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Carrier dynamics in an organic magnetic superconductor and related salts κ , λ -(BETS)₂MCl₄ (M = Fe, Ga)

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Abstract

In order to compare the carrier dynamics and reveal the origin of differences in their electrical behaviour, time-resolved reflectivity changes were measured on single crystals of the title compounds. The observed relaxation behaviour explained well their electrical behaviour, and indicated that different conduction mechanisms dominated κ - and λ -type BETS salts, irrespective of local spins, at about 8–100 K; the electrical behaviour of the κ -type salts is governed by relaxation times of carriers and/or density of states at the Fermi levels, while that of the λ -type salts is dominated by the latter.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Superconductivity has now been found in various materials including \sim 120 organic (or molecular) charge transfer salts [1]. A number of data suggest that there should be a universal physics in their superconductivity mechanism, which many researchers are interested in and extensively seek [2]. One of the practical and most straightforward strategies to understand the mechanism is to carry out a comparative study of a systematic series of samples. The organic charge transfer salts form a unique class of superconductors (SCs) because they realize superconductivity *without doping*, which excludes any ambiguity in the structures and band filling of the samples. In addition, their electronic band structures are generally well described by a tight-binding band approximation with simple Fermi surfaces.

Among organic SCs and related salts, the BETS (BETS = bis(ethylenedithio)tetraselenafulvalene; figure 1) salts attract particular attention because of the unique features stated below, though the number of BETS salts is limited compared with that of major organic SCs like ET (ET = bis(ethylenedithio)tetrathiafulvalene) salts

because of difficulty in synthesis, and thus little is known on their conducting properties except for the intensively studied λ -(BETS)₂FeCl₄ and related salts [3]. The charge transfer salts of BETS include SCs called λ - and κ -type structures (figure 1). Both non-magnetic $(GaCl_4^-)$ and magnetic (FeCl₄⁻) ions yield κ - and λ -type BETS salts with identical structures to each other in the respective types. In addition, they include superconducting and nonsuperconducting materials, exhibiting various ground states (figure 2). The superconducting $(T_{\rm C})$ and antiferromagnetic (T_N) transition temperatures and local spins (S) of the salts are as follows: $T_{\rm C}~pprox~0.1$ K, $T_{\rm N}~pprox~0.65$ K, S~=~5/2 for κ -(BETS)₂FeCl₄ (κ -Fe) [4], $T_N = 8$ K, S = 5/2 for λ - $(BETS)_2FeCl_4$ (λ -Fe) [5], and $T_C = 8$ K, S = 0 for λ -(BETS)₂GaCl₄ (λ -Ga) [5]. κ -(BETS)₂GaCl₄ (κ -Ga; S = 0) remains metallic from 300 to 2 K, and no transition has been found in this salt [5]. It is noteworthy that magnetic ordering and superconductivity coexist in the ground state of the κ -Fe salt [4]. The λ -Fe salt is an antiferromagnetic insulator in the ground state under ambient pressure, but exhibits pressure-induced superconductivity [6] and even magneticfield-induced superconductivity [7]. Accordingly, the title compounds are the samples of choice for comparative study for the (super)conduction mechanism.

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Figure 1. (a) Molecular structure of BETS and crystal structures of (b) λ - and (c) κ -(BETS)₂GaCl₄. Hydrogen atoms are omitted for clarity in (b) and (c).

Experimental facts indicate that local spins should play an important role in the conduction properties of the Fe-containing BETS salts. Meanwhile, as for the mechanism of superconductivity, important questions remain unanswered such as the connection between superconductivity and local spins. The correlation between crystal/electronic structures and conducting properties is very complicated in the organic SCs, and (dis)similarity in crystal structures and/or absence/presence of local spins alone simply fail to explain their electrical behaviour even in a qualitative way. The most fundamental and puzzling problems on their electrical behaviour are as follows.



Figure 2. Temperature dependences of electrical resistivity of (a) λ - and (b) κ -type BETS salts. Reproduced from [5] with permission. Copyright 1993 by the Chemical Society of Japan.

- (1) λ -(BETS)₂MCl₄ (M = Fe, Ga) have nearly identical band structures [8] and temperature dependence of resistivity ($\rho'(T)$) to those of the κ -type ET SCs, in spite of totally different molecular arrangements between κ and λ -type structures.
- (2) κ -(BETS)₂MCl₄ (M = Fe, Ga) have nearly identical crystal and band structures [8] to those of the κ -type ET SCs, in spite of totally different $\rho'(T)$ between κ -type BETS and ET salts.

In such cases, direct observation of carrier dynamics should provide an important piece of information.

In this paper, we present the carrier dynamics in κ -, λ -(BETS)₂MCl₄ (M = Fe, Ga) obtained from the timeresolved polarized reflectance spectra. This method can detect any interaction affecting electrical behaviour, and actually revealed the differences of dominant factors in their conduction mechanisms.

2. Experimental details

The single crystalline samples were prepared according to the literature [8]. Polarized pump and probe beams (~10 μ m Ø) were incident on the conduction planes (the crystallographic ac-planes) of all the crystals. Polarization of the incident light was aligned with the a-axes, which was checked by x-ray oscillation photographs. Polarization dependence will be reported elsewhere [15], and is not discussed here. For all the salts, pump and probe beams (76 MHz) were 8600 cm⁻¹ (1160 nm-1 eV) and 12 500 cm⁻¹ (800 nm-1.5 eV), respectively. Based on the calculated band structures [8, 10, 11], they are considered to be off-resonance optical transitions between HOMO and LUMO bands of the BETS salts (figure 3), where HOMO and LUMO respectively mean the highest occupied molecular orbital and the lowest unoccupied molecular orbital. Using this combination of wavelengths one can perturb and probe the carriers at the Fermi level $(E_{\rm F})$, which is accommodated in the HOMO band⁴. The intensities of beams were 20–150 μ W (pump) and 50–85 μ W (probe), respectively⁵. The time resolution was ~ 200 fs. All the temperatures indicated in this paper are corrected for heating effects by laser irradiation, which were estimated by varying the laser power. The experimental details and analysis of the time-resolved spectroscopy are described in previous papers [13–15]. By the optical measurement described herein, one obtains the difference in reflectivity (R) from that of the equilibrium state as a function of time: $\Delta R(t)$. The sign of ΔR does not depend on experimental conditions. However, we used a lock-in amplifier in the detection system, which allowed us to know only relative signs of ΔR in this study. The obtained ΔR was analysed by curve-fitting using the following equation:

$$\Delta R = A \exp(-t/\tau) + C \tag{1}$$

where A, τ , and C imply the amplitude of the response of carriers, relaxation time, and offset required to express a long relaxation (>10 ps), respectively.



Figure 3. Schematic energy diagram of molecular orbitals of BETS calculated on the basis of the extended Hückel approximation. Reproduced from [11] with slight modification with permission. Copyright 2002 by the Physical Society of Japan.

3. Results and discussion

3.1. Outline of relaxation behaviour

Figures 4(a) and (b) show selected $\Delta R(t)$ of the κ - and the λ -Fe salts, respectively; the $\Delta R(t)$ of the corresponding Ga salts are nearly identical to the counterparts in figures 4(a)and (b), as shown later. All the salts exhibited $\Delta R(t)$ well approximated by a single-exponential-component decay curve (equation (1)) at ca. 8–100 K except for $\Delta R(t)$ at $T \leq 50$ K of the λ -type salts. As a result of curve-fitting analysis of $\Delta R(t)$, the parameter C was always zero (not shown) except for $\Delta R(t)$ of the λ -type salts at $T \leq 8$ K, in which very slow relaxations suddenly appeared at the transition temperatures ($T_{\rm C}$, $T_{\rm N}$ = 8 K). Accordingly, finite values of C suddenly appeared at $T_{\rm C}$ ($T_{\rm N}$) (figure 4(c)). The finite offsets C are considered to correspond to the relaxation of carriers across the superconducting (λ -Ga) and band (λ -Fe) gaps, respectively [14]. At a closer examination, only the λ type salts exhibited fine structures in $\Delta R(t)$ at $T \leq 50$ K, which can be attributed to coherent phonons. For $\Delta R(t)$ at $T \leq 50$ K, we carried out curve-fitting analysis using equation (2)

$$\Delta R(t) = A \exp(-t/\tau) + B \exp(-\gamma t) \sin\{(\omega t - \phi)\pi/180\} + C$$
(2)

where B, γ , ω , and ϕ are amplitude, linewidth, angular frequency, and phase of the coherent oscillation, respectively, and the remaining parameters have the same meanings as in equation (1). The results showed that the oscillation frequency was ~0.7 THz (23 cm⁻¹) for both λ -Fe ($T_N = 8$ K) and λ -Ga ($T_C = 8$ K) salts; the observed frequency (~0.7 THz ≈ 34 K) was slightly higher than the transition temperatures (T_N , T_C). The frequency and the amplitudes of the coherent phonon remained constant around 8 K for both salts. Therefore, this phonon mode does not relate to the superconducting transition in the λ -Ga salt, whether the mechanism is within a framework of the BCS theory or not. At present, we have carried out time-resolved spectroscopy on five kinds of materials having the κ -type structures, κ -(ET)₂X, X = Cu[N(CN)₂]Br

⁴ In this work, the role of photo-excitation is different from that of standard methods of spectroscopy without time resolution in the following sense. The former is utilized to *perturb* the electronic state at the Fermi level, and the assignment of the resultant optical transition is unimportant as long as the transition involves electrons at the Fermi level. We observe *only* the temporal change of the electronic state (mainly, electron density) *at the Fermi level* through the reflectivity, and do not obtain any information from the other band/energy level to/from which the optical transition occurs. This is why we can select and utilize a high photon energy to observe low-lying excitation such as carrier dynamics. For details, see [12].

⁵ In order to avoid a complex mixing of the successive relaxation processes due to the pump and the probe beams, the energy of the probe beam is selected to well exceed that of the pump beam. This makes the electrons (carriers) be excited to a far higher level by the probe beam than that by the pump beam. This, in turn, makes the relaxation of probe excitation slower by (an) order(s) of magnitude than the other, and they will not mix with each other. Therefore we can ignore the effect of relaxation by the probe light itself on the observed signal, irrespective of the probe light intensity.



Figure 4. Transient reflectivity change $\Delta R(t)$ at selected temperatures: (a) κ -Fe and (b) λ -Fe. (c) $\Delta R(t)$ of λ -Fe salt at 8 K with a fitted curve using equation (2). Note that the fitted curve shows independent contributions separately by the sum of the main relaxation (equation (1)) and coherent oscillation ('damp sine', i.e. the second term in equation (2)). (d) Normalized $\Delta R(t)$ of κ -Fe and κ -Ga salts.

 $(T_{\rm C} = 12 \text{ K})$ [14], Cu[N(CN)₂]Cl (Mott insulator at $T \leq 45$ K) [14], Cu(NCS)₂ ($T_{\rm C} = 9.7$ K) [9] and κ - $(BETS)_2MCl_4$ (M = Fe, Ga) [9], and none of them exhibited coherent oscillations down to the lowest temperature of measurements (~6-8 K). Observation of coherent oscillation means that there is an electron-phonon (e-ph) interaction. Since strong electron-molecular-vibration (emv) coupling was always observed in infrared reflectance spectra of various κ type ET salts [16–19], it is hardly considered that the κ type salts generally do not have e-ph (or quasiparticle-ph) interactions. There are two possible origins for the difference in appearance of coherent oscillation between the κ - and the λ type salts; as for the phonons of the κ -type BETS and ET salts, (1) the width of our laser pulse (\sim 130 fs) is not sufficiently small compared with their periods, or (2) coherent phonons with lower frequencies are yet to be observed, requiring lower temperature for observation.

3.2. Comparison of Fe and Ga salts

Figure 4(d) shows a close comparison of $\Delta R(t)$ of the κ -type salts⁶. One could hardly find any difference (beyond

an experimental error of ± 0.1 ps) in relaxation behaviour between Fe and Ga salts of each structural type, though strong interaction between conduction electrons on BETS (π) and local spins on Fe(III) (d), i.e. strong π -d interaction, is pointed out in the λ -Fe salt based on various experiments and theoretical calculations [3], while some researchers insist that π -d interaction in the λ -Fe salt in the metallic phase (i.e. at T > 8 K) is reduced compared with that in the insulating phase (T < 8 K) [20] and that π -d interaction in the κ -Fe salt is small [11, 21]. Our results appear to indicate a weak π -d interaction in not only the κ -type but also the λ -type salts at T > 8 K. However, because there is a possibility that π -d interaction should not *dominate* carrier dynamics in the λ -type salts, our results cannot exclude the possibility of strong π -d interaction in the λ -type salts at T > 8 K. Further study is required before conclusion on this point.

3.3. Comparison of κ - and λ -type salts

Figures 5(a) and (b) show the temperature dependence of amplitude (A'(T)) of all the salts. The parameter A reflects the density of states (DOS) at $E_{\rm F}$ in this case. The observed A

⁶ The normalized $\Delta R(t)$ of the λ-Fe and the λ-Ga salts are similarly identical to each other (not shown) except for the sign of the offset *C*; *C* > 0 for λ-

Fe and C < 0 for λ -Ga when we assume the sign of the faster relaxation component is positive.



Figure 5. Temperature dependences of *A* of (a) κ -type and (b) λ -type salts.

exhibited different behaviour between κ - and λ -salts, and the trend was shared by the Fe and the Ga salts in the respective structures. For the κ -type salts, A exhibited a gradual increase from 103 down to 6 K (figure 5(a)). This behaviour agrees well with $\rho'(T)$ of the κ -type salts; their resistivity ($\rho(T)$) decreases from 300 to 2 K in a fairly monotonic way [5]. On the other hand, A of the λ -type salts exhibited more complex behaviour with temperature variation (figure 5(b)), exhibiting a maximum at 85 K and a minimum at \sim 65 K. This behaviour agrees well with $\rho'(T)$ of the λ -type salts: nearly constant or slightly increasing $\rho(T)$ from 300 to ~90 K, where $\rho(T)$ takes a broad maximum, and then it begins to rapidly decrease down to $T_{\rm C}$ (8 K) [5]; 85 and 65 K correspond to the maximum and a flexion point of $\rho(T)$, respectively. Thus carrier dynamics is considered to be governed by DOS at $E_{\rm F}$ in the λ -type BETS salts. The increase in A toward the lowest temperature is considered to reflect the increase in DOS at $E_{\rm F}$ due to the relaxation of thermal excitation in the electronic structure with decreasing temperature.

Figures 6(a) and (b) show the temperature dependences of relaxation time $(\tau'(T))$ of all the salts. The κ - and the λ -salts exhibited different behaviour from each other, while the Fe and the Ga salts of each structural type respectively



Figure 6. Temperature dependences of τ of (a) κ -type and (b) λ -type salts.

exhibited identical behaviour. The former observation means that relaxation mechanisms of carriers are different between the κ - and the λ -type salts. In the κ -type salts, τ gradually and monotonically increased with decreasing temperature from $\tau \sim 0.4$ ps at $T \approx 80$ K to $\tau \sim 0.8$ –0.9 ps at $T \approx 6$ K. This observation corresponds well to the electrical behaviour of the κ -type salts as stated above⁷. Also taking the behaviour of A into consideration, one can conclude that the electrical behaviour of the κ -type salts is dominated by DOS at $E_{\rm F}$ and/or τ . As for the λ -type salts, τ was nearly independent of temperature, i.e. nearly constant around 0.4–0.5 ps, except for the cusp-like anomalies at 25 and 65 K, both of which temperatures well agree with those of small anomalies (flexion points) in their $\rho(T)$ [5]. Generally speaking, such anomalies in τ could be an indication of a phase transition or a crossover [14], and could involve e-ph interaction: further investigation of τ values of other related BETS salts would clarify these points, leading to a unified phase diagram of organic SCs. Anyway, the nearly temperature-independent

⁷ Since we do not know the explicit relation between the relaxation in electrical behaviour and that in optical excitation, here we tentatively assume that the former should be proportional to the latter. The discussion hereafter is a possible but not the only explanation. The validity of this assumption should be examined by further study.

behaviour of τ does not account for the peculiar $\rho'(T)$ of the λ -type salts, and thus $\rho(T)$ of the λ -type salts is not considered to be dominated by τ . The observed τ (0.4–0.9 ps) for the κ - and the λ -type salts are significantly prolonged compared with a typical τ (≤ 0.1 ps at any temperature) in the electron systems which can be regarded as Fermi liquids. The carrier dynamics of the λ -type BETS salts resembles that of the κ -type ET SCs [14]; nearly temperature-independent τ except around the temperature of some anomalies in $\rho(T)$, and nearly constant A except for its gradual and steady increase at $T \leq 40-60$ K.⁸ On the other hand, the carrier dynamics of the κ -type BETS salts is qualitatively different from either the κ -type ET SCs or the λ -type BETS salts. The experimental findings presented in this paper enable us to relate the difference in electrical behaviour among the title compounds to that of carrier dynamics.

3.4. Possible explanation on some aspects of carrier dynamics

Now let us briefly discuss possible factors dominating the observed carrier dynamics above. The temperature dependence of lattice parameters of κ -(BETS)₂MCl₄ (M = Fe, Ga) is unknown. If we could assume that the temperature dependence of lattice parameters of κ -(BETS)₂MCl₄ (M = Fe, Ga) should be similar to that of the isostructural salt κ -(BETS)₂FeBr₄ (orthorhombic, *Pnma*), the temperature dependence of τ agrees well with that of the lattice parameter *a* in κ -(BETS)₂MCl₄ (M = Fe, Ga). Since *c* remains almost constant between 7 and 300 K, the temperature dependence of τ is considered to be dominated by the thermal behaviour of the *a*-axis.

The gradual change in DOS with decreasing temperature can be connected with lattice shrinkage, particularly the shrinkage of the conduction plane (the *ac*-plane) ΔS . Here we should examine ΔS defined by

$$\Delta S = \frac{S(T_1) - S(T_2)}{S(T_1)} \times 100,$$
(3)

where $S(Å^2) = (lattice parameter a (Å)) \times (lattice parameter c (Å) × sin(<math>\beta$ (deg))) at the given temperature T (K) and $T_1 > T_2$. From the low-temperature structural studies, ΔS (%) between 100 and 7 K (the temperature range of measurements in this study) can be calculated: 0.15 for κ -(ET)₂Cu[N(CN)₂]Br [22, 23], 0.61 for λ -(BETS)₂MCl₄ (M = Fe, Ga) [8, 24], 1.3 for κ -(BETS)₂FeBr₄ [25], respectively⁹. ΔS is much larger in κ -(BETS)₂MCl₄ (M = Fe, Ga) than in the remaining salts. This explains that the marked increase in DOS, which was indicated as an increase in A, was observed only in the κ -type BETS salts with decreasing temperature, and that merely slight increases in A were observed in the remaining salts (see footnote 7). Therefore,

it is concluded that the thermal behaviour of ΔS , i.e. the *a*and the *c*-axes, is closely related to A'(T) (i.e. DOS at E_F), which in turn affects (the κ -type salts) or dominates (the λ type salts) $\rho(T)$ in each salt. However, on closer examination, $\tau'(T)$ and A'(T) are not completely parallel with $\rho'(T)$ or the temperature dependences of lattice parameters in every salt. The remaining problems are as follows:

- (1) what dominates $\tau'(T)$ and A'(T) in each salt;
- (2) what determines the relation among $\tau'(T)$, A'(T) and $\rho'(T)$.

Further study is required to answer these questions.

4. Conclusion

Time-resolved spectroscopy revealed the difference in temperature-dependent carrier dynamics in κ - and λ -(BETS)₂MCl₄ (M = Fe, Ga): $\rho(T)$ is governed by τ and/or DOS at $E_{\rm F}$ in the κ -type salts, while by DOS at $E_{\rm F}$ in the λ -type salts. In terms of $\tau'(T)$ and A'(T), the λ -type BETS salts resemble the κ -type ET SCs rather than κ -type BETS salts, which qualitatively explains the resemblance/contrast in their electrical behaviour.

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⁸ We should note here that the increases in A and τ at $T \le 30-35$ K (Y = Br) or $T \le 45-50$ K (Y = Cl) observed in κ -(ET)₂Cu[N(CN)₂]Y [14] are due to some electronic transition or crossover, and cannot be compared directly with those in the BETS salts.

⁹ As for the λ-type salts, the change of β with decreasing temperature is ignored here. Actually, β remains nearly constant: ~96.7° at 298 K and ~95.8° at 10 K for λ-Fe. β remains nearly identical at all the temperatures between λ-Ga and λ-Fe [8, 24].

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