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Many-body effect on the superconducting transition temperature in layered organic superconductors

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We have calculated bare cyclotron masses of layered organic superconductors, κ-type bis(ethylenedithio)tetrathiafulvalene (ET) and bis(ethylenedithio)tetraselenafulvalene (BETS) salts, in which the effective cyclotron masses have been determined by quantum oscillations. The higher superconducting transition temperature (T_c) materials show the larger ratios of the observed to the bare cyclotron masses. This indicates that the mass enhancement, i.e., strong many-body effect is quite important for a high-T_c organic superconductor. The κ-type BETS salts need a stronger many-body interaction than the ET salts to be a superconductor, and the magnetic exchange interaction with magnetic anions realizes this requirement.

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A superconducting phase appears near an antiferromagnetic state in strongly correlated electron materials including the copper-oxide (high-T_c) superconductors,[1] heavy fermion compounds,[2] and organic molecular crystals.[3,4] Current theoretical models account for these phase diagrams in view of the role of spin fluctuations in mediating the superconductivity.[5] Although the ground state of high-T_c superconductors is controlled by the carrier number, that of organic compounds is regulated by pressure. For example, in κ-(ET)$_2X$, where ET is bis(ethylenedithio)tetrathiafulvalene (Fig. 1) and X is an anion, the antiferromagnetic insulating state changes to a superconducting phase by applying pressure. This phase diagram, called Kanoda's diagram,[3] is well explained by the strength of the electronic correlation.

The κ-type donor arrangement is shown in Fig. 1. The donor molecules form face-to-face orthogonal dimers connected by the transfer integral t_{b1}; that is, they are rotated by approximately 90° with respect to each other. Since a dimer has one carrier, the effective on-site Coulomb repulsion U_{eff} is defined for a dimer ($U_{\mathrm{eff}} \sim 0.4-0.6$ eV).[3,6–8] Two ET highest occupied molecular orbitals (HOMO's) in the dimer are split into bonding and antibonding orbitals, each of which forms a conduction band due to interdimer transfer integrals. The two bands are separated by a finite gap, and the Fermi level lies in the upper energy band with the bandwidth $W \sim 0.4-0.6$ eV.[3,9] Therefore, κ-(ET)$_2X$ can be treated as a strongly correlated electron material with an effective half-filled band. An external pressure controls the ratio U_{eff}/W, then Kanoda's diagram strongly suggests that the superconductivity is mediated by not only electron-phonon interaction but also other many-body effects, i.e., electron-electron interaction. Actually, Caulfield *et al.* have found that the higher T_c state has the heavier effective cyclotron mass from the high-pressure Shubnikov–de Haas oscillations of κ-(ET)$_2$Cu(NCS)$_2$.[10]

Many-body effects clearly appear in the effective masses of quasiparticles. From the analysis of the quantum oscillation measurements, the de Haas–van Alphen (dHvA) and Shubnikov–de Haas (SdH) oscillations, we can estimate the effective cyclotron mass of the carrier and the shape of the Fermi surface (FS).[11] This effective mass includes all interacting effects. The FS of the κ-type organic superconductors has been calculated by the tight-binding approximation as shown in Fig. 2. The FS is composed of the overlapping cylinders and there are two fundamental α and β orbits. Although the α pocket area depends on the transfer integrals ratio, the β orbit area is equal to 100% of the first Brillouin zone (BZ) and is independent of the transfer integral values. This simple FS is in agreement with the results of the quantum oscillation measurements.[4,11]

The effective cyclotron masses for the quasiparticles are obtained from the temperature dependence of the oscillation amplitude, which is proportional to the temperature reduction factor R_T. This damping factor is expressed as

$$R_T = \frac{K(m^*/m_0)T/(B\cos\theta)}{\sinh[K(m^*/m_0)T/(B\cos\theta)]}, \tag{1}$$

where B is the strength of the magnetic field, θ is the tilt angle between the magnetic field and the axis perpendicular to the conducting plane, m^* is the effective cyclotron mass at

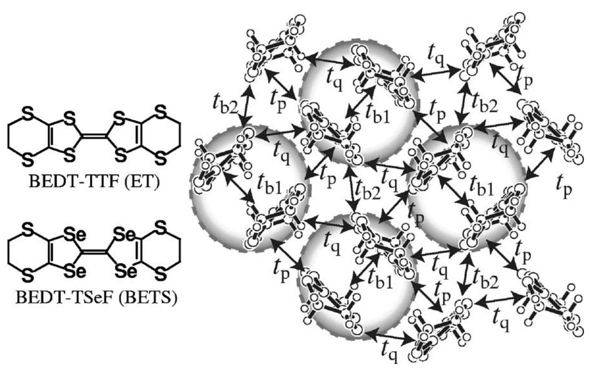

FIG. 1. The donor molecules and the κ-type arrangement of donor molecules projected along the molecular long axis. A shaded circle means a dimer.

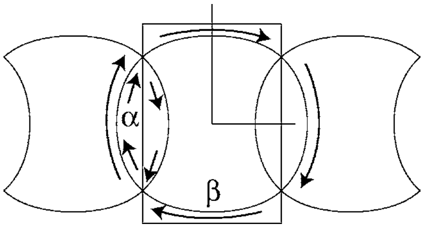

FIG. 2. α and β orbits in a κ-(ET)$_2X$ superconductor. The arrows indicate the trajectory of holes on each orbit in the presence of a magnetic field perpendicular to the conducting layers.

$\theta = 0°, m_0$ is the free electron mass, and K is equal to 14.69 T/K.[11]

The bare cyclotron mass is defined with the cyclotron frequency by

$$\omega_c = \frac{eB}{m_c}. \tag{2}$$

This mass involves an average of the dispersion relation along the periodic orbit. The experimentally determined mass includes not only the band dispersion but also all interactions, i.e., electron-phonon and electron-electron interactions. Therefore, we have written the observed effective cyclotron mass as m^* to distinguish the bare cyclotron mass m_c. The effective cyclotron mass of the quasiparticle is expressed as

$$m^* = (1 + \lambda_{ep})(1 + \lambda_{ee})m_c = (1 + \lambda^*)m_c, \tag{3}$$

where λ_{ep} is an electron-phonon interaction, λ_{ee} is an electron-electron interaction, and λ^* is a parameter including all interactions.

Equation (2) can be rearranged to give

$$m_c = \frac{\hbar^2}{2\pi} \frac{\partial A_F(E)}{\partial E}\bigg|_{E=E_F}, \tag{4}$$

where $A_F(E)$ is the cross sectional area of the closed FS defined by the circuit of the carrier motion in the presence of a magnetic field B.[12] We can calculate m_c by this equation.

The present paper reports the relation between the calculated bare cyclotron mass and the observed cyclotron mass of the κ-type organic superconductors based on not only the ET salts but also the BETS salts, where BETS is bis(ethylenedithio)tetraselenafulvalene (Fig. 1). Our results show that it is important to develop a strongly correlated material for a high-T_c organic superconductor.

The energy-band structure was calculated on the basis of the extended Hückel method and the tight-binding approximation from the atomic coordinates found by the x-ray crystal structure analysis.[13–15] The same atomic orbital parameters as those in Ref. 13 for the ET salts and those in Ref. 14 for the BETS salts were used. In our calculation, $\frac{\partial A_F(E)}{\partial E}\big|_{E=E_F}$ is treated as $[A_F(E_F+\Delta E) - A_F(E_F-\Delta E)]/(2\Delta E)$, where we set ΔE as 1 meV. For some materials, the β orbit has small gaps at the zone boundary because of the crystallographic symmetry, and this orbit becomes a magnetic breakdown orbit. However, we have divided the first BZ into 600×500 meshes, and numerically calculated $A_F(E)$ by counting the meshes inside the Fermi wave number.

Our results are shown in Table I with the experimental results. Merino and Mckenzie have calculated the bare-band mass of several κ-(ET)$_2X$ conductors by some methods.[36] Our results are in agreement with their results based on the extended Hückel approximation.

The calculated total density of states $N(E_F)$ and the experimentally determined Debye temperature Θ_D of the κ-type organic superconductors based on ET and BETS are independent of T_c. For both the ET and BETS salts, the α-orbit masses are lighter than the free-electron mass, and the β orbit masses are heavier than m_0. The ratio m^*/m_c of the α orbit is the same as that of the β orbit in the same material. This is also the same as that in Ref. 36.

For κ-(ET)$_2$Cu(NCS)$_2$, the cyclotron resonance spectra have been measured and the cyclotron mass (m_λ) of the α orbit, which includes only electron-phonon interaction, has been found to be $1.18m_0$.[6] The electron-phonon coupling constant is obtained as $\lambda_{ep} = 0.33$ using m_λ and m_c. On the other hand, the detailed analysis of the optical reflectance spectra has given us the electron-molecular vibration coupling constant as 0.20 along the b axis and 0.25 along the c axis.[37] This value is slightly smaller than the above-determined λ_{ep}. We can estimate the electron-electron interaction strength as $\lambda_{ee} = 2.0$ using m_λ, m_c, and Eq. (3); this indicates that m^* is enhanced by mainly electron-electron interaction.

Figure 3 shows the relation between T_c and the averaged λ^* for the α and β orbits. For both ET and BETS salts, T_c strongly depends on λ^* and the behavior shows $\exp\left(\frac{-1}{C\lambda^*}\right)$ dependence, where C is a constant. The highest-T_c ET material has the largest value of λ^*. This is consistent with Kanoda's phase diagram for κ-(ET)$_2X$, because the Cu[N(CN)$_2$]Br salt exists at the border between the superconductor and the antiferromagnetic insulator, i.e., in the strongly correlated state.[3] On the other hand, the I$_3$ salt with low T_c has a small λ^*. The behavior of the ET salts in Fig. 3 indicates that the electronic correlation is important for a high-T_c organic superconductor.

The BETS salts also show the same tendency as the ET salts in Fig. 3. It seems that larger λ^* than that of the ET salts is required for κ-(BETS)$_2X$ to be a superconductor. The lowest T_c BETS salt ($T_c \sim 0.1$ K) is the FeCl$_4$ salt with $\lambda^* = 2.3$. The Cu[N(CN)$_2$]Br, C(CN)$_3$, and GaCl$_4$ salts do not show superconductivity in experiments above $T \sim 0.5$ K, and their λ^*s are smaller than that of the FeCl$_4$ salt. The fitted line in Fig. 3 speculates that the BETS salt with $\lambda^* = 1.9$ shows superconductivity at $T_c \sim 38$ mK. Three salts (the Cu[N(CN)$_2$]Br, C(CN)$_3$, and GaCl$_4$ salts) will not be superconductors in the experimentally accessible temperature range using a dilution refrigerator, $T \sim 35$ mK.

Only κ-(BETS)$_2X$ with a magnetic anion (FeY_4^-; Y = Cl, Br) shows superconductivity. κ-(BETS)$_2$FeBr$_4$ shows field-induced superconductivity (FISC), and the maximum T_c in the FISC phase appears under the external field of 12.6 T.[38] This means that the internal field originating in the π-d magnetic exchange interaction between the

TABLE I. Superconducting transition temperatures under zero magnetic field, the calculated density of states at the Fermi level for the electron of one-spin orientation $N\ (E_F)$, the Debye temperatures Θ_D, the calculated bandwidths of the upper band W, the observed SdH or dHvA frequencies F_{expt}, the effective cyclotron mass ratios m^*/m_0, the calculated cyclotron mass ratios m_c/m_0, and the ratio between the effective and calculated cyclotron masses m^*/m_c. The total density of states $N\ (E_F)$ is given in units of states eV^{-1} $\mathrm{molecule}^{-1}$ spin^{-1}.

Materials	T_c (K)	$N\ (E_F)$[a]	Θ_D (K)	W (eV)[a]	F_{expt} (T)	$\frac{m^*}{m_0}$	$\left(\frac{m_c}{m_0}\right)^{\mathrm{a}}$	$\left(\frac{m^*}{m_c}\right)^{\mathrm{a}}$	Refs.
κ-$(\mathrm{ET})_2\mathrm{Cu}[\mathrm{N(CN)}_2]\mathrm{Br}$	11.8	1.94	210±15	0.60	— (α)	—	0.84	—	16,17
					3810 (β)	6.7	1.7	3.9	18
κ-$(\mathrm{ET})_2\mathrm{Cu(NCS)}_2$	10.4	1.80	215±10	0.58	625 (α)	3.5	0.89	3.9	19–21
					3800 (β)	6.9	1.7	4.0	21
κ-$(\mathrm{ET})_2\mathrm{Ag(CN)}_2\cdot\mathrm{H_2O}$	5.0	1.95	—	0.55	?[b] (α)	2.7	0.93	2.9	22,23
					— (β)	—	1.9	—	
κ-$(\mathrm{ET})_2\mathrm{I}_3$	3.6	1.81	218±7	0.61	571 (α)	1.85	0.83	2.3	24–26
					3883 (β)	3.9	1.7	2.3	26
κ-$(\mathrm{BETS})_2\mathrm{FeBr}_4$	1.0	1.53	—	0.71	847 (α)	4.7	0.81	5.8	27,28
					4292 (β)	8.0	1.4	5.7	28
κ-$(\mathrm{BETS})_2\mathrm{FeCl}_4$	0.1	1.60	—	0.68	864 (α)	2.8	0.88	3.2	29,30
					4296 (β)	5.3	1.6	3.3	30
κ-$(\mathrm{BETS})_2\mathrm{Cu}[\mathrm{N(CN)}_2]\mathrm{Br}$	Metal	1.09	—	1.04	— (α)	—	0.49	—	31
	(>0.44K)				3799 (β)	2.7	0.96	2.8	32
κ-$(\mathrm{BETS})_2\mathrm{C(CN)}_3$	Metal	1.43	—	0.84	950 (α)	1.7	0.89	1.9	33
	(>1.3K)				4480 (β)	3.3	1.4	2.3	33
κ-$(\mathrm{BETS})_2\mathrm{GaCl}_4$	Metal	1.57	—	0.76	816 (α)	1.2	0.89	1.3	34,35
	(>0.5K)				4350 (β)	2.4	1.5	1.6	35

[a] This work.

[b] The observed frequency is not described.

BETS and magnetic anion molecules $J_{\pi d}$ is 12.6 T. For κ-$(\mathrm{BETS})_2\mathrm{FeBr}_4$, the internal field is estimated as 14.7 T from the calculated $J_{\pi d}$.[14] Therefore, the calculated $J_{\pi d}$ of the κ-$(\mathrm{BETS})_2\mathrm{Fe}Y_4$ will be a good estimation. The ratio of calculated $J_{\pi d}$ between the FeBr_4 and FeCl_4 salts ($J_{\pi d,\mathrm{FeBr}_4}/J_{\pi d,\mathrm{FeCl}_4}$) is 2.5;[14] this is close to the ratio $\lambda^*_{\mathrm{FeBr}_4}/\lambda^*_{\mathrm{FeCl}_4}=2.2$. The origin of the large λ^* in κ-$(\mathrm{BETS})_2\mathrm{Fe}Y_4$ is probably mainly the π-d interaction.

We should discuss a reason why κ-$(\mathrm{BETS})_2X$ needs larger λ^* than that of κ-$(\mathrm{ET})_2X$ to be a superconductor. The transfer integrals of the BETS salts are larger than those of the ET salts because of the size difference between S and Se atoms. As a result, the bandwidths of the upper band of the BETS salts are larger than those of the ET salts as shown in Table I. The effective on-site Coulomb repulsion for a dimer will be the same value for both molecules. The strength of the electronic correlation is strongly related to U_{eff}/W.[3] Therefore, the parameter of interactions λ^* of the BETS salts, which is mainly affected by the electronic correlation based on the result of $\lambda_{ee}/\lambda_{ep}\sim 6$ of κ-$(\mathrm{ET})_2\mathrm{Cu(NCS)}_2$, is smaller than that of the ET salts. Our results clearly demonstrate that the many-body effects are important for the κ-type salts to be superconductors.

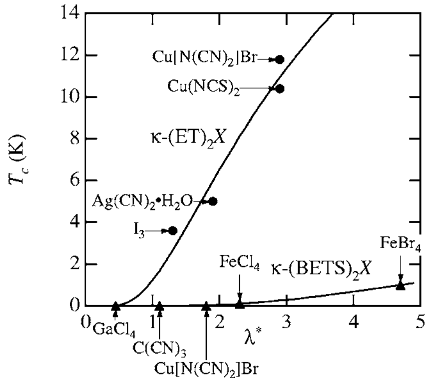

FIG. 3. λ^* dependence of T_c. The solid lines show $\exp(\frac{-1}{C\lambda^*})$ dependences.

In summary, we have calculated the bare cyclotron masses and the interaction parameter (λ^*) of layered organic superconductors. The higher T_c materials have the larger λ^*. This indicates that the mass enhancement, i.e., strong many-body effect is quite important for us to obtain a high-T_c organic superconductor. A large λ^* value is required for κ-$(\mathrm{BETS})_2X$ to be a superconductor, and the π-d interaction realizes this requirement.

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