Superconductivity and pseudogap in λ-(BETS)2GaCl4 observed from microwave conductivity measurements

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§ 1 Introduction

λ-$(BETS)_2GaCl_4$ (the $GaCl_4$ salt), where BETS is an abbreviation of bis(ethylenedithio) tetraselenafulvalene, is a quasi-two dimensional organic superconductor with $T_C = 4.8$ K. On the other hand, an isostructural analogue with the magnetic Fe^{3+} ion, the $FeCl_4$ salt, which is known as the first magnetic molecular conductor, shows a metal-toinsulator (MI) transition at T_{MI} = 8.3 K. The mixed salts λ -(BETS)$_2$Fe$_x$Ga$_{1-x}$Cl$_4$ (x = 0-1) are synthesized. The mixed salts are the first compounds that undergo successive metal- superconductor-insulator transitions. These facts clearly indicate that the condensation energies in between superconducting and insulating states are in close proximity with each other in this λ -type BETS donor based salts.

In the FeCl$_4$ salt, a π -d interaction between π electrons and 3d spins localized on the Fe^{3+} ion lead to antiferromagnetic (AFM), charge and dielectric orders in the insulating state. A variety of fascinating phenomena such as a field-induced superconducting (SC) state, non-linear transport with a negative resistance, colossal magnetodielectricity and so on are originated from the π -d interaction. In addition, the previous microwave conductivity, ^{1}H-NMR and X-ray structural studies on the FeCl$_4$ salt have identified the presence of the anomalous metallic states (AMS) at $T_{MI} < T < T_{FM}$ = 70 K, where a relaxer ferroelectric domain appears in a metallic background forming a heterogeneous structure.

Then, a fundamental question arises as for how the π -electronic system without π -d interaction responds to an external electromagnetic wave. Any differences in the electronic and phononic properties are hardly expected in between the FeCl$_4$ and GaCl$_4$ salts, except for the presence of localized spins in the former salt. The purpose of this thesis is to clarify an electrodynamics of the π -electronic system in the nonmagnetic GaCl$_4$ salt. Since microwave conductivity measurements are a very useful experimental technique as evidenced by the studies on the FeCl$_4$ salt, we investigate microwave responses both in the SC and metallic states of the GaCl$_4$ salt.

We also study the T-x phase diagram in the mixed salts via magnetic susceptibility measurements. The experimentally determined T-x phase will help a future progress in understandings of π -d interaction related phenomena.

§ 2 Experimental Techniques

The microwave conductivity at 45 GHz are measured at 0.6 K < T < 150 K based on a cavity perturbation technique. The principle of the technique is to measure twice both of a resonant frequency f and a resonance width Γ, with (s) and without (0) a sample installed in the cavity. The frequency shift $\Delta f/f_0 = (f_s - f_0)/f_0$ and the width change $\Delta \Gamma/2f_0 = (\Gamma_s - \Gamma_0)/2f_0$ relate to a change of a microwave phase and a microwave loss, respectively. Both components of the complex conductivity are derived from these values.

The magnetic susceptibility is measured using a SQUID magnetometer above 2 K, and a Faraday force magnetometer at 0.5 K < T < 4 K combined with a ^{3}He cryostat at Center for Low Temperature Science, IMR, Tohoku University.

The BETS donor molecule is synthesized with a new synthetic route developed by our group. The single crystals of λ -(BETS)$_2$Fe$_x$Ga$_{1-x}$Cl$_4$ are successfully grown by an electrochemical oxidation method in the optimum condition identified by us.

§ 3 Microwave conductivity studies on λ -(BETS)$_2$GaCl$_4$

3.1 Superconducting states

The inter-plane upper critical field-temperature ($\mu_0 H_{c2}$-T) phase diagram of the GaCl$_4$ salt is determined from the temperature dependence of microwave loss under magnetic fields applied perpendicular to the ac-conducting plane. It is found that the ($\mu_0 H_{c2}$-T) phase diagram is well explained within a theoretical framework for a conventional type-II superconductor. With the value of the initial slope at T_C, the Ginzburg-Landau coherence length ξ_{GL} in the conducting plane is estimated to be 8.7 nm. The superconductivity of the $GaCl_4$ salt is found to be in the pure limit because $\xi_{GL} << l = 110$ nm, where l is the mean free path. The inter-plane upper critical field at 0 K is estimated to be about 3 T based on the GLAG-WHH theory.

With decreasing temperature, the real part of the microwave conductivity σ_1^c along the *c*-axis decreases monotonously and saturates toward zero. It is found that there is no indication of a coherence peak in σ_1^c. The imaginary part σ_2^c takes a finite value even at T_C and shows saturation well below T_C. The London penetration depth λ_L along the *c*-axis calculated from σ_2^c is almost temperature independent below $T/T_C = 0.5$. This saturation indicates that the superconducting gap opens over the entire Fermi surface.

3.2 Metallic States

In the metallic state, σ_1^c well coincides with σ_{dc}^c above about 60 K, and then becomes smaller than σ_{dc}^c toward T_C. σ_2^c is almost zero above about 20 K, and then increases exponentially toward T_C. σ_2^c shows a continuous increase at T_C.

3.3 Discussions

According to a Drude model describing electrodynamics in a conventional metallic state, $\sigma_1 = \sigma_{dc}$ and $\sigma_2 \sim 0$ at the present microwave frequency. However, there is a prominent dispersion in σ_1 and the huge upturn in σ_2 with positive finite values in the metallic state of the $GaCl_4$ salt.

Since an excitation of quasi-particles near the Fermi level by a microwave contributes to σ_1, the decrease of σ_1 compared to σ_{dc} indicates an appearance of some gap-like features around the Fermi level for a microwave excitation. We refer to this gap-like feature as a so-called pseudogap fluctuating in the time scale of the microwave frequency. A following situation is assumed in the pseudogap state of the $GaCl_4$ salt. A part of quasi-particles around the Fermi level, which contribute to σ_1, changes dynamically into a state that contribute to σ_2 fluctuating in a time scale of the microwave frequency. In this case, the reduction of σ_1 is simply attributed to a decrease of a number density of quasi-particles.

While the π-d interaction leads to dielectric anomalies in the $FeCl_4$ salt, there appears the pseudogap around the Fermi level for the microwave excitation in the nonmagnetic $GaCl_4$ salt. Two possible candidates are discussed as the origin of the pseudogap. One is the fluctuating development of a density wave or charge ordering. Another is the appearance of the incoherent pre-formed Cooper pairs.

The fluctuation of the density wave is considered to cause a so-called T^* anomaly in the κ-type BEDT-TTF based salts. Also in these salts, the appearance of the pseudogap and an increase of σ_2 with positive finite values are observed. The pseudogap observed in the microwave study on the $GaCl_4$ salt may indicate one aspect of T^* anomaly.

The precursory appearance of the pre-formed Cooper pairs is also discussed in the pseudogap issue in high-T_C cuprates. In the case that the pseudogap in the $GaCl_4$ salt originates from the appearance of pre-formed pairs, the positive finite σ_2 may represent an electrodynamics of such pairs with a lifetime of the order of microwave frequency.

§ 4 Temperature-composition (*T-x*) Phase Diagram of λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$

The *T-x* phase diagram of the mixed salt is determined by magnetic susceptibility measurements. There exist three different phases in the diagram; SC, AFMI and paramagnetic metallic (PM) states. It is found that T_C hardly depends on x. An AFMI transition temperature T_N is almost proportional to x. From the T-x phase diagram, the AFMI region is found to exist above $x = 0.2$.

The discontinuous change in the magnetization is discussed quantitatively. It is assumed that all localized π spins align antiferromagnetically with each other even in the rather diluted mixed salts.

§ 5 Summary

This thesis clarifies new aspects of λ -type BETS based compounds as follows. 1) The μ_0H_{c2}-T phase diagram of the $GaCl_4$ salt is one of a conventional type-II superconductor. 2) The metallic state of the $GaCl_4$ salt is in a so-called pseudogap state. 3) The T-x phase diagram of the mixed salt is experimentally determined. It has an AFMI region above $x = 0.2$. T_C is almost independent on x, while T_N is proportional to x.

論文審査の結果の要旨

TMTTF,BEDT-TTF(ET)分子と並ぶ有機導体の分野で重要な物質である。特に現在BETS分子は、陽イオン状態となるBETS分子と陰イオン状態となる分子を組み合わせてできる錯体が伝導と磁性の両方の観点から物性物理として興味ある物性を発現することで大きな注目を集めている。また、最近そのBETS分子は、四塩化鉄錯体の形態で巨大誘電率の異常を示すことでも大きな注目を集めている。

これまでの研究で、BETS-FeCl4錯体は、TMI=8.3Kで金属-絶縁体転移を生じるが、磁場の存在下では超伝導転移を示す興味ある物性が報告されていた。一方、BETS-$GaCl_4$錯体は、Tc=4.8Kで超伝導体転移を示すことが報告されていた。従って本物質系の全体の描像としては、ps軌道混成を中心とする電子状態から、d軌道を取り込んだ場合の電子状態へ興味ある物性変化として考えることができる。しかし、従来の研究では、BETS-$GaCl_4$錯体においては、様々な研究にもかかわらず、高温相である常磁性金属状態ならびに低温状態である超伝導相に関する詳細な理解が十分ではなかった。

本研究では、マイクロ波摂動法という特殊な電子状態の観測実験手法を適用して、従来十分ではなかった超伝導状態の物理的パラメータを総合的に決定するとともに、常磁性金属状態においても従来の電気抵抗測定では観測されていなかった擬ギャップの存在を観測することに初めて成功した。この観測した擬ギャップの存在は、超伝導相とも密接な関係を有している可能性を指摘した。擬ギャップが発現する原因としては、電荷整列（Charge-Order）関係した微小ドメイン構造の発現、あるいは超伝導状態になる前に形成される前駆的ボゾン（Preformed　Boson）などが候補に挙げられる。

本研究の成果は、有機導体の研究分野において、BETS-GaCl4錯体の電子状態をマイクロ波共振摂動法を適用して、正確な超伝導パラメータを決定するとともに、従来常金属相と考えられていた高温相に擬ギャップが発現することを新たに見出した。本研究は、有機伝導体の分野で注目を集めているBETS系伝導体において、物性理解を深めるとともに、擬ギャップの発現という他の物質とも関係する普遍性のある結果を観測した。以上により、本人が自立して研究活動を行うのに必要な高度な研究能力と学識を有することは明らかである。したがって、鈴木貴博氏提出の論文は博士（理学）の学位論文として合格と認める。