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Abstract of Doctoral Dissertation

Degree requested Doctor of Science Applicant's name Taehoon Lee

Title of Doctoral Dissertation

Microscopic Studies of *π-d* Molecular Conductor λ-$(BETS)_2FeCl_4$ by ESR

(電子スピン共鳴を用いた *π-d* 系分子性導体 λ-$(BETS)_2FeCl_4$ の微視的研究)

The molecular conductor λ-$(BETS)_2FeCl_4$ consists of conducting *π*–electrons from the BETS molecule and the magnetic *d*-electrons in $FeCl_4$ anion. Due to the short atomic distance between the BETS molecule and $FeCl_4$ anion, it is expected that a strong interaction exists between *π*- and *d*-electron. Thanks to this strong *π-d* interaction, the λ-$(BETS)_2FeCl_4$ has a fascinating phase diagram as a function of temperature and magnetic field, such as an antiferromagnetic insulating (AFI) phase, a paramagnetic metal (PM) phase, and a field-induced superconducting (FISC) phase [1,2]. The FISC phase is well-understood by the Jaccarino-Peter compensation mechanism. However, the ground state of the AFI phase is under debate for the past decades.

The metal-insulator (MI) transition has been thought for a long time to be triggered by the antiferromagnetic long-range order of the *d*-electrons [3]. However, Akiba *et al.* reported a large excess specific heat below T_{MI} = 8.3 K [4]. The origin of the excess specific heat was explained by the 'paramagnetic Fe model', where the conducting π-electrons become localized and antiferromagnetic due to the Mott transition at T_{MI}, meanwhile, the Fe spins still remain paramagnetic below T_{MI}. Nevertheless, this explanation is not consistent with the existence of strong exchange interaction between the π- and the *d*-electrons. Moreover, it contradicts with the previous electron spin resonance (ESR) studies, where no paramagnetic resonance is observed below T_{MI} [3,5,6].

Meanwhile, many anomalous dielectric behaviors were reported nearby the phase boundary of the AFI phase [5]. Rutel *et al*. observed a huge change of the high-frequency response, which is related to the permittivity, within the AFI phase, where they have attributed the origin to the metastable state of the π-electrons. The metastable state is a mixed state of conducting and localized π-electrons. If such metastable state of π-electrons exists, it might affect the magnetic properties of this system due to the strong *π-d* interaction. And, this metastable state of the π-electrons might induce the excess specific heat. Hence, in this study, we have performed the precise ESR measurements of the AFI phase as a function of magnetic field and temperature.

The antiferromagnetic resonance (AFMR) has several modes such as the hard-axis mode of AFMR, the easy-axis mode of AFMR, and the spin-flop resonance. These modes are related to the AF easy-axis. Hence, the AF easy-axis must be known to investigate antiferromagnetic properties of the system. The AF easy-axis of λ-$(BETS)_2FeCl_4$ is known to be 30° from the *c*-axis to the *b**-axis [7]. Although the *c*-axis is the needle-axis, the *a**- and the *b**-axes are difficult to define due to the small needle-shape single crystal. Hence, we have first investigated the relation between the crystal-axes and principal-axes of the *g*-tensor from the electron paramagnetic resonance (EPR).

For finding the AF easy-axis, we have measured the angular dependence of EPR. Typical angular dependence of the *g*-value has a sinusoidal curve. However, two minima of the *g*-value are observed in low temperature region when the magnetic field is parallel to the *a*b**-plane. The two minima of the *g*-value are related to the short contacts between Cl in $FeCl_4$ anion and Se/S in the BETS molecule. Moreover, the anomalies of the *g*-value are developing with decreasing temperature, which are due to the developments of the *π-d* correlations. Thanks to this characteristic structure, the crystal-axes of λ-$(BETS)_2FeCl_4$ can be easily defined, and now, the AF easy-axis can also be obtained from the EPR measurements [8].

By finding the easy-axis using EPR, the AFMR behaviors within the AFI phase were investigated in detail. We find out from the X-band ESR measurements that the AF easy-axis changes with temperature, which might be due to the metastable state of the π-electrons. Moreover, a double-peak structure is observed in AFMR, where the double-peak structure suggests two different environments of Fe spins. Two different environments of Fe spins are consistent with previous Mössbauer measurements [9]. Two different

environments might be also related to the metastable state of the π-electrons. Moreover, the AFMR signal is observed above T_{MI}. This suggests the MI transition is triggered by antiferromagnetic long-range ordered of Fe spins.

Furthermore, the splitting ESR signals are observed above 6 T, where the splitting ESR signals consist of AFMR and EPR. These splitting signals show the change of the contribution between AFMR and EPR with temperature and the magnetic field. We suppose the change of contribution suggests the existence of slow transition between antiferromagnetic and paramagnetic state with temperature and the magnetic field.

In summary, we have studied the electronic ground state of λ-$(BETS)_2FeCl_4$ by ESR. We have find that strong *π*-*d* correlations indeed exist from the characteristic angular dependence of EPR. Thanks to this specific angular dependence, the AF easy-axis and the crystal axes are easily find. From the precise angular dependence of AFMR, the change of the AF easy-axis is observed around the AFI phase boundary. Moreover, the AFMR and EPR are both observed above 6 T, and the change of the contribution between AFMR and EPR are observed with temperature and the magnetic field. These observations support the existence of the metastable state of the π-electrons with temperature and magnetic field. Hence, we conclude that the metastable state affects magnetic properties of λ-$(BETS)_2FeCl_4$ due to the strong *π*-*d* interaction.

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