

Review

Magnetic and Electronic Properties of π - d Interacting Molecular Magnetic Superconductor κ -(BETS) $_2$ FeX $_4$ (X = Cl, Br) Studied by Angle-Resolved Heat Capacity Measurements

Shuhei Fukuoka ^{1,*}, Sotarou Fukuchi ², Hiroki Akutsu ² , Atsushi Kawamoto ¹ and Yasuhiro Nakazawa ²

¹ Department of Condensed Matter Physics, Graduate School of Science, Hokkaido University, Kita-ku Sapporo, Hokkaido 060-0810, Japan; atkawa@phys.sci.hokudai.ac.jp

² Department of Chemistry, Graduate School of Science, Osaka University, Machikaneyama 1-1, Toyonaka, Osaka 560-0043, Japan; fukuchis17@chem.sci.osaka-u.ac.jp (S.F.); akutsu@chem.sci.osaka-u.ac.jp (H.A.); nakazawa@chem.sci.osaka-u.ac.jp (Y.N.)

* Correspondence: fukuoka@phys.sci.hokudai.ac.jp; Tel.: +81-01-706-4424

Received: 8 December 2018; Accepted: 19 January 2019; Published: 26 January 2019



Abstract: Thermodynamic picture induced by π - d interaction in a molecular magnetic superconductor κ -(BETS) $_2$ FeX $_4$ (X = Cl, Br), where BETS is bis(ethylenedithio)tetraselenafulvalene, studied by single crystal calorimetry is reviewed. Although the $S = 5/2$ spins of Fe $^{3+}$ in the anion layers form a three-dimensional long-range ordering with nearly full entropy of $R\ln 6$, a broad hump structure appears in the temperature dependence of the magnetic heat capacity only when the magnetic field is applied parallel to the a axis, which is considered as the magnetic easy axis. The scaling of the temperature dependence of the magnetic heat capacity of the two salts is possible using the parameter of $|J_{dd}|/k_B$ and therefore the origin of the hump structure is related to the direct magnetic interaction, J_{dd} , that is dominant in the system. Quite unusual crossover from a three-dimensional ordering to a one-dimensional magnet occurs when magnetic fields are applied parallel to the a axis. A notable anisotropic field-direction dependence against the in-plane magnetic field was also observed in the transition temperature of the bulk superconductivity by the angle-resolved heat capacity measurements. We discuss the origin of this in-plane anisotropy in terms of the $3d$ electron spin configuration change induced by magnetic fields.

Keywords: π - d system; thermodynamic measurement; superconductivity; antiferromagnetism; single crystal heat capacity measurement; magnetic conductor

1. Introduction

There are increasing interests in studying magnetic properties of molecule-based materials from fundamental science and application, since they show a variety of functionalities related to spin degrees of freedom, which have different appearance manners from those of intermetallic compounds, such as transition metal oxides and pnictide, etc. Not only the development of new materials, which have ferromagnetic or ferrimagnetic ordering of molecular spins, but also the synthesis of new compounds with large cluster spins, such as single-molecule magnets (SMM), single-chain magnets (SCM), and those with spin crossover features, have been performed [1,2]. Some molecular magnets show a large magnetocaloric effect (MCE) derived from the large magnetic entropy change, which is applicable to cryogenic coolants [3,4]. The fabrication of devices applicable to spintronics and topological phenomena are becoming challenging subjects both for synthetic chemists and

physicists [5–7]. The molecule-based magnets studied up to now contain organic radical compounds, assembled magnetic metal complexes with open shell metal cations, and coordination polymers of them, etc. [8–11]. The unpaired π electrons in the singly occupied molecular orbital (SOMO), the highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) of organic molecules in the radical compounds possess delocalized character over the molecules and have strong quantum mechanical features [12–14]. The magnetic metal complexes have potential for showing various net magnetic properties of d - or f - electrons in the inorganic ions in various coordination fields produced by surrounding organic ligands [15,16]. The design and synthesis of new molecules and the provision of new functionalities are extensively performed as interesting challenges in chemistry. The rich variety of structures and relatively sensitive responses against external stimuli are advantages for applications of them [17,18]. Due to these characteristic natures, molecule-based magnets are considered as promising materials for studying important topics, such as spin crossover, spin frustration, light irradiation-induced magnetic structures, and single molecule magnets [19–22].

In addition to these materials, the magnetic properties of charge transfer complexes are also attracting attention, since they show various conducting and magnetic properties inherent in the multi-composition of molecules with different electronic structures and functionalities [23,24]. The π - d interacting systems, which consist of organic donor molecules and counter anions containing magnetic ions, such as Cu^{2+} , Fe^{3+} , Mn^{2+} , etc., with localized $3d$ electron spin moments have been studied in terms of the developing cooperative phenomena between conducting electrons and localized spins. They are recognized as organic-inorganic hybrid molecular magnets. Until now, several π - d interacting compounds with D_2A composition, where D denotes a donor molecule, such as BETS and BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene), and A denotes monovalent magnetic counter anions, such as FeX_4^- ($X = \text{Cl}, \text{Br}$), have been studied [25–30]. In such π - d interacting systems, the charge transfer from donor molecules to counter anion molecules occurs and unpaired π electrons and $3d$ electron spins coexist in a crystal. Since the donor molecules and the magnetic counter anion molecules form respective layers, the π electrons show two-dimensional conducting and magnetic properties with strong electron correlations. In addition, magnetic interaction between the π electrons and the $3d$ electrons, which is called π - d interaction, appears in the systems [31]. By combining the π - d interacting effect and the electron correlation, these π - d systems show various unique magnetic and conducting properties. For example, the metal-insulator transition and the coexistent state of a magnetic long-range ordering and superconductivity are observed in them [32–36]. Furthermore, a rich variety of electronic and magnetic phases appear with the tuning of external parameters, such as temperature, pressure, and magnetic and electric fields, etc., in these compounds. A magnetic-field-induced superconducting (FISC) state observed in λ -(BETS) $_2\text{FeCl}_4$ under extremely large magnetic fields higher than 17 T is a representative phenomenon that the electronic state shows drastic change by controlling external parameters [37].

In this article, we review the results of the thermodynamic experiments for π - d interacting systems of κ -(BETS) $_2\text{FeX}_4$ ($X = \text{Cl}, \text{Br}$) performed by single crystal calorimetry as well as the development of the calorimetry system using the measurements and discuss the physical properties of these compounds in relation to the π - d interacting effects.

2. Electronic Structure of the κ -(BETS) $_2\text{FeX}_4$ Systems

The crystal structures of κ -(BETS) $_2\text{FeX}_4$ are shown in Figure 1. The BETS molecules and the FeX_4^- anions form conducting π electron layers and insulating FeX_4^- layers, respectively, in the ac plane and these layers are stacked alternately in the direction parallel to the b axis [34]. In the donor layers, these molecules form dimers with face to face contact in the layers. The dimer units are arranged in a nearly orthogonally tilted structure to form a zig-zag lattice. This structure is called a κ -type structure and various superconductors with relatively high T_c have this structure. Since one electron is removed from two BETS molecules, namely one dimer, to form a charge transfer complex with FeX_4^- anions, the 3/4-filled band is expected in BETS layers as is usual for the compounds with a 2:1 concentration.

However, since the degree of dimerization in the κ -type structure is higher than the other packing, the 3/4-filled band splits into bonding and antibonding bands, changing the 3/4-filled band into an effective half-filled band system with strong electron correlation. In the FeX_4^- layers, Fe^{3+} ions have localized 3d electrons with $S = 5/2$ spins. The localized 3d electrons and the conducting π electrons are strongly coupled through the π -d interaction, and the conducting and magnetic properties of the π electrons and the 3d electrons influence each other.

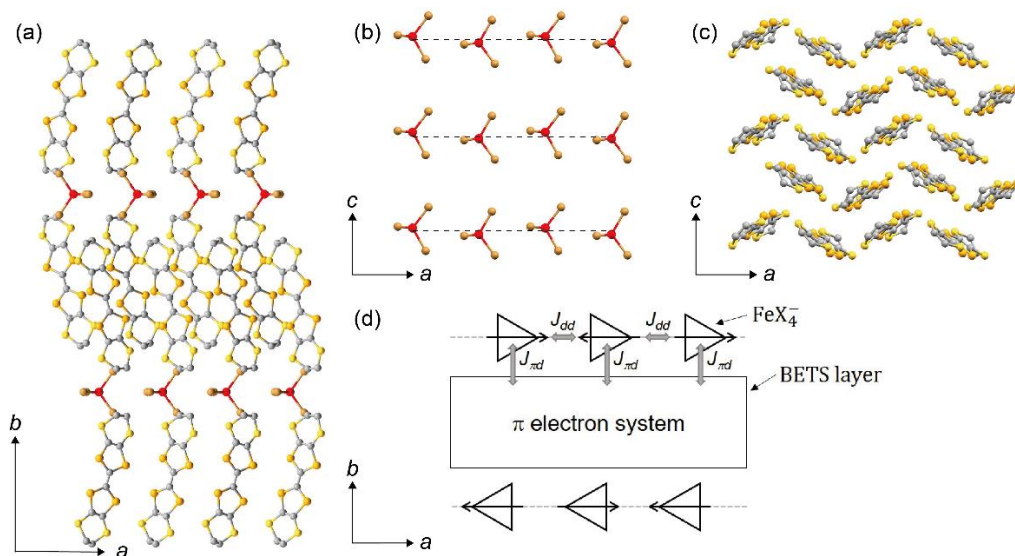


Figure 1. (a) Crystal structure of κ -(BETS)₂FeX₄ projected along the c axis. Molecular arrangement of the (b) anion (FeX_4^-) layer and (c) donor (BETS) layer in the ac plane. BETS and FeX_4^- are drawn in ball-and-stick representation. Carbon, sulfur, selenium, iron, and halogen atoms are shown in gray, yellow, orange, red, and brown, respectively. The dashed lines represent the one-dimensional direct magnetic interaction network. (d) Schematic view of the magnetic interaction network in the κ -(BETS)₂FeX₄ system.

3. Transport and Magnetic Properties

The mechanism of magnetic interaction between π electron spins and 3d electron spins and the possibility of π -d hybridization in electronic bands have been discussed theoretically and experimentally. The conducting and magnetic properties of κ -(BETS)₂FeX₄ have been studied in the previous works by Fujiwara and Otsuka et al. and they reported that both κ -(BETS)₂FeBr₄ and κ -(BETS)₂FeCl₄ show superconductivity coexisting with an antiferromagnetic long-range ordering [34–36]. The 3d electrons in the Fe^{3+} show an antiferromagnetic transition at 2.47 K in κ -(BETS)₂FeBr₄ and 0.47 K in κ -(BETS)₂FeCl₄, respectively, while the π electrons are metallic in a wide temperature range. At extremely low temperatures, they show superconducting transitions. The transition temperature is 1.5 K in κ -(BETS)₂FeBr₄ and 0.1 K in κ -(BETS)₂FeCl₄, respectively. The superconducting ordering and the antiferromagnetic ordering occur independently at a glance, since only a small kink is observed around T_N in the temperature dependence of resistivities [34,35]. Furthermore, the superconducting transition occurs at almost the same temperature in κ -(BETS)₂GaX₄ ($X = \text{Cl}, \text{Br}$), which have non-magnetic counter anions [38]. However, the electronic phase diagram under magnetic fields indicates the anisotropy against magnetic field direction, which demonstrates that the internal field produced by the 3d electron spin ordering affects the superconductivity of the π electrons through the π -d interaction [34,39]. The electron correlation of the π electrons which not only induces antiferromagnetic fluctuations but also produces charge fluctuations is also considered as an important factor to determine the magnetic phase diagram of these compounds. Moreover, it is reported that κ -(BETS)₂FeBr₄ shows a FISC state similar to the case of well-known λ -(BETS)₂FeCl₄ [39]. Since the mechanism of the FISC state is explained by the Jaccarino-Peter compensation effect realized

by the internal field produced by the aligned $3d$ electron spins, the existence of the π - d interactions should be taken into account [40,41]. These results demonstrate that the coupling of the π electrons and the $3d$ electrons is crucial to characterize the conducting and magnetic properties of these systems and this coupling can give unique features as molecular magnets.

4. Calorimetry System Applicable to Tiny Single Crystals of Molecular Magnetic Materials

The heat capacity measurements were performed by the thermal relaxation method, which is suitable for single crystal measurements at a low temperature region. Since the crystals of the κ -(BETS) $_2$ FeX $_4$ system are tiny thin plates, we used custom-made calorimetry cells of which details were already reported in [42]. The sample stage consists of a RuOx thermometer of which the room temperature resistance is 1 k Ω , and a strain gauge (EFLK-1000) heater with 1 k Ω in resistance. By using ϕ 13 μ m constantan wires as the electric leads for the heater and the thermometer, it is possible to adjust the thermal relaxation time between 0.1 s to 100 s depending on the sample size and the experimental temperature region. The temperature of the sample was monitored by an ac resistance bridge (LakeShore model 370N) with a scanner system and a pre-amplifier. The calorimetry cells are also designed for conducting angle-resolved heat capacity measurements under in-plane magnetic fields. The sample stage was suspended by thin stainless wires to prevent the sample from tilting by the magnetic torque produced by a magnetic field. We confirmed that the in-plane direction is kept just parallel to the magnetic field direction by monitoring the resistance of Hall sensor. We succeeded in reducing the misalignment of the field-angle direction within $\pm 1^\circ$ in all magnetic fields, which is satisfactory for the present experiments. Therefore, investigations of the anisotropy of the superconducting transition against the in-plane magnetic field were possible with high accuracy by using the calorimetry cells. The angle-resolved system was subsequently modified to reduce the blank heat capacity by Imajo et al. of which details were reported in [43].

In the experiments, the calorimetry cells were mounted on a top loading type 3 He cryostat and a dilution refrigerator (TS-3H100 Taiyo Nissan), which are available in the variable temperature insert (VTI) system with superconducting magnets. The minimum temperature of the former is 0.6 K and that of the latter is 100 mK.

In the heat capacity measurements in this study, we used a single crystal of κ -(BETS) $_2$ FeBr $_4$ with 94 μ g and that of κ -(BETS) $_2$ FeCl $_4$ with 45 μ g. The BETS molecules were solved in the solvent of 1,1,2-trichloroethane with tetrabutylammonium salts of FeX $_4^-$. The electrochemical oxidation technique was used to grow the single crystals. The sample was adhered on the sample stage with a small amount of Apiezon N grease to attain good thermal contact. We confirmed that the thermal relaxation curves of the measurements obey the simple single exponential function in all temperature range between 100 mK and 10 K, which means that the thermal contact between the sample and the stage is adequate to attain absolute values of the heat capacity. As a matter of fact, the absolute values of the heat capacity, including the height of the peak, coincide well with the data of previous works [34,35].

5. Thermodynamic Properties of Antiferromagnetic Ordered State of κ -(BETS) $_2$ FeX $_4$

Here, we review the magnetic nature of the $3d$ electron systems investigated by heat capacity measurements. Temperature dependences of the magnetic heat capacity of κ -(BETS) $_2$ FeBr $_4$ and κ -(BETS) $_2$ FeCl $_4$ are shown in Figure 2 by the $C_{\text{mag}}T^{-1}$ vs. T plot [44]. The contribution of the $3d$ electron spins were evaluated by subtracting the lattice heat capacity. Although the π electrons contribute to the total heat capacity (C_p), the entropic contribution of them is almost negligible in this plot. Their electronic state can be explained by the band state, and the electronic heat capacity should give a simple formula of $C_{\text{el}} = \gamma T$. The value of the γ term is expected to be about 10–30 mJ K $^{-2}$ mol $^{-1}$ if the π electron band gives a similar band width, W , as for the case of metallic compounds of κ -(BEDT-TTF) $_2$ X systems [45–49]. This indicates that the contribution of the π electrons should be two orders of magnitude smaller than that of the $3d$ electrons. The sharp peaks at 2.47 K and 0.47 K are attributed to

the formation of the long-range ordering of the 3d electron spins in the anion layers. The temperature of the magnetic transition coincides well with the results of magnetic susceptibility measurements by Fujiwara and Otsuka et al. [34–36]. As a matter of fact, the evaluated magnetic entropy reaches $S_{\text{mag}} = 14.9 \text{ JK}^{-1}\text{mol}^{-1}$ at 8 K for $\kappa\text{-(BETS)}_2\text{FeBr}_4$ and 2 K for $\kappa\text{-(BETS)}_2\text{FeCl}_4$. These values are consistent with the full entropy of the 3d electron spins in FeX_4^- possessing the spin multiplicity of $S = 5/2$ spins, namely, $S_{\text{mag}} = R\ln 6$. This result means that the magnetic orders occur with a bulk feature in both compounds in which all the 3d electron spins form an antiferromagnetic structure.

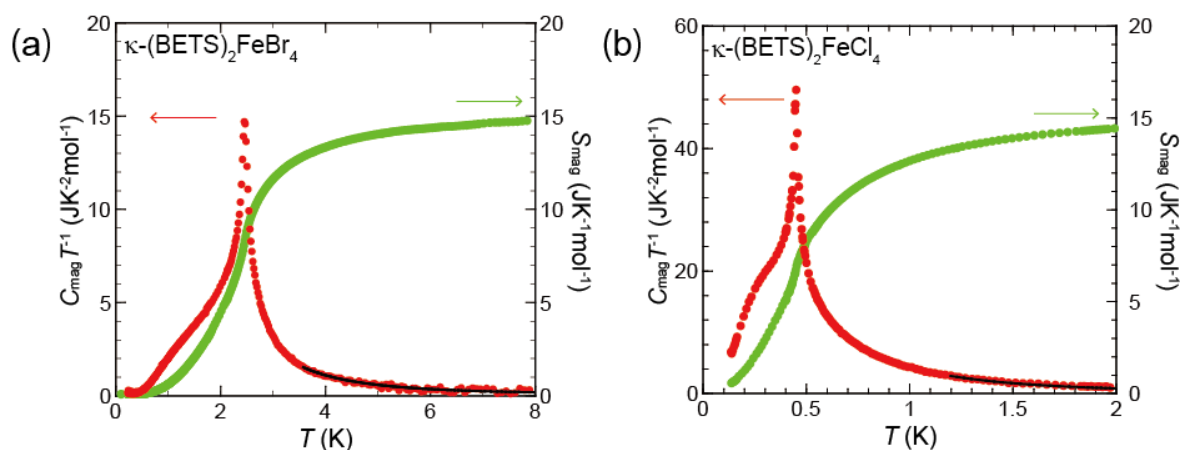


Figure 2. Temperature dependence of the magnetic heat capacity (red) and the magnetic entropy (green) of (a) $\kappa\text{-(BETS)}_2\text{FeBr}_4$ and (b) $\kappa\text{-(BETS)}_2\text{FeCl}_4$. The solid lines represent the fitting curves of high-temperature magnetic heat capacity data using the AT^{-2} term. Reproduced with permission from [44].

The temperature dependence of the magnetic entropy shown in Figure 2 indicates that most of the magnetic entropy is distributed around T_N . However, a nearly symmetric peak shape of C_p against temperature and the existence of the higher-temperature tail of the magnetic heat capacity prompted us to consider a kind of low dimensional fluctuation effect. From the data in Figure 2, it is notable that nearly 40% of the contribution for the magnetic entropy is distributed above T_N . There are two types of magnetic interactions between the 3d electron spins in the FeX_4^- sites in these two compounds [31,50]. One is the direct magnetic interaction expressed as J_{dd} , and the other is the indirect magnetic interaction mediated by the coupling between the 3d electron spins and the π electron spins on the BETS layers, which is expressed as $J_{\pi\text{d}}$. The schematic view of the interaction is shown in Figure 1d. Although both interactions are antiferromagnetic, the contribution for the antiferromagnetic ordering of the direct magnetic interaction is expected to be relatively larger than that of the indirect magnetic interaction. Mori et al. estimated the contribution of the direct magnetic interaction and the indirect magnetic interaction to T_N by theoretical calculation and revealed the dominant contribution of the direct magnetic interaction [50]. Since the counter anions of FeX_4^- form one-dimensional chain like structures along the a axis, as is shown in the crystal structure in Figure 1b, the J_{dd} forms a one-dimensional interaction network. The direct magnetic interactions along the inter-chain (parallel to the c axis) and the inter-layer (parallel to the b axis) directions are one order of magnitude smaller and are almost negligible. However, the indirect magnetic interaction between the 3d electron spins works in all directions to form a three-dimensional magnetic interaction network. In the inter-chain and the inter-layer directions, magnetic interactions are dominated by this indirect magnetic interaction. In the case of the a axis direction, the direct magnetic interaction and the indirect interaction coexist. Therefore, the short-range ordering of the 3d electron spins due to the dominant direct magnetic interaction with one-dimensional character should develop from the higher-temperature region above T_N , leading to the distribution of the magnetic entropy above T_N . The J_{dd} values can be evaluated by fitting the high-temperature magnetic heat capacity data using the AT^{-2} term [51,52]. The fitting results

give the value of $|J_{\text{dd}}|/k_B = 0.27$ K for $\kappa\text{-(BETS)}_2\text{FeBr}_4$ and $|J_{\text{dd}}|/k_B = 0.081$ K for $\kappa\text{-(BETS)}_2\text{FeCl}_4$, respectively. The fitting curves of the high-temperature magnetic heat capacity using the AT^{-2} term is shown by black solid lines in Figure 2. Here, we must mention that the single-ion anisotropy of Fe^{3+} is not taken into account and these values contain ambiguity. Although the one-dimensional fluctuations appear at high temperatures, the indirect magnetic interaction through the π electron layers works cooperatively and forms three-dimensional ordering.

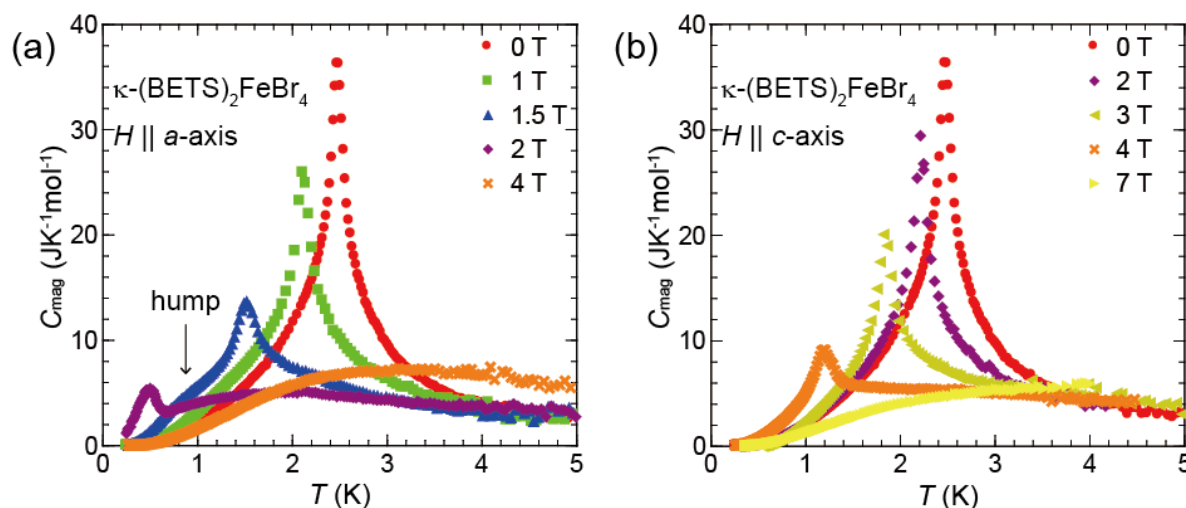


Figure 3. Temperature dependences of the magnetic heat capacity of $\kappa\text{-(BETS)}_2\text{FeBr}_4$ under magnetic fields parallel to (a) the a axis and (b) the c axis. Reproduced with permission from [44].

The magnetic field dependences of the magnetic heat capacity of the $3d$ electron spins of the two compounds were also investigated. By applying magnetic fields, the transition temperature decreases with the increase of magnetic fields, which is a typical behavior of conventional antiferromagnetic compounds. The temperature dependence of the magnetic heat capacity of $\kappa\text{-(BETS)}_2\text{FeBr}_4$ obtained under magnetic fields is shown in Figure 3. The magnetic fields are applied to the a axis and the c axis directions in the plane. The a axis is the magnetic easy axis of the $3d$ electron spins, which is confirmed by the single crystal magnetic susceptibility measurements [34]. The suppression of the T_N is largest in the a axis direction and T_N decreases down to about 2.07 K at 1 T and 0.45 K at 2 T, while that of the $H \parallel c$ axis direction is 2.21 K at 2 T and 1.18 K at 4 T, respectively.

Figure 4a shows the temperature dependences of the heat capacity under magnetic field at 1 T applied in several directions from the b axis (out-of-plane direction) to the a axis (in-plane direction) in the ab plane measured by the long relaxation method using the same calorimetry cell. By tilting the field direction from the b axis to the a axis, T_N shifts to the lower temperature region. The field-direction dependence of the T_N at 1 T and 2 T are summarized in Figure 4b. The T_N is 2.37 K at 1 T and 2.24 K at 2 T, respectively, in the b axis direction. The degree of the suppression of T_N by the magnetic field is almost the same between the b axis direction and the c axis direction, which is also consistent with the previous magnetic susceptibility measurements [34].

The curious features appear in the temperature dependence of the magnetic heat capacity when the magnetic fields are applied to the a axis direction. As confirmed in Figure 3, the magnetic field works to suppress the peak gradually and a kind of hump structure appears. In the data of Figure 3a, the hump structure is observed clearly at 1.5 T and 2 T. It is important to mention that the magnetic entropy at 8 K is retained as $R\ln 6$ even though the temperature dependence of the magnetic heat capacity shows such a drastic change. This result indicates that the hump structure is derived from the spin degrees of freedom of the $3d$ electron spins and the magnetic nature is gradually changed inside the antiferromagnetic phase. Note that the temperature dependences of the magnetic heat

capacity under the magnetic field parallel to the b axis and the c axis are almost the same, and the hump structure is not observed when the magnetic field is applied in both directions.

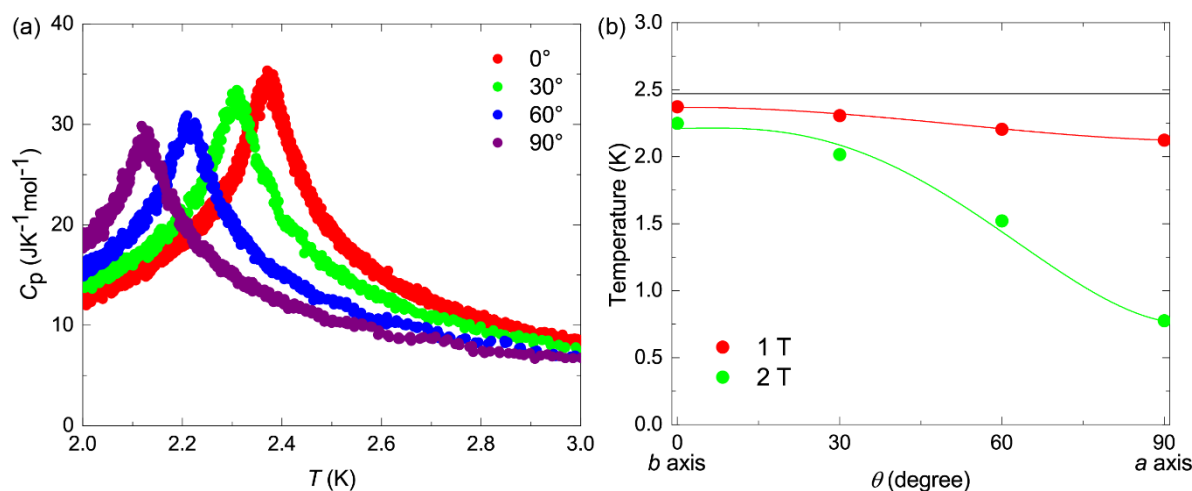


Figure 4. (a) Temperature dependences of the heat capacity of κ -(BETS) $_2$ FeBr $_4$. The magnetic field of 1 T is applied in several directions from the b axis (0°) to the a axis (90°). (b) Field-direction dependence of the antiferromagnetic transition temperature at 1 T (red) and 2 T (green). The black line represents the antiferromagnetic transition temperature of 2.47 K at 0 T.

A similar tendency is observed in κ -(BETS) $_2$ FeCl $_4$, though the magnetic features are shifted to the lower energy scale. Figure 5 shows the temperature dependences of the magnetic heat capacity under magnetic fields applied parallel to the a axis and the c axis. The hump structure is also observed in κ -(BETS) $_2$ FeCl $_4$ at 0.5 T as is indicated in Figure 5a. These results certainly suggest that the same magnetic nature in κ -(BETS) $_2$ FeBr $_4$ also appears in κ -(BETS) $_2$ FeCl $_4$.

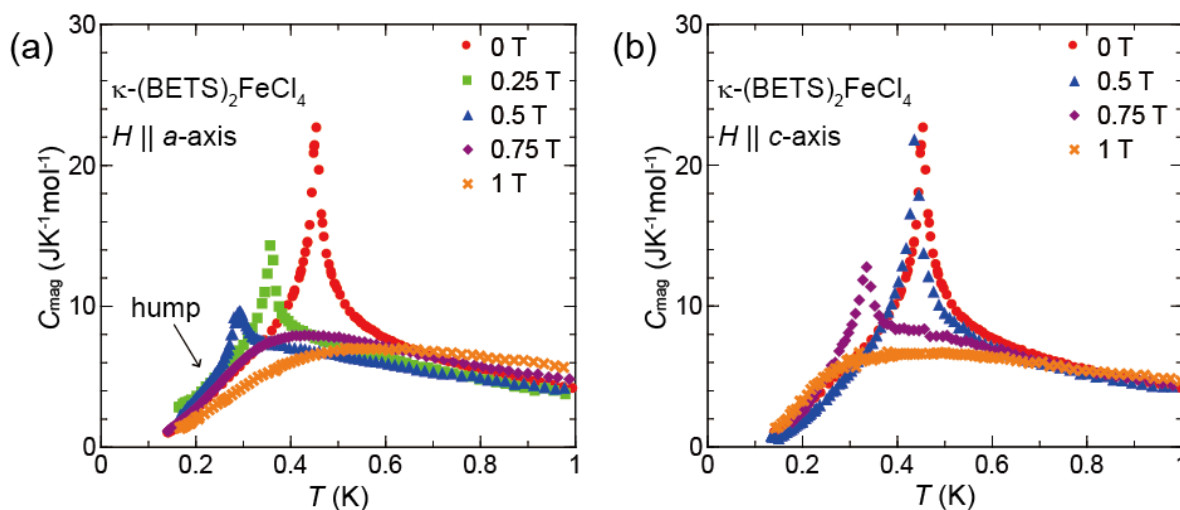


Figure 5. Temperature dependences of the magnetic heat capacity of κ -(BETS) $_2$ FeCl $_4$ under magnetic fields parallel to (a) the a axis and (b) the c axis. Reproduced with permission from [44].

In order to compare the data of the two compounds in the same framework, the magnetic heat capacity data obtained in the configuration of the $H \parallel a$ axis of the two compounds are displayed in the same figure in Figure 6. In this figure, the temperatures are scaled by the dominant direct magnetic interaction, $|J_{dd}|/k_B$, of each compound. It is worthy of note that not only the high temperature tails derived from the short-range ordering, but also the hump structures scale well between the two compounds, suggesting that the origin of the hump structure is related to the energy scale of the direct

magnetic interaction. The temperature dependence of the magnetic heat capacity of the κ -(BETS)₂FeCl₄ at 0 T coincides with that of κ -(BETS)₂FeBr₄ at 1.5 T. The magnetic field of 1.5 T corresponds to the difference of the magnitude of the direct magnetic interactions between κ -(BETS)₂FeBr₄ and κ -(BETS)₂FeCl₄ compounds. From this scaling result and quantitative evaluation of the magnetic interactions, we can claim that even though the 3d electron spin systems undergo the antiferromagnetic ordered state by the indirect magnetic interaction, the characteristics of the direct magnetic interactions, J_{dd} , still remains as internal degrees of freedom below T_N , which is observed as a hump structure in the magnetic heat capacity.

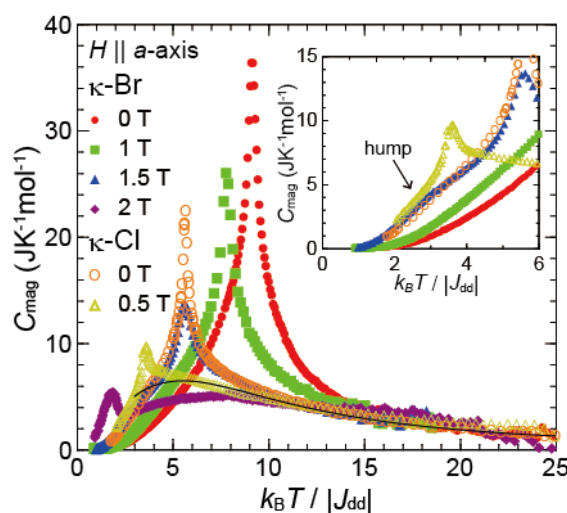


Figure 6. Temperature dependences of the magnetic heat capacities of κ -(BETS)₂FeBr₄ (κ -Br) and κ -(BETS)₂FeCl₄ (κ -Cl). The solid line represents the theoretical curve of the $S = 5/2$ one-dimensional Heisenberg chain [53]. Reproduced with permission from [44].

It is generally recognized that the compounds possessing a low dimensional structure of the magnetic ions or molecules usually show short-range fluctuations in their thermodynamic and magnetic properties. In the case of κ -(BETS)₂FeX₄ systems, the tail structure in the magnetic heat capacity observed at higher temperatures is due to the short-range ordering derived from the dominant direct magnetic interaction, and the long-range ordering is induced by the indirect magnetic interaction. Numerous works to investigate the thermodynamic nature of such low dimensional magnetic systems by heat capacity measurements have been performed and comprehensive discussion is given in several review papers and textbooks [52,54,55]. However, the situation of the present compounds is quite different from the conventional low dimensional magnetic systems. The inter-layer magnetic interactions between the π electrons and the 3d electrons are relatively large and in the same order with the direct magnetic interactions in the a axis direction. As is shown schematically in Figure 1d, the indirect magnetic interaction between the 3d electron spins through the π - d interaction exists in all directions and they can form a three-dimensional ordering at rather high temperatures. However, only in the a axis direction, the direct magnetic interaction of J_{dd} exists with a similar order as the indirect magnetic interaction. This interaction is quite anisotropic, like one-dimensional magnetic systems. Although the three-dimensional ordering occurs as a cooperative effect of the direct and the indirect magnetic interactions, the effect of the direct magnetic interaction remains as internal degrees of freedom even though the three-dimensional ordering is established at T_N . The low dimensional magnetic system, which has direct and indirect magnetic interactions with a similar order, is quite rare and probably the unique point for this material. Moreover, the strong electron correlation among the π electrons also influences the magnetic nature of the 3d electron spin system. Such situation characteristic in the π - d interacting system changes the three-dimensional ordered state to the unconventional magnetic state such that the nature of the one-dimensional direct magnetic

interaction remains even below T_N . Interestingly, the similar hump structure is also observed more clearly in the λ -(BETS) $_2$ FeCl $_4$, which is another π - d interacting system, which is reviewed in [56]. Recently, some theoretical studies on the emergence of the hump structure in the π - d interacting system have been reported [57]. These results claim that the curious magnetic behaviors reviewed in this section are characteristic behavior of the π - d interacting systems and shed light on a new aspect of molecular magnets.

6. Anisotropic Magnetic Field Dependence of the Superconducting Transition of κ -(BETS) $_2$ FeBr $_4$

The coupling of the 3d electrons and the π electrons also influences the superconducting nature. Below the antiferromagnetic transition temperature, κ -(BETS) $_2$ FeBr $_4$ and κ -(BETS) $_2$ FeCl $_4$ show a superconducting transition at 1.5 K and 0.1 K, respectively [34–36]. The superconductivity of the κ -type compounds has two-dimensional characters with line-nodes in the cylindrical Fermi surface and the pairing state is considered as the anisotropic $d_{x^2-y^2}$ or d_{xy} type depending on the magnitude of dimerization and frustration factor inherent in the triangularity of the κ -type packing [58,59]. To discuss the superconducting nature, it is necessary to extract the electronic heat capacity of the π electrons. In the case of κ -(BETS) $_2$ FeBr $_4$, the magnetic heat capacity originating from the 3d electron spins gives a dominant contribution to the total heat capacity, and this situation makes it difficult to analyze the accurate electronic heat capacity of the π electrons. However, by subtracting the appropriate magnetic heat capacity by the procedure explained in [60], the thermal anomaly due to the superconducting transition was evaluated. Figure 7 shows the temperature dependence of the heat capacity of κ -(BETS) $_2$ FeBr $_4$ around the superconducting transition temperature and the thermal anomaly due to the superconductivity. The magnitude of the heat capacity jump at $T_c = 1.5$ K is about $\Delta C_p \sim 50$ mJ K $^{-1}$ mol $^{-1}$, which is a typical value for organic superconductors [45–49]. The deviation from the Bardeen-Cooper-Schrieffer (BCS) curves may imply a possible nodal superconductor. However, it should be emphasized that the ambiguity of the background evaluation exists as a serious factor for further discussion and it is difficult to discuss the temperature dependence of ΔC_p and pair symmetry using BCS theory or other models. We cannot discuss the origin of the small anomaly around 0.8 K at present, since we cannot exclude an extrinsic origin due to the slight change of the thermal conductivity of the wires used as a heat leak in the calorimetry cell.

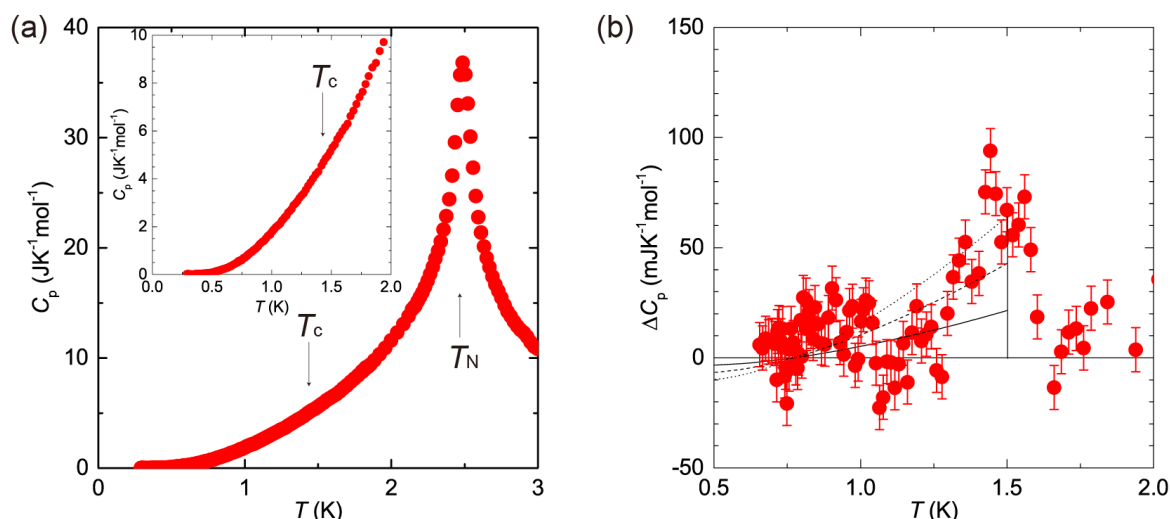


Figure 7. (a) C_p vs. T curve of κ -(BETS) $_2$ FeBr $_4$ at 0 T. The inset shows the enlarged view around the superconducting transition temperature. (b) ΔC_p vs. T curve of κ -(BETS) $_2$ FeBr $_4$ at 0 T. The solid, dashed, and dotted lines represent the BCS curves assuming that the γ values are 10, 20, 30 mJ K $^{-2}$ mol $^{-1}$, respectively [61]. Reproduced with permission from [60].

The magnetic field dependence of the peak temperature due to the superconductivity shows unusual in-plane anisotropy. Although the exact estimation of the electronic heat capacity under the magnetic field is difficult, the relative field-dependent change of the thermal anomaly and the superconducting transition temperature can be traced by comparing the heat capacity data under magnetic fields parallel to the b axis, which is the perpendicular direction of the conducting layers as was reported in [60]. Figure 8 shows the ΔC_p vs. T curves at several magnetic fields applied parallel to the c axis. The anomaly shows no significant field dependence up to 2 T. Above 2 T, the superconducting transition temperature is gradually decreased and disappears around 2.5 T.

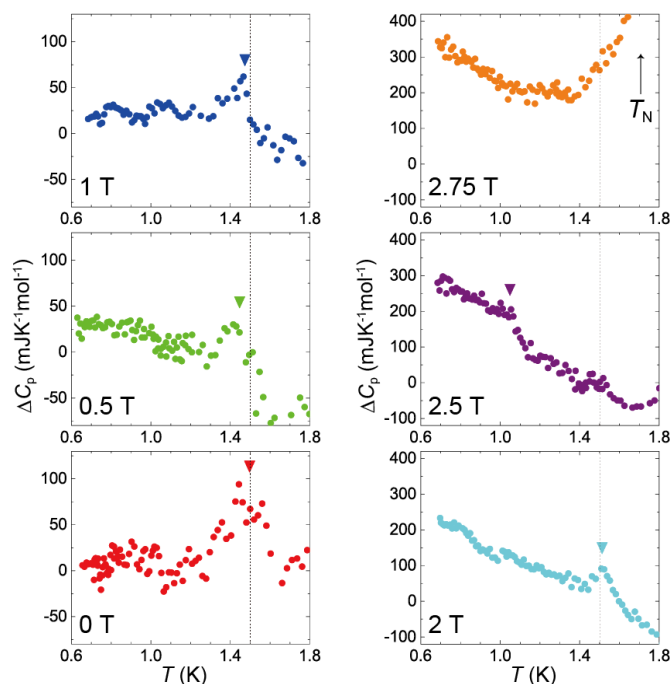


Figure 8. ΔC_p vs. T curves of κ -(BETS) $_2$ FeBr $_4$ at several magnetic fields applied parallel to the c axis. The dashed lines represent the superconducting transition temperature of 1.5 K at 0 T. Reproduced with permission from [60].

Figure 9 shows the field-direction dependence of the ΔC_p vs. T curves at 1 T and 2 T. Although several ΔC_p curves contain large offset inherent in the ambiguity of the estimation of the magnetic contribution derived from the $3d$ electron spins, the anomaly associated with the superconducting transition can be traced. Although the superconducting transition shows almost isotropic field-direction dependence at 1 T, it shows significant anisotropic field-direction dependence at 2 T. When the magnetic field-direction is tilted from the c axis to the a axis, the superconducting transition shifts to the lower temperature region drastically, and it is no longer observed above 30° from the c axis in the experimentally available temperature range down to 0.65 K. Such field-direction dependence is not explained by the anisotropy of the Fermi surfaces and the symmetry of the superconducting gap structure [62–64].

Figure 10 shows a magnetic field vs. temperature (B - T) phase diagram determined by the heat capacity measurements. This phase diagram is almost the same with that determined by the transport and magnetic susceptibility measurements by Fujiwara et al. [26,34]. Since the magnetic fields are applied parallel to the in-plane direction of the donor layers, the pair breaking by the orbital effect is not so large. Therefore, in this configuration, the suppression mechanism of electron pairs is mainly determined by the Zeeman effect [65]. The Pauli limit of the weak coupling superconductor is given as $H_P = 1.84T_c$, which corresponds to the 2.6 T for κ -(BETS) $_2$ FeBr $_4$. This field is close to the field where the thermal anomaly due to the superconducting transition disappears when the magnetic field is

applied parallel to the c axis [66]. The origin of the anisotropy produced above 1 T is attributed to the change of internal magnetic fields induced by the change of antiferromagnetic spin structures. From the magnetization measurement, it is confirmed that when the magnetic field is applied parallel to the a axis, corresponding to the magnetic easy axis of the $3d$ electron spins, the $3d$ electron spins show a metamagnetic transition around 2 T, leading to the drastic change of the internal field [34]. Fujiwara et al. calculated the field dependence of the effective magnetic field for several directions and suggested that the drastic increase of the internal field occurs at the metamagnetic transition field [67]. From these results, it is considered that the increase of the effective magnetic field induced by the change of the antiferromagnetic spin structure destabilizes the superconducting state even below the Pauli limit. In contrast to this, only a slight change is expected for the antiferromagnetic spin arrangement below the metamagnetic transition field. Therefore, the suppression of the superconducting transition temperature is moderate at the weak magnetic field region. On the other hand, only a gradual change of the internal field occurs up to the Pauli-limit value when the magnetic field is applied parallel to the c axis. In this direction, the magnetic field is perpendicular to the magnetic easy axis and the magnetic field gradually cants the direction of the $3d$ electron spins while keeping the antiferromagnetically ordered structure. Therefore, the change of the internal field is gradual and the drastic suppression of the superconducting transition temperature is not observed up to the Pauli-limit value. These results suggest that the magnetic state of the $3d$ electron spins influences the superconducting state of the π electron system through the π - d interaction as the change of the effective magnetic field.

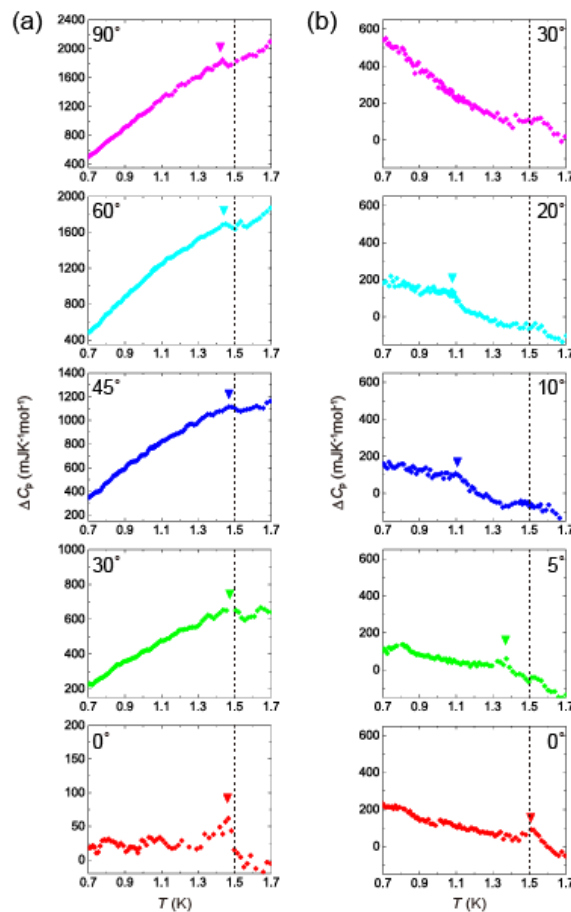


Figure 9. Field-direction dependences of the ΔC_p vs. T curves of κ -(BETS) $_2$ FeBr $_4$ under the in-plane magnetic field at (a) 1 T and (b) 2 T. 0° and 90° correspond to the c axis and the a axis, respectively. Dashed lines represent the superconducting transition temperature of 1.5 K at 0 T. Reproduced with permission from [60].

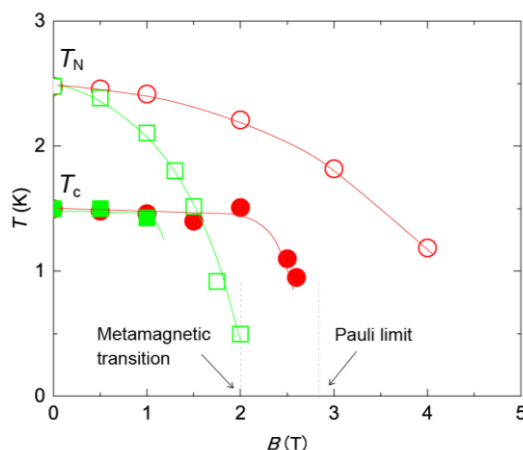


Figure 10. B - T phase diagram of κ -(BETS) $_2$ FeBr $_4$ determined by heat capacity measurements. The closed and open symbols represent the superconducting transition temperature and the antiferromagnetic transition temperature. The magnetic field is applied parallel to the a axis (green) and the c axis (red). Reproduced with permission from [60].

7. Summary

In this article, the unique magnetic and superconducting properties of κ -(BETS) $_2$ FeX $_4$ ($X = \text{Cl}, \text{Br}$) investigated by single crystal heat capacity measurements were reviewed. In the former part, we showed the results of the magnetic heat capacity of the $3d$ electron spin system. The heat capacity measurements revealed that both κ -(BETS) $_2$ FeBr $_4$ and κ -(BETS) $_2$ FeCl $_4$ showed hump structures only when the external magnetic fields were applied parallel to the a axis, which is the easy axis of the $3d$ electron spins. The hump structures scale well between two compounds by using the value of dominant direct magnetic interaction, $|J_{\text{dd}}|/k_{\text{B}}$. Such anisotropic magnetic properties were produced by the coexistence of the direct and the indirect magnetic interactions in this direction. In the latter part, we showed the results of the electronic heat capacity of the π electron system. The superconducting transition anomaly in the electronic heat capacity was observed in κ -(BETS) $_2$ FeBr $_4$ at 1.5 K, although the ambiguity of the subtraction of the large magnetic heat capacity of the $3d$ electron spins remains. When the magnetic field was applied parallel to the conducting layers, the superconducting transition temperature also showed anisotropic field dependence even though the superconductivity itself has two-dimensional characters. Although the superconducting transition could be observed near the Pauli limit if the magnetic field was applied parallel to the c axis, it was drastically suppressed if the magnetic field was applied parallel to the a axis similar to the case of T_{N} . The anisotropic field-direction dependence in the in-plane configuration can be understood by considering the change of the internal magnetic field produced by the $3d$ electron spin system. It should be emphasized that the coexistence of the direct magnetic interaction and the indirect magnetic interaction through the π - d interaction plays a crucial role for both the origin of the unconventional magnetic properties of the $3d$ electron spins and that of the anisotropic field-direction dependence of the superconducting transition temperature.

Author Contributions: Conceptualization, S.F. (Shuhei Fukuoka) and Y.N.; Investigation, S.F. (Shuhei Fukuoka) and S.F. (Sotarou Fukuchi); Writing—original draft preparation, S.F. (Shuhei Fukuoka) and Y.N.; Writing—review and editing, H.A. and A.K.; Funding acquisition, S.F. (Shuhei Fukuoka) and Y.N.

Funding: This work was partly supported by a Grant-in-Aid for JSPS Fellow.

Acknowledgments: Authors are grateful to S. Yamashita and T. Yamamoto for fruitful discussion, and H. Fujiwara, T. Shirahata, and K. Takahashi for the synthesis of large high quality κ -(BETS) $_2$ FeX $_4$ ($X = \text{Cl}, \text{Br}$) crystals.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Miyasaka, H.; Nakata, K.; Lecren, L.; Coulon, C.; Nakazawa, Y.; Fujisaki, T.; Sugiura, K.; Yamashita, M.; Clérac, R. Two-dimensional networks based on Mn_4 complex linked by dicyanamide anion: From single-molecule magnet to classical magnet behavior. *J. Am. Chem. Soc.* **2006**, *128*, 3770–3783. [[CrossRef](#)] [[PubMed](#)]
2. Miyasaka, H.; Madanbashi, T.; Sugimoto, K.; Nakazawa, Y.; Wernsdorfer, W.; Sugiura, K.; Yamashita, M.; Coulon, C.; Clérac, R. Single-chain magnet behavior in an alternated one-dimensional assembly of a Mn^{III} Schiff-base complex and a TNCQ radical. *Chem. Eur. J.* **2006**, *12*, 7028–7040. [[CrossRef](#)] [[PubMed](#)]
3. Fitta, M.; Peřka, R.; Konieczny, P.; Bařanda, M. Multifunctional molecular magnets: Magnetocaloric effect in octacyanometallates. *Crystals* **2019**, *9*, 9. [[CrossRef](#)]
4. Liu, J.-L.; Chen, Y.-C.; Guo, F.-S.; Tong, M.-L. Recent advances in the design of magnetic molecules for use as cryogenic magnetic coolants. *Coord. Chem. Rev.* **2014**, *281*, 26–49. [[CrossRef](#)]
5. Miller, J.S.; Epstein, A.J.; Reiff, W.M. Ferromagnetic molecular charge-transfer complexes. *Chem. Rev.* **1988**, *88*, 201–220. [[CrossRef](#)]
6. Qiu, Z.; Uruichi, M.; Hou, D.; Uchida, K.; Yamamoto, H.M.; Saitoh, E. Spin-current injection and detection in κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Br. *AIP Adv.* **2015**, *5*, 057167. [[CrossRef](#)]
7. Liu, M.; Chuang, Z.; Malissa, H.; Groesbeck, M.; Kavand, M.; McLaughlin, R.; Jamali, S.; Hao, J.; Sun, D.; Davidson, R.A.; et al. Organic-based magnon spintronics. *Nat. Mater.* **2018**, *17*, 308–312. [[CrossRef](#)] [[PubMed](#)]
8. Kinoshita, M.; Turek, P.; Tamura, M.; Nozawa, K.; Shiomi, D.; Nakazawa, Y.; Ishikawa, M.; Takahashi, M.; Awaga, K.; Inabe, T.; et al. An organic radical ferromagnet. *Chem. Lett.* **1991**, *20*, 1225–1228. [[CrossRef](#)]
9. Tamura, M.; Nakazawa, Y.; Shiomi, D.; Nozawa, K.; Hosokoshi, Y.; Ishikawa, M.; Takahashi, M.; Kinoshita, M. Bulk ferromagnetism in the β -phase crystal of the *p*-nitrophenyl nitroxide. *Chem. Phys. Lett.* **1991**, *186*, 401–404. [[CrossRef](#)]
10. Korshak, Y.V.; Medvedeva, T.V.; Ovchinnikov, A.A.; Spector, V.N. Organic polymer ferromagnet. *Nature* **1987**, *326*, 370–372. [[CrossRef](#)]
11. Miller, J.S.; Epstein, A.J. Organic and organometallic molecular magnetic materials—Designer magnets. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 385–415. [[CrossRef](#)]
12. Tamura, M.; Hosokoshi, Y.; Shiomi, D.; Kinoshita, M.; Nakazawa, Y.; Ishikawa, M.; Sawa, H.; Kitazawa, T.; Eguchi, A.; Nishio, Y.; et al. Magnetic properties and structures of the α - and δ -phases of *p*-NPN. *J. Phys. Soc. Jpn.* **2003**, *72*, 1735–1744. [[CrossRef](#)]
13. Okabe, T.; Yamaguchi, H.; Kittaka, S.; Sakakibara, T.; Ono, T.; Hosokoshi, Y. Magnetic properties of the $S = 1/2$ honeycomb lattice antiferromagnet 2-Cl-3,6-F $_2$ -V. *Phys. Rev. B* **2017**, *95*, 075120. [[CrossRef](#)]
14. Kono, Y.; Kittaka, S.; Yamaguchi, H.; Hosokoshi, Y.; Sakakibara, T. Quasi-one-dimensional Bose-Einstein condensation in the spin-1/2 ferromagnetic-leg ladder 3-I-V. *Phys. Rev. B* **2018**, *97*, 100406. [[CrossRef](#)]
15. Caneschi, A.; Gatteschi, D.; Ray, P.; Sessoli, R. Structure and magnetic ordering of a ferrimagnetic helix formed by manganese (II) and a nitronyl nitroxide radical. *Inorg. Chem.* **1991**, *30*, 3936–3941. [[CrossRef](#)]
16. Kumagai, H.; Inoue, K. A chiral molecular based metamagnet prepared from manganese ions and a chiral triplet organic radical as a bridging ligand. *Angew. Chem. Int. Ed.* **1999**, *38*, 1601–1603. [[CrossRef](#)]
17. Gatteschi, D.; Sessoli, R.; Villain, J. *Molecular Nanomagnets*; Oxford University Press: Oxford, UK, 2010.
18. Sato, O. Dynamic molecular crystals with switchable physical properties. *Nat. Chem.* **2016**, *8*, 644–656. [[CrossRef](#)] [[PubMed](#)]
19. Nihei, M.; Shiga, T.; Maeda, Y.; Oshio, H. Spin crossover iron(III) complexes. *Coord. Chem. Rev.* **2007**, *251*, 2606–2621. [[CrossRef](#)]
20. Shimizu, Y.; Miyagawa, K.; Kanoda, K.; Maesato, M.; Saito, G. Spin liquid state in an organic Mott insulator with a triangular lattice. *Phys. Rev. Lett.* **2003**, *91*, 107001. [[CrossRef](#)]
21. Christou, G.; Gatteschi, D.; Hendrickson, D.N.; Sessoli, R. Single-molecule magnets. *Mrs Bull.* **2000**, *25*, 66–71. [[CrossRef](#)]
22. Ohkoshi, S.; Imoto, K.; Tsunobuchi, Y.; Takano, S.; Tokoro, H. Light-induced spin-crossover magnet. *Nat. Chem.* **2011**, *3*, 564–569. [[CrossRef](#)] [[PubMed](#)]
23. Enoki, T.; Miyazaki, A. Magnetic TTF-based charge-transfer complexes. *Chem. Rev.* **2004**, *104*, 5449–5477. [[CrossRef](#)] [[PubMed](#)]

24. Coronado, E.; Day, P. Magnetic molecular conductors. *Chem. Rev.* **2004**, *104*, 5419–5448. [[CrossRef](#)] [[PubMed](#)]
25. Kobayashi, H.; Kobayashi, A.; Cassoux, P. BETS as a source of molecular magnetic superconductors (BETS = bis(ethylenedithio)tetraselenafulvalene). *Chem. Soc. Rev.* **2000**, *29*, 325–333. [[CrossRef](#)]
26. Kobayashi, H.; Cui, H.B. Organic metal and superconductors based on BETS (BETS = Bis(ethylenedithio)tetraselenafulvalene). *Chem. Rev.* **2004**, *104*, 5265–5288. [[CrossRef](#)] [[PubMed](#)]
27. Kikuchi, K.; Nishikawa, H.; Ikemoto, I.; Toita, T.; Akutsu, H.; Nakatsuji, S.; Yamada, J. Tetrachloroferrate (III) salts of BDH-TTP [2,5-Bis(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene] and BDA-TTP [2,5-Bis(1,3-dithian-2-ylidene)-1,3,4,6-tetrathiapentalene]: Crystal structures and physical properties. *J. Solid State Chem.* **2002**, *168*, 503–508. [[CrossRef](#)]
28. Fujiwara, H.; Wada, K.; Hiraoka, T.; Hayashi, T.; Sugimoto, T.; Nakazumi, H.; Yokogawa, K.; Teramura, M.; Yasuzuka, S.; Murata, K.; et al. Stable metallic behavior and antiferromagnetic ordering of Fe(III) *d* spins in (EDO-TTFVO)₂·FeCl₄. *J. Am. Chem. Soc.* **2005**, *127*, 14166–14167. [[CrossRef](#)] [[PubMed](#)]
29. Xiao, X.; Hayashi, T.; Fujiwara, H.; Sugimoto, T.; Noguchi, S.; Weng, Y.; Yoshino, H.; Murata, K.; Aruga-Katori, H. An antiferromagnetic molecular metal based on a new bent-donor molecule. *J. Am. Chem. Soc.* **2007**, *129*, 12618–12619. [[CrossRef](#)] [[PubMed](#)]
30. Coronado, E.; Galán-Mascarós, J.R.; Gómez-García, C.J.; Laukhin, V. Coexistence of ferromagnetism and metallic conductivity in a molecule-based layered compound. *Nature* **2000**, *408*, 447–449. [[CrossRef](#)]
31. Hotta, C.; Fukuyama, H. Effects of localized spins in quasi-two dimensional organic conductor. *J. Phys. Soc. Jpn.* **2000**, *69*, 2577–2596. [[CrossRef](#)]
32. Kobayashi, A.; Udagawa, T.; Tomita, H.; Naito, T.; Kobayashi, H. New organic metals based on BETS compounds with MX₄[−] anions (BETS = bis(ethylenedithio)tetraselenafulvalene; M = Ga, Fe, In; X = Cl, Br). *Chem. Lett.* **1993**, *22*, 2179–2182. [[CrossRef](#)]
33. Kobayashi, H.; Tomita, H.; Naito, T.; Kobayashi, A.; Sakai, F.; Watanabe, T.; Cassoux, P. New BETS conductors with magnetic anions (BETS = bis(ethylenedithio)tetraselenafulvalene). *J. Am. Chem. Soc.* **1996**, *118*, 368–377. [[CrossRef](#)]
34. Fujiwara, H.; Fujiwara, E.; Nakazawa, Y.; Narymbetov, B.Z.; Kato, K.; Kobayashi, H.; Kobayashi, A.; Tokumoto, M.; Cassoux, P. A novel antiferromagnetic organic superconductor κ-(BETS)₂FeBr₄ [Where BETS = Bis(ethylenedithio)tetraselenafulvalene]. *J. Am. Chem. Soc.* **2001**, *123*, 306–314. [[CrossRef](#)] [[PubMed](#)]
35. Otsuka, T.; Kobayashi, A.; Miyamoto, Y.; Kiuchi, J.; Nakamura, S.; Wada, N.; Fujiwara, E.; Fujiwara, H.; Kobayashi, H. Organic antiferromagnetic metals exhibiting superconducting transitions κ-(BETS)₂FeX₄ (X = Cl, Br); Drastic effect of halogen substitution on the successive phase transitions. *J. Solid State Chem.* **2001**, *159*, 407–412. [[CrossRef](#)]
36. Otsuka, T.; Kobayashi, A.; Miyamoto, Y.; Kikuchi, J.; Wada, N.; Ojima, E.; Fujiwara, H.; Kobayashi, H. Successive antiferromagnetic and superconducting transitions in an organic metal, κ-(BETS)₂FeCl₄. *Chem. Lett.* **2000**, *29*, 732–733. [[CrossRef](#)]
37. Uji, S.; Shinagawa, H.; Terashima, T.; Yakabe, T.; Terai, Y.; Tokumoto, M.; Kobayashi, A.; Tanaka, H.; Kobayashi, H. Magnetic-field-induced superconductivity in a two-dimensional organic conductor. *Nature* **2001**, *410*, 908–910. [[CrossRef](#)]
38. Tanaka, H.; Ojima, E.; Fujiwara, H.; Nakazawa, Y.; Kobayashi, H.; Kobayashi, A. A new κ-type organic superconductor based on BETS molecules, κ-(BETS)₂GaBr₄ [BETS = bis(ethylenedithio)tetraselenafulvalene]. *J. Mater. Chem.* **2000**, *10*, 245–247. [[CrossRef](#)]
39. Konoike, T.; Uji, S.; Terashima, T.; Nishimura, M.; Yasuzuka, S.; Enomoto, K.; Fujiwara, H.; Zhang, B.; Kobayashi, H. Magnetic-field-induced superconductivity in the antiferromagnetic organic superconductor κ-(BETS)₂FeBr₄. *Phys. Rev. B* **2004**, *70*, 094514. [[CrossRef](#)]
40. Jaccarino, V.; Peter, M. Ultra-high-field superconductivity. *Phys. Rev. Lett.* **1962**, *9*, 290–292. [[CrossRef](#)]
41. Fujiyama, S.; Takigawa, M.; Kikuchi, J.; Cui, H.-B.; Fujiwara, H.; Kobayashi, H. Compensation of effective field in the field-induced superconductor κ-(BETS)₂FeBr₄ observed by ⁷⁷Se NMR. *Phys. Rev. Lett.* **2006**, *96*, 217001. [[CrossRef](#)]
42. Fukuoka, S.; Horie, Y.; Yamashita, S.; Nakazawa, Y. Development of heat capacity measurement system for single crystals of molecule-based compounds. *J. Therm. Anal. Calorim.* **2013**, *113*, 1303–1308. [[CrossRef](#)]

43. Imajo, S.; Fukuoka, S.; Yamashita, S.; Nakazawa, Y. Construction of relaxation calorimetry for 10^{1-2} μg samples and heat capacity measurements of organic complexes. *J. Therm. Anal. Calorim.* **2016**, *123*, 1871–1876. [[CrossRef](#)]
44. Fukuoka, S.; Yamashita, S.; Nakazawa, Y.; Yamamoto, T.; Fujiwara, H.; Shirahata, T.; Takahashi, K. Thermodynamic properties of antiferromagnetic ordered states of π - d interacting systems of κ -(BETS)₂FeX₄ (X = Br, Cl). *Phys. Rev. B* **2016**, *93*, 245136. [[CrossRef](#)]
45. Andraka, B.; Kim, J.S.; Stewart, G.R.; Carlson, K.D.; Wang, H.H.; Williams, J.M. Specific heat in high magnetic field of κ -di[Bis(ethylenedithio)tetrathiafulvalene]-di(thiocynano)Cuprate [κ -(ET)₂Cu(NCS)₂]; Evidence for strong-coupling superconductivity. *Phys. Rev. B* **1989**, *40*, 11345. [[CrossRef](#)]
46. Andraka, B.; Jee, C.S.; Kim, J.S.; Stewart, G.R.; Carlson, K.D.; Wang, H.H.; Crouch, A.V.S.; Kini, A.M.; Williams, J.M. Specific heat of the high T_c organic superconductor κ -(ET)₂Cu[N(CN)₂]Br. *Solid State Commun.* **1991**, *79*, 57–59. [[CrossRef](#)]
47. Wosnitzer, J.; Liu, X.; Schweitzer, D.; Keller, H.J. Specific heat of the organic superconductor κ -(BEDT-TTF)₂I₃. *Phys. Rev. B* **1994**, *59*, 12747. [[CrossRef](#)]
48. Nakazawa, Y.; Yamashita, S. Thermodynamic properties of κ -(BEDT-TTF)₂X salts: Electron correlation and superconductivity. *Crystals* **2012**, *2*, 741–761. [[CrossRef](#)]
49. Nakazawa, Y.; Imajo, S.; Matsuoka, Y.; Yamashita, S.; Akutsu, H. Thermodynamic picture of dimer-Mott organic superconductors revealed by heat capacity measurements with external and chemical pressure control. *Crystals* **2018**, *8*, 143. [[CrossRef](#)]
50. Mori, T.; Katsuhara, M. Estimation of πd -interaction in organic conductors including magnetic anions. *J. Phys. Soc. Jpn.* **2002**, *71*, 826–844. [[CrossRef](#)]
51. Gopal, E.S.R. *Specific Heats at Low Temperature*; Heywood Books: London, UK, 1966.
52. De Jongh, L.J.; Miedema, A.R. Experiments on simple magnetic model systems. *Adv. Phys.* **1974**, *23*, 1–260. [[CrossRef](#)]
53. Blöte, H.W. The heat capacities of linear Heisenberg chains. *Physica* **1974**, *78*, 302–307. [[CrossRef](#)]
54. Sorai, M.; Nakazawa, Y.; Nakano, M.; Miyazaki, Y. Calorimetric investigation of phase transitions occurring in molecule-based magnets. *Chem. Rev.* **2013**, *113*, PR41–PR122. [[CrossRef](#)] [[PubMed](#)]
55. Blundell, S. *Magnetism in Condensed Matter*; Oxford University Press: Oxford, UK, 2001.
56. Akiba, H.; Shimada, K.; Tajima, N.; Kajita, K.; Nishio, Y. Paramagnetic metal-antiferromagnetic insulator transition in π - d system λ -BETS₂FeCl₄, BETS = Bis(ethylenedithio)tetraselenafulvalene. *Crystals* **2012**, *2*, 984–995. [[CrossRef](#)]
57. Ito, K.; Shimahara, H. Mean field theory of a coupled Heisenberg model and its application to an organic antiferromagnet with magnetic anions. *J. Phys. Soc. Jpn.* **2016**, *85*, 024704. [[CrossRef](#)]
58. Nakazawa, Y.; Kanoda, K. Low-temperature specific heat of κ -(BEDT-TTF)₂Cu[N(CN)₂]Br in the superconducting state. *Phys. Rev. B* **1997**, *55*, R8670–R8673. [[CrossRef](#)]
59. Taylor, O.J.; Carrington, A.; Schlueter, J.A. Specific-heat measurements of the gap structure of the organic superconductors κ -(ET)₂Cu[N(CN)₂]Br and κ -(ET)₂Cu(NCS)₂. *Phys. Rev. Lett.* **2007**, *99*, 057001. [[CrossRef](#)] [[PubMed](#)]
60. Fukuoka, S.; Yamashita, S.; Nakazawa, Y.; Yamamoto, T.; Fujiwara, H. Anisotropic field dependence of the superconducting transition in the magnetic molecular superconductor κ -(BETS)₂FeBr₄. *J. Phys. Soc. Jpn.* **2017**, *86*, 014706. [[CrossRef](#)]
61. Muhlschlegel, B. Die thermodynamischen Funktionen des Supraleiters. *Z. Phys.* **1959**, *155*, 313–327. [[CrossRef](#)]
62. Sasaki, T.; Toyota, N. Anisotropic galvanomagnetic effect in the quasi-two-dimensional organic conductor α -(BEDT-TTF)₂KHg(SCN)₄, where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene. *Phys. Rev. B* **1994**, *49*, 10120–10130. [[CrossRef](#)]
63. Wang, H.H.; Vanzile, M.L.; Schlueter, J.A.; Kini, A.M.; Sche, P.P. In-plane ESR microwave conductivity measurements and electronic band structure studies of the organic superconductor β'' -(BEDT-TTF)₂SF₅CH₂CF₂SO₃. *J. Phys. Chem. B* **1999**, *103*, 5493–5499. [[CrossRef](#)]
64. Ishiguro, T.; Kajimura, K.; Bando, H.; Murata, K.; Anzai, H. Electronic state of (TMTSF)₂ClO₄ in metallic region. *Mol. Cryst. Liq. Cryst.* **1985**, *119*, 19–26. [[CrossRef](#)]
65. Tinkham, M. *Introduction to Superconductivity*, 2nd ed.; McGraw-Hill: New York, NY, USA, 1996.

66. Clogston, A.M. Upper limit for the critical field in hard superconductors. *Phys. Rev. Lett.* **1962**, *9*, 266–267. [[CrossRef](#)]
67. Fujiwara, H.; Kobayashi, H.; Fujiwara, E.; Kobayashi, A. An indication of magnetic-field-induced superconductivity in a bifunctional layered organic conductor, κ -(BETS) $_2$ FeBr $_4$. *J. Am. Chem. Soc.* **2002**, *124*, 6816–6817. [[CrossRef](#)] [[PubMed](#)]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).