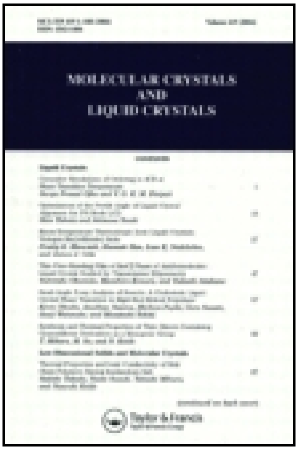

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ELECTRONIC STRUCTURES OF ORGANIC CONDUCTORS, $(BEDT\text{-}TTF)_2CsM(SCN)_4$ (M=Co, Zn)

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Abstract ^{1}H-NMR and EPR investigations of new organic conductors, $(BEDT\text{-}TTF)_2CsM(SCN)_4$ (M=Co, Zn), have been performed. In the Co containing salt, the ^{1}H-NMR spin-lattice relaxation rate, $T_1{}^{-1}$, is governed by the fluctuation of the localized magnetic moments on the Co^{2+} ions. The evaluated exchange interaction, J/k_B, is 0.09 K. A large increase in the ^{1}H-NMR linewidth has been observed below 20 K for the Co salt, which can be explained as the effect of the static magnetization of the paramagnetic Co^{2+} ions. For the Zn containing salt, which has a closed d-shell, the ^{1}H-NMR $T_1{}^{-1}$ and EPR properties exhibit anomalous behavior below 20 K, indicating a change in the electronic structure of the π-system around 20 K. The low-temperature electronic structure of the title compounds is discussed in the microscopic view.

INTRODUCTION

$(BEDT\text{-}TTF)_2CsCo(SCN)_4$ and $(BEDT\text{-}TTF)_2CsZn(SCN)_4$ are isostructural compounds having two-dimensional conducting layers composed of the BEDT-TTF molecules.[1] (Hereafter we abbreviate them to Co and Zn salts, respectively.) According to a tight-binding band calculation, both salts have a two-dimensional cylindrical Fermi surface. A clear difference between these salts exists in the insulating anion layer: The Co^{2+} ion (d_7) in the Co salt has a localized magnetic moment ($S = 3/2$), while the Zn^{2+} ion (d_{10}) is nonmagnetic. The Co salt is thus expected to be a possible π-d hybrid system. The electric resistivity of the title compounds shows a weak metallic behavior down to about 50 K and an abrupt increase below 20 K.[1,2] The mechanism of the Metal to Insulator transition (or crossover), and the electronic structure of the low-temperature phase have not been clarified so far. The aims of this study are 1) to estimate the magnitude of the possible π-*d* interaction from the experiments of the Co salt, and 2) to understand the electronic structure of the π-system in the low-temperature insulating phase from those of the Zn salt.

EXPERIMENTAL

Samples were prepared by the electrochemical oxidation of BEDT-TTF using CsSCN, $M(SCN)_2$ (M=Co, Zn), and 18-crown-6 ether in a 1,1,2-trichloroethane solution including 10 vol. % ethanol under a constant current of 1.5 μA. A polycrystalline sample with the total amount of about 20 mg was used for the ^{1}H-NMR measurements. The spin-lattice relaxation rate was determined from the recovery of the nuclear magnetization after a set of saturation comb pulses. The measurements of absorption lineshape were carried out by using a conventional continuous-wave method. For the EPR measurements of the Zn salt, a single crystal of 0.64 mg in weight was used. Magnetic susceptibility was also measured by a SQUID magnetometer for an assembly of small single crystals with the total amount of 17.73 mg. The core diamagnetization was corrected using the the absolute value of the spin susceptibility at 290 K determined by EPR.

RESULTS AND DISCUSSION

The Co salt

The ^{1}H-NMR relaxation curve observed in the Co salt at low temperatures was not single exponential, indicating the existence of inhomogeneity in the relaxation rate, T_1^{-1}. Hence we determined the ^{1}H-NMR T_1^{-1} from the initial slope of the relaxation curve as a weighted average of the relaxation rate. The T_1^{-1} of the Co salt is almost temperature independent in a wide temperature range, as shown in Fig. 1(a). The absolute value of about 8000 sec^{-1} is much larger than those of typical BEDT-TTF conductors. From these two facts, we conclude that the relaxation is governed by the fluctuation of the localized Co^{2+} spins, and the contribution of the itinerant electrons is screened out. T_1^{-1} in the paramagnetic states is given by the following relation;

$$T_1^{-1} = 2\gamma^2 < H_d^2 > \tau_c/(1 + \omega_0^2\tau_c^2),$$

where τ_c, $< H_d^2 >$ and γ are the correlation time of the fluctuation of the localized spin at the ^{1}H-sites, the second moment of the local magnetic fields, and the nuclear gyromagnetic ratio, respectively. Taking $\tau_c \sim \hbar/J$, one can estimate the magnitude of the exchange interaction between Co^{2+} ions, J, from the absolute

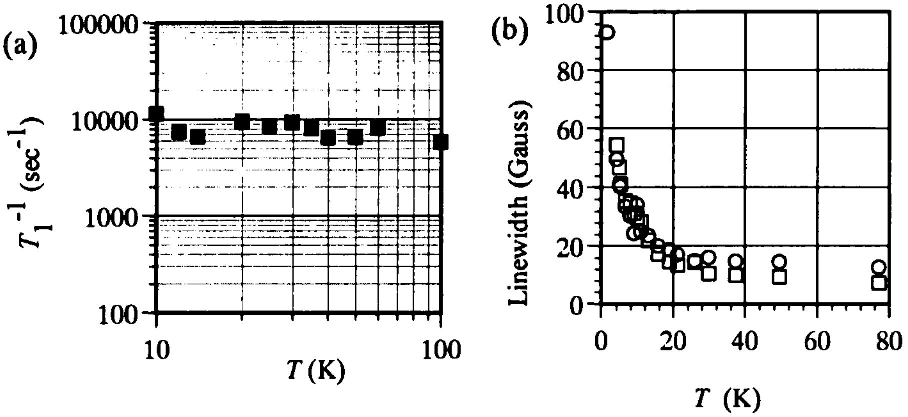

FIGURE 1 (a)Temperature dependence of the ^{1} H-NMR spin-lattice relaxation, $T_1{}^{-1}$, of the Co salt. (b)Temperature dependence of the ^{1}H-NMR absorption linewidth. The circles indicate the peak-to-peak linewidth of the absorption derivative. The squares show the square root of the second moment of the numerically integrated absorption line. Both of them are consistent with each other.

value of T_1^{-1}. Assuming that the Co^{2+} ion has a $S = 3/2$ spin with $g = 2$, we calculated the magnitude of $< H_d^2 >$ of the 4 crystallographically independent ^{1}H-sites as 83800, 153000, 11000 and 6800 Gauss^2, respectively. One can divide the ^{1}H-sites into two groups in the aspect of the magnitude of the local magnetic fields. Since the observed T_1 of 100 μsec is comparable to the T_2^* of 20 μsec estimated from FID signal, the ^{1}H-sites with different magnitude of the local fields are considered to be decoupled with each other. The non-single exponential relaxation mentioned above should be due to the existence of the decoupled ^{1}H-sites. If we use the averaged $<H_d{}^2>$ of 62800 Gauss^2, the magnitude of the exchange interaction between Co^{2+}, J/k_B, is given as 0.09 K. Although significant exchange interaction exists in the Co salt, the magnitude is much smaller than that of (BEDT-TTF) $_3$CuBr$_4$ ($J/k_B\sim$ 20 K).[3]

Figure 1(b) shows the temperature dependence of ^{1}H-NMR linewidth. The linewidth above 20 K is temperature independent, and the absolute value of 10 Gauss is considered as the effect of the nuclear dipolar interaction between the neighboring ^{1}H nuclei. (The dipolar fields from the Co^{2+} ions are narrowed due to their rapid fluctuation mentioned above.) On the contrary, the linewidth exhibits an abrupt increase below 20 K without any obvious change in the lineshape. The width at 1.6 K reached up to 90 Gauss. Although an abrupt increase of NMR

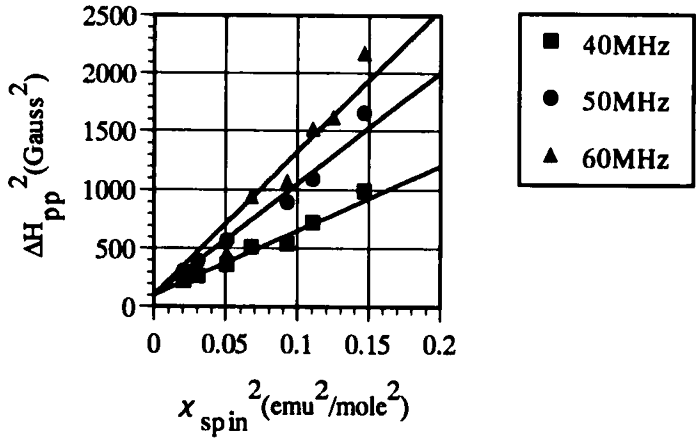

FIGURE 2 External field dependence of the ^{1}H-NMR linewidth. The squares, circles and triangles represent the results of the resonance frequency of 40 MHz (0.94 T), 50 MHz (1.17 T) and 60 MHz (1.41 T), respectively. The data are plotted against the square of the spin susceptibility [see Text].

linewidth is frequently observed in the formation of magnetic ordering, this possibility is ruled out for the Co salt as follows: Firstly, no anomaly in T_1^{-1} has been observed. Secondly, the broadening of the linewidth does not obey the Brillouin function but looks Curie-like. Since the static magnetization of Co^{2+} ions is quite large at low temperatures even in the paramagnetic states, we expect that it possibly causes a significant local field at the ^{1}H sites. To clarify the reason of the line broadening, we have measured the external field dependence of the linewidth. In Fig. 2, the ^{1}H-NMR linewidth at the resonance frequencies of 40, 50, and 60 MHz is plotted against the observed spin susceptibility of the Co salt. It is clearly seen that the linewidth follows an equation of $\Delta H^2 = A + B\chi_{\rm spin}^2$. Moreover, the constant, A, is corresponds to the square of the nuclear dipole field, and the coefficient, B, increases with the external fields. These facts support our expectation. We thus conclude that the increase of the ^{1}H-NMR linewidth is due to the static magnetization of the paramagnetic Co^{2+} ions, and that there is no significant change in the nature of the Co^{2+} ions down to 1.6 K.

The Zn salt

Next we turn to the Zn salt which has a closed *d*-shell. In order to understand the electronic structure of the π-system in the low-temperature insulating phase, we have carried out ^{1}H-NMR measurements for the Zn salt. Figure 3(a) show the

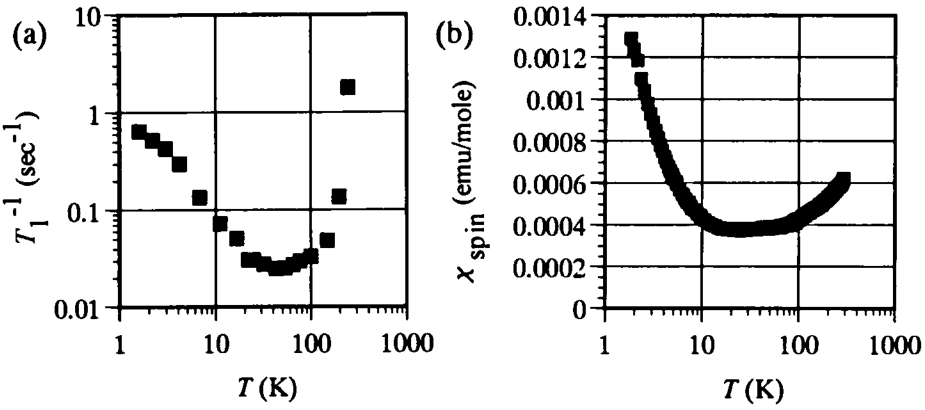

FIGURE 3 (a)Temperature dependence of the ^{1}H-NMR spin-lattice relaxation, T_1^{-1}, of the Zn salt. (b) Temperature dependence of the spin susceptibility of the Zn salt determined by SQUID measurement.

temperature dependence of the ^{1}H-NMR spin-lattice relaxation rate, T_1^{-1} in the Zn salt. In contrast with the Co salt, T_1^{-1} of the Zn salt exhibits a characteristic temperature dependence. Hereafter, we will discuss the experimental results dividing the measured temperature region into three.

(1) Above 100 K: T_1^{-1} exhibits a large enhancement, which is due to the thermal motions of the outer ethylene groups of BEDT-TTF molecules.

(2) Between 20 and 100 K: T_1^{-1} of the Zn salt shows a weak temperature dependence, and the absolute value is small, suggesting that the nuclear relaxation is due to itinerant π-electrons. The magnitude of the $(T_1 T)^{-1}$ of 3.5×10^{-4} sec^{-1}K^{-1} is close to that of a typical organic superconductor, β-(BEDT-TTF)$_2$I$_3$ (5.8×10^{-4} sec^{-1}K^{-1}),[4] but smaller than those of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (9.1×10^{-4} sec^{-1}K^{-1}),[5] and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br (2.2×10^{-3} sec^{-1}K^{-1}).[6] No significant enhancement of the $(T_1 T)^{-1}$ was observed in the Zn salt. Hence it seems that the π-electrons behave as a conventional metal in this temperature range.

(3) Below 20 K: T_1^{-1} exhibits an anomalous increase with decreasing temperature. It is interesting to note that this temperature corresponds to that of the abrupt increase of resistivity. The enhancement of T_1^{-1} is quite large; the value of T_1^{-1} at 1.6 K is about 40 times as large as that of the minimum of T_1^{-1} at 50 K. Such a large enhancement of T_1^{-1} is not expected in conventional itinerant systems, and reminds us a precursor of a magnetic order. However, no significant change in the FID has been observed down to 1.6 K, so that the possibility of any magnetic or-

dering is ruled out at least down to 1.6 K. Our EPR and SQUID results show an anomalous behavior around 20 K as follows. As seen in Fig. 3(b), the spin susceptibility is almost temperature independent down to 20 K, indicating a Pauli-like behavior. The absolute value of 6.0×10^{-4} emu/mole is close to those of the organic superconductors, κ-(BEDT-TTF)$_2X$.[7] Below 20 K, the spin susceptibility turns to increase and goes up to 1.3×10^{-3} emu/mole at 1.8 K which is about three times as large as the value at 20 K.[8] Although the enhancement of the spin susceptibility is remarkable, the absolute value is extremely small compared to that expected in a perfectly localized electron system. Since the title compounds are half-filled metal, it seems natural to consider that the low temperature phase is concerned with a Mott insulator. In the same temperature region, the principal axes of the g-tensor were found to change their directions, keeping the principal values constant.[9] It suggests that a kind of structural change occurs around 20 K resulting in a drastic change in the electronic structure.

In conclusion, we discovered an anomalous low-temperature phase in the π-system, while no obvious change takes place in the localized d-system. The low-temperature phase is probably due to a Mott-like transition accompanied by a possible structural change.

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REFERENCES

1. H. Mori et al., Bull. Chem. Soc. Jpn., 68, 1136(1995).
2. H. Mori et al., Mol. Cryst. Liq. Cryst., to be published.
3. R. Tsuchiya et al. Synth. Metals, 70, 967(1995).
4. Y. Maniwa et al., J. Phys. Soc. Jpn., 55, 47(1986).
5. T. Takahashi et al., Physica C, 153-155, 487(1988).
6. K. Kanoda et al., Physica C, 185-189, 2667(1991).
7. T. Nakamura et al. J. Phys. Soc. Jpn. , 63, 4110(1994).
8. It should be also mentioned that the possibility of formation of a conventional SDW or CDW is ruled out since the spin freedom exists down to the lowest temperature. It is confirmed by EPR analysis that the observed spin susceptibility is originated from the intrinsic spins.
9. Detailed analysis of the g-tensor of the Zn salt will be discussed elsewhere.