



Title	Carrier dynamics in an organic magnetic superconductor and related salts , $-(\text{BETS})_2\text{MCl}_4$ (M = Fe, Ga)
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# Carrier dynamics in organic magnetic superconductor and related salts $\kappa$ , $\lambda$ -(BETS)<sub>2</sub>MCl<sub>4</sub> (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 well explained their electrical behaviour, and indicated that different conduction mechanisms dominated  $\kappa$ - and  $\lambda$ -type BETS salts, irrespective of local spins, at *ca.* 8-100 K; the electrical behaviour of the  $\kappa$ -type salts is governed by relaxation times of carriers and/or density of states at the Fermi levels, while that of the  $\lambda$ -type salts is dominated by the latter.

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## 1. Introduction

Now superconductivity has been found in various materials including ~120 of 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 for [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 every ambiguity on 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; Fig. 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 its difficulty in the synthesis and thus little is known on their conducting properties except for intensively studied  $\lambda$ -(BETS)<sub>2</sub>FeCl<sub>4</sub> and related salts [3]. The charge-transfer salts of BETS include SCs called  $\lambda$ - and  $\kappa$ -type structures (Fig. 1). Both non-magnetic (GaCl<sub>4</sub><sup>-</sup>) and magnetic (FeCl<sub>4</sub><sup>-</sup>) ions yield  $\kappa$ - and  $\lambda$ -type BETS salts with identical structures to each other in the respective type. In addition, they include superconducting and

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non-superconducting materials, exhibiting various ground states (Fig. 2). The superconducting ( $T_C$ ) and antiferromagnetic ( $T_N$ ) transition temperatures and local spins ( $S$ ) of the salts are as follows;  $T_C \approx 0.1$  K,  $T_N \approx 0.65$  K,  $S = 5/2$  for  $\kappa$ -(BETS) $_2$ FeCl $_4$  ( $\kappa$ -Fe) [4],  $T_N = 8$  K,  $S = 5/2$  for  $\lambda$ -(BETS) $_2$ FeCl $_4$  ( $\lambda$ -Fe) [5], and  $T_C = 8$  K,  $S = 0$  for  $\lambda$ -(BETS) $_2$ GaCl $_4$  ( $\lambda$ -Ga) [5].  $\kappa$ -(BETS) $_2$ GaCl $_4$  ( $\kappa$ -Ga;  $S = 0$ ) remains metallic from 300 K 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  $\kappa$ -Fe salt [4]. The  $\lambda$ -Fe salt is an antiferromagnetic insulator at the ground state under ambient pressure, but exhibits pressure-induced superconductivity [6] and even magnetic-field-induced superconductivity [7]. Accordingly, the title compounds are the samples of choice for comparative study for (super)conduction mechanism.

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 to be 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;

(1)  $\lambda$ -(BETS) $_2$ MCl $_4$  ( $M = \text{Fe, Ga}$ ) have nearly identical band structures and the temperature dependence of resistivity ( $\rho'(T)$ ) with those of the  $\kappa$ -type ET SCs, in spite of totally different molecular arrangements between  $\kappa$ - and  $\lambda$ -type structures.

(2)  $\kappa$ -(BETS) $_2$ MCl $_4$  ( $M = \text{Fe, Ga}$ ) have nearly identical crystal and band structures with those of the  $\kappa$ -type ET SCs, in spite of totally different  $\rho'(T)$  between  $\kappa$ -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  $\kappa$ -,  $\lambda$ -(BETS) $_2$ MCl $_4$  ( $M = \text{Fe, Ga}$ ) obtained from the time-resolved 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

The single crystalline samples were prepared according to the literature [8]. Polarized pump and probe beams ( $\sim 10 \mu\text{m}\phi$ ) 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, and is not discussed here. For all the salts, pump and probe beams (76 MHz) were of  $8600 \text{ cm}^{-1}$  ( $1160 \text{ nm} \sim 1 \text{ eV}$ ) and of  $12500 \text{ cm}^{-1}$  ( $800 \text{ nm} \sim 1.5 \text{ eV}$ ), respectively. Based on the calculated band structures [8-10], they are considered to be optical transitions of off-resonance between HOMO-LUMO bands of the BETS salts (Fig. 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 ( $E_F$ ), which is accommodated in the HOMO band [11]. The intensities of beams were 20-150  $\mu\text{W}$  (pump), and 50-85  $\mu\text{W}$  (probe), respectively [12]. The time resolution was  $\sim 200 \text{ fs}$ . All the temperatures indicated in this paper are corrected for heating effects by laser irradiation, which were estimated by varying the laser power. The details of our experimental 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 equilibrium state as a function of time;  $\Delta R(t)$ . The sign of  $\Delta R$  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  $\Delta R$  in this study. The obtained  $\Delta R$  was analyzed by curve-fitting using the following equation,

$$\Delta R = A \exp(-t/\tau) + C. \quad (1)$$

where  $A$ ,  $\tau$ , and  $C$  imply amplitude of the response of carriers, relaxation time, and offset required to express a long relaxation ( $> 10 \text{ ps}$ ), respectively.

### 3. Results and Discussion

#### 3.1 Outline of relaxation behaviour

Figures 4(a) and (b) show selected  $\Delta R(t)$  of the  $\kappa$ -, and the  $\lambda$ -Fe salts, respectively;  $\Delta R(t)$  of the corresponding Ga salts are nearly identical to the counterpart in Figs. 4(a) and (b), as shown later. All the salts exhibited  $\Delta R(t)$  being well approximated by a single-exponential-component decay curve (eq. (1)) at *ca.* 8-100 K except for  $\Delta R(t)$  at  $T \leq 50 \text{ K}$  of the  $\lambda$ -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  $\lambda$ -type salts at  $T \leq 8 \text{ K}$ , in which very slow relaxations suddenly appeared at the transition temperatures ( $T_C$ ,  $T_N = 8 \text{ K}$ ). Accordingly, the finite values of  $C$  suddenly appeared at  $T_C$  ( $T_N$ ) (Fig. 4(c)). The finite offsets  $C$  are considered to correspond to the relaxation of carriers across the superconducting ( $\lambda$ -Ga) and band ( $\lambda$ -Fe) gaps, respectively [14]. At a closer examination, only the  $\lambda$ -type salts exhibited fine structures in  $\Delta R(t)$  at  $T \leq 50 \text{ K}$ , which can be attributed to coherent phonons. For  $\Delta R(t)$  at  $T \leq 50 \text{ K}$ , we carried out curve-fitting analysis using eq. (2)

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

where  $B$ ,  $\gamma$ ,  $\omega$ , and  $\phi$  are amplitude, linewidth, angular frequency, and phase of the coherent

oscillation, respectively, and the remaining parameters have the same meanings in eq. (1). The results showed that the oscillation frequency was  $\sim 0.7$  THz ( $23 \text{ cm}^{-1}$ ) for both of  $\lambda$ -Fe ( $T_N = 8$  K) and  $\lambda$ -Ga ( $T_C = 8$  K) salts; the observed frequency ( $\sim 0.7$  THz  $\approx 34$  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  $\lambda$ -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  $\kappa$ -type structures;  $\kappa$ -(ET)<sub>2</sub>X, X = Cu[N(CN)<sub>2</sub>]Br ( $T_C = 12$  K) [14], Cu[N(CN)<sub>2</sub>]Cl (Mott insulator at  $T \leq 45$  K) [14], Cu(NCS)<sub>2</sub> ( $T_C = 9.7$  K) [16] and  $\kappa$ -(BETS)<sub>2</sub>MCl<sub>4</sub> (M = Fe, Ga) [16], and none of them exhibited coherent oscillations down to the lowest temperature of measurements ( $\sim 6$ -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  $\kappa$ -type ET salts [17-20], it is hardly considered that the  $\kappa$ -type salts generally do not have  $e$ -ph (or quasiparticle-ph) interactions. There are two possible origins for difference in appearance of coherent oscillation between the  $\kappa$ - and the  $\lambda$ -type salts; as for the phonons of the  $\kappa$ -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  $\kappa$ -type salts [21]. One could hardly find any difference (beyond an experimental error of  $\pm 0.1$  ps) in relaxation behaviour between Fe and Ga salts of each structural type, though strong interaction between conduction electrons on BETS ( $\pi$ ) and local spins on Fe(III) (d), *i.e.* strong  $\pi$ -d interaction is pointed out in the  $\lambda$ -Fe salt based on various experiments and theoretical calculations [3], while some researchers insist that  $\pi$ -d interaction in the  $\lambda$ -Fe salt in the metallic phase (*i.e.* at  $T > 8$  K) is reduced compared with that in the insulating phase ( $T < 8$  K) [22] and that  $\pi$ -d interaction in the  $\kappa$ -Fe salt is small [10] or little [23]. Our results appear to indicate a weak  $\pi$ -d interaction in not only the  $\kappa$ -type but also the  $\lambda$ -type salts at  $T > 8$  K. However, because there is a possibility that  $\pi$ -d interaction should not *dominate* carrier dynamics in the  $\lambda$ -type salts, our results can not exclude the possibility of strong  $\pi$ -d interaction in the  $\lambda$ -type salts at  $T > 8$  K. Further study is required before conclusion on this point.

### 3.3 Comparison of $\kappa$ - and $\lambda$ -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  $E_F$  in this case. The observed  $A$  exhibited

different behaviour between  $\kappa$ - and  $\lambda$ -salts, and the trend was shared by the Fe and the Ga salts in the respective structures. For the  $\kappa$ -type salts,  $A$  exhibited a gradual increase from 103 K down to 6 K (Fig. 5(a)). This behaviour well agrees with  $\rho'(T)$  of the  $\kappa$ -type salts; their resistivity ( $\rho(T)$ ) decrease from 300 K to 2 K in a rather monotonous way [5]. On the other hand,  $A$  of the  $\lambda$ -type salts exhibited more complex behaviour with temperature variation (Fig. 5(b)), exhibiting a maximum at 85 K and a minimum at  $\sim 65$  K. This behaviour well agrees with  $\rho'(T)$  of the  $\lambda$ -type salts; nearly constant or slightly increasing  $\rho(T)$  from 300 K to  $\sim 90$  K, where  $\rho(T)$  takes a broad maximum, and then it begins to rapidly decrease down to  $T_C$  (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  $E_F$  in the  $\lambda$ -type BETS salts. The increase in  $A$  toward the lowest temperature is considered to reflect the increase in DOS at  $E_F$  due to the relaxation of thermal excitation in the electronic structure with decreasing temperature.

Figures 6(a) and (b) show the temperature dependence of relaxation time ( $\tau(T)$ ) of all the salts. The  $\kappa$ - and the  $\lambda$ - salts exhibited different behaviour from each other, while the Fe and the Ga salts of each structural type respectively exhibited identical behaviour. The former observation means that relaxation mechanisms of carriers are different between the  $\kappa$ - and the  $\lambda$ -type salts. In the  $\kappa$ -type salts,  $\tau$  gradually and monotonously 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 well corresponds to the electrical behaviour of the  $\kappa$ -type salts as stated above [24]. Taking the behaviour of  $A$  also into consideration, one can conclude that the electrical behaviour of the  $\kappa$ -type salts is dominated by DOS at  $E_F$  and/or  $\tau$ . As for the  $\lambda$ -type salts,  $\tau$  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  $\tau$  could be an indication of a phase transition or a crossover [14], and could involve  $e$ -ph interaction: further investigation of  $\tau$  of other related BETS salts would clarify these points, leading to a unified phase diagram of organic SCs. Anyway, the nearly-temperature-independent behaviour of  $\tau$  does not account for the peculiar  $\rho'(T)$  of the  $\lambda$ -type salts, and thus  $\rho(T)$  of the  $\lambda$ -type salts is not considered to be dominated by  $\tau$ . The observed  $\tau$  (0.4-0.9 ps) for the  $\kappa$ - and the  $\lambda$ -type salts are significantly prolonged compared with a typical  $\tau$  ( $\leq 0.1$  ps at any temperature) in the electron systems which can be regarded as Fermi liquids. The carrier dynamics of the  $\lambda$ -type BETS salts resembles that of the  $\kappa$ -type ET SCs [14]; nearly temperature-independent  $\tau$  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 [25]. On the other hand, the carrier dynamics of the  $\kappa$ -type BETS salts is qualitatively different from either the  $\kappa$ -type ET SCs or the  $\lambda$ -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  $\kappa$ -(BETS)<sub>2</sub>MCl<sub>4</sub> (M = Fe, Ga) is unknown. If we could assume that the temperature dependence of lattice parameters of  $\kappa$ -(BETS)<sub>2</sub>MCl<sub>4</sub> (M = Fe, Ga) should be similar to that of the isostructural salt  $\kappa$ -(BETS)<sub>2</sub>FeBr<sub>4</sub> (Orthorhombic, Pnma), the temperature dependence of  $\tau$  well agree with that of the lattice parameter  $a$  in  $\kappa$ -(BETS)<sub>2</sub>MCl<sub>4</sub> (M = Fe, Ga). Since  $c$  remains almost constant between 7-300 K, the temperature dependence of  $\tau$  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 conduction plane (the  $ac$ -plane)  $\Delta S$ . Here we should examine  $\Delta S$  defined by

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

where  $S [\text{\AA}^2] = (\text{lattice parameter } a [\text{\AA}]) \times (\text{lattice parameter } c [\text{\AA}] \times \sin(\beta[^\circ]))$  at the given temperature  $T$  [K] and  $T_1 > T_2$ . From the low-temperature structural studies,  $\Delta S$  (%) between 100 K and 7 K (the temperature range of measurements in this study) can be calculated; 0.15 for  $\kappa$ -(ET)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Br [26,27], 0.61 for  $\lambda$ -(BETS)<sub>2</sub>MCl<sub>4</sub> (M = Fe, Ga) [8,28], 1.3 for  $\kappa$ -(BETS)<sub>2</sub>FeBr<sub>4</sub> [29], respectively [30].  $\Delta S$  is much larger in  $\kappa$ -(BETS)<sub>2</sub>MCl<sub>4</sub> (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  $\kappa$ -type BETS salts with decreasing temperature, and that merely slight increases in  $A$  were observed in the remaining salts [24]. Therefore it is concluded that the thermal behaviour of  $\Delta S$ , *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  $\kappa$ -type salts) or dominates (the  $\lambda$ -type salts)  $\rho(T)$  in each salt. However, at a 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.

### 3. Conclusion

Time-resolved spectroscopy revealed the difference in temperature-dependent carrier dynamics in  $\kappa$ -, and  $\lambda$ -(BETS)<sub>2</sub>MCl<sub>4</sub> (M = Fe, Ga);  $\rho(T)$  is governed by  $\tau$  and/or DOS at  $E_F$  in the  $\kappa$ -type salts, while by DOS at  $E_F$  in the  $\lambda$ -type salts. In terms of  $\tau'(T)$  and  $A'(T)$ , the  $\lambda$ -type BETS salts resemble the  $\kappa$ -type ET SCs rather than  $\kappa$ -type BETS salts, which qualitatively explains resemblance/contrast in

their electrical behaviour.

### Acknowledgment

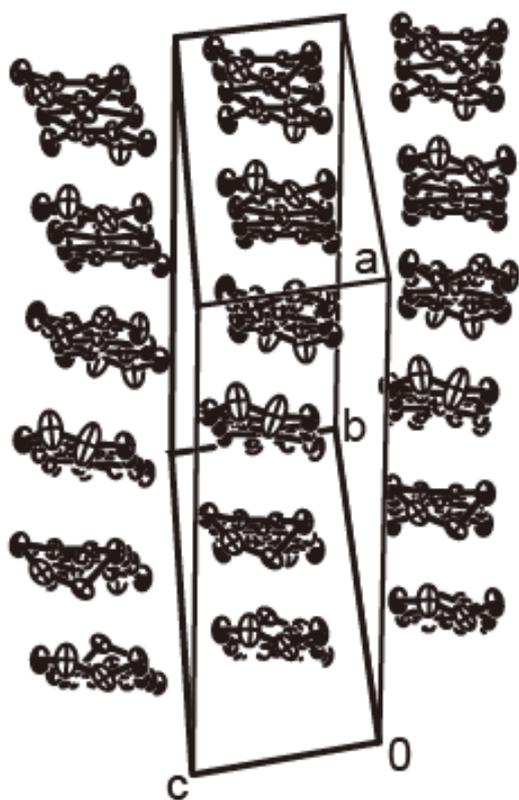
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beam. This, in its turn, makes the relaxation of probe-excitation slower by (an) order(s) of magnitude than the other, and they will not mix each other. Therefore we can ignore the effect of relaxation by the probe light itself on the observed signal, irrespective of the probe light intensity.

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(a)



(b)

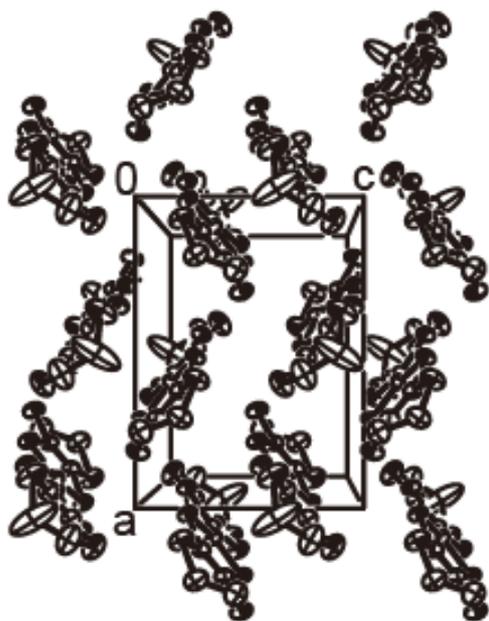


Fig. 1. Crystal structures of (a)  $\lambda$ -, and (b)  $\kappa$ -(BETS) $_2$ GaCl $_4$ . Hydrogen atoms are omitted for clarity.

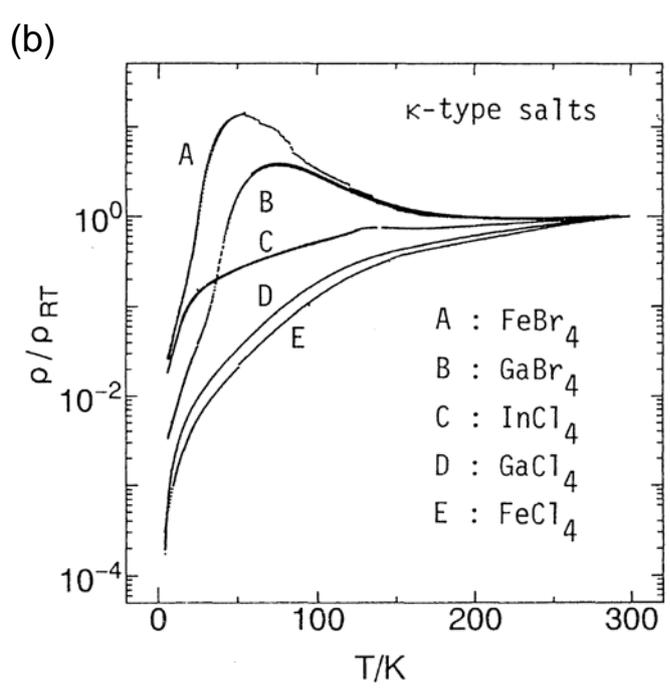
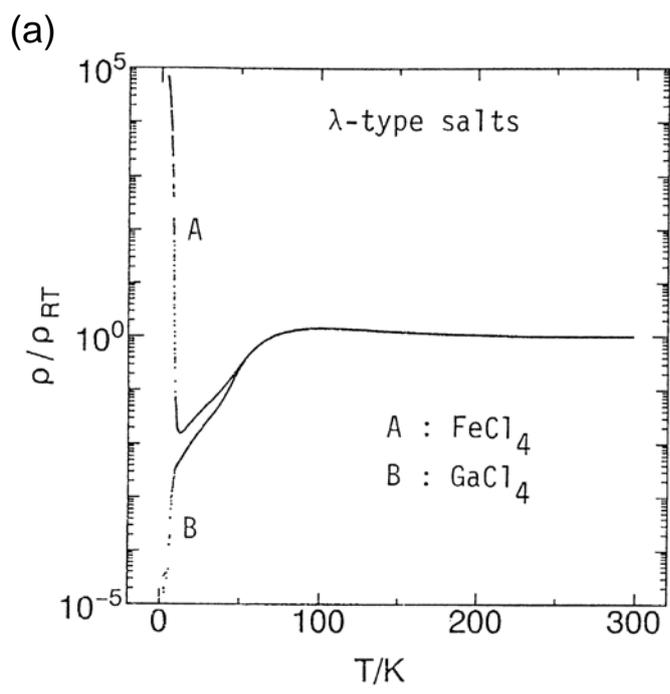
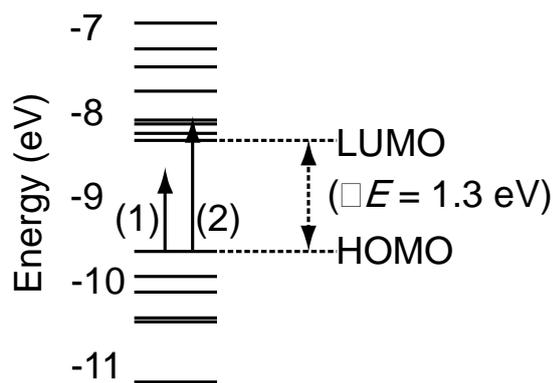
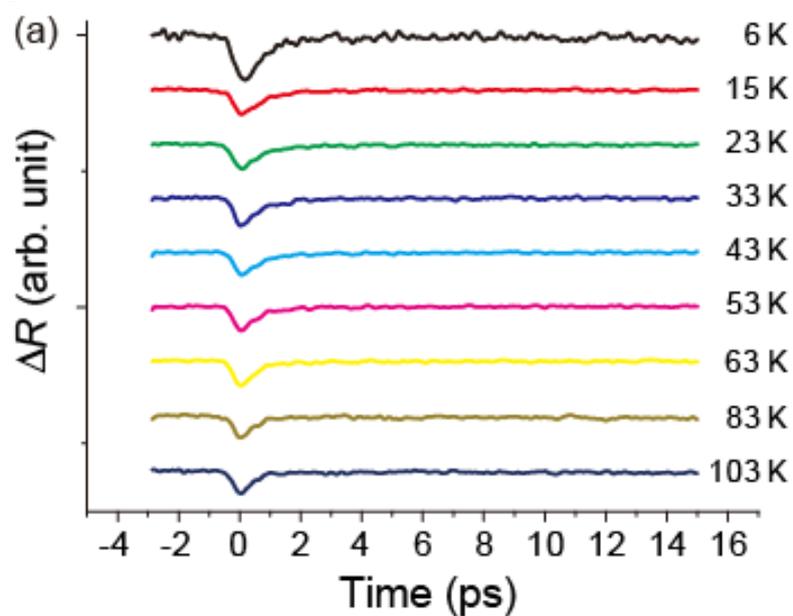


Fig. 2. Temperature dependences of electrical resistivity of (a)  $\lambda$ -, and (b)  $\kappa$ -type BETS salts. Reproduced from ref. 5 under permission.



- (1) Pump (1 eV)
- (2) Probe (1.5 eV)

Fig. 3. Schematic energy diagram of molecular orbitals of BETS calculated on the basis of the extended Hückel approximation. Reproduced from ref. 10 with slight modification under permission.



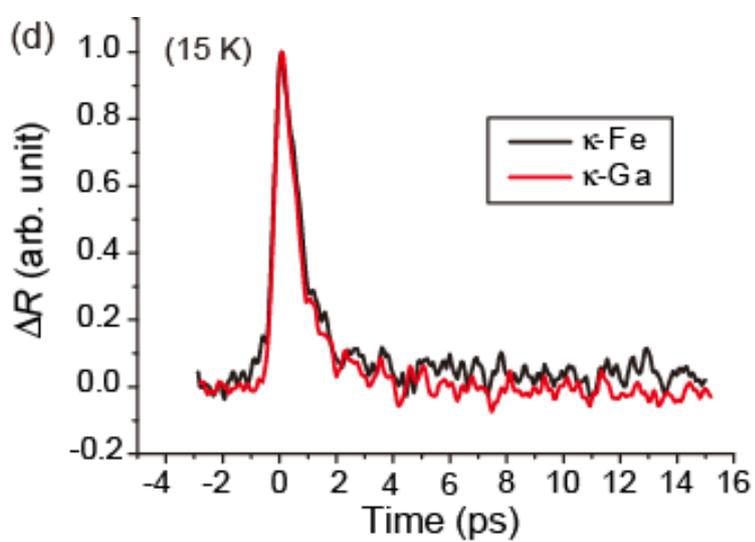
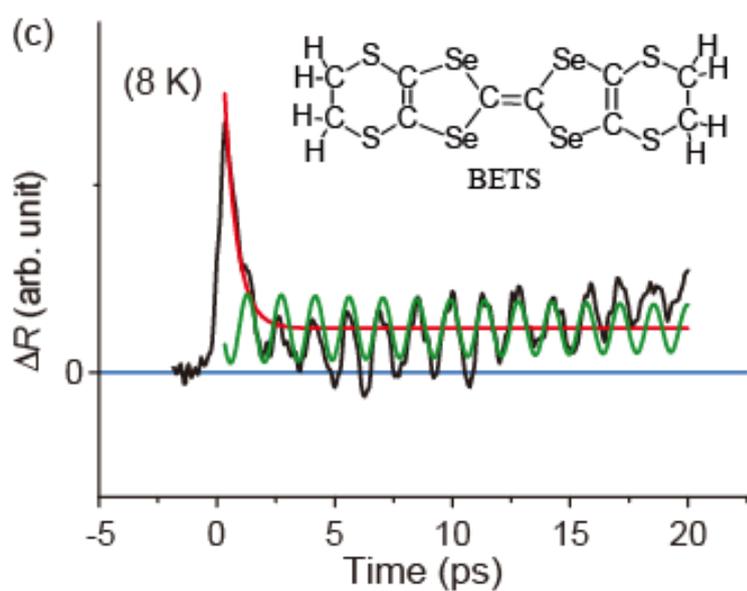
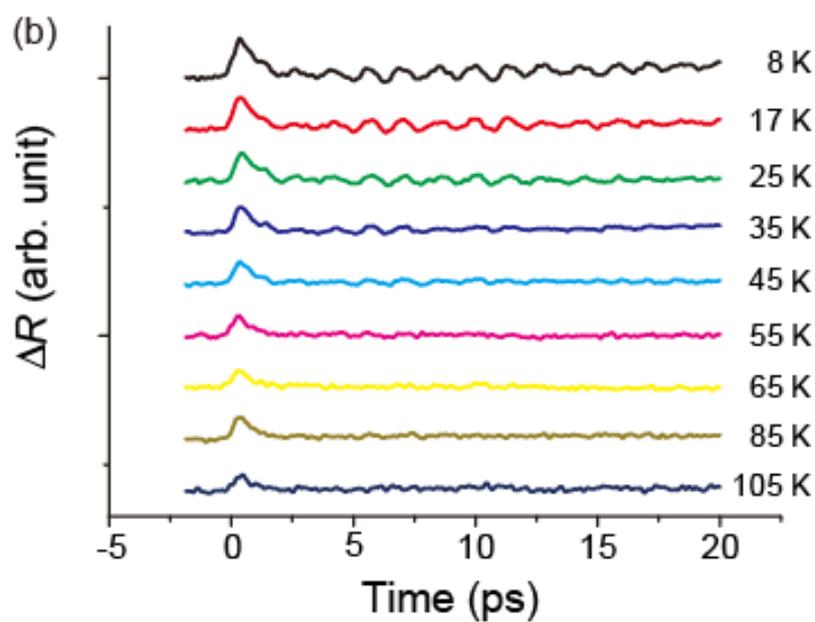


Fig. 4. Transient reflectivity change  $\Delta R(t)$  at selected temperatures; (a)  $\kappa$ -Fe and (b)  $\lambda$ -Fe. (c)  $\Delta R(t)$  of  $\lambda$ -Fe salt at 8 K with a fitted curve using eq. (2). Note that the fitted curve shows independent contributions separately by sum of the main relaxation (eq. (1)) and coherent oscillation (“damp sine”, *i.e.* the second term in eq. (2)). (d) Normalized  $\Delta R(t)$  of  $\kappa$ -Fe and  $\kappa$ -Ga salts.

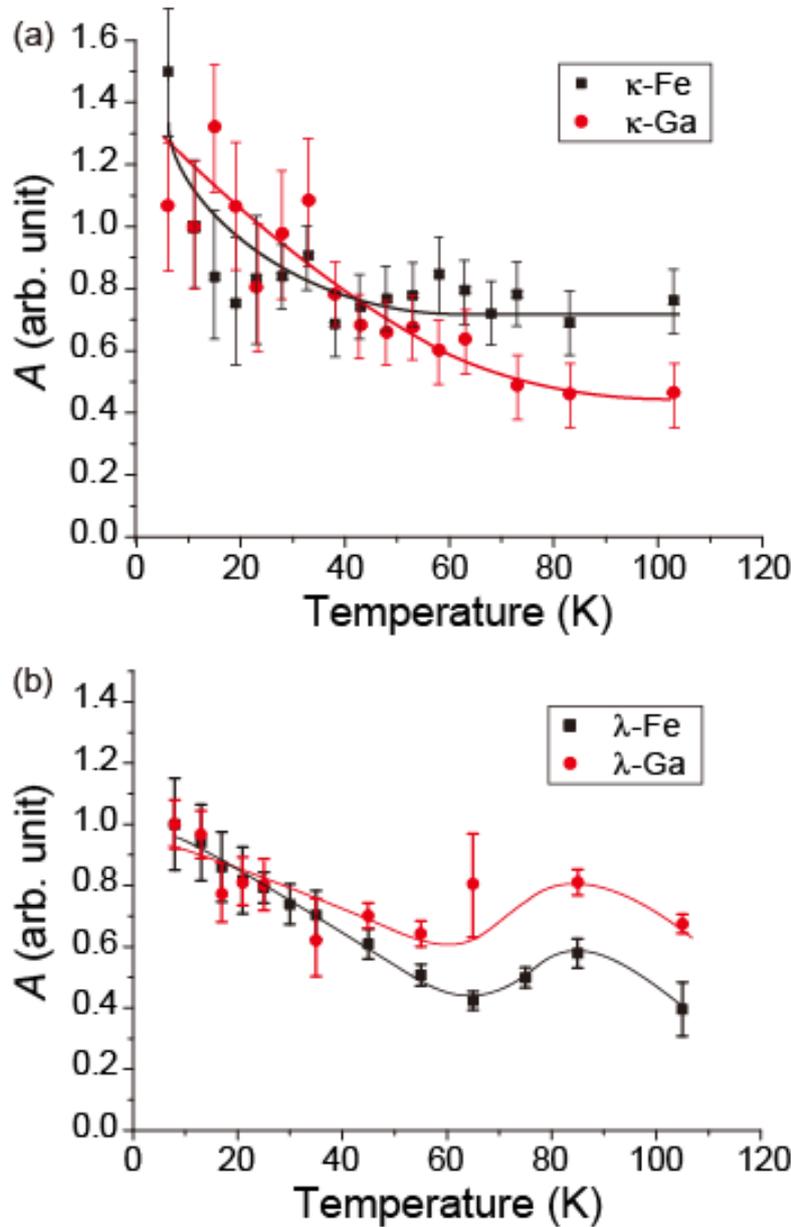


Fig. 5. Temperature dependences of  $A$  of (a)  $\kappa$ -type, and (b)  $\lambda$ -type salts.

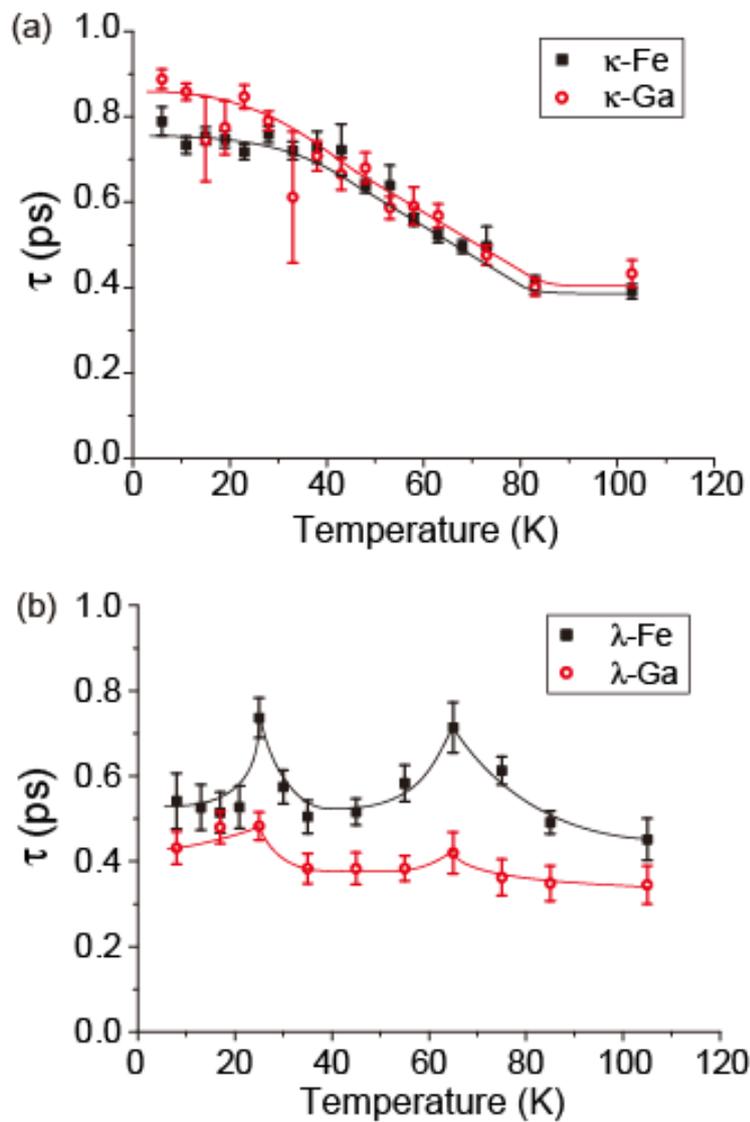


Fig. 6. Temperature dependences of  $\tau$  of (a)  $\kappa$ -type, and (b)  $\lambda$ -type salts.