposed a model for the influence of ethylene ordering transformation on the electronic structure in a closely related $\kappa-(\text{BEDT-TTF})_2\text{Cu}[\text{N}(\text{CN})_2]^+\text{I}_3$. In this salt, ordering leads to a formation of the superstructure, destroying partially the open sheet of the Fermi surface. A similar effect is implied by an influence of annealing on the electronic properties of Br salt. The disappearance of the superstructure under pressure may explain a notable increase of the coherence lengths without drastic change in $T_c$, since superstructural gaps on the Fermi surface can notably modify the orbital motion within the plane, and for some particular positions on the Fermi surface even completely remove closed orbits.

B. Transcendence over BCS Pauli paramagnetic limit

When the orbital magnetic effect on $H_{c2}$ becomes weak, the pair breaking due to the Pauli paramagnetism becomes important for a singlet superconductor. This idea is supported by the shape of the phase diagram at ambient pressure, but the observed $H_{c2}$ far exceeds $H_{P}^{\text{BCS}}$. Several contributions can lead to the transcendence over the $H_{P}^{\text{BCS}}$. The effect of the spin-orbit scattering, however, seems to be too weak, since the material is clean, as evidenced by the observation of clear magnetoquantum oscillations. On the other hand, the reduced value of the effective $g$ factor of the electrons in the normal state and the strong-coupling scenario of the superconductivity should be considered. It was shown that the value of the effective $g$ factor for paramagnetic suppression should be the same as deduced from the de Haas--van Alphen effect. For Br salt, the $g$ value determined from the angle-dependent magnetoquantum oscillation is 1.5. Furthermore from the magnitude of the specific-heat jump at $T_c$ at ambient pressure $\alpha$ was determined as 2.7, implying the enhancement in the coupling by a factor of 1.5. The strong-coupling scenario is supported also in other specific-heat and tunneling experiments. The reduction of the $g$ factor by a factor of 1.33 and an approximately 1.5 times increase of the superconducting gap $\Delta$ give the value of $H_{P}^{\text{BCS}} \sim 2H_{P}^{\text{BCS}}$, in reasonable agreement with the experimental estimation.

C. Pressure dependence

The linear temperature dependence of the $H_{c2}$ near $T_c$ is derived from the GL model in which the orbital motion is taken into account. In this case, the $H_{c2}$ tends to saturate near 0 K, so as to obey an empirical temperature dependence as $[1 - (T/T_c)^2]$. The observed linear temperature dependence of $H_{c2}$ under pressure in $T \approx T_c/2$ indicates that the orbital pair-breaking mechanism is not negligible even for the parallel field. This is because the pressure increases the interplane transfer, as evidenced by a 3.84 times decrease of interplane resistance at $T$ slightly higher than $T_c$ on going from 0 to 1.5 kbar. In concert with this, $H_{c2}/H_{P}^{\text{BCS}}$ (Fig. 4) becomes gradually lower than that at ambient pressure where it is determined by the paramagnetic effect. This is in agreement with the increase in $\xi_\perp$ and $\xi_\parallel$ in the pressurized crystals as shown in Table I.

It is noteworthy that $\xi_\parallel$ increases more rapidly with pressure than $\xi_\perp$. This result is related to the anisotropy in the crystal compressibility: the in-plane spacing determined by the interaction between BEDT-TTF molecules is more compliant to pressure than the inter-plane spacing determined by the ionic interaction between charged BEDT-TTF molecules and counter anions. The ratio of $R_j$ under $P=0$ kbar to that under 1.5 kbar became 4.91, which is slightly larger than that for $R_\parallel$. However, the change in the coherence lengths on the pressure application reaches 2.8–4.2 times for $\xi_\perp$ and 3.8–6.1 times $\xi_\parallel$, according to Table I. They are too large to be explained in terms of the GL model, given that the coherence length is inversely proportional to the square root of the effective electron mass. This supports the view that the change on the pressure application is connected to a phase transition in the electronic states.

D. Comparison with $\kappa-(\text{BEDT-TTF})_2\text{Cu(NCS)}_2$

It was claimed recently that the high $H_{c2}$ and the non-saturating temperature dependence in NCS salt can be due to the formation of an FFLO state. This state, characterized by a nonzero momentum of the Cooper pair and a spatial oscillation of the order parameter, can appear as a solution of the gap equation when the Zeeman energy becomes comparable to the condensation energy. For an FFLO state it is predicted that $H_{c2}$ exceeds the Pauli paramagnetic limit in the temperature region below 0.56$T_c$, associated with the transcendence increasing towards 0 K.

For Br salt, the formation of the FFLO state, which is strongly sensitive to impurities and defects, is not probable at ambient pressure due to the disorder in the ethylene fragments. The depression of the disorder by pressure is expected to promote the formation of the FFLO state, but the simultaneous increase in the interlayer transfer enhances the orbital magnetic effect. As a result, under pressure $H_{c2}$ is affected by the orbital effect together with the Pauli paramagnetic effect. The decrease in $H_{c2}/H_{P}^{\text{BCS}}$ near 0 K to 1.2–1.3 under the pressure from the value (about 2) estimated at ambient pressure is ascribed to the mixing of the orbital effect.

It is interesting then to see the change of the behavior in $H_{c2}$ under pressure for NCS salt. The results shown in Fig. 6 indicate that the temperature dependence tends to show a downward curvature with the increase in pressure so as to show the form of $[1 - (T/T_{c2})^2]$. Simultaneously the value of $H_{c2}(0)/H_{P}^{\text{BCS}}$ decreases to 1.3 at $\sim 1.5$ kbar from 1.9 at ambient pressure. This indicates that the orbital magnetic effect is enhanced by pressure also in NCS salt and, because of that, even if the FFLO state is formed at ambient pressure, it is not probable under pressure due to the in-
volvement of the orbital magnetic effect. Thus the results on $H_c(0)$ for the pressurized samples indicate that the states for Br salt and NCS salt are connected as expected from the similarity in the electronic structure but the states at ambient pressure split into different directions, according to the degree of the ethylene disorder.

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