Magnetic Properties of Coexistent System of Itinerant and Localized Electrons, (BEDT-TTF)2MCo(SCN)4 (M=K, Rb, Cs)
Hatsumi Mori, Shoji Tanaka, Takehiko Mori

To cite this version:

HAL Id: jpa-00247293
https://hal.archives-ouvertes.fr/jpa-00247293
Submitted on 1 Jan 1996

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Magnetic Properties of Coexistent System of Itinerant and Localized Electrons, \((\text{BEDT-TTF})_2\text{MCo(SCN)}_4\) \((M = \text{K, Rb, Cs})\)

Hatsumi Mori (1,*). Shoji Tanaka (1) and Takehiko Mori (2)

(1) International Superconductivity Technology Center, Shinonome, Tokyo 135, Japan
(2) Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Tokyo 152, Japan

(Received 30 April 1996, revised 8 July 1996, accepted 19 August 1996)

PACS.71.20.Rv - Polymers and organic compounds
PACS.71.30.+h - Metal-insulator transitions and other electronic transitions
PACS.71.70.Ch - Crystal and ligand fields

Abstract. — A coexistent system of itinerant and localized electrons was prepared and the magnetic properties of both electrons were investigated. \(\alpha\)-(BEDT-TTF)\(_2\)CsCo(SCN)\(_4\) (abbreviated as the CsCo salt), \(\alpha\)-(BEDT-TTF)\(_2\)RbCo(SCN)\(_4\) (the RbCo salt), and \(\alpha''\)-(BEDT-TTF)\(_2\)K\(_4\)Co(SCN)\(_4\) (the KCo salt), undergo metal-insulator transitions at 20 K, 190 K, and 130 K, respectively. The ESR measurement of the RbCo salt indicates that the electronic state below transition temperature, 190 K, is magnetic insulator due to the strong electron correlation. The static magnetic susceptibility of the CsCo salt measured by SQUID is mostly originated from the localized electrons, Co\(^{2+}\) \((S = 3/2)\), and obeys the Curie-Weiss law with \(\theta = -3\) K above 20 K, where the weak interaction between Co\(^{2+}\) might be caused by the superexchange through coordinated SCN\(^-\) anion. Below 20 K, the rapid decrease of \(\chi T\) is observed because of the crystal field around Co\(^{2+}\)

1. Introduction

The coexistent system of localized and itinerant electrons has afforded us interesting topics. In 1951, Zener discussed the ferromagnetism of Fe in terms of the interaction of unfilled d shell electrons of Fe through 4s conducting electrons [1]. His idea has been developed by Ruderman, Kittel, Kasuya, and Yoshida, been called RKKY interaction [2], and is discussed in rare earth metals, dilute alloys, etc. The negative s-d exchange interaction in a dilute alloy gives rise to a resistance minimum with \(\log T\) dependence below the minimum temperature, so called Kondo temperature [3]. Not only s-d but \(\pi\)-d interaction has been eagerly investigated in inorganic and organic conductors. For the intercalated graphite with a localized moment as \(C_6\)Eu, Eu\(^{2+}\) spin which constructs a triangle lattice has a RKKY-type interaction through \(\pi\)-itinerant electron in graphite and gives the curious magnetization curve by applying magnetic field [4]. In Cu(DMeDCNQI)_2 (DMeDCNQI: dimethyl-N,N-dicyanoquinoxalidime) system, the band of Cu\(^{+4/3}\) is mixed with that of \(\pi\)-electron in DCNQI, but the couple of the Jahn-Teller effect

(*) Author for correspondence

© Les Éditions de Physique 1996
around Cu cation and the instability of one-dimensional chain of DCNQI affords a variety of physical properties under pressure [5]. Recently it has been reported that \( \lambda \)-(BETS)_2GaCl_4 (BETS; bis(ethylenedithio)tetrathiafulvalene) shows the superconductivity at 8 K, while the isostructural \( \lambda \)-(BETS)_2FeCl_4 with localized spins of Fe^{3+} (S = 5/2) indicates a metal-insulator transition at the same temperature. This transition is explained by the antiferromagnetic order of Fe^{3+} that introduces the condensation of conduction electrons [6]. Under magnetic field, the condensed conduction electrons are evaporated so that the metal-insulator transition is suppressed [7].

Recently we prepared new organic conductors which contain the localized electron of Co^{2+} (S = 3/2), \( \alpha \)-(BEDT-TTF)_2CsCo(SCN)_4 (BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene), abbreviated as the CsCo salt), \( \alpha \)-(BEDT-TTF)_2RbCo(SCN)_4 (the RbCo salt), and \( \alpha'' \)-(BEDT-TTF)_2K_{1.4}Co(SCN)_4 (the KCo salt) [8, 9]. The CsCo and RbCo salts are isostructural to \( \alpha \)-(BEDT-TTF)_2CsZn(SCN)_4 (the CsZn salt) and \( \alpha \)-(BEDT-TTF)_2RbZn(SCN)_4 (the RbZn salt) which do not have a localized moment; a donor layer and a thick anion sheet of 8 Å stack alternately and the arrangement of the donors is \( \alpha \)-type (strictly speaking \( \theta \)-type [10]). The donors stack regularly and the side-by-side interaction, where a dihedral angle of donor planes is 120°, is larger than that of the stacking direction. The interaction spreads in the \( ac \) plane to construct a closed Fermi surface. In an anion sheet, Co^{2+} (or Zn^{2+}) is coordinated distorted-tetrahedrally to N atom of SCN⁻ to form an anion polymer chain.

The metal-insulator transition occurs at 20 K for the CsCo and CsZn salts and at 190 K for the RbCo and RbZn salts (Fig. 1). Since the unit cells of two rubidium salts are slightly smaller than those of two cesium salts, the rubidium salts seem to be the chemically pressurized system of the cesium salts. With applying pressure, overlap of molecular orbitals usually
increases, instability is suppressed, and transition temperature is decreased. The metal-insulator transition for the rubidium pressurized system, however, occurs at higher temperatures. The same effect is observed by applying the external pressure in the CsCo and CsZn salts. That is, the metal-insulator transition temperatures increase with the pressure for the CsCo and CsZn salts [8,9,11]. It might be due to the fact the transverse interaction reduces under pressure with changing the dihedral angles of donor planes [12]. Even though the CsCo salt has a localized moment, magnetic field does not influence the metal-insulator transition [11] dissimilar to $\lambda$-(BETS)$_2$FeCl$_4$ [7].

In order to observe the magnetic properties of itinerant and localized spins for the coexistent system of the CsCo, RbCo, and KCo salts, ESR and SQUID measurements were carried out and a mechanism of a metal-insulator transition, the behavior of a localized moment, and the interaction of both kind of spins are discussed in this paper.

2. Experimental

Single crystals are prepared by electrochemical oxidation of BEDT-TTF by using MSCN ($M = K, Rb, Cs$), $M'$ (SCN)$_2$ ($M' = Co, Zn$), and 18-crown-6 ether in 1,1,2-trichloroethane and 10% ethanol. Electrical resistivities were measured by the conventional four-probe method with applying a low ac current and the contacts were prepared by a gold paint (Tokuriki 8560). The ESR spectra were obtained from 4 K to 300 K with utilizing a JEOL JES-RE3X (9.2 GHz, X-band) spectrometer equipped with an Air Product and Chemicals inc. LTR-3 cryostat and a Scientific Instrument model 5500 temperature controller. The temperature was controlled and monitored with chromel vs. gold with 0.07 atomic % iron thermocouples. Li+TCNQ$^-$ ($g = 2.0026$) was used as a standard. The magnetization data were collected by SQUID (Quantum Design model MPMS7) and the angle dependent measurements were carried out with an original quartz glass probe. The diamagnetic contribution was corrected using Pascal’s law: $\chi_{core} = 5.64 \times 10^{-4}, 5.62 \times 10^{-4}, 5.75 \times 10^{-4}, 5.73 \times 10^{-4}$, and $5.62 \times 10^{-4}$ emu mol$^{-1}$ for the RbCo, RbZn, CsCo, CsZn, and KCo salts, respectively.

3. Results and Discussion

In order to investigate the behaviors of itinerant electrons, ESR measurements were carried out. All ESR signals attributed to BEDT-TTF$^+$ are Lorentzian and the angular dependencies of linewidth and g-value at room temperature are shown in Figure 2. The g-values of the CsCo and CsZn salts varies from 2.0135 to 2.0033 when the magnetic field applies parallel to the b-axis (the direction of molecular long axis) and to the a-axis (the direction tilted by 35° to the molecular plane), respectively. The KCo salt has the same tendency. These g-values are close to those of $\alpha$-(BEDT-TTF)$_2$I$_3$, $\beta$-(BEDT-TTF)$_2$I$_3$, (BEDT-TTF)$_2$SbF$_6$, and (BEDT-TTF)$_2$AsF$_6$ in which the principal values of the molecular g-tensor are $g_1 = 2.011 - 2.012$, $g_2 = 2.006 - 2.007$, and $g_3 = 2.002 - 2.003$ for the directions of molecular long axis, short axis, and normal to the molecular plane, respectively [13]. Since the g-values of the RbCo and CsCo salts are similar to those of other BEDT-TTF salts without localized spins and do not shift to that of Co$^{2+}$ ($g = 2.2 - 2.3$ [14]) in a distorted-tetrahedral crystal field, there is no interaction between the localized moment (Co$^{2+}$) and the itinerant electron (BEDT-TTF$^+$).

Figure 3 shows the temperature dependence of linewidth, intensity, and g-value. For the CsCo and CsZn salts, the linewidth at room temperature are 80-72 G, slightly increases with lowering temperature to 91-78 G around 70-110 K, which corresponds to the minimum temperature of the resistivity, and decreases rapidly below these temperatures. The intensities are kept down to 20 K and the origin of the metal-insulator transitions at 20 K are under
Fig. 2. — Angular dependences of ESR linewidths and $g$-values for $\alpha$-(BEDT-TTF)$_2$CsCo(SCN)$_4$, $\alpha$-(BEDT-TTF)$_2$CsZn(SCN)$_4$, and $\alpha''$-(BEDT-TTF)$_2$K$_{1.4}$Co(SCN)$_4$. The data are obtained by $b-a-b$, $b-a-b$ and $a^*-c-a^*$ rotation of the static magnetic field, respectively.

The measurements of temperature dependence of ESR for the RbZn and RbCo salts were carried out with applying the magnetic field nearly parallel to the $b$-axis (the direction of the molecular long axis) and closely to the $a$-axis (the direction tilted to the molecular plane), respectively. The observed linewidth is 90 G and the $g$-value is 2.0154 for the RbZn salt and 65 G and 2.0064 for the RbCo salt, which is similar behavior to the CsCo and CsZn salts. The characteristic feature is that the linewidth decreases suddenly from 69 G to 28 G for the RbZn salt and from 50 G to 24 G for the RbCo salt at the metal-insulator transition temperature around 190 K, but that the intensities for both salts remain. The preliminary result of magnetic measurement by SQUID for the RbZn salt shows that the question due to the Curie impurity. The $g$-values are constant from room temperature to 50 K and reductions below that temperature for both CsCo and CsZn salts suggests the change of the electronic state. For the KCo salts, the linewidth at room temperature is relatively narrow, 32 G and sharpens with lowering temperature. The intensity reduces rapidly below the metal-insulator transition temperature of 130 K with narrowing of linewidth, which might be attributed to the CDW instability.
Fig. 3. — Temperature dependences of ESR linewidths, intensities, and $g$-values for $\alpha$-(BEDT-TTF)$_2$CsCo(SCN)$_4$ ($H \parallel \alpha$), $\alpha$-(BEDT-TTF)$_2$CsZn(SCN)$_4$ ($H \parallel \alpha$), $\alpha$-(BEDT-TTF)$_2$RbCo(SCN)$_4$ ($H \parallel \alpha$), $\alpha$-(BEDT-TTF)$_2$RbZn(SCN)$_4$ ($H \parallel b$), and $\alpha''$-(BEDT-TTF)$_2$K$_4$Co(SCN)$_4$ ($H \parallel c$).
susceptibility with \(6.1 \times 10^{-4} \text{ emu mol}^{-1}\) at room temperature approaches to the calculated value based on two-dimensional Heisenberg model with \(J = -100 \text{ K}\) and follows it below 190 K down to 50 K, suggesting the Mott transition at 190 K [12]. The sudden decrease of linewidth around 190 K is related to the disappearance of the screening of itinerant electrons and the elongation of the relaxation rate. On the other hand, the linewidth of the CsCo and CsZn salts also decrease rapidly below the transition temperature (20 K). but the intrinsic intensity is not clear due to the Curie impurity component at low temperatures. Whether the metal-insulator transition of the cesium salts are the same electron-correlated type as the rubidium salts or not is not clear by ESR measurements, but the other magnetic observation of NMR suggests a similar electron-correlated type transition [15].

In order to observe the behavior of the localized electron of the CsCo salt, the temperature dependence of magnetic susceptibility parallel to the \(a\), \(b\), and \(c\)-axes are measured as shown in Figure 4. Since the total susceptibility is \(2 \times 10^{-2} \text{ emu mol}^{-1}\) at 100 K and \(3 \times 10^{-1} \text{ emu mol}^{-1}\) at 2 K, the contribution of the itinerant electron of around \(6 \times 10^{-4} \text{ emu mol}^{-1}\) [16] is \(3 - 0.2\%\), so that most of the moment is originated from the localized electron of Co\(^{2+}\) (\(S = 3/2\)). The specific feature is the decrease of \(\chi T\) below 20 K along the three axes. This deviation from the Curie-law behavior may be related to the zero field splitting due to the crystal field around Co\(^{2+}\) with distorted-tetrahedral coordination of NCS\(^-\). Figure 5 indicates the energy level diagram of Co\(^{2+}\) in a tetrahedral ligand field [17]. Subject to a crystal field by an exact tetrahedron of point charges, the \(4\text{F}\) ground term of Co\(^{2+}\) as a free-ion is split to make the lowest term in a cubic field as \(4\text{A}_2\) of four-fold degeneracy. The \(4\text{T}_2\) term also split from the free-ion \(4\text{F}\) term usually lies at about 3000 cm\(^{-1}\) above the \(4\text{A}_2\) term observed by spectroscopic methods [18]. A distortion from the exact tetrahedral coordination, combined with second-order spin-orbit coupling, split up this four-fold degeneracy into two Kramers doublets with an energy separation of 2D. Therefore, the susceptibility data have been fitted in the following manner. First, the energy levels in a magnetic field were calculated by using the Hamiltonian
Magnetic properties of (BEDT-TTF)$_2$MCo(SCN)$_4$

of equation (1) [19].

\[ H = D[S^2 - S(S+1)/3] + \mu_B \sum_i g_i H_i S_i \]  

(1)

\( D \): zero field splitting; \( \mu_B \): Bohr magneton; \( S \): spin quantum number as 3/2 for Co$^{2+}$.

These energy levels are readily inserted into Van Vleck’s equation [20] to yield equation (2) [19].

\[
\chi'_{||} = N \sum_n [(E_n^{(1)})^2/kT - 2E_n^{(2)}] \exp(-E_n^{(0)}/kT) \\
\sum_n \exp(-E_n^{(0)}/kT)
\]

\[
= \frac{N \mu_B^2 g_i^2 [1 + 9 \exp(-2D/kT)]}{4kT[1 + \exp(-2D/kT)]}
\]

\[ E_n = H^0 E_n^{(0)} + H^1 E_n^{(1)} + H^2 E_n^{(2)} + \ldots \]

\[
\chi'_{\perp} = \frac{N \mu_B^2 g_i^2}{kT[1 + \exp(-2D/kT)]} + \frac{3N \mu_B^2 g_i^2 [\exp(2D/kT) - 1]}{4D[\exp(2D/kT) + 1]}
\]  

(2)

\( 2D \): energy separation of Kramers doublet; \( k \): Boltzmann constant; \( g_{||}, g_{\perp} \): \( g \)-values parallel and perpendicular to the \( z \) axis.

Then the macroscopic susceptibilities were corrected for the presence of exchange by means of a molecular-field approximation with \( zJ \) to afford equation (3) [18].

\[
\chi_s = \frac{\chi'_{||}}{1 - \left( \frac{2zJ \chi'_{||}}{N g_i^2 \mu_B^2} \right)}
\]  

(3)

\( z \): nearest neighbor; \( J \): exchange parameter.

The fitting of the data using these equations resulted in \( 2D/k = -7.0 \) K, \( g_a = 2.2 \), \( g_b = 2.1 \), \( g_c = 1.95 \), and \( zJ/k = -1.3 \) K as shown in Figure 4 as solid lines. Horrocks and Burlone calculated the relation between the distortion of the tetrahedral coordination and the separation of Kramers doublet [21]. By applying their calculation, the N-Co-N angle containing \( d_z^2 \) (\( = a \)) axis (104.5°) obtained by crystal structure analysis of the CsCo salt [8] computed the separation.
1994 JOURNAL DE PHYSIQUE I N°12

Fig. 6. — Temperature dependences of magnetic susceptibilities for \( \alpha-(\text{BEDT-TTF})_2\text{CsCo(SCN)}_4 \), \( \alpha-(\text{BEDT-TTF})_2\text{RbCo(SCN)}_4 \), and \( \alpha''-(\text{BEDT-TTF})_2\text{K}_4\text{Co(SCN)}_4 \).

Table I. — The Weiss temperatures (\( \theta \)) and \( g \)-values of \((\text{BEDT-TTF})_2M\text{Co(SCN)}_4\) (\( M = K, \text{Rb}, \text{Cs} \)).

<table>
<thead>
<tr>
<th>( \theta / K )</th>
<th>( \alpha''-(\text{ET})_2\text{K}_4\text{Co(SCN)}_4 )</th>
<th>( \alpha-(\text{ET})_2\text{RbCo(SCN)}_4 )</th>
<th>( \alpha-(\text{ET})_2\text{CsCo(SCN)}_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( g )</td>
<td>2.23</td>
<td>2.38</td>
<td>2.48</td>
</tr>
</tbody>
</table>

of two Kramers doublets to be \( 2D/k = -7 \) K. This is in good agreement with our fitting data of \( 2D/k = -7.0 \) K. When \( D < 0 \), the level of \( M_s = \pm 3/2 \) is lower than that of \( M_s = \pm 1/2 \) and an antiferromagnetic order following the Ising model (\( S = 1/2 \)) is anticipated at a low temperature and the deviation of \( \chi T \) from the fitting line along the \( a \)-axis suggests its precursor of antiferromagnetism (Fig. 4).

In order to find out the averaged magnetic properties, the temperature dependences of magnetic susceptibilities at 5 T for powder samples of \((\text{BEDT-TTF})_2M\text{Co(SCN)}_4\) (\( M = K, \text{Rb}, \text{Cs} \)) were measured by a SQUID (Fig. 6). From 300 K to 20 K, the magnetic susceptibility obeys the Curie-Weiss law and the fitted Weiss temperature (\( \theta \)) and \( g \)-value are listed in Table I. The Weiss temperatures are relatively large compared with other BEDT-TTF salts like \((\text{BEDT-TTF})_4\text{KFe(C}_2\text{O}_4)_3\text{C}_6\text{H}_5\text{CN} \) (\( \theta = -0.25 \) K) [22], \((\text{BEDT-TTF})_4\text{H}_2\text{O}\text{Fe(C}_2\text{O}_4)_3\text{C}_6\text{H}_5\text{CN} \) (\( \theta = -0.2 \) K) [23], \((\text{BEDT-TTF})\text{[MoOCl}_4\text{(H}_2\text{O})]\) (\( \theta = -0.23 \) K) [21]. In the present salt, the Co\(^{2+} \) localized spins interact weakly with each other through the coordinated SCN\(^- \) anions.

In conclusion, the localized moments (Co\(^{2+} \)) are introduced into the anion layers of the organic conductors as \( \alpha-(\text{BEDT-TTF})_2\text{CsCo(SCN)}_4 \), \( \alpha-(\text{BEDT-TTF})_2\text{RbCo(SCN)}_4 \), and \( \alpha''-(\text{BEDT-TTF})_2\text{K}_4\text{Co(SCN)}_4 \). According to the ESR measurement, the linewidth decreases rapidly at 190 K and the intensity remained down to 50 K for the RbCo and RbZn salts.
The static susceptibility by SQUID also remained and follows the two-dimensional Heisenberg model \((J = -100 \text{ K})\) below 190 K, although the metal-insulator transition occurs at 190 K, suggesting that the electronic state below transition temperature is magnetic insulator owing to the strong electron correlation. On the other hand, whether the transition of the CsCo and CsZn salts is electron-correlated type or not is under investigation by different magnetic probes. The magnetic susceptibility measurement by SQUID of the CsCo, RbCo, and KCo salts shows that the behavior of Co\(^{2+}\) \((S = 3/2)\) follows the Curie-Weiss law \((\theta = -3.1 \text{ K}, -3.7 \text{ K and } -4.6 \text{ K for the CsCo , RbCo, and KCo salts})\) above 20 K, and deviates from the Curie-Weiss law below 20 K as the rapid decrease of \(\chi T\). This behavior is explained by the crystal field where Co\(^{2+}\) is coordinated by SCN\(^-\) distorted-tetrahedrally to produce the zero field splitting of 7 K between \(M_s = \pm 3/2\) and \(\pm 1/2\) orbitals. Van Vleck’s equation which includes the terms of \(H^0\), \(H^1\), and \(H^2\) in addition to the small exchange by means of a molecular-field approximation fits well the temperature dependence of the susceptibility curve. Moreover, the distortion of tetrahedral coordination is well correlated to the calculations of the zero-field splitting energy. The small interaction originates from the superexchange through the coordinated SCN\(^-\) anions.

References

[16] The isostructural CsZn salt without the localized moment shows the Pauli paramagnetism from the room temperature down to 20 K with the constant value of \(5.69 \times 10^{-4} \text{ emu mol}^{-1}\).