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Magnetic field induced transition in the charge-glass former θ-(BEDT-TTF)$_2$CsCo(SCN)$_4$

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We perform thermodynamic and transport measurements on a magnetic charge-glass former, θ-(BEDT-TTF)$_2$CsCo(SCN)$_4$, to discuss the π-d interaction occurring in the interlayer direction. An anomalous temperature dependence and sharp peak structure of the heat capacity are observed in magnetic fields, indicating a field-induced transition in this compound. Furthermore, a sharp peak of the thermoelectric power is also observed in magnetic fields, supporting the presence of the field-induced transition. Comparison with a nonmagnetic analog compound indicates that the introduction of magnetic Co^{2+} ions ($S = 3/2$) triggers this transition. This strongly suggests that the π-d interaction effectively works in this compound and affects the physical properties. To explain the field-induced phenomenon in this compound, we propose a speculative scenario in which the π-d interaction between the π spins in the insulating domains and the d spin of Co^{2+} induces the reconstruction of the domain structure in the CG state.

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I. INTRODUCTION

A charge-glass (CG) state is a metastable electronic state driven by electron correlations and geometrical frustration [1]. In 1/4-filled hole-band systems in organic charge-transfer complexes, a charge-order (CO) state often emerges at low temperatures owing to the strong intersite Coulomb repulsion, V. The CO state is usually a long-range ordered state in which electrons form a superlattice periodicity of charge-rich and charge-poor sites. However, in geometrically frustrated systems such as a triangular lattice, several patterns of CO states energetically compete with each other, preventing the formation of a long-range CO state [2–5]. As a result, a coexisting state of several types of short-range CO domains with local charge patterns emerges at low temperatures. This state is known as a CG state. A CG state is not derived from impurities or disorders in a crystal but is caused by the quantum mechanical effect in the charge and lattice degrees of freedom. It is conceptually similar to a quantum spin liquid state, in which geometrical frustration suppresses a long-range ordering of antiferromagnetically coupled spins [6].

Quasi-two-dimensional organic conductors θ-(BEDT-TTF)$_2X$ series have been studied extensively as CG formers, where BEDT-TTF donates bis(ethylenedithio) tetrathiafulvalene. In these compounds, the conducting BEDT-TTF layers and insulating anion X layers are stacked alternatively to construct the hybrid systems of π-electron and insulating layers. The BEDT-TTF molecules form a frustrated triangular lattice and accommodate one hole per two molecules, resulting in a 1/4-filled hole-band system. The low-temperature electronic states of θ-type compounds can range from a CO state to a superconducting state depending on the monovalent X [7,8], and a phase diagram of this system parameterized by the dihedral angle, ϕ, between two BEDT-TTF molecules has been proposed [9]. In θ-type systems, the compounds with a geometrically frustrated lattice show a CG state in low temperatures. For example, θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ and θ-(BEDT-TTF)$_2$TlCo(SCN)$_4$ show a CG state when the formation of a long-range CO state is suppressed by rapid cooling [1,10–12]. On the other hand, θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ (hereafter θ-CsZn salt) and θ-(BEDT-TTF)$_2$CsCo(SCN)$_4$ (hereafter θ-CsCo salt) (Fig. 1) exhibit a CG state even under slow cooling conditions because of the high CG forming ability of these compounds, which is determined by the anisotropy of V [10,13–15].

There are CG formers with and without magnetic d-block elements in the insulating layers, however, how the presence or absence of magnetic ions affects the physical properties has not been discussed in depth. It is known that localized spins of d electrons can magnetically interact with π electrons in the conduction layer (π-d interaction), which often induces anomalous transport properties and magnetic-field responsivity. The effect of π-d interaction has been studied in, for example, (BETS)$_2$FeCl$_4$ and (BETS)$_2$FeBr$_4$ systems [16–18]. Even in the case of magnetic CG formers, it is possible that the π-d interaction effectively operates and makes their properties different from those of the non-magnetic analog compound. The research on π-d interactions in CG formers may provide another pathway not only to control the physical properties but also to find a unique electronic state in the frustrated lattice system.

Here, we focus on the physical properties of θ-CsCo salt, which contains magnetic Co^{2+} ($S = 3/2$) ions in the insulator layer, to discuss the existence of the π-d interactions in CG formers. According to previous studies, the CG state consisting of two types of short-range CO domains with different wave vectors, $\boldsymbol{q_1} = (2/3, k, 1/3)$ and $\boldsymbol{q_2} = (0, k, 1/2)$, is

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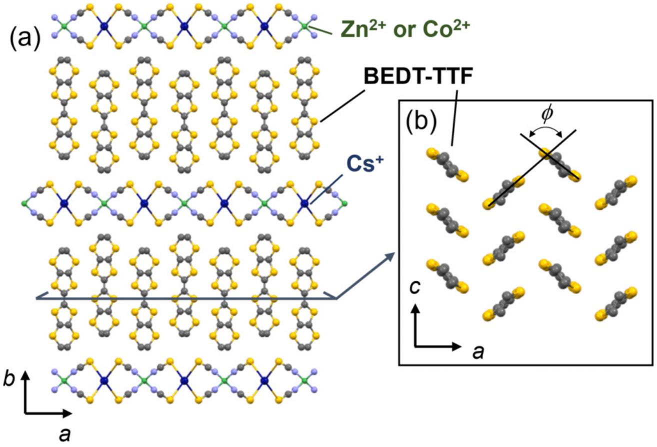

FIG. 1. (a) Crystal structure of θ-(BEDT-TTF)$_2$CsM(SCN)$_4$ (M = Zn, Co). (b) Molecular arraignment in the conducting layers where BEDT-TTF molecules form an anisotropic triangular lattice. ϕ denotes the dihedral angle of the BEDT-TTF molecules.

formed in θ-CsCo salt at low temperatures [19,20]. The low-temperature electronic state of θ-CsCo salt is quite similar to those of a nonmagnetic analog of θ-CsZn salt [19,20]. Since the domains of $\boldsymbol{q_1}$ and $\boldsymbol{q_2}$ are charge gapless (metallic) and charge gaped (insulating), respectively, the CG state is a percolated state of metallic and insulating regions. Below 20 K, the domains of $\boldsymbol{q_2}$ grow spatially, leading to a metal-insulator transition around 20 K [21]. Since the π spins in the $\boldsymbol{q_2}$ domains can behave as a localized spin, it is possible that the π spins magnetically interact with the d spins at low temperatures. Presently, it remains unclear whether the presence of the d spins of Co^{2+} affect the properties of the π electrons in the CG state, although there are several studies on the physical properties of θ-CsCo salt [13,22]. In the case of θ-CsZn salt, the π spin in the insulating domains forms a nonmagnetic singlet state with a neighboring π spin below 20 K [14,23] and the CG state is not affected by weak magnetic fields. If the π spins of θ-CsCo salt are also in a singlet state below 20 K, they would not interact with the d spins, and no unique properties related to the π-d interaction would be observed. However, it is possible that the introduction of magnetic ions changes the magnetic state from a nonmagnetic singlet state, creating a situation in which the π-d interaction effectively works [24]. In such case, unlike the magnetically robust CG state in θ-CsZn salt, the π electrons in θ-CsCo salt can be significantly influenced by magnetic fields through the π-d interaction and a magnetic-field response in the physical properties is expected to be observed. Therefore, a detailed study of the physical properties of θ-CsCo under magnetic fields may lead to unique insights into the π-d interaction in CG formers.

In this paper, we report the thermodynamic, transport, and magnetic properties of θ-CsCo salt under zero and several magnetic fields. We found a field-induced transition of θ-CsCo salt as anomalies in the heat capacity and the thermoelectric power. Because the field-induced transition cannot be observed in θ-CsZn salt, the emergence of the transition suggests the π-d interaction in the CG formers. We propose the reconstruction phenomenon of π electrons in the CG state by magnetic fields as a possible origin of the field-induced transition.

II. EXPERIMENTAL

Single crystals were grown using the standard electric oxidation method [9]. The heat capacity, C_p, measurements with external magnetic fields using single crystals were performed using the thermal relaxation technique. We adopted the long (sweeping) relaxation method which is applicable even in materials that exhibit a drastic change in heat capacity or a phase transition with latent heat [25,26]. All data for the heat capacity correspond to data from the cooling process because the heat capacity was calculated from the time variation of the temperature during the thermal relaxation process of the sample heated to high temperatures by a heater. The sample weights were 97.3 μg for θ-CsCo salt and 72.7 μg for θ-CsZn salt, respectively. For the heat capacity measurements, we used an RuO$_2$ chip resistance as a thermometer and a heater. The samples were attached to the sample stage using Apiezon N grease to obtain good thermal contact. Thermal conductivity measurements were performed by the standard steady-state method [27]. The sample dimensions were 0.70 mm × 0.30 mm × 0.30 mm. The temperature gradient, ΔT, for the thermal conductivity measurement was produced by heating an RuO$_2$ heater and was set to 5% of the measurement temperature. The direction of heat flow was parallel to the c axis of θ-CsCo salt. The sample, heater, two thermometers, and heat sink (copper block) were thermally linked by gold wires (ϕ = 20 μm) and gold pastes. Thermoelectric power measurement was also performed using the steady-state method. ΔT for the thermoelectric power measurement was adjusted to 5% of the measurement temperature. In the thermoelectric power measurements, the measurement temperature was cooled by the cooling rate of approximately 0.1 K min^{-1}. Magnetic susceptibility measurements using a single crystal of θ-CsCo salt were performed by the SQUID system (Quantum Design, Inc.). The sample weight for the magnetic susceptibility was 1.06 mg. Finally, magnetoresistance (MR) was measured using the standard four-terminal method under exchange gas conditions. During the MR measurement, the external magnetic field was slowly increased at a sweeping rate of approximately 50 Oe s^{-1}.

III. RESULTS

A. Heat capacity under zero field

Figure 2(a) shows the temperature dependence of C_p of θ-CsCo and θ-CsZn salts under zero field. The absolute value and temperature dependence of C_p of θ-CsZn salt is consistent with those in previous studies [28,29]. The C_p value of θ-CsCo salt is larger than that of θ-CsCo salt over the entire temperature range, which is due to the Schottky-type heat capacity of the paramagnetic Co^{2+} spins ($C_{\rm Sch}$). In the case of Co^{2+} in the tetrahedral field, the lowest level is $^4A_{2g}$. The quadruple degenerated states are split into two Kramers doublets with zero-field splitting (ZFS) energy D owing to the distortion of the SCN$^-$ structure, which induces a two-level Schottky-type heat capacity [22]. Since θ-CsZn and θ-CsCo salts have very similar electronic and spectroscopic

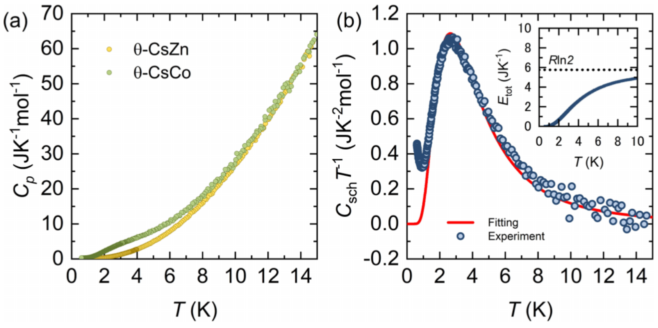

FIG. 2. (a) Temperature dependence of the heat capacity of θ-CsCo salt (green series) and θ-CsZn salt (yellow series). (b) Temperature dependence of the magnetic heat capacity $C_{\rm Sch}$ of θ-CsCo salt (blue series). The red solid line is the fitting curve expected by the two-level Schottky-type heat capacity, where the fitting parameters $D/k_{\rm B}$ is -4.3 K. Inset: The total entropy $E_{\rm tot}$ of spins calculated by integrating the $C_{\rm Sch}T^{-1}$. The $E_{\rm tot}$ saturates to Rln2 ($= 5.76$ JK^{-1}mol^{-1}) shown as the dotted line in the figure.

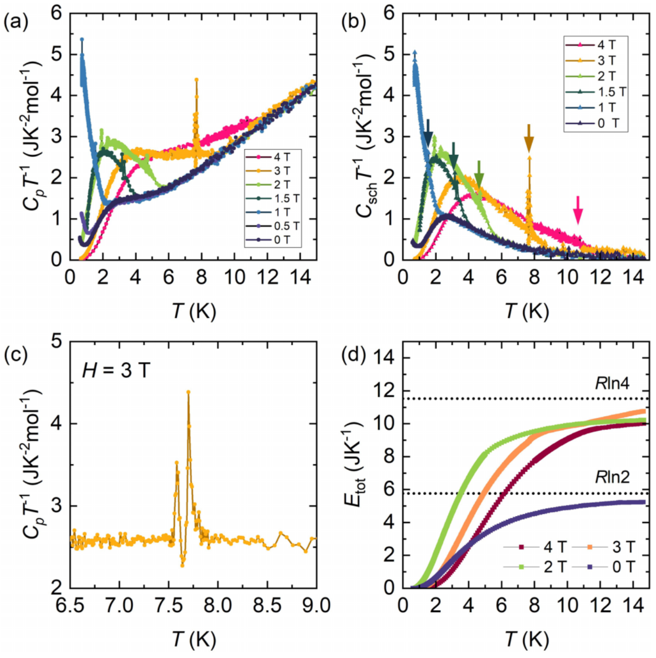

FIG. 3. (a) Temperature dependence of the heat capacity of θ-CsCo salt under several magnetic fields. Magnetic fields H were applied in parallel to the a axis. (b) Temperature dependence of the magnetic heat capacity $C_{\rm Sch}$. (c) The enlarged figure of C_pT^{-1} around the $T_{\rm peak}$ under $H = 3$ T. (d) The total entropy of spins calculated by the data of zero-field and several fields. The two dotted lines represent Rln2 and Rln4 ($= 11.5$ JK^{-1}mol^{-1}), respectively.

properties as well as crystal structures [9], it is reasonable to estimate the $C_{\rm Sch}$ by subtracting the heat capacity of θ-CsZn salt from that of θ-CsCo salt. Figure 2(b) shows the temperature dependence of $C_{\rm Sch}$ when plotted as $C_{\rm Sch}T^{-1}$ versus T. We observed a peak structure of $C_{\rm Sch}T^{-1}$ around 3 K, which could be fitted by the two-level Schottky equation as follows:

$$C_{\rm Sch} = Nk_{\rm B}\left(\frac{2D/k_{\rm B}T}{1+e^{-2D/k_{\rm B}T}}\right)^2 e^{-2D/k_{\rm B}T}, \qquad (1)$$

where N is the number of electronic spins and $k_{\rm B}$ is the Boltzmann constant ($= 1.38 \times 10^{-23}$ JK^{-1}). From the fitting curve shown in Fig. 2(b), we evaluated the fitting parameter $D/k_{\rm B} = -4.3$ K and $Nk_{\rm B} = 0.91R$, where R is the gas constant ($= 8.31$ K^{-1}mol^{-1}), which is consistent with the D value estimated by the magnetic susceptibility measurement in Ref. [22]. The total entropy $E_{\rm tot}$ saturated to Rln2 ($= 5.76$ JK^{-1}mol^{-1}), as shown in the inset of Fig. 2(b), indicates that the lowest level of the system is the two-degenerated sublevel corresponding to $M_s = \pm 3/2$. We note that $C_{\rm Sch}T^{-1}$ increased below 1 K, suggesting that the degeneracy is lifted marginally probably due to a lattice disorder or hyperfine interaction. These results reveal that the heat capacity of θ-CsCo salt under zero field shows no anomalous behavior, and its temperature dependence can be explained by the Schottky-type heat capacity model.

B. Heat capacity under magnetic fields

The temperature dependence of C_pT^{-1} and $C_{\rm Sch}T^{-1}$ for θ-CsCo salt under several magnetic fields is shown in Figs. 3(a) and 3(b). In the calculation of $C_{\rm Sch}$, we assumed that $C_{\rm lat}$ does not change even in magnetic fields. Because the doubly degenerated sublevels are split into four discrete levels under magnetic fields by the Zeeman effect, the magnetic heat capacity is expected to follow a four-level Schottky model. However, C_pT^{-1} under magnetic fields exactly agrees with that of the zero field at high temperatures and then exhibits a sudden increase at certain temperatures, resulting in a humplike curve of C_pT^{-1}. Such an abrupt change in heat capacity cannot be fitted simply by the four-level Schottky heat capacity model. Furthermore, we observed sharp peak anomalies in the heat capacity near the starting temperature of the humplike anomalies. As shown in Fig. 3(c), these peaks have a doublet structure. The temperature of these peaks, $T_{\rm peak}$, increases with increasing magnitude of the applied magnetic field, as well as the temperature of the humplike anomaly, as shown in Fig. 3(b). These findings suggest that the heat capacity of the θ-CsCo salt cannot be explained within the framework of a typical paramagnetic compound and that this compound exhibits a field-induced transition. Since no field-induced transition is observed in θ-CsZn salt [28], the transition we found may be caused by the introduction of the d spins of Co^{2+}. The $E_{\rm tot}$ measured under magnetic fields saturate to Rln4 ($= 11.5$ JK^{-1}mol^{-1}) as shown in Fig. 3(d), indicating the four discrete sublevels, $M_s = \pm 3/2$ and $\pm 1/2$. This suggests that the magnetic heat capacity in θ-CsCo is dominated only by the paramagnetic d spins even under magnetic fields, and the contribution of π-spins ($S = 1/2$) is not included. Since the contribution of π spins is not observed, the possible state of π spins in the insulating domains is considered to be either a nonmagnetic singlet state like θ-CsZn salt or an antiferromagnetic state like π-d systems with λ-type crystal structure [30].

C. Thermoelectric power

Next, we performed the thermoelectric power measurements to confirm the presence of field-induced transition in

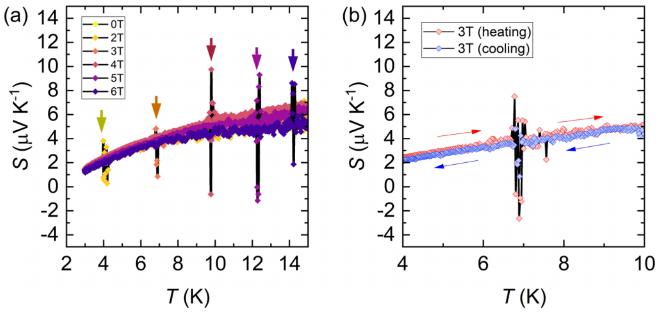

FIG. 4. (a) Temperature dependence of the Seebeck coefficient of θ-CsCo under zero and several magnetic fields. The arrows point to the temperature of the anomalous sharp peak (T_s) at each magnetic field. (b) Comparison of the measurement data under 3 T in the cooling process (blue series) and the heating process (red series). No temperature hysteresis was observed.

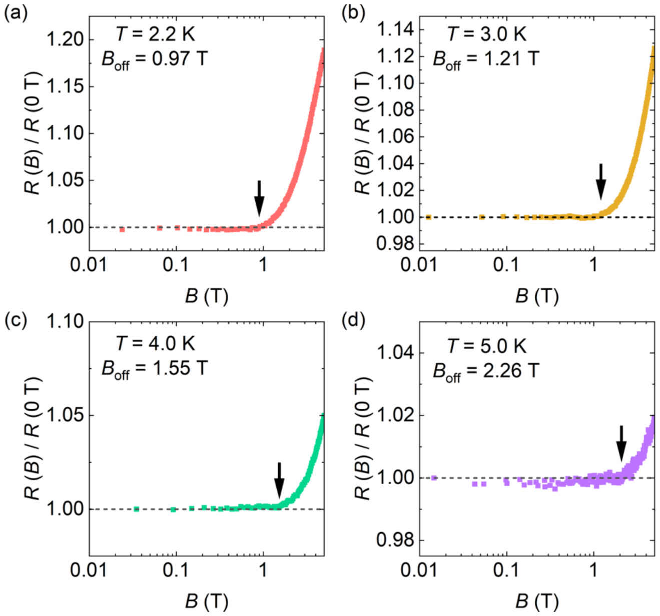

FIG. 5. MR of θ-CsCo measured at (a) 2.2 K, (b) 3.0 K, (c) 4.0 K, and (d) 5.0 K, respectively. The black arrows point to the threshold field (B_{off}) at each temperature. Above B_{off}, the MR increased proportional to B.

θ-CsCo salt. Figure 4(a) shows the temperature dependence of S between 15 and 2 K measured under several magnetic fields. In the case of $H = 0$ T, S monotonically decreases with decreasing temperature toward 0 $\mu\mathrm{VK}^{-1}$ at $T = 0$ K, which is usually observed in metals. The absolute value of $S \sim 5$ $\mu\mathrm{VK}^{-1}$ in this temperature region agrees with the literature value for θ-CsCo salt [13]. Even under magnetic fields, the metallic temperature dependence and absolute value of S were not changed significantly. However, a new sharp peak of S emerged in magnetic fields as shown in Fig. 4(a). The temperature of the peak, T_s, increases proportionally with the applied magnetic fields, which is the similar trend of T_{peak} observed in the heat capacity measurement. Figure 4(b) is the comparison of the S obtained in the cooling (blue series) and heating (red series) processes. The T_s in the cooling process and heating process agreed well, and no hysteresis behavior was observed in our measurements.

In the CG state below 20 K, the metallic q_1 domains and insulating q_2 domains coexist. The insulator domains do not contribute to the Seebeck coefficient because the carrier number is not changed by a small temperature gradient. Thus, it is considered that only a small thermoelectric power owing to the metallic domains was observed. Such a metallic behavior has been reported in the coexisting systems of metallic and insulating regions such as high-T_c copper oxides [31] and other CG formers [32]. Since the temperature dependence of S does not change under magnetic fields, the electronic state in magnetic fields is considered to be the CG state consisting of metallic and insulating CO domains. However, the observation of new peaks due to the application of magnetic fields suggests that a magnetic field induced transition occurs in θ-CsCo salt. Since the thermoelectric power signal is sensitive to the sample temperature, a sharp peak of S can be observed when the temperature of a sample changes rapidly. Therefore, the magnetic field induced transition is possibly a first-order phase transition accompanied by latent heat. If a first-order transition exists in this compound, it is natural to observe a sharp peak in the heat capacity in a magnetic field. Although a first-order transition usually exhibits the hysteresis of the transition temperature, we could not detect such a hysteresis behavior as shown in Fig. 4(b). Thus, it is not clear whether this transition is a first-order phase transition or not. One possible reason that we could not observe the hysteresis is because the speed of temperature sweeping was limited to be slow ($\sim$0.1 Kmin^{-1}).

D. Magnetoresistance

Figure 5 shows the MR of θ-CsCo salt measured at several temperatures. At all measurement temperatures, a negligibly small MR was observed in the low-field region and a positive B-linear MR was observed above a certain field. This is qualitatively different from MR owing to the Lorentz force, which is proportional to B^2. In CG formers, a large positive MR owing to impurity spins is observed at extremely low temperatures [33]. However, this anomalous increase in the MR can be observed at much higher temperatures as $T = 5$ K. The threshold field B_{off}, where the MR starts to increase, increases with increasing measurement temperature, which is similar to the anomalies observed in the heat capacity and thermoelectric power.

Figure 6 shows the relationship between the anomalies observed in the thermodynamic and transport measurements and applied magnetic fields. The temperature or field at which the anomaly was observed, T_{peak}, T_s, and B_{off} shows a good agreement, suggesting that these anomalies have the same origin. The temperature of the thermal anomalies increases linearly with increasing the magnetic fields, similar to a ferromagnetic compound.

E. Thermal conductivity

Figure 7 shows the temperature dependence of the thermal conductivity, κ, of θ-CsCo salt measured under several magnetic fields. Since θ-CsCo salt behaves as an insulator below

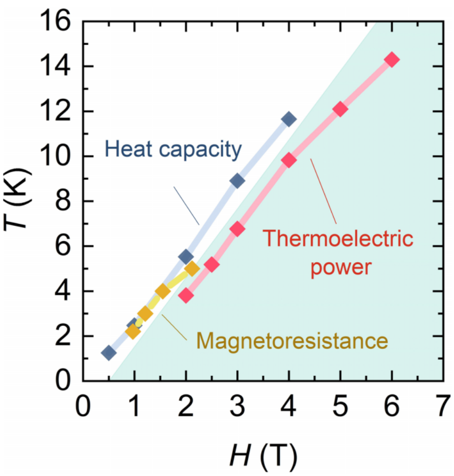

FIG. 6. Relationship between the observed thermal anomalies and the applied magnetic fields in θ-CsCo salt. T_{peak} (red series), T_{s} (blue series), and B_{off} (yellow series).

20 K, the dominant contribution to κ is thermal conduction by phonons. κ shows a monotonic decrease proportional to T down to 6 K and forms a plateau structure between 6 and 2 K. Below 2 K, κ starts to decrease again and exhibits a T-linear dependence. Such a temperature dependence of κ is a characteristic of CG formers in which the strong charge fluctuation changes the lattice properties from a crystalline state to a glassy state through the electron-phonon coupling [34]. When the magnetic fields were applied, the absolute value of κ slightly increased. However, the glasslike temperature dependence of κ did not change significantly and no thermal anomaly was observed in contrast to the heat capacity and thermoelectric power. This result suggests that a field-induced phase transition is not a type of transition that fundamentally alters the CG state in θ-CsCo salt, which is consistent with the result that the metallic temperature dependence of the thermoelectric power does not change by magnetic fields. The slight increase in κ around 2 K under magnetic fields may be caused by the increase in the phonon mean-free path related to the suppression of spin-phonon scattering by applying magnetic fields. However, this effect is not very large, and the main factor determining the thermal conductivity is the glassy features of phonons owing to the CG state. The absence of signs of the first-order transition in thermal conductivity, as seen in heat capacity and thermoelectric power, could be attributed to a difference in temperature control; thermal conductivity was measured at a fixed temperature, whereas heat capacity and thermoelectric power were measured while sweeping the temperature.

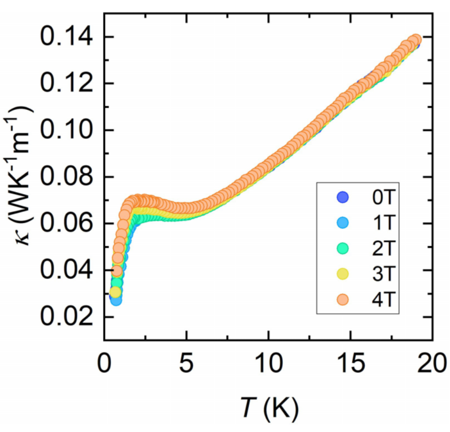

FIG. 7. Temperature dependence of the thermal conductivity of θ-CsCo salt under several magnetic fields. The T-liner decrement and the plateau structure of thermal conductivity were observed in all magnetic field data.

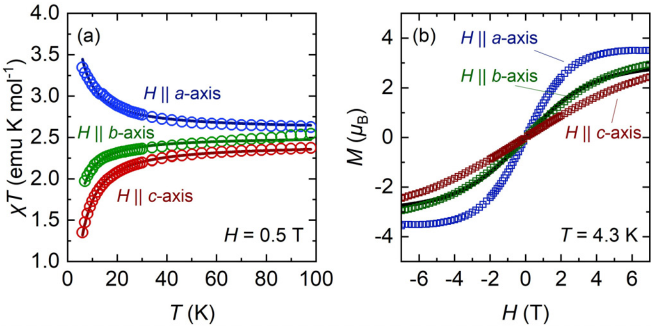

FIG. 8. (a) Temperature dependence of the magnetic susceptibility of θ-CsCo salt plotted as χT versus T plot. The solid lines are fitting curves by Eqs. (2) and (3) in the main text. (b) Magnetization curves between +7 T and −7 T at 4.3 K. The black solid line is the Brillouin function assuming $g = 2$ at 4.3 K.

F. Magnetic properties

Figure 8(a) shows the temperature dependence of magnetic susceptibility as a χT versus T plot measured at $H = 0.5$ T. According to the magnetic susceptibility results for nonmagnetic analog compounds, the magnetic susceptibility of localized π spins is approximately 2–3 × 10^{-4} emu mol^{-1}, which is about 1% of the contribution of Co^{2+} spins [9]. In the $H \parallel b$ and c axes, an almost constant χT in the high-temperature metallic region and a decreasing behavior below 20 K were observed. In contrast, in the $H \parallel a$ axis, χT increased at low temperatures like a ferromagnetic system. A similar anisotropy of χT was observed for analog compounds [35]. This anisotropy can be attributed to the anisotropy of the ZFS [36]. In spin-3/2 systems with ZFS, the magnetic susceptibility of the parallel component ($\chi_\parallel$) and the perpendicular component ($\chi_\perp$) to the z axis are described as follows:

$$\chi_\parallel = \frac{C_0 g_\parallel^2}{4T} \times \frac{1 + 9\exp(-2D/k_{\mathrm{B}}T)}{1 + \exp(-2D/k_{\mathrm{B}}T)}, \tag{2}$$

$$\chi_\perp = \frac{C_0 g_\perp^2}{T}\left[1 + \frac{3k_{\mathrm{B}}T}{4D} \times \frac{1 - \exp(-2D/k_{\mathrm{B}}T)}{1 + \exp(-2D/k_{\mathrm{B}}T)}\right], \tag{3}$$

$$C_0 = \frac{N_{\mathrm{A}}\mu_{\mathrm{B}}^2}{3k_{\mathrm{B}}}, \tag{4}$$

where N_{A} is the Avogadro constant, $g_\parallel$ and $g_\perp$ are the g factors of the parallel and perpendicular directions, respectively, and D is the axial ZFS parameter. In θ-CsCo salt, the N-Co-N angular direction forms a 104.5°angle, namely, the a-axis direction is the parallel direction ($\chi_\parallel = \chi_a$, $g_\parallel = g_a$), and the b- and c-axis directions are perpendicular

$(\chi_\perp = \chi_b, \chi_c, g_\perp = g_b, g_c)$ [37]. As indicated by the solid lines in Fig. 8(a), these formulas can reproduce the temperature dependence of χT. The g values obtained by the fitting are $g_a = 2.03$, $g_b = 2.00$, and $g_c = 1.96$. The fitting parameter D gives negative values for all directions ($D/k_\mathrm{B} = -2.6$ K for the a axis, -3.4 K for the b axis, -6.1 K for the c axis), which indicates that the spins behave as the Ising-type spins. These values are consistent with the D values estimated from the heat capacity measurement. Since the formula does not assume in-plane anisotropy in which the effect of π-d interaction is involved, the discrepancy in D values may originate from in-plane anisotropy. Figure 8(b) shows the magnetization curve of θ-CsCo salt measured at 4.3 K. The magnetization curve is highly anisotropic and does not follow the normal Brillouin function ($g = 2$), as indicated by the solid black line in Fig. 8(b). In the case of the $H \parallel a$ axis, the magnetization curve saturates to 3.5 μ_B at a high magnetic field. This saturation value corresponds to $g_a \sim 2.3$. The value reported in Ref. [22], estimated by the temperature dependence of the magnetic susceptibility, was $g_a = 2.2$, which agrees well with our data. In addition, the trend of the magnetization curve is consistent with that of the g values calculated by the χT versus T plot. In summary, we demonstrate that the magnetic properties of θ-CsCo salt are highly anisotropic with respect to the ZFS. We observed no drastic change in the magnetization process, suggesting that the field-induced transition cannot be attributed to a change in the magnetic state of the Co^{2+} spins.

IV. DISCUSSION

Our results demonstrate that θ-CsCo salt exhibits a magnetic field induced transition inducing anomalous behaviors in the transport and thermodynamic properties. Since the magnetic susceptibility and heat capacity measurements rule out any ordering of Co^{2+} spins, the field-induced transition is attributed to the change in the π electrons in the CG state. In θ-CsZn salt, no anomaly is observed even in magnetic fields, indicating the introduction of localized d spins is considered to be a trigger of the transition in θ-CsCo salt. This strongly suggests that the π-d interaction effectively works in θ-CsCo salt. The presence of π-d interactions simultaneously implies that the magnetic ground state of π spins may not be a nonmagnetic singlet state like θ-CsZn salt but a different magnetic state, such as a short-range antiferromagnetic ordered state.

Here, we discuss the origin of the anomalous magnetic-field responses in the physical properties of θ-CsCo salt based on the presence of the π-d interaction. The heat capacity under magnetic fields cannot be explained as the normal Schottky-type heat capacity modulated by the Zeeman effect, indicating that the energy scheme of the quadruple-degenerated states of Co^{2+} ions may be perturbed by the transition. The energy scheme of the d-electron orbitals can be varied when the coordination environment or magnetic interactions around Co^{2+} ions are changed. Considering the small change in the thermal conductivity by magnetic fields, it is unlikely that the coordination environment is drastically altered by the transition. In addition, the effect of the d-d interaction is presumed to be small [9]. Therefore, it is plausible that the anomalous field dependence of the heat capacity can be attributed to the change in the intensity of the π-d interaction between the Co^{2+} ions and the localized π electrons. Since the thermal conductivity and thermoelectric power show a characteristic feature of CG states even in magnetic fields, the basic structure of the CG state, in which the two kinds of CO domains coexist, is considered to remain under magnetic fields. Therefore, it is assumed that the field-induced transition is a transition between metastable states, from a CG state to another CG state with a different CO domain distribution. It is possible that the change in the spatial distribution of the CO domains interacting with the d spins affects the intensity of π-d interaction, resulting in the anomalous field dependence of the magnetic heat capacity in θ-CsCo salt. Moreover, since the electron-phonon coupling in CG formers is significantly strong [28,29,34], the change in the domain structure possibly induces a local structure change accompanied by latent heat. We believe that the sharp peaks observed in the heat capacity and thermoelectric power measurements, which imply temperature change in the sample, can also be interpreted as endothermic or exothermic effects caused by the domain structure change in the π-electron system.

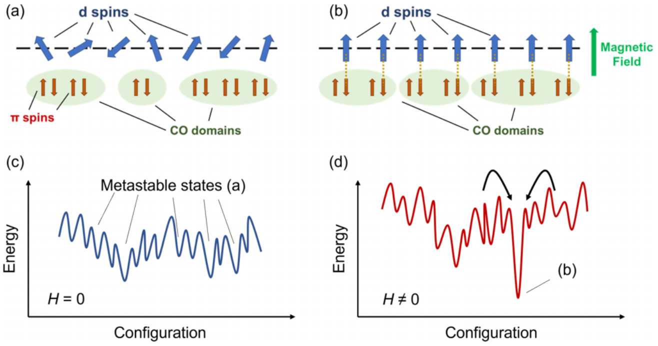

FIG. 9. (a), (b) Schematic illustration of (a) a freely dispersed CG state and (b) a spin-constrained CG state. (c), (d) Energy landscape of the CG state (c) under zero-field and (d) several magnetic fields. Under magnetic fields, a spin-constrain state is more stable than other metastable states, resulting in small configuration changes in the CG state.

The state of π electrons and π spins under magnetic fields remains unclear at present and further experimental and theoretical investigations are required. To explain the physical properties of θ-CsCo salt under magnetic fields, we propose a speculative scenario in which reconstruction of the CG structure occurs under several magnetic fields. In the CG state, the metallic and insulating CO domains are randomly distributed and fluctuate in slow dynamics. There are no energetic constraints on the spin orientation at each CO domain under zero field (a freely dispersed CG state), and thus one metastable state can change into another metastable state with a different orientation of CO domains. In contrast, under magnetic fields, it would be energetically advantageous for the antiparallel orientation state of π spins to the Co^{2+} spins which are in a forced ferromagnetic state. This may lead to a spin-orientation-related constraint on the possible structure of the short-range CO domain as shown in Fig. 9. When a magnetic field is applied, the short-range domains may reorganize from a freely dispersed CG state to a spin-constrained

CG state, which is considered to be the origin of the field-induced transition in θ-CsCo salt. In the case of θ-CsZn salt, such a field-induced transition is not expected to be observed since spin-related energy difference between individual metastable states of the CG state occurs even in magnetic fields. In the case of molecular glass materials and organic polymers, a broad peak is expected to be observed when a reorientation in metastable states with various energies occurs [38], which seems to be inconsistent with the sharp peaks we observed. We believe that the temperature range where the CO domains are pinned and stuck by spin-related constraints is determined by the magnitude of π-d interaction, and thus the transition to the spin-constrained phase occurs simultaneously at a certain temperature, leading to the sharp peaks in various measurements. Since this change only arranges the distribution of CO domains, it is natural that the temperature dependence and absolute value of the thermal conductivity and thermoelectric power do not change significantly. The reconstruction is likely to occur at higher temperatures when a larger magnetic field is applied because the spin-parallel orientation of localized electrons becomes more unstable. Therefore, this scenario can explain the B-linear increase of the transition temperature as shown in Fig. 6. In addition, it is likely that the charge fluctuations are suppressed owing to the spin-orientation-related constraints, which is consistent with our result that the MR increases in the field-induced phase.

Our findings suggest that it is necessary to consider the effects of spin degrees of freedom as well as charge degrees of freedom when considering the stability of the low-temperature electronic states in CO and CG systems. Even in other θ-type compounds, including magnetic ions and CO systems consisting of different types of organic molecules (e.g., DI-DCNQI systems) [39,40], unique physical properties originating from π-d interactions may also be observed. Interestingly, CO systems show a variety of unique physical properties and functionalities have been reported such as giant nonlinear conduction and the DC-AC conversion effect [20,41]. It is expected that the magnetic interaction between magnetic ions and π electrons can be utilized to provide unique functionalities to CO systems that can be controlled by an external magnetic field. The detailed mechanism of the magnetic field induced phase transition and the magnetic structure of π electrons in magnetic fields have not been clarified yet. Further investigation on the field-induced phase in θ-CsCo salt is required in the future.

V. CONCLUSION

In conclusion, we measure the thermodynamic, transport, and magnetic properties of θ-(BEDT-TTF)$_2$CsCo(SCN)$_4$ to observe the phenomenon induced by the magnetic interaction between the π electrons in the CG state and the localized d spins. We discover a magnetic field induced transition in this compound by the heat capacity and thermoelectric power measurements. We speculatively propose that the reconstitution of the CG state with a small structural change is driven by the π-d interactions.

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