Temperature Dependence of Internal Field by Analysis of Specific Heat on an Organic Conductor $\lambda$-BETS$_2$FeCl$_4$

Kazuo SHIMADA*, Hiroshi AKIBA, Naoya TAJIMA, Koji KAJITA, Yutaka NISHIO, Reizo KATO$^1$, Akiko. KOBAYASHI$^2$ and Hayao. KOBAYASHI$^2$

Department of Physics, Toho University, Chiba, 274-8510, Japan

$^1$Condensed Molecular Materials Lab. RIKEN, Saitama, 351-0198, Japan

$^2$Department of Humanities and Sciences, Nihon University, Tokyo 156-8550, Japan

E-mail: k.shimada19880520@gmail.com

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$\lambda$-BETS$_2$FeCl$_4$ (BETS = bis (ethylenedithio) tetraselenafulvalene) system exhibits a mysterious paramagnetic metal (PM) -antiferromagnetic insulator (AFI) phase transition. Just after AF ordering, the large entropy of Fe 3$d$ localized spin still remains. To investigate why the mysterious free 3$d$ spin exists in the $\pi$ spin AF ordering state, we measured the specific heat in the vicinity of the PM-AFI transition. The formation process of this AF ordering is discussed in the context of a low-dimensional spin network. It is proposed that the FeCl$_4$ crystal field plays a crucial role in this magnetic ordering via a $\pi$–$d$ interaction.

**KEYWORDS:** Metal-insulator transition, $\pi$–$d$ interaction, Low-dimensional antiferromagnetic order

1. Introduction

Several researchers have studied $\lambda$- and $\kappa$-type BETS based (BETS = bis (ethylenedithio) tetraselenafulvalene) organic conductors to discuss the relationship between magnetic ordering and superconductivity [1-3]. Quasi two-dimensional organic superconductor $\lambda$-BETS$_2$FeCl$_4$ has a layered structure in which BETS molecule conductive layers, and insulating layers composed of FeCl$_4$ molecules with localized high spin states of Fe ($s = 5/2$) are arranged alternately [1]. This compound exhibits magnetic-field-induced superconductivity above 17 T [4]. At zero magnetic field, it also undergoes a novel phase transition from paramagnetic metal (PM) to antiferromagnetic insulator (AFI) at a transition temperature, $T_{MI} \approx 8.3$ K [5, 6].

Recently, we found a six-level Schottky hump in the specific heat of $\lambda$-BETS$_2$FeCl$_4$ system in the AFI phase [7-9], where Tokumoto reported that the magnetic susceptibility decreases rapidly with an anomalous shoulder [5]. Just below the $T_{MI}$, approximately 80 % of the 3$d$ spin degree of freedom remain free. This free 3$d$ spin force us to consider the reason why $\pi$ electron doesn’t form the AF order in isostructural $\lambda$-BETS$_2$GaCl$_4$ system, and the AFI phase is established only in the $\lambda$-BETS$_2$FeCl$_4$ system. These questions directly ask what the role of free 3$d$ spin in the AFI ground state is.

In the present article, we investigate an internal magnetic field formation process in
the vicinity of the PM-AFI phase transition using the 3d spin as a microprobe to elucidate the role of the 3d spin and π–d interaction.

2. Experimental

We measured the specific heat by the thermal relaxation method over a wide temperature range from 0.2 to 12 K. We attached several pieces of a single crystal of the sample to a bolometer using Apiezon N grease (total sample weight: 25-120 µg).

3. Result and Discussion

We studied the thermal properties of the λ-BETS₂FeCl₄ system focusing on the states of the π electron and 3d spin during the PM-AFI phase transition. Figure 1 shows the excess specific heat, ΔC, of sample #10, which was obtained by subtracting the lattice contribution estimated from λ-BETS₂GaCl₄ [7]. The specific heats of sample #10 and λ-BETS₂GaCl₄ are shown in the inset of Fig. 1. At the TMI ~ 8.3 K, we observed a sharp peak that was ascribed to the PM-AFI transition. We found that a large excess specific heat exists on lower temperatures, which can be fitted using the six-level Schottky specific heat with Zeeman energy and anisotropic energy that originate from the constant internal magnetic field and FeCl₄ crystal field, respectively: gμBH₀/kB = 5.5 K and D/kB = 0.15 K (solid curve in Fig.1).

Figure 2 shows an excess entropy ΔS calculated by integrating the ΔC over temperature. Combining the lower broad hump with the sharp peak contribution, total excess entropy reaches to the Fe 3d spin degrees of freedom; R ln(6) ( = R ln(2s+1), s = 5/2). Just below the TMI, 80% of its degrees of freedom remain. Below 6 K, the excess entropy also can be fitted by the calculation curve estimated from Schottky specific heat.

As shown in figure 1, up to the transition temperature from lower temperatures, the experimental data ΔC deviates from a solid curve due to the

![Fig. 1. Temperature dependence of excess specific heat of λ-BETS₂FeCl₄, as obtained by subtracting lattice contribution. Solid curve shows fitting line of the data using six-level Schottky specific heat. Inset shows temperature dependence of specific heats of λ-BETS₂FeCl₄ (closed circles) and λ-BETS₂GaCl₄ (open circles).](image1)

![Fig. 2. Excess entropy of λ-BETS₂FeCl₄ (closed circles), calculated entropy curves with various internal magnetic fields (solid line and dashed lines), and Fe 3d spin degrees of freedom, R ln(6) (broken line).](image2)
formation of the sharp peak; this sharp peak is attributed to rapid enhancement of the internal magnetic field, $H_{\text{int}}$, at the Fe sites accompanied by the development of spontaneous magnetization of the $\pi$ spin system. It should be noted that the sharp peak does not directly represent a critical behavior of the $\pi$ spin system: instead, indirectly represents the formation process of $\pi$ AF order as internal field at the 3$d$ spin site. When the $\pi$ magnetization reaches saturation value, $\Delta C$ follows the Schottky curve calculated under fixed internal magnetic field $H_0$.

As shown in figure 2, the excess entropy also deviated from the solid curve as it approaches the $T_{\text{MI}}$. We also plotted the calculation curves under various weaker magnetic fields, as shown by the dashed lines. The weaker the internal magnetic field, the more the degrees of freedom remains. We can evaluate the temperature dependence of the internal magnetic fields, $H_{\text{int}}$, from the intersection of excess entropy data and calculated entropy curves.

Figure 3 shows a temperature dependence of normalized internal field, $H_{\text{int}}/H_0$. The temperature dependence of $H_{\text{int}}$ is in good agreement with the hyperfine field observed by the Mössbauer effect [10]. We also plotted the critical behaviors in the class of the 2D Ising model (solid line) and three-dimensional (3D) Ising model (dotted line). The experimental results more closely match the 2D Ising line.

If anisotropy is not introduced into the isotropic strong $\pi$–$\pi$ spin network that has low-dimensional character, this network does not exhibit AF magnetic ordering. This is why strong $\pi$–$\pi$ interactions cannot form magnetic order at higher temperatures and in non-magnetic $\lambda$-BETS$_2$GaCl$_4$ system. In the $\lambda$-BETS$_2$FeCl$_4$ system, the $\pi$–$d$ interaction begins to affect the $\pi$–$\pi$ spin network as it approaches the transition temperature. Then, anisotropy is introduced into isotropic $\pi$ spin system by the FeCl$_4$ crystal field via the $\pi$–$d$ interaction. This anisotropy suppresses 2D fluctuation. Thus, the $\pi$ spin system is able to establish the 2D Ising-like AF ordering.

4. Summary

We studied the temperature dependence of the internal magnetic field on the Fe 3$d$ spin site around the PM-AFI phase transition in the $\lambda$-BETS$_2$FeCl$_4$ system. To investigate the role of the $\pi$ electron and 3$d$ spin for the mysterious PM-AFI transition, we measured the excess specific heat derived from the 3$d$ spin. The excess specific heat shows the large
hump in the AFI ground state and the sharp peak at $T_M$. Thus, we investigated the formation process of the $\pi$ spin AF ordering in the vicinity of the transition temperature. The internal magnetic field exhibited 2D behavior. We proposed that the 3$d$ spin supports the formation of 2D Ising-like $\pi$ spin ordering via crystal anisotropy through the strong $\pi$–$d$ interaction.

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