Hyperfine structure and exchange coupling with conduction electrons in the quasi-one-dimensional organic metal $Co_{0.01}Ni_{0.99}Pc(AsF_6)_{0.5}$

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We found an anisotropic hyperfine structure in the magnetically diluted alloy system, quasi-one-dimensional organic conductor, $Co_{0.01}Ni_{0.99}Pc(AsF_6)_{0.5}$ ($Pc=C_{32}N_8H_{16}$), and confirmed that the doped CoPc was relevantly substituted. The hyperfine signal was replaced by a broad Lorentzian signal at ~ 30 K. The $H \perp c$ broad signal shifted and narrowed with increasing temperatures. We interpreted the temperature-dependent g value and linewidth based on Hasegawa's phenomenological theory for dilute magnetic alloys. The density of state at the Fermi level and the exchange energy between the local spin of Co^{2+} and itinerant π hole of the Pc chain were estimated, respectively, as $D_F = 3.8 \pm 0.2$ eV and $|J_{\pi d}| = 0.013 \pm 0.002$ eV.

The quasi-one-dimensional phthalocyanine conductors $MPc(X)_y$ ($M = H_2^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+}, Pt^{2+}; $Pc = (C_{32}N_8H_{16})^{2-}$; $y = 0.5$ for $X = AsF_6^-$, ClO_4^-, SbF_6^-, $y = 0.33$ for I_3^-) constitute a unique system that involves magnetic metal ions near the conducting pathway. Both the paramagnetic ($M = Co^{2+}, Cu^{2+}$) and diamagnetic ($M = H_2^{2+}, Ni^{2+}, Pt^{2+}$) phthalocyanines yield nearly isostructural conductive crystals. Owing to this property, comparative study of the phthalocyanine-based conductors with paramagnetic and diamagnetic phthalocyanine ($M^{2+}Pc^{2-}$) and alloy systems have been studied in order to elucidate the influence of the localized spins on the conduction electrons. The first study was reported by Ogawa *et al.*, on $CuPc(I_3)_{0.33}$, in which a magnetic order was suggested below 8 K by electron spin resonance (ESR) static susceptibility, and NMR measurements.[1] They suggested a strong coupling between the localized spin of Cu^{2+} ($S = 1/2$) and the conduction electron of the Pc chain. Subsequently, they suggested the presence of the cross-relaxation process between the localized spin and itinerant electron through the analysis of the temperature-dependent linewidth of ESR.[2] The influence of the localized spin of Cu^{2+} on the conductivity was studied by Quirion *et al.*, on $CuPc(I_3)_{0.33}$ and analogous compounds, which in the microwave resistivity experiment they found a huge negative magnetoresistance and proposed a spin-flip scattering process produced by Cu^{2+} local spin.[3,4] The essential idea was consistent with the findings of a study of the alloys, $Cu_xNi_{1-x}Pc(I_3)_{0.33}$[5,6] and $Cu_xH_{2(1-x)}Pc(I_3)_{0.33}$.[7]

Martinsen *et al.* reported the phthalocyanine conductor of another paramagnetic ion, Co^{2+} ($S = 1/2$), on $CoPc(I_3)_{0.33}$, in which the central metal spine was responsible for the conductivity.[8] The microwave conductivity of the alloy $Co_xNi_{1-x}Pc(I_3)_{0.33}$ provided the same conclusion.[9,10] On the other hand, the authors reported a similar Co-containing phthalocyanine conductor $CoPc(AsF_6)_{0.5}$.[11] In contrast to $CoPc(I_3)_{0.33}$, the Pc chain played a part in the electrical conductivity, and thus the Co^{2+} ions were anticipated to play the same role as Cu^{2+} in $CuPc(I_3)_{0.33}$. However, the magnetic moment of Co^{2+} was suppressed by the direct Co-Co exchange interaction.[12] The resistivity of $CoPc(AsF_6)_{0.5}$ showed a minimum near the room temperature,[12] whereas the nearly isostructural diamagnetic phthalocyanine conduc-

tor, $NiPc(AsF_6)_{0.5}$, was metallic down to ~ 40 K and increased its resistivity below ~ 40 K.[13] The role of the Co^{2+} spin in this compound remains unclear. An important factor in our understanding of the properties of $CoPc(AsF_6)_{0.5}$ is the exchange energy $J_{\pi d}$ between the localized spin of Co^{2+} and itinerant spin of π holes. To reduce the direct Co-Co exchange interaction, we prepared the alloy $Co_xNi_{1-x}Pc(AsF_6)_{0.5}$ and characterized it using the methods of elementary analysis, crystal structure analysis, reflection spectroscopy, Raman spectroscopy, and ESR.[14] In this paper we present the hyperfine structure of Co^{2+} ($I = 7/2$) and estimate the exchange energy $J_{\pi d}$ in the magnetically diluted alloy $Co_{0.01}Ni_{0.99}Pc(AsF_6)_{0.5}$.

The single crystals of $Co_xNi_{1-x}Pc(AsF_6)_{0.5}$ were grown electrochemically in 1-chloronaphthalene solution.[15] The crystals of CoPc and NiPc (Aldrich) were grounded together with the weighting factor of NiPc:CoPc$=100:1$. The mixtures were sublimed four times under a high vacuum to ensure intimate mixing. After allowing the electrochemical reaction to proceed for three weeks, all the starting materials were transformed into the AsF_6 salts. The atomic ratio between Ni and Co in the $Co_xNi_{1-x}Pc(AsF_6)_{0.5}$ single crystals was determined on an electron probe microanalyzer system (Hitachi S-450). The alloy Kovar, $CoPc(AsF_6)_{0.5}$, and $NiPc(AsF_6)_{0.5}$ were used as the standards for the analysis of cobalt and nickel concentrations. The analysis of several points on each single crystal indicated that the distribution of Co and Ni atoms in the samples was homogeneous. In all cases, the Co to Ni ratio agreed with the ratio of the initial mixture within 10%. ESR measurements were carried out on an ESR spectrometer with an x-band cavity (Bruker ESP-300E). The temperature was controlled within ± 0.1 K using a helium-gas flow-type cryostat (Oxford Instruments). For the angular dependent ESR experiment, aligned single crystals were mounted on a quartz rod. The static magnetic susceptibility was measured on a superconducting quantum interference device magnetometer (Quantum Design MPMS 7000). About 1 mg of single crystals was aligned on a quartz plate to detect the anisotropy. Electrical resistivity was measured by means of a conventional four-probe method. Silver or graphite pastes were used for making the electrical contact between the sample and the 10 μm gold or annealed platinum wire.
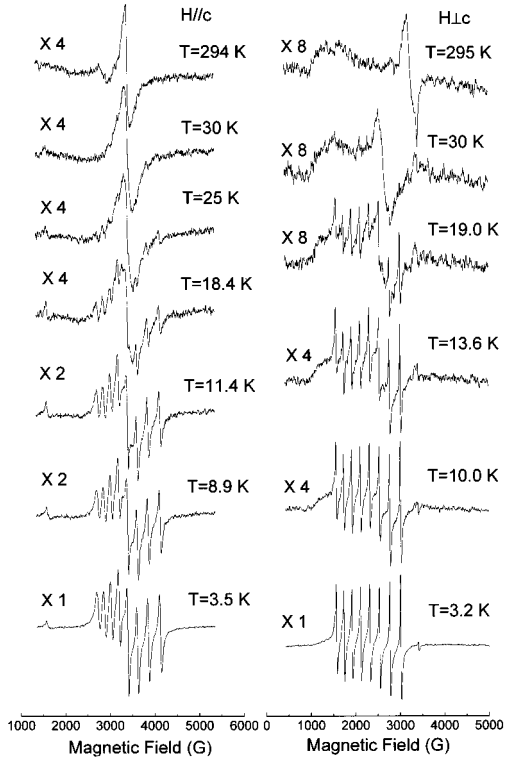
FIG. 1. Temperature-dependent ESR signals of H∥c (left) and H⊥c (right).

We have determined the crystal structure of $Co_xNi_{1-x}Pc(AsF_6)_{0.5}$ with $x=0$, 0.25, 0.55, and 1. As the crystals of $x=0.25$ and 0.55 are isostructural to orthorhombic $NiPc(AsF_6)_{0.5}$ $(x=0)$ (Ref. 16) and tetragonal $CoPc(AsF_6)_{0.5}$ $(x=1)$,[12] respectively, the boundary of the tetragonal and orthorhombic systems is located between $x=0.25$ and 0.55 in this alloy system. We thus consider that $Co_{0.01}Ni_{0.99}Pc(AsF_6)_{0.5}$ is isostructural to $NiPc(AsF_6)_{0.5}$. The unit cell of $NiPc(AsF_6)_{0.5}$ involves two conducting columns with a metal-over-metal stack, half of the unit cell being almost same as the unit cell of $CoPc(AsF_6)_{0.5}$. Based on this crystal structure the mean separation between the magnetic dopants along the stacking axis in $Co_{0.01}Ni_{0.99}Pc(AsF_6)_{0.5}$ is estimated to be 66 Å. It is determined from the analysis of the anisotropic Curie constants for $H\|c$ and $H\perp c$ that the magnetic species consist of 0.77% of CoPc and 0.21% of a defect. $Co_{0.01}Ni_{0.99}Pc(AsF_6)_{0.5}$ shows metallic conductivity from near room temperature at least down to 200 K. At present, however, we have not determined the complete con-

ductivity temperature dependence, since the crystals are too fragile to withstand temperature change.

As shown in Fig. 1, we found well-resolved anisotropic hyperfine structures of Co^{2+} $(I=7/2)$ at 3.5 K $(H\|c)$ and 3.2 K $(H\perp c)$. The individual hyperfine resonance line has a derivative peak-to-peak linewidth of $\Delta H_\| = 60$ G and $\Delta H_\perp = 23$ G. The separation between the hyperfine lines significantly increases toward higher fields. The g value is determined at the mid-field between $M_I = \pm 1/2$ lines. The NiPc molecules are stacked along the c axis making their molecular planes exactly parallel to the ab plane. Therefore the c axis of the crystal is parallel to the fourfold rotation axis of the NiPc molecule, and the a and b axes are nearly equivalent with each other. If CoPc is substituted at the position of NiPc, this characteristic structure requires the following angular dependence for the g value,

$$g(\theta) = (g_\|^2 \cos^2 \theta + g_\perp^2 \sin^2 \theta)^{1/2}. \quad (1)$$

The experimentally obtained angular dependence of g value perfectly agrees with the theoretical curve calculated by Eq. (1). This agreement means that the doped CoPc is relevantly substituted in the alloy.

Hyperfine structure is interpreted according to the Hamiltonian, which is used to analyze the ESR signal of the magnetically diluted CoPc in β-NiPc and α-ZnPc crystals.[17] The hyperfine constants A for $H\|c$ and B for $H\perp c$ are determined by the least-squares calculation to reproduce the 16 lines shown in Fig. 1. Table I presents the g values and hyperfine parameters in $Co_{0.01}Ni_{0.99}Pc(AsF_6)_{0.5}$, along with those of CoPc diluted in the insulating β-NiPc and α-ZnPc crystals. The hyperfine constants of the Co^{2+} ion in $Co_{0.01}Ni_{0.99}Pc(AsF_6)_{0.5}$ resemble those in β-$Co_{0.001}Ni_{0.999}Pc$ rather than α-$Co_{0.001}Zn_{0.999}Pc$ because the local environment of the Co^{2+} ion doped in $NiPc(AsF_6)_{0.5}$ resembles that in β-NiPc.[17] No super-hyperfine structure from the nearest four nitrogen atoms is observed in $Co_{0.01}Ni_{0.99}Pc(AsF_6)_{0.5}$. This result indicates that the unpaired electron occupies the $3d_{z^2}$ orbital of Co^{2+}, and this orbital is not extended to the nitrogen atoms.[18] The very anisotropic g value also supports the $3d_{z^2}$ orbital for the location of the unpaired electron in CoPc.[19] The resemblance of the anisotropic g values as well as the anisotropic hyperfine constants to the magnetically diluted CoPc in β-NiPc indicates that the ESR signal of this compound is coming from the $CoPc^0$ substituted in the molecular column of $NiPc^{0.5+}$. It should be noted that the magnetic impurity in this alloy is well characterized by the analysis of the hyperfine structure.

TABLE I. q values and hyperfine splitting constants A and B.

Material	Temperature (K)	$g_\|$	$g_\perp$	A (cm^{-1})	B (cm^{-1})
$Co_{0.01}Ni_{0.99}Pc(AsF_6)_{0.5}$	3.2, 3.5	2.056(4)	3.045(4)	0.019(1)	0.029(1)
β-$Co_{0.001}Ni_{0.999}Pc^a$	77, 27	1.89(1)	2.94(1)	0.015(1)	0.028(1)
α-$Co_{0.001}Zn_{0.999}Pc^a$	300, 77, 27	2.007(3)	2.422(3)	0.0116(3)	0.0066(3)

[a]This data is taken from Ref. 17. Numerical values in parentheses are the estimated errors. The error is defined by 3σ in the case of $Co_{0.01}Ni_{0.99}Pc(AsF_6)_{0.5}$, where σ is the standard deviation in the least-squares calculation.
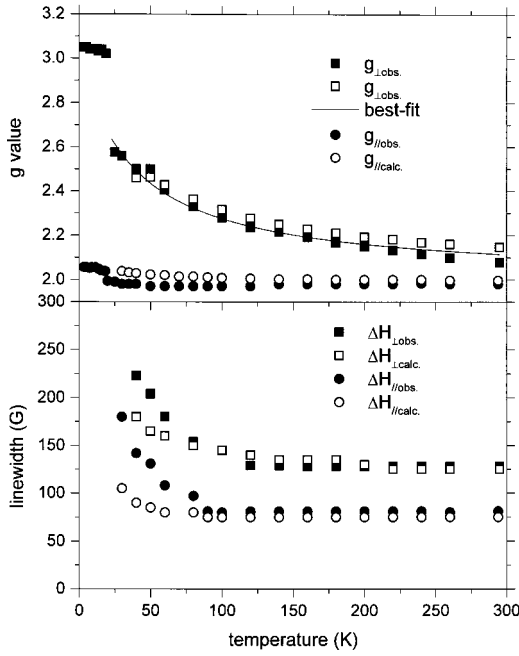
FIG. 2. Temperature dependence of $g_\perp$ and $g_\parallel$ values (top) and linewidths of the broad signals (bottom). See the text for the calculation of the best-fit curve, g values, and linewidths.

With increasing temperatures, the hyperfine structure weakens each line without increasing its linewidth, finally being replaced by the broad signal above 30 K as shown in Fig. 1. Above 30 K, the broad signal narrows the linewidth with increasing temperatures, and the $H \perp c$ signal in particular shows a significant g shift. At room temperature, the signal becomes a single Lorentzian with $\Delta H_\perp = 130$ G, $g_\perp = 2.078$ and $\Delta H_\parallel = 81$ G, $g_\parallel = 1.98$. Figure 2 shows the temperature dependence of the g values and linewidths, which suggest that the exchange interaction between the localized $3d$ spin and itinerant π hole is involved in the relaxation process. If an itinerant π hole strongly interacts with a localized $3d$ electron, the ESR lines of itinerant π and localized $3d$ spins merge into a single line. In fact, the high-temperature ESR signal suggests this case. This situation corresponds to the so-called ''bottleneck regime'' in dilute magnetic alloys.[20] In this regime, the cross-relaxation rates between itinerant and local spins are much faster than the spin-lattice relaxation rates of the local and itinerant spins, and the effective g value is given by the following equation:[20]

$$g_{\text{eff}_{\perp,\parallel}} = \frac{g_\pi \chi_\pi + g_{d\perp,\parallel} \chi_{d\perp,\parallel}}{\chi_\pi + \chi_{d\perp,\parallel}}, \qquad (2)$$

where $g_{d\perp,\parallel}$ is the g value of Co^{2+} ions, and g_π the isotropic g value of π holes [$g_\pi = 2.0023$ for NiPc(AsF$_6$)$_{0.5}$]. If we take the molecular field approximation, χ_d and χ_π are given by the following equations:[20]

$$\chi_d = \frac{\chi_d^0(1 + \lambda \chi_\pi^0)}{1 - \lambda^2 \chi_d^0 \chi_\pi^0} \quad \text{and} \quad \chi_\pi = \frac{\chi_\pi^0(1 + \lambda \chi_d^0)}{1 - \lambda^2 \chi_d^0 \chi_\pi^0}, \qquad (3)$$

where χ_d^0 is the magnetic susceptibility by the bare local moment on Co^{2+}, χ_π^0 the susceptibility of the Pauli paramagnetism in NiPc(AsF$_6$)$_{0.5}$, and λ the molecular field coefficient. They are given by the following equations:

$$\chi_\pi^0 = \frac{N_A}{2}(g_\pi \mu_B)^2 D_F, \qquad (4)$$

$$\chi_d^0 = \frac{N_A c_0 (g_d \mu_B)^2 S(S+1)}{3 k_B T}, \qquad (5)$$

$$\lambda = \frac{2 J_{\pi d}}{N_A g_\pi g_d \mu_B^2}, \qquad (6)$$

where D_F is the density of state per hole and per spin at the Fermi level, c_0 the concentration of the magnetic ion, N_A the Avogadro number, and $J_{\pi d}$ the exchange energy between the local and itinerant spins. The temperature dependence of the effective g value is expressed by the two independent parameters, D_F and $J_{\pi d}$. Equation (2) reproduces the observed $g_\perp(T)$ curve for the broad signal (20 K$<$T$<$300 K) very closely, if we use $D_F = 3.8 \pm 0.2$ eV^{-1} and $J_{\pi d} = -0.001 \pm 0.03$ eV. The calculated $g_\perp(T)$ curve is illustrated by the solid line in the top panel of Fig. 2. The density of state is calculated as $D_F = 1.5$ eV^{-1} when we take the 3/4-filled one-dimensional tight-binding band with the transfer integral of $t = 0.3$ eV.[16] Due to a strong correlation effect, the density of state is usually enhanced in organic metals. Taking this correlation effect into account, the agreement is satisfactory. Owing to the relation $g_{d\parallel} \approx g_\pi$, the effective $g_\parallel$ value is expected to be close to temperature independent g_π. In fact, the $g_\parallel$ value is nearly temperature independent as shown in the top panel of Fig. 2. The standard deviation for D_F is small enough, but $J_{\pi d}$ is insensitive to $g_\perp(T)$.

To estimate $J_{\pi d}$ more precisely, we conducted a numerical calculation of the ESR line shape based on Hasegawa's phenomenological theory for a dilute random alloy, which was solved by Barnes et al., including a hyperfine structure.[21] Equations (3)–(5) derived from the molecular field approximation are used in this model. The Korringa relaxation rate is introduced as $1/T_{d\pi} = 4\pi(D_F J_{\pi d})^2 k_B T/\hbar$. to describe the relaxation rate of the local spin via the interaction with the itinerant π spin. The spin-lattice relaxation rate is assumed to be temperature independent. $1/T_{dL\perp} = 23$ G and $1/T_{dL\parallel} = 61$ G are taken from the ESR linewidth of the individual hyperfine line, and $1/T_{\pi L\perp} = 100$ G and $1/T_{\pi L\parallel} = 70$ G are taken so as to adjust the room-temperature linewidth. The resonance magnetic fields of the hyperfine lines are taken from the experimentally observed values. In this model, the line broadening at low temperature is ascribed to the hyperfine interaction. With the density of state $D_F = 3.8$ eV^{-1}, we simulated the line shape by changing the exchange energy $J_{\pi d}$. For example, $|J_{\pi d}| = 0.001$ eV is too small to explain the observed broad signal because in this case a narrow signal of π spins appears separately from hyperfine signals of $3d$ spins in the whole temperature range. The simulation with $|J_{\pi d}| = 0.02$ eV, on the other hand, reproduces the g shift but does not reproduce the line broad-

ening upon cooling. In this case, the linewidth is already narrowed above 20 K. The open squares and circles in Fig. 2 show the g value (top) and linewidth (bottom) obtained from the line shape calculated with $|J_{\pi d}| = 0.013$ eV. This simulation properly explains both the temperature-dependent g shift and line narrowing above 30–40 K. Below this temperature, the observed ESR line shape is very different from the calculation. In the temperature range of $10\,\text{K} < T < 30\,\text{K}$, the hyperfine signal coexists with the broad line, and the replacement by the broad line appears to be continuous. Below 10 K, the hyperfine structure increases the line intensity according to Curie law. The weak broad line disappears in the strong hyperfine signals. The above model with $|J_{\pi d}| = 0.013$ eV cannot reproduce the well-resolved hyperfine structure. This means that some part of Co^{2+} spins are decoupled with π holes below 30 K. Furthermore, the hyperfine signal decreases more strongly than predicted by the Curie law above 30 K. We thus speculate that the π holes may be weakly localized in this alloy below 30 K.

Ogawa *et al.*, estimated the dynamical exchange term between the local and mobile spins in $Cu_xNi_{1-x}Pc(I_3)_{0.33}$, and presented the coefficient of T as 0.055.[5] If we interpret this coefficient as $4\pi(D_F J_{\pi d})^2$ in the Korringa relaxation rate, the exchange energy is estimated as $|J_{\pi d}| \lesssim 0.017$ eV, since D_F in the 5/6-filled band is larger than that of the 3/4-filled band.[22] This $|J_{\pi d}|$ value is comparable to that in $Co_{0.01}Ni_{0.99}Pc(AsF_6)_{0.5}$. The exchange parameter in the phthalocyanine conductor is much smaller than that in inorganic alloy, the corresponding value being ≈ 1 eV for $3d$ ions and ≈ 0.05 eV for $4f$ ions.[20] Using the parameters, D_F and $|J_{\pi d}|$, the Kondo and Ruderman-Kittel-Kasuya-Yosida

temperatures are estimated as $T_K \approx W\exp(-1/D_F|J_{\pi d}|) = 2 \times 10^{-5}$ K and $T_{RKKY} \approx |J_{\pi d}|^2 D_F = 7$ K, where W is the bandwidth ($= 1.2$ eV) of $NiPc(AsF_6)_{0.5}$.[16] This estimation is consistent with the Curie-Weiss behavior of the low-temperature magnetic susceptibility.

$J_{\pi d}$ involves on-molecule exchange term J_{mo} and covalent mixing term J_{cm}, thereby $J_{\pi d} = J_{mo} + J_{cm}$. J_{mo} is estimated from the following Coulomb energy:

$$\int\int \phi_\pi(r_2)\varphi_d(r_1)\frac{e^2}{r_{12}}\phi_\pi(r_1)\varphi_d(r_2)dr_1 dr_2,$$

where ϕ_π and φ_d are the highest occupied molecular orbitals (HOMO) of Pc^{2-} and $3d_{z^2}$ orbital of Co^{2+}, respectively. According to the molecular orbital calculation of NiPc, HOMO has nodes at Ni and N sites, and the $3d_{z^2}$ orbital is also localized near the Ni site.[23] They mutually occupy separate sites in the phthalocyanine molecule, so the differential overlap $\phi_\pi(r)\varphi_d(r)$ seems to be very small in every site in the molecule. If the molecular orbital of CoPc resembles NiPc, the above Coulomb energy seems to be very small. Covalent mixing comes from the hybridization of the Co $3d_{z^2}$ orbital and Pc HOMO of the neighbor molecule. The small value of J_{cm} suggests the small hybridization. This suggestion is consistent with the characteristic feature of the HOMO and $3d_{z^2}$ orbital.

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[1] M. Y. Ogawa, B. M. Hoffman, S. Lee, M. Yudkowski, and W. P. Halperin, Phys. Rev. Lett. **57**, 1177 (1986).

[2] M. Y. Ogawa, J. Martinsen, S. M. Palmer, J. L. Stanton, J. Tanaka, R. L. Green, B. M. Hoffman, and J. A. Ibers, J. Am. Chem. Soc. **109**, 1115 (1987).

[3] G. Quirion, M. Poirier, K. K. Liou, M. Y. Ogawa, and B. M. Hoffman, Phys. Rev. B **37**, 4272 (1988).

[4] G. Quirion, M. Poirier, C. Ayache, K. K. Liou, and B. M. Hoffman, J. Phys. I **2**, 741 (1992).

[5] M. Y. Ogawa, S. M. Palmer, K. K. Liou, G. Quirion, J. A. Thompson, M. Poirier, and B. M. Hoffman, Phys. Rev. B **39**, 10 682 (1989).

[6] G. Quirion, M. Poirier, K. K. Liou, and B. M. Hoffman, Phys. Rev. B **43**, 860 (1991).

[7] J. Thompson, K. Murata, R. Durcharne, M. Poirier, and B. M. Hoffman, Phys. Rev. B **60**, 523 (1999).

[8] J. Martinsen, J. L. Stanton, R. L. Green, J. Tanaka, B. M. Hoffman, and J. A. Ibers, J. Am. Chem. Soc. **107**, 6915 (1985).

[9] G. Quirion, M. Poirier, M. Castonguay, K. K. Liou, and B. M. Hoffman, Phys. Rev. B **42**, 2831 (1990).

[10] K. K. Liou, C. S. Jacobsen, and B. M. Hoffman, J. Am. Chem. Soc. **111**, 6616 (1989).

[11] K. Yakushi, H. Yamakado, T. Ida, and A. Ugawa, Solid State Commun. **78**, 919 (1991).

[12] H. Yamakado, T. Ida, A. Ugawa, K. Yakushi, K. Awaga, Y. Maruyama, K. Imaeda, and H. Inokuchi, Synth. Met. **62**, 169 (1994).

[13] H. Yamakado, A. Ugawa, T. Ida, and K. Yakushi, *The Physics and Chemistry of Organic Superconductors*, edited by G. Saito and S. Kagoshima (Springer-Verlag, Berlin, 1999), p. 311.

[14] This will be published separately. A part of the results is published in Y. Yonehara and K. Yakushi, Synth. Met. **103**, 2214 (1999).

[15] T. Hiejima and K. Yakushi, J. Chem. Phys. **103**, 3950 (1995).

[16] K. Yakushi, H. Yamakado, M. Yoshitake, N. Kosugi, H. Kuroda, T. Sugano, M. Kinoshita, A. Kawamoto, and J. Tanaka, Bull. Chem. Soc. Jpn. **62**, 687 (1989).

[17] J. M. Assour and W. K. Kahn, J. Am. Chem. Soc. **87**, 207 (1965).

[18] B. A. Goodman and J. B. Paynon, Adv. Inorg. Chem. Radiochem. **13**, 135 (1972).

[19] Y. Nishida and S. Kida, Inorg. Nucl. Chem. Lett. **7**, 325 (1971).

[20] S. E. Barnes, Adv. Phys. **30**, 801 (1981).

[21] S. E. Barnes, J. Dupraz, and R. Orbach, J. Appl. Phys. **42**, 1659 (1971).

[22] The density of state is given as $D_F = [\pi t \sin(ck_F)]^{-1}$ in the one-dimensional tight-binding model. Since the band-filling factor of $CuPc(I_3)_{0.33}$ is larger, k_F so that D_F is larger than those of $NiPc(AsF_6)_{0.5}$.

[23] F. W. Kutzler and D. E. Ellis, J. Chem. Phys. **84**, 1033 (1986).