Disorder effect on superconductivity in organic superconductor $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$

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Abstract. The relation between the superconductivity and the scattering time $\tau$ of the quasiparticle in the organic superconductor $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ has been investigated by measuring the de Haas-van Alphen (dHvA) oscillations. The single crystals substituted partly with BMDT-TTF molecules, $\kappa$-[(BEDT-TTF)$_{1-x}$(BMDT-TTF)$_x$]$_2$Cu(NCS)$_2$ are synthesized for introducing the nonmagnetic impurities. The oscillation frequency $F = 600 \pm 5$ T and the effective mass ratio $m^*/m_0 = 3.2 \pm 0.2$ are the same with those of no substituted crystal. On the other hand, the BMDT-TTF molecule substitution reduces the quasiparticle scattering time $\tau \sim 2.5$ psec for $x = 0$ to $\sim 0.5$ psec for $x = 0.15$. The relation between $T_c$ and $\tau$ in the nonmagnetic molecule substituted crystals is discussed in comparison with the Abrikosov-Gorkov relation.

The superconductivity in the organic charge transfer salts, $\kappa$-(BEDT-TTF)$_2$X, where BEDT-TTF 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 BEDT-TTF molecules. In 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 could 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 [2]. A superconductivity nearby an AF Mott insulator has been theoretically expected to possess unconventional $d$-wave order parameter. Experimental results on the unconventional superconductivity, however, have not been settled fully yet [3]. 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 anisotropy. There have been several attempts to introduce disorder into the organic superconductors; electron, proton, and x-ray irradiation [4, 5, 6], freeze of the conformational disorder of terminal ethylene group in ET [7, 8, 9], and the anion X or donor molecule substitution [10, 11, 12].

In this paper, we present the effect of the impurity/disorder introduced by the BMDT-TTF molecule partial substitution, where BMDT-TTF denotes bis(methylenedithio)tetrathiafulvalene, in $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ on the superconducting transition temperature $T_c$ and the scattering time $\tau$ obtained by the de Haas-van Alphen (dHvA) effect.

Single crystals of $\kappa$-[(BEDT-TTF)$_{1-x}$(BMDT-TTF)$_x$]$_2$Cu(NCS)$_2$ were grown by an electrochemical oxidation method. Crystals with the substitution ratio up to $x = 0.15$ could be grown. The substitution ratio was examined by using the molecular vibration amplitude
Figure 1. Temperature dependence of the magnetic susceptibility in $\kappa$-[\((\text{BEDT-TTF})_{1-x}(\text{BMDT-TTF})_x\)\text{Cu(NCS)}$_2$]. Inset shows the substitution ratio $x$ dependence of $T_c$. The bars indicate the transition width. See the text for the details.

Figure 2. The dHvA oscillations observed in $\kappa$-[\((\text{BEDT-TTF})_{1-x}(\text{BMDT-TTF})_x\)\text{Cu(NCS)}$_2$] with $x = 0.01$, 0.05 and 0.15 at 0.5 K in the magnetic field perpendicular to the $b$-$c$ plane. Each amplitude is normalized by the value at 15 T.

of the terminal ethylene group in the infrared reflectance spectra. The substitution ratio $x$ measured was almost the same with the nominal value in the preparation. The magnetic susceptibility at 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 for detecting the dHvA oscillations by using a precision capacitance torquemeter [13].

Figure 1 shows the temperature dependence of the magnetic susceptibility $4\pi\chi$ in $\kappa$-[\((\text{BEDT-TTF})_{1-x}(\text{BMDT-TTF})_x\)\text{Cu(NCS)}$_2$] and the substitution ratio $x$ dependence of $T_c$. The demagnetization effect is corrected by using an ellipsoidal approximation. The width of the superconducting transition is evaluated to be the half width of the temperature derivative curve of the susceptibility. The BMDT-TTF molecule substitution reduces $T_c$ almost linearly with $x$ up to $\sim 0.1$. In addition, the transition width increases gradually with the decrease of $T_c$. The observed large suppression of the superconductivity may be caused by the impurity and disorder effects with the nonmagnetic BMDT-TTF molecule substitution. The present substitution effect is different from the previous results of the deuterated BEDT-TTF molecule substitution [14]. The deuterated BEDT-TTF molecule substitution does not affect so much on the superconductivity as a role of the impurities/disorders, but it works as a good tunable parameter for $W$ as a chemical pressure [11]. The increase of the transition width indicates that the BMDT-TTF molecule substitution causes also the inhomogeneity of the superconductivity. Above $x = 0.1$, $T_c$ does not decrease seemingly in proportion to $x$. This may be due to the definition of $T_c$ which tends to reflect higher $T_c$’s in inhomogeneous superconductivity by disorder.

Figure 2 shows the de Haas-van Alphen (dHvA) oscillations in the BMDT-TTF molecule substituted samples at 0.5 K in the magnetic field perpendicular to the conductive $b$-$c$ plane. The molecule substitution reduces the oscillation amplitude and then the magnetic fields at which the oscillations are observable shift to higher fields with the substitution. From the oscillations,
the cross sectional area of the Fermi surface, 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 [15]. The amplitude \( A_{LK} \) is described as, 
\[
A_{LK} \propto H^n R_D R_T R_S,
\]
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, \( \lambda \equiv 2\pi^2 \epsilon k_B/e\hbar = 14.69 \) 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 of \( F = 600 \pm 5 \) T and the effective mass ratio \( m^*/m_0 = 3.2 \pm 0.2 \), which are attributed to the \( \alpha \)-orbit, do not depend on \( x \) as shown in Figs. 3(a) and 3(b). It is noted here that the magnetic breakdown \( \beta \)-orbit is not observed in the present measurements up to 15 T at 0.5 K. On the other hand, the scattering time \( \tau \) decreases rapidly with the substitution from \( \tau \simeq 2.5 \) psec for \( x = 0 \) to 0.5 psec for \( x = 0.15 \). The decrease of \( \tau \) is considered to be mostly due to the impurity scattering induced by the substituted BMDT-TTF molecules because of unchanged \( F \) and \( m^*/m_0 \) with \( x \). In the region of large substitution, however, inhomogeneity may be caused by the substitution. The inhomogeneity could influence upon the decrease of \( \tau \) obtained by the dHvA effect in addition to the impurity scatterings [16, 17]. As we pointed out above, the increase of the transition width of \( T_c \) with \( x \gg 0.1 \) may be reflective of the inhomogeneity. The mean free path \( l \simeq 20 \) nm for \( x = 0.15 \), however, is still longer than the in-plane coherence length \( \xi \simeq 5 - 6 \) nm, where \( l = v_F \tau \) and \( v_F \simeq 5 \times 10^4 \) m/s for the \( \alpha \)-orbit [3, 12]. This means that the superconductivity of this substituted system can be treated as a clean limit case.

We finally discuss the impurity scattering effect on the superconductivity by the BMDT-
TTF 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 [18]. Indeed, a noticeable reduction of $T_c$ by nonmagnetic impurities has been successfully applied to the AG formula to confirm the unconventional superconductivity [19]. It is therefore interesting to examine whether the present substitution is also the case or not. The transition temperature $T_c^{AG}$ affected by the impurity scattering is described in the AG formula as \[ \ln \left( \frac{T_c}{T_c^{AG}} \right) = \psi \left( \frac{1}{2} + \frac{\hbar}{4\pi k_B T_c^{AG} \tau} \right) - \psi \left( \frac{1}{2} \right), \] where $T_{c0}$ is $T_c$ in perfectly pure system with $\tau \to \infty$ and $\psi(x)$ is the digamma function. Figure 4 shows the comparison between the substitution ratio $x$ dependence of the observed $T_c$ and the calculated $T_c^{AG}$. The dashed curve is the calculated $T_c^{AG}$ based on the AG formula with $T_{c0} = 10.3$ K. The observed $T_c$ is in fairly good agreement with $T_c^{AG}$ for $x < 0.1$. For $x > 0.1$, however, the scattering time observed deviates from the AG formula. This deviation may be caused by an additional scattering time by the inhomogeneity resulting from a large number of the substituted BMDT-TTF molecules. The scattering time obtained from the dHvA effect is affected also by the inhomogeneity due to spatial variations in the potential for the quasiparticles [16, 17] in addition to the elastic impurity scattering. On the other hand, the scattering for the pair breaking mechanism in the AG formula is considered to be originated from the elastic impurity scattering. The present results suggest that the nonmagnetic impurity scattering induced by the molecule substitution works as the pair-breaker expected in the unconventional superconductivity, while the inhomogeneity/disorder appearing in larger $x$ region does not affect so much on the reduction of $T_c$ but has an influence on the dHvA effect. It must be necessary to investigate further the impurity and inhomogeneity/disorder effects on both the superconductivity and quasiparticle scatterings.

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