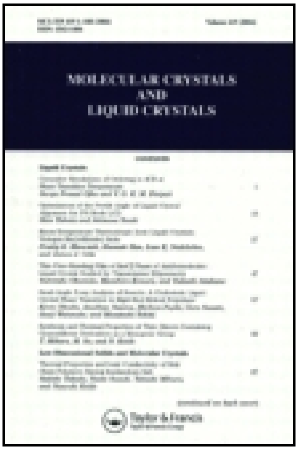

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Three-Component Organic Conductors; (BEDT-TTF)$_2$MM′(SCN)$_4$

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THREE-COMPONENT ORGANIC CONDUCTORS; $(BEDT\text{-}TTF)_2MM'(SCN)_4$

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Abstract New organic conductors which contain a magnetic cation of Co^{2+} (d^7, S=3/2), $(BEDT\text{-}TTF)_2MCo(SCN)_4$ [M=K, Rb, Cs], and related materials were prepared. The crystal structure analyses clarify that α-$(BEDT\text{-}TTF)_2MM'(SCN)_4$ [M=Rb, Cs, M'=Co, Zn] are isostructural and that these donor arrangements are α-type (strictly speaking θ-type). Although the band structure calculation affords the closed Fermi surface due to the large transverse overlap integrals, a metal-insulator (M-I) transition occurs at 20 K for α-$(BEDT\text{-}TTF)_2CsM'(SCN)_4$ [M'=Co, Zn] and at 190 K for α-$(BEDT\text{-}TTF)_2RbCo(SCN)_4$, respectively. The M-I transition temperatures of the former M=Cs salts are elevated by applying pressure. The magnetic susceptibilities of the M'=Co salts obey the Curie-Weiss law with θ=3-6K from 300 K to 20K. The relatively large θ might be originated from the superexchange of an anion network like ...Co^{2+}...NCS^- as well as interaction through itinerant electrons in BEDT-TTF layer. Below 20 K the anomaly of χT was observed, which can be explained by a crystal field around Co^{2+}.

INTRODUCTION

The study of an interaction between s-electron as a conducting carrier and d-electron for a localized spin (s-d interaction) begins since C.Zener discussed a ferromagnetism of iron as an interaction of 3d localized electron through 4s electron in 1951.[1] M.A.Ruderman, C.Kittel, T.Kasuya, and K.Yoshida developed the idea of an interaction of a localized spin through an itinerant electron in a study of a rare earth metal and a dilute alloy, so called RKKY interaction.[2] This s-d interaction strength is characterized by Kondo temperature as logT dependence of the resistivity.[3] Not only an investigation of an iron family, a dilute alloy, a rare earth metal or alloy, or a heavy Fermion but also that of organic conductors like M(pc)I (M=Cu, Ni),[4] $Cu(DCNQI)_2$,[5] etc., has been proceeded in terms of a π-d interaction.

Lately an introduction of a localized spin to an insulating anion sheet in an organic cation radical salt has been examined and a π-d interaction has been studied. Coexistence of an itinerant electron and a localized spin at a low temperature is, however, rare due to an instability of low-dimensional organic system. A few successful systems are (perylene)[M(mnt)$_2$] (M=Cu,Ni; mnt=malononitriledithiolate, $C_4N_2S_2{}^{2-}$) metallic down to 20K,[6] (BEDT-TTF)$_3$CuCl$_4$H$_2$O to 0.2K,[7] (BEDT-TTF)$_4$(H$_2$O)Fe(C$_2$O$_4$)$_3$·C$_6$H$_5$CN of Tc=8K,[8] and (BETS)$_2$MX$_4$ [M=Fe, Co, Mn, Ni, Cu, X=Cl, Br, CN].[9] The former three salts obey the Curie-Weiss law with near zero Weiss temperature, likely that an itinerant electron and a localized spin are almost independent. Only the last salt seems that an order of Fe^{3+} at 8K influences an itinerant electron of BETS and causes a metal-insulator transition. Owing to a low-dimensional properties of an organic system, a study of π-d interaction accompanied with an instability like CDW, SDW, or spin-Peierls as well as a magnetic order will be curious to have a possibility of a new physics.

Recently we have prepared a three-component system that contains a localized spin, Co^{2+} (d^7, S=3/2), as (BEDT-TTF)$_2$MCo(SCN)$_4$ [M=K, Rb, Cs] where the M=Cs salts retain metallic conductivity down to 20K. In the present paper, crystal and electronic structures, electrical resistivities, thermopower, ESR and SQUID measurements of α-(BEDT-TTF)$_2$MCo(SCN)$_4$ [M=K, Rb, Cs] and related materials are reported in order to clarify a π-d interaction and an origin of the metal-insulator transition.

EXPERIMENTAL

Single crystals were prepared by electrochemical crystallization of BEDT-TTF in the presence of MSCN (M=Li, Na, K, NH$_4$, Rb, or Cs), M'(SCN)$_2$ (M'=Co, Zn, Cd), and 18-crown-6 ether in 1,1,2-trichloroethane or 1,2-dichloroethane with 10% volume of ethanol. Obtained crystals are listed in Table 1.

Table 2 lists the crystal data of α-(BEDT-TTF)$_2$MM'(SCN)$_4$ (M=K, Rb, Cs, M'=Co, Zn). Intensity data were measured by the ω-θ scan technique on a Rigaku automated four-circle diffractometer AFC-5R with graphite monochromatized Mo-Kα radiation and corrected for the Lorentz and polarization effects and absorption by the Ψ-scan method. The structures were solved by the Patterson method and the succeeding Fourier syntheses, and refined by the full-matrix least squares procedure. All non-hydrogen atoms were refined anisotropically.

Electrical resistivities were measured by four-probe method with applying low-frequency current and the contacts were prepared by a gold paint (Tokuriki 8560). The

Table 1. Preparations, crystal shapes, and electrical resistivities of $MM'(SCN)_n$ complex.

Complexes	Crystal shape	Electrical resistivity
$(ET)_2Co(SCN)_4$[a,c]	black plate	$\sigma_{RT}=1Scm^{-1}$, $Ea=0.06eV$
α''-$(ET)_2\mathbf{K}_{\mathbf{1.4}}Co(SCN)_4$[b]	black plate	$\sigma_{RT}=6Scm^{-1}$,$T_{MI}=300K$, $Ea=0.05eV$
α-$(ET)_2\mathbf{Rb}Co(SCN)_4$[b]	black plate	$\sigma_{RT}=2Scm^{-1}$, $T_{MI}=190K$
α-$(ET)_2\mathbf{Cs}Co(SCN)_4$[b]	black plate	$\sigma_{RT}=14Scm^{-1}$, $T_{MI}=20K$
$(ET)_2\mathbf{K}Zn(SCN)_4$[c]	black needle	$\sigma_{RT}=28Scm^{-1}$, $Ea=0.07eV$
$(ET)Zn(SCN)_3$[b]	black plate	$\rho_{RT}=180\Omega cm$, $Ea=0.18eV$
α-$(ET)_2\mathbf{Rb}Zn(SCN)_4$[b]	black plate	$\sigma_{RT}=26Scm^{-1}$, -
α-$(ET)_2\mathbf{Cs}Zn(SCN)_4$[b]	black plate	$\sigma_{RT}=110Scm^{-1}$, $T_{MI}=20K$
$(ET)_2\mathbf{K}Cd(SCN)_4$[c]	black plate	-
α-$(ET)Cd_{0.66}(SCN)_2$[b]	black plate	$\sigma_{RT}=4Scm^{-1}$, $Ea=0.11eV$
$(ET)_2\mathbf{Cs}Cd(SCN)_4$[b]	black plate	$\sigma_{RT}=10Scm^{-1}$, $Ea=0.02eV$

a:ET=BEDT-TTF.

b:The stoichiometries are determined by EDX measurements and crystal structure analyses.

c:The stoichiometries are determined by EDX measurements.

measurements under pressure were carried out with pressure cell of clamp type with an oil as a pressure medium. The pressure was determined by a manganin wire and corrected to the low-temperature value.

The ESR data were obtained by utilizing a JEOL JES-RE3X (9.2GHz) with a cylindrical cavity (TE_{011}) from room temperature to 4K. Li^+TCNQ^- (g=2.0026) was used as a standard sample of g-value. Magnetic susceptibilities were measured by SQUID (Quantum Design model MPMS7) and the angle dependent measurements were carried out with an original quarts glass probe.

RESULTS AND DISCUSSION

CRYSTAL STRUCTURE

The complexes whose crystal structure analyses are completed are underlined in Table 1. Among them, α-$(BEDT\text{-}TTF)_2MM'(SCN)_4$ [M=Rb, Cs, M'=Co, Zn][10] are isostructural as shown in Table 2. Since the radius of Cs^+ (1.81Å) is larger than that of Rb^+ (1.75Å), the volume of α-$(BEDT\text{-}TTF)_2CsM'(SCN)_4$ [M'=Co (2074Å^3), Zn (2077Å^3)] is bigger than that of α-$(BEDT\text{-}TTF)_2RbM'(SCN)_4$ [M'=Co (2046Å^3),

Table 2. The lattice parameters of α-$ET_2MM'(SCN)_4$ (M=K, Rb, Cs, M'=Co, Zn).

	α''-$(ET)_2K_{1.4}Co(SCN)_4$	α-$(ET)_2RbCo(SCN)_4$	α-$(ET)_2CsCo(SCN)_4$
Chemical formula	$K_{1.4}CoS_{20}N_4$-$C_{24}H_{16}$	$RbCoS_{20}N_4$-$C_{24}H_{16}$	$CsCoS_{20}N_4$-$C_{24}H_{16}$
FW	1113.4	1146.0	1193.6
system	monoclinic	orthorhmbic	orthorhmbic
space group	C2/c	I222	I222
a/Å	44.639(6)	10.176(6)	9.804(4)
b/Å	4.93(1)	43.258(4)	43.416(3)
c/Å	19.18(1)	4.650(5)	4.873(4)
α/°	90	90	90
β/°	102.39(2)	90	90
γ/°	90	90	90
V/Å^3	4125(9)	2046(1)	2074(3)
Z	4	2	2
R	0.13	0.062	0.038
D_c	1.79	1.86	1.91
No. of ref.	905 ($\|I_o\|>5\sigma\|I_o\|$)	727 ($\|I_o\|>3\sigma\|I_o\|$)	757 ($\|I_o\|>3\sigma\|I_o\|$)
$2\theta_{max}$/°	55	60	60
λ/Å	0.71073	0.71073	0.71073
reference	this work	this work	10

	α-$(ET)_2RbZn(SCN)_4$	α-$(ET)_2CsZn(SCN)_4$
Chemical formula	$RbZnS_{20}N_4$-$C_{24}H_{16}$	$CsZnS_{20}N_4$-$C_{24}H_{16}$
FW	1152.6	1200.0
system	orthorhmbic	orthorhmbic
space group	I222	I222
a/Å	10.175(9)	9.816(4)
b/Å	43.301(9)	43.443(5)
c/Å	4.65(1)	4.870(4)
α/°	90	90
β/°	90	90
γ/°	90	90
V/Å^3	2047(3)	2077(2)
Z	2	2
R	0.091	0.12
D_c	1.87	1.92
No. of ref.	562 ($\|I_o\|>3\sigma\|I_o\|$)	728 ($\|I_o\|>3\sigma\|I_o\|$)
$2\theta_{max}$/°	60	60
λ/Å	0.71073	0.71073
reference	this work	10

Zn (2047Å^3)]. The M'=Co [r(Co^{2+})=0.79Å] and Zn [r(Zn^{2+})=0.74Å] salts have the similar unit cell volume because Co^{2+} (Zn^{2+})...NCS is chemically coordinated. In a series of MHg(SCN)$_4$ [M=Li, Na, K, Tl, NH$_4$, Rb, Cs] based upon BEDT-TTF, the M=K, Tl, NH$_4$, and Rb salts are isostructural, whereas these MM'(SCN)$_4$ system [M'=Co and Zn] affords the isostructural M=Rb and Cs salts except for the M=K one.

The crystal structure of α-(BEDT-TTF)$_2$RbCo(SCN)$_4$ is depicted in Figure 1. A BEDT-TTF molecule is on the two-fold axis, Rb$^+$ and Co$^+$ are located on the cross point of two-fold axes, and a SCN anion is on a general position. Therefore a half of BEDT-TTF, 1/4 of Rb$^+$ and Co$^+$, and one SCN are crystallographically independent. The conducting donor plane and the anion sheet of 8.1 Å, which is thicker than that of α-

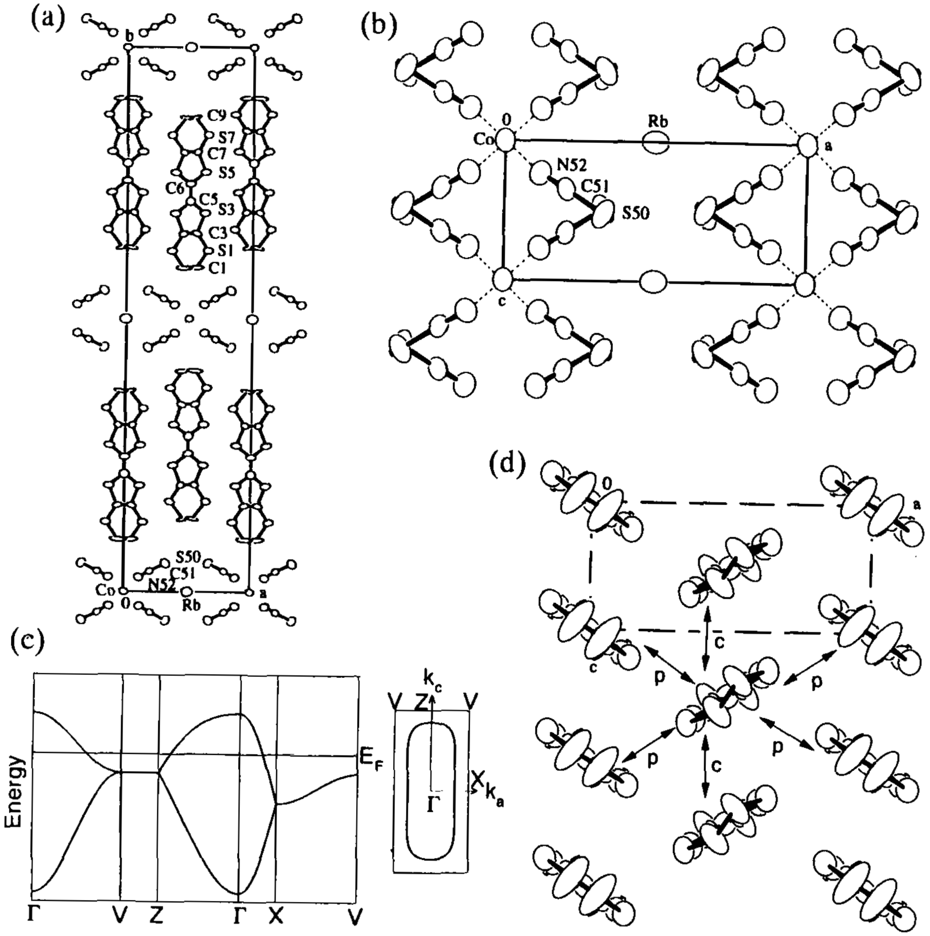

Figure 1. a)Crystal structure, b)anion arrangement, c)band structure, and d)donor arrangement of α-(BEDT-TTF)$_2$RbCo(SCN)$_4$.

Table 3. Overlap integrals (x10^{-3}) of α-$ET_2MM'(SCN)_4$ (M=Rb, Cs, M'=Co, Zn).

direction	α-$(ET)_2RbCo(SCN)_4$	α-$(ET)_2CsCo(SCN)_4$	α-$(ET)_2RbZn(SCN)_4$	α-$(ET)_2CsZn(SCN)_4$
c	3.3	0.5	2.4	1.0
p	-9.9	-10.6	-9.4	-10.8

$(BEDT\text{-}TTF)_2KHg(SCN)_4$ (6.8 Å),[11] are stacked along the b-axis. Figure 1d shows the α-type (strictly speaking θ-type) donor arrangement and Figure 1b depicts the arrangement in an anion layer. Co^{2+} has a distorted tetrahedral coordination to four N atoms of the NCS [$r(Co^{2+}...N52)=1.97$ Å < $r(Co^{2+})+r(N)=0.79+1.55=2.34$ Å[12]] and the closest S50...S50 separates 3.47 Å, which is shorter than sum of Van der Waals radii, 3.6 Å. Therefore one dimensional array of anion is elongated along the c-axis.

In order to understand the intermolecular interaction, the overlap integrals of four isostructural salts were listed in Table 3. The transverse interaction p is by 3 to 20 times larger than the interaction c along the donor stacking direction, which is characteristic of α-type (strictly speaking θ-type) BEDT-TTF complexes. Owing to the transverse interaction spreading over the two-dimensional plane, the closed Fermi surface is inevitably obtained for the θ-phase salts (Figure 1c). However, a metallic behavior due to the two-dimensional feature is not necessarily obtained; These α-$(BEDT\text{-}TTF)_2RbCo(SCN)_4$ and α-$(BEDT\text{-}TTF)_2CsM'(SCN)_4$ [M'=Co, Zn] become insulators around 190K and 20K, respectively and θ-$(BEDT\text{-}TTF)_2Cu(CN)[N(CN)_2]$[13] and θ-$(BEDT\text{-}TTF)_2Ag_{1.6}(SCN)_2$[14] are semiconducting even at room temperature. The electronic states of some θ-type salts can not be explained by the band calculation due to their special donor arrangement. Because of the straight part of the Fermi surface, the present salts might have the nesting of the Fermi surface along the transverse direction parallel to the a-axis, but the origin and the direction of the instability around 190 K or 20 K are under investigation.

Figure 2 illustrates the crystal and band structures of α"-$(BEDT\text{-}TTF)_2K_{1.4}Co(SCN)_4$. One BEDT-TTF molecule, two SCN^- anions, and a K^+ cation are located on general positions and a Co^{2+} is on a two-fold axis, so that the crystallographically independent molecules are one BEDT-TTF, two SCN^-, a K^+ whose occupancy is about 70%, and a half of Co^{2+}. The thick anion layer (8.5Å) and the donor sheet are stacked along the a-axis. The donor arrangement is similar to $(BEDT\text{-}TTF)_2Cu_5I_6$[15] and $(BEDT\text{-}TTF)_2CsHg(SCN)_4$[16], so called α"-phase. Although the band structures of $(BEDT\text{-}TTF)_2Cu_5I_6$ and $(BEDT\text{-}TTF)_2CsHg(SCN)_4$ are calculated to be pseudo one dimensional along the donor stacking direction, the former is metallic down to 1.3K and the latter undergoes a metal-insulator transition at 210 K. On the other hand, the present salt has both open and closed Fermi surfaces (Figure 2c) because of the relatively large transverse interactions (p1=-10.5, p2=-9.3x10^{-3}), but a metal-insulator transition occurs around 300 K. (Table 1) This α"-phase also falls into a group of some exceptional complexes where the calculated band structure is inconsistent with the electronic properties. The anion arrangement (Figure 2b) indicates that Co^{2+} is tetrahedraly coordinated by four N atoms of the NCS^- and that the distances of K^+...S [r(K...S50)=3.60(4),3.65(4), r(K...S60)=3.44(4),3.49(4)Å] are slightly larger than the sum of the ionic and Van der Waals radii, r(K^+...S)=r(K^+)+r(S)=1.52+1.80=3.32 Å. The existence of K^+ was confirmed by EDX (Energy Dispersion X-ray spectroscopy)

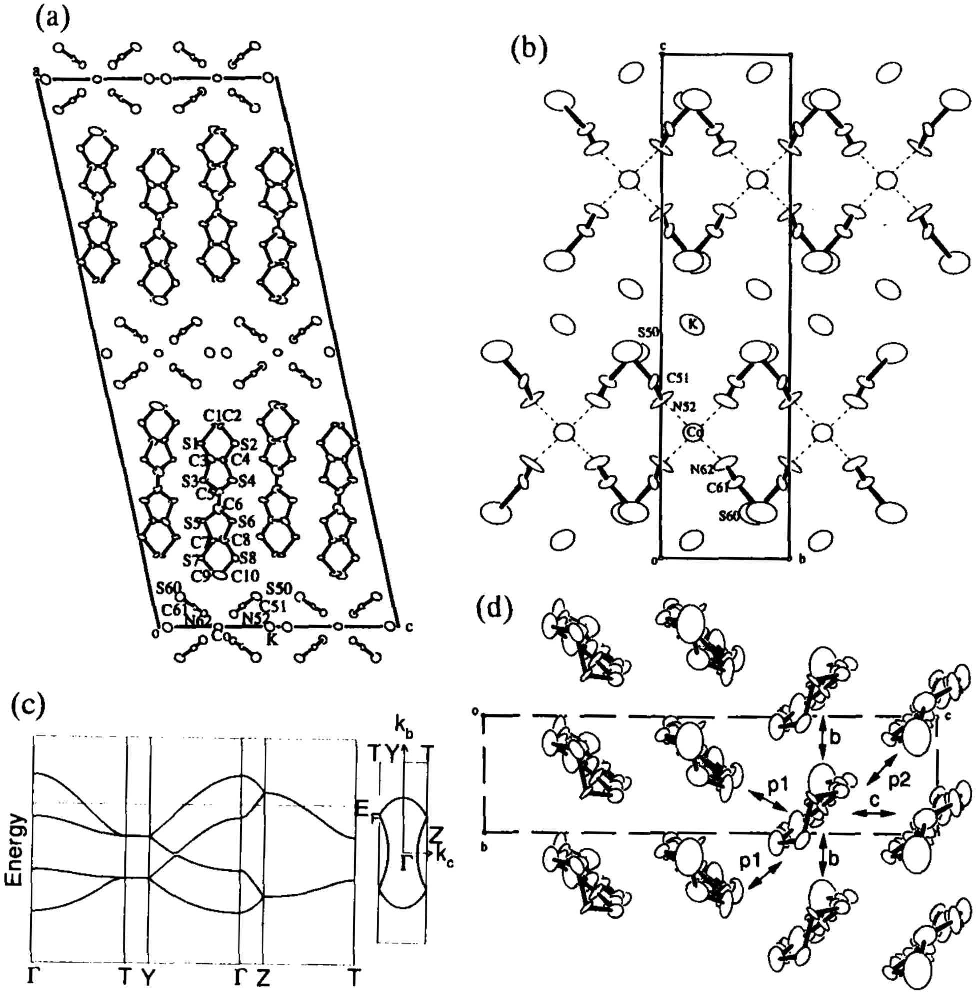

Figure 2. a)Crystal structure, b)anion arrangement, c)band structure, and d)donor arrangement of α"-$(BEDT\text{-}TTF)_2K_{1.4}Co(SCN)_4$. The overlap integrals are b=-1.5, c=-0.1, p1=-10.5, p2=-9.3 (x10^{-3}).

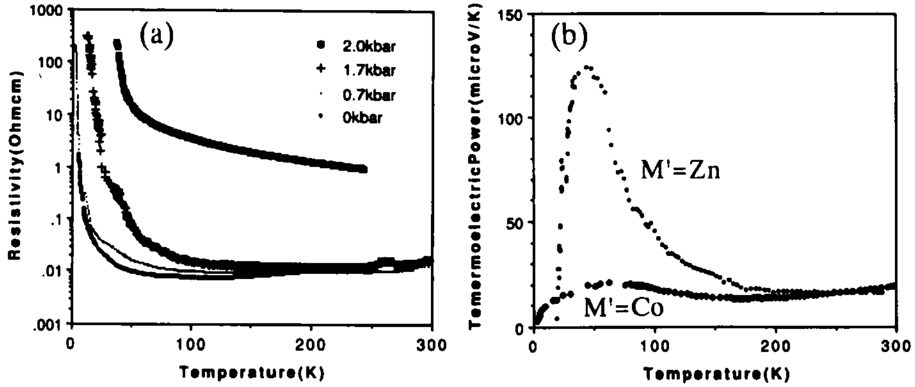

Figure 3. a)A temperature dependence of an electrical resistivity at various pressures for α-$(BEDT\text{-}TTF)_2CsCo(SCN)_4$ and b)thermoelectric power of α-$(BEDT\text{-}TTF)_2CsM'(SCN)_4$ [M'=Co, Zn].

and the calculated occupancy by the crystal structure analysis amounts to about 70%. Because the calculated charge of BEDT-TTF is +0.3, the energy band is (2-0.3)/2=0.85 filled as shown in Figure 2c.

TRANSPORT PROPERTIES

In order to suppress the instability at 20 K in α-$(BEDT\text{-}TTF)_2CsCo(SCN)_4$, the pressure dependence of electrical resistivity was measured. Above the critical pressure (~1.7kbar), the resistivity increases rapidly on the contrary to our expectation. By applying a pressure, the temperature of the metal-insulator is elevated. (Figure 3a) A similar behavior of pressure induced semiconducting state has been observed in $(BEDT\text{-}TTF)_5Hg_3Br_{11}$.[17]

Figure 3b shows the temperature dependence of thermoelectric power. From 300 K to 200K, thermopower is proportional to temperature, indicating a metallic behavior. Below 200K, the thermopower deviates from the linearity and has a peak or an anomaly around 70 K, at which the resistivity start to increase with decreasing temperature. Below 70 K, the thermopower of α-$(BEDT\text{-}TTF)_2CsCo(SCN)_4$ goes towards zero again, whereas the thermopower of α-$(BEDT\text{-}TTF)_2CsZn(SCN)_4$ decreases rapidly and crosses zero around 20 K, though a semiconducting resistivities are observed for both salts at low temperatures.

MAGNETIC PROPERTIES

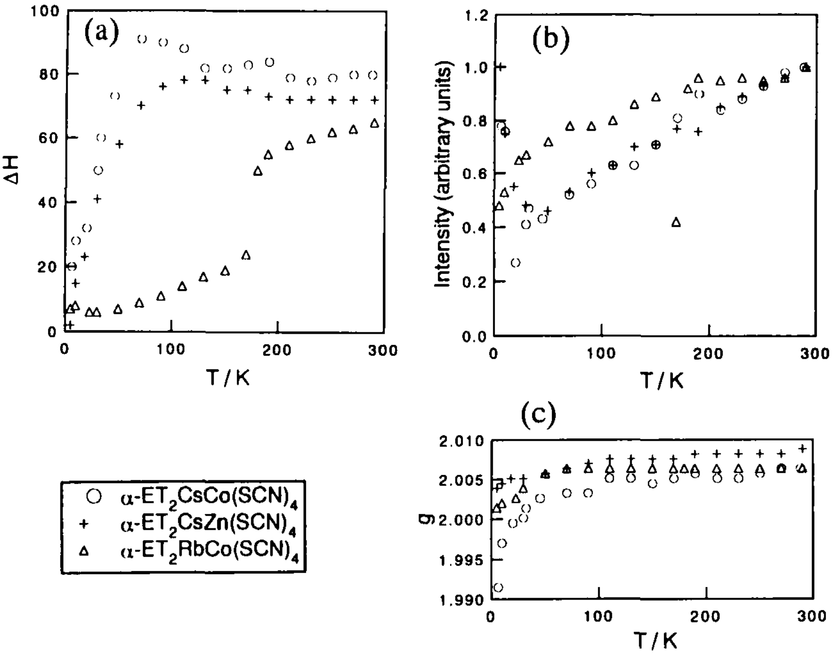

Figure 4. Temperature dependence of a)linewidth, b)intensity, and c)g-value for α-(BEDT-TTF)$_2$CsM'(SCN)$_4$ [M'=Co, Zn] and α-(BEDT-TTF)$_2$RbCo(SCN)$_4$.

It is characteristic of α-(BEDT-TTF)$_2$MCo(SCN)$_4$ [M=K, Rb, Cs] that a localized spin and an itinerant electron co-exist in a crystal. ESR and SQUID measurements of these samples have been carried out from three viewpoints: first to observe the origin of the metal-insulator transition related to the itinerant electron, second to investigate the feature of the localized spin, and third to know whether there is interaction between the itinerant electron and the localized spin or not. The results of the ESR measurement are shown in Figure 4. For the isostructural α-(BEDT-TTF)$_2$CsM'(SCN)$_4$ [M'=Co, Zn], the Lorentzian signals with the linewidth of 80 G at room temperature were observed. With lowering temperature, the linewidth increases slightly and reduces rapidly below 70 K, where the g-values also deviate from the constant value. The transition temperature is in agreement with that of the resistivity minimum, at which the fluctuation of the sharp transition at 20 K begins. The intensities of both salts finite even at 20 K and below it the Curie tail due to impurities or defects of the crystal appear. Owing to this Curie tail, we could not discuss about the origin of the M-I transition. Below 60K, a broad signal (~2000G) from Co^{2+} and a sharp one from BEDT-TTF are slightly coupled, indicating the interaction between itinerant electrons and localized spins. For α-(BEDT-TTF)$_2$RbCo(SCN)$_4$ the sudden decrease of linewidth at 180K was observed, where the

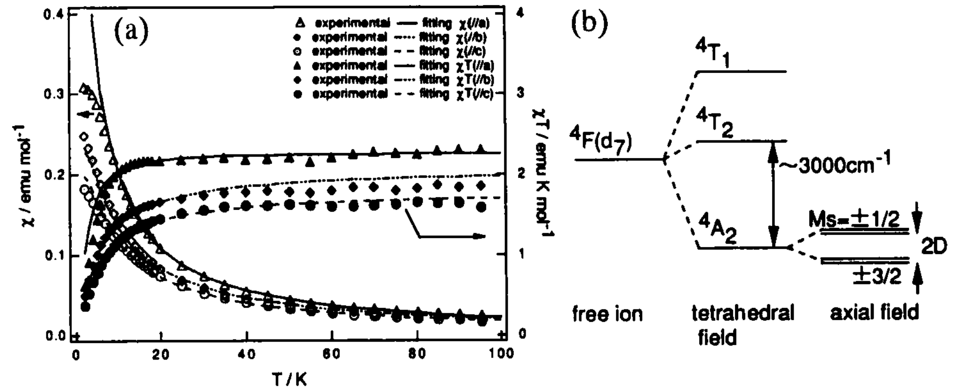

Figure 5. a)Temperature dependence of χT and χ parallel to the a-,b-, c-axes for α-(BEDT-TTF)$_2$CsCo(SCN)$_4$ and b)energy diagram in a crystal field of Co^{2+}.

sharp metal-insulator transition has been observed in the electrical resistivity. The intensity of the spin, however, is retained even at low temperature. The possibilities of the Mott transition at 180 K is under investigation.

Figure 5a shows the temperature dependence of magnetic susceptibility measured by SQUID applying 5T parallel to the a, b, and c-axes for α-(BEDT-TTF)$_2$CsCo(SCN)$_4$. This magnetic susceptibility is almost originated from the localized Co^{2+} spins (d^7, S=3/2). The low-temperature decrease of χT as shown in Figure 5a is attributable to the crystal field splitting; although the d-orbitals of a Co^{2+} free ion are degenerated, the states are separated to three in a tetrahedral field and the further distortion of the tetrahedral coordination gives rise to two doublets states (Kramers doublets) from the ^{4}A$_2$ state as shown in Figure 5b. The large separation of the Kramers doublets (2D) makes the deviation from the Curie law. The fitting to the Van Vleck equation with a weak exchange interaction reproduces the curve as g_a=2.2, g_b=2.1, g_c=1.95, 2D/k=-7.0K, and zJ/k=-1.3K. W.D.Horrocks, Jr. et al. calculated the relation between the distortion of the tetrahedral coordination and the sprit of Kramers doublet.^{18} By applying their calculation, the N-Co-N angle (104.5°)^{10} affords the separation of two Kramers doublets to be 2D/k=-7 K This is in a good agreement with our data of 2D/k=-7.0K. When D<0, the level of M$_S$=±3/2 is lower than that of M$_S$=±1/2 and an antiferromagnetic order following the Ising model (S=1/2) is anticipated at a low temperature and the deviation of χT from fitting line along the a-axis suggests its precursor. (Figure 5a)

In order to know the averaged magnetic properties, the temperature dependences of magnetic susceptibilities at 5T for powder samples of α-(BEDT-TTF)$_2$MCo(SCN)$_4$

Table 4. The Weiss temperatures and g-values of $(BEDT\text{-}TTF)_2MCo(SCN)_4$. [M=K, Rb, Cs]

	$\alpha''\text{-}(ET)_2K_{1.4}Co(SCN)_4$	$\alpha\text{-}(ET)_2RbCo(SCN)_4$	$\alpha\text{-}(ET)_2CsCo(SCN)_4$
θ/K	-4.6	6.5	-3.1
g	2.23	2.22	2.48

[M=K, Rb, Cs] were measured by SQUID.(Figure 6) From 300K to 20K, the magnetic susceptibility obeys the Curie-Weiss law and the fitted Weiss temperature (θ) and g-value are listed in Table 4. The Weiss temperatures are relatively large compared with other BEDT-TTF salts like $(BEDT\text{-}TTF)_4KFe(C_2O_4)_3\cdot C_6H_5CN$ (θ=-0.25K),[19] $(BEDT\text{-}TTF)_4(H_2O)Fe(C_2O_4)_3\cdot C_6H_5CN$ (θ=-0.2K),[8] $(BEDT\text{-}TTF)[MoOCl_4(H_2O)]$ (θ=-0.23K).[19] In the present salt, the Co^{2+} localized spins interact weakly to each other through superexchange in a two-dimensional anion network as well as through itinerant electrons in the BEDT-TTF sheet.

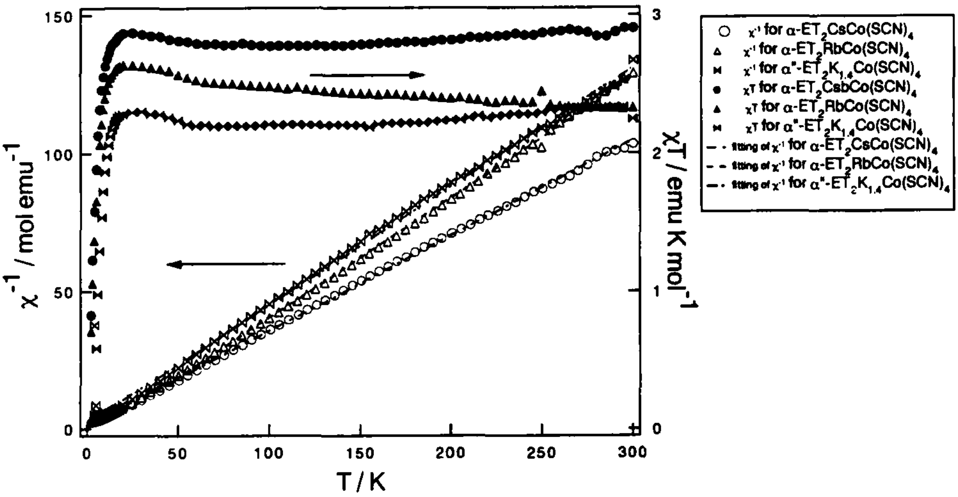

Figure 6. Temperature dependence of χT and χ^{-1} of powder samples for $(BEDT\text{-}TTF)_2MCo(SCN)_4$ [M=K, Rb, Cs].

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