Disorder effect on the superconductivity of the organic superconductor $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ partly substituted by the deuterated molecules

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Abstract. The effect of the disorder induced by the deuterated BEDT-TTF ($d$-BEDT-TTF) molecule substitution on the superconductivity has been investigated in the quasi two dimensional organic superconductor $\kappa$-[$(h$-BEDT-TTF)$_{1-x}(d$-BEDT-TTF)$_x$]$_2$Cu(NCS)$_2$. The scattering time $\tau$ obtained by the de Haas-van Alphen effect changes in the form of $1/\tau \propto x(1-x)$, which is known as Nordheim relation. Although the scattering time takes minimum around $x = 0.5$, the superconducting transition temperature $T_c$ increases linearly with $x$. The relation between the scattering time and $T_c$ is not simply explained by the nonmagnetic impurity effect in the unconventional superconductivity expected in this organic superconductor.

The superconductivity in the organic charge transfer salts, $\kappa$-(BEDT-TTF)$_2X$, where BEDT-TTF or ET denotes bis(ethylenedithio)tetrathiafulvalene, has been investigated extensively. Its remarkable feature is that the native quarter filled band is modified to the effective half filled band by the strong dimer structure consisting of two ET molecules. In such a strongly correlated electronic system, several electronic phases appear and the transitions among these phases are controlled by applying pressure and slight chemical substitution of the molecules, which should change the conduction band width $W$ with respect to the effective Coulomb repulsion $U$ between two electrons on a dimer [1]. The first order metal - insulator Mott transition divides the phase diagram into the superconducting and antiferromagnetic (AF) Mott insulator phases. Such a superconductivity nearby an AF Mott insulator has been theoretically expected to possess unconventional $d$-wave order parameter. Experimental results on the anisotropy of the superconductivity, however, have not been settled fully yet [2]. To clarify the pair breaking mechanism, the investigation of impurity effects on the superconductivity are indispensable, because it can give information on the symmetry of the order parameter and the gap formation. There have been several attempts to introduce disorder into the organic superconductors; electron, proton, and x-ray irradiation [3] [4], freeze of the conformational disorder of terminal ethylene group in ET [5] [6] [7], and the anion $X$ or donor molecule substitution [8] [9].

In this paper, we present the effect of the disorder induced by deuterated BEDT-TTF ($d$-ET) molecule substitution in $\kappa$-(ET)$_2$Cu(NCS)$_2$ on the superconducting transition temperature $T_c$ and the scattering time $\tau$ obtained by the de Haas-van Alphen (dHvA) effect, where $h$-ET is hydrogenated ET.

Single crystals of $\kappa$-[$(h$-ET)$_{1-x}(d$-ET)$_x$]$_2$Cu(NCS)$_2$ were grown by an electrochemical oxidation method. Crystals with the substitution ratio of $x = 0, 0.2, 0.5, 0.8$ and $1.0$ were
prepared. The substitution ratio was examined by using the molecular vibration amplitude of the terminal ethylene group in the infrared reflectance spectra. The ratio $x$ measured was almost the same with the nominal value in the preparation. The magnetic susceptibility in 0.3 mT was measured by a SQUID magnetometer. $T_c$ was determined as the crossing point of the interpolation lines in the normal and superconducting regions. The magnetic torque measurements were performed by using a precision capacitance torquemeter [10]. The holder with the samples was cooled from room temperature to 4.2K in 24 hours and directly immersed in liquid $^4$He of a refrigerator combined with a 15-T superconducting magnet at the High Field Laboratory for Superconducting Materials (HFLSM), IMR, Tohoku University.

Figure 1 shows the substitution ratio $x$ dependence of $T_c$ and $-4\pi\chi$ at 2 K in 0.3 mT. The horizontal pressure value is a relative scale for the fully deuterated $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br.

Figure 2 shows the torque-\(d\)HvA oscillations in $\kappa$-[(h-ET)$_{1-x}$d-ET)$_x$$_2$Cu(NCS)$_2$ with $x = 0.5$ and 1 at 0.5 K in the magnetic field nearly perpendicular to the conductive $b$-$c$ plane. Inset shows the Dingle plot of the oscillations.
the effective mass and the scattering time of the cyclotron orbiting electrons on the Fermi surfaces are obtained from the oscillation frequency $F$, the temperature and magnetic field dependence of the oscillation amplitude, respectively, on the basis of the Lifshitz-Kosevich formula [13]. The amplitude $A_{\text{LK}}$ is described as, $A_{\text{LK}} \propto H^n R_D R_T R_S$, where the temperature factor $R_T = (\lambda \mu_c T/H) / \sinh(\lambda \mu_c T/H)$, the Dingle factor $R_D = \exp(-\lambda \mu_c T_D/H)$ and the spin factor $R_S = \cos(\pi g \mu_b / 2)$. Here, $\lambda \equiv 2\pi^2 c k_B/e\hbar = 14.69$ T/K, $\mu_b$ and $\mu_c$ are the band and cyclotron effective mass ratio, and $T_D$ is the Dingle temperature related to the scattering time $\tau$ with $T_D = \hbar / 2\pi k_B \tau$. For the torque-dHvA amplitude in the 3D (2D) case, $n$ is 3/2 (1).

The oscillation frequency in the magnetic field perpendicular to the $b$-$c$ plane is $F = 597 \pm 2$ T, which is attributed to the $\alpha$-orbit, in all samples with $x = 0, 0.2, 0.5, 0.8$ and 1, which is consistent with the previous report in $x = 0$ and 1 [14]. The magnetic breakdown $\beta$-orbit is not observed in the present measurements up to 14.5 T at 0.5 K. The effective mass ratio $\mu$ of approximately 3.2 does not depend on $x$ as shown in Fig. 3(a), whereas the Dingle temperature obtained by the magnetic field dependence of the oscillation amplitude markedly varies with $x$ in spite of a fairly large sample dependence shown in $x = 0$ and $x = 0.5$. The oscillation amplitude in $x = 0.5$ has larger field dependence compared with that in $x = 1$, which indicates that the former has smaller $\tau$ than the latter, as shown in the inset of Fig. 2. The downward deviation from the straight line in low field region results from the superconducting fluctuation [10].

The $x$ dependences of $\mu$ and $\tau$ are shown in Figs. 3(a) and 3(b), respectively. It should be noted that $\tau$ is reduced by the partial substitution and takes the minimum around $x \approx 0.5$. The value in $x = 0.5$ becomes almost 70% of $\tau$ obtained in $x = 0$ and 1, contrasting to the value of $\mu$ almost independent of $x$. The dashed curve in Fig. 3(b) shows a relation of $1/\tau \propto x(1-x)$, known as the Nordheim relation in the residual resistivity of the metal alloys like as copper-gold

**Figure 3.** Substitution ratio $x$ dependence of (a) the effective mass ratio and (b) the scattering time obtained by the torque-dHvA effect. The dashed curve in the lower panel shows the Nordheim relation.
The scattering time obtained by the dHvA effect should be affected also by the small angle scattering in addition to the large angle scattering dominant in the residual resistivity. In preliminary resistivity measurements of the present substitution system, the residual resistivity does not show the significant $x$ dependence. Thus the deuterated molecule substitution may induce mainly the small angle scattering. The mean free path calculated by $\tau \bar{\tau}$ becomes about $120 \text{ nm in } x = 0.5$. This is still so longer than the in-plane coherence length $\xi \approx 5 \text{ nm}$ that the substituted samples are still classified into clean limit superconductors for all $x$.

We finally discuss the impurity scattering effect on the superconductivity by the deuterated molecular substitution. The Abrikosov-Gorkov (AG) formula has originally described the magnetic impurity effect on the reduction of $T_c$ in the conventional superconductivity. The same formulation has been expected to be applicable to the nonmagnetic impurity effect in the unconventional case with non $s$-wave symmetry [17]. Indeed, a noticeable reduction of $T_c$ by nonmagnetic impurities have been successfully applied to the formula to confirm the unconventional superconductivity [18]. It is therefore interesting to examine whether the present substitution is also the case or not, because it is expected to give nonmagnetic disorders into the present unconventional superconductor. The transition temperature $T_{c}^{AG}$ affected by the impurity scattering is described in the AG formula as

$$\ln \left( \frac{T_{c0}}{T_{c}} \right) = \psi \left( \frac{1}{2} + \frac{h}{4\pi k_{B}T_{c}\sqrt{\tau}} \right) - \psi \left( \frac{1}{2} \right),$$

where $T_{c0}$ in pure system and $\psi(x)$ is the digamma function. Figure 4 shows the substitution $x$ dependence of $T_c$ measured and the calculated $T_{c}^{AG}$. The dashed curve is the calculated $T_{c}^{AG}$ based on the AG formula with $\tau$ obtained from the Nordheim approximation. $T_{c0}(x)$ originated from the chemical pressure effect ($-0.35 \text{ K/MPa}$ corresponding to $-0.23 \text{ K/MPa}$) is also potted (dash-dotted line). The observed $T_c$ does not show so large reduction expected in the AG formula although the clear reduction of $\tau$ is observed. This result suggests that the disorder induced by substitution does not work as the pair-breaker expected in the unconventional superconductivity if it is realized. It must be necessary to investigate further the impurity effect on the superconductivity.

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