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FORMATION OF MIXED CRYSTAL SYSTEM $Co_xNi_{1-x}Pc(AsF_6)_{0.5}$

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The mixed crystal system $Co_xNi_{1-x}Pc(AsF_6)_{0.5}$ ($0 < x < 1$) was prepared and characterized by elementary analysis of EPMA, X-ray diffraction, ESR, and Raman spectra. It is shown that the mixed crystal system is formed in a wide range of x, although the $CoPc(AsF_6)_{0.5}$ is not exactly isomorphous to $NiPc(AsF_6)_{0.5}$. The ESR and Raman spectra established the formation of mixed crystal in a whole range of x.

Keywords: phthalocyanine; organic conductor; mixed crystal; molecular alloy; reflectivity

INTRODUCTION

The quasi-one-dimensional phthalocyanine conductors $MPc(X)_y$ ($M = H_2^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+}; $Pc = (C_{32}N_8H_{16})^{2-}$; $y = 0.5$ for $X = AsF_6^-$, $y = 0.33$ 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+}) phthalocyanines yield nearly isostructural conductive crystals. Comparative study of the phthalocyanine-based conductors with paramagnetic and diamagnetic molecules and their alloy system have been conducted in order to elucidate the influence of the localized spins on the conduction electrons. Ogawa et al. suggested a strong coupling between the localized spin of Cu^{2+} ($S = 1/2$) and the conduction electron of the Pc chain in $CuPc(I_3)_{0.33}$ [1,2]. 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, in which in the microwave resistivity experiment they found a huge negative magneto-resistance and proposed a spin-flip scattering process produced by Cu^{2+} local spin [3,4]. They studied 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].

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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 authors reported a similar Co-containing phthalocyanine conductor $CoPc(AsF_6)_{0.5}$ [9]. 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 $CuPc(I_3)_{0.33}$. The resistivity of $CoPc(AsF_6)_{0.5}$ showed a minimum near the room temperature, [8], whereas the nearly isostructural diamagnetic phthalocyanine conductor $NiPc(AsF_6)_{0.5}$, was metallic down to ~40 K [10]. To elucidate the role of the Co^{2+} spin in $CoPc(AsF_6)_{0.5}$, we prepared the alloy $Co_xNi_{1-x}Pc(AsF_6)_{0.5}$. In this paper, we characterized the alloy using the methods of elementary analysis, crystal structure analysis, ESR, and Raman spectrum.

ELEMENTARY ANALYSIS AND CRYSTAL STRUCTURE

The single crystals of $Co_xNi_{1-x}Pc(AsF_6)_{0.5}$ were grown electrochemically in 1-chloronaphthalene solution [11]. For the preparation of $Co_xNi_{1-x}Pc(AsF_6)_{0.5}$, crystals of crude CoPc and NiPc were carefully weighed and ground together with corresponding weighting factor. The resulting mixtures were sublimed 4 times under 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 by means of EPMA (Hitachi S-450). The analysis of several points on each single crystal indicated that the distribution of Co and Ni atoms in the samples was homogeneous.

We have determined the crystal structure of $Co_xNi_{1-x}Pc(AsF_6)_{0.5}$ with $x = 0.25$ and 0.55. The lattice parameters were listed in (Table 1) along with those of $NiPc(AsF_6)_{0.5}$ ($x = 0$) [12] and $CoPc(AsF_6)_{0.5}$ ($x = 1$) [13]. The boundary of the tetragonal and orthorhombic systems is located between $x = 0.25$ and 0.55 in this alloy system. The unit cell of $NiPc(AsF_6)_{0.5}$

TABLE 1 Lattice Parameters of $Co_xNi_{1-x}Pc(AsF_6)_{0.5}$

	$NiPc(AsF_6)_{0.5}$	$Ni_{0.75}Co_{0.25}Pc(AsF_6)_{0.5}$	$Ni_{0.55}Co_{0.45}Pc(AsF_6)_{0.5}$	$CoPc(AsF_6)_{0.5}$
Crystal class space group	Orthorhombic Pnc2	Orthorhombic Pnc2	Tetragonal P4/mcc	Tetragonal P4/mcc
a	14.015(1)	14.033(4)	14.226(2)	14.234(2)
b	28.485(2)	28.54(1)	14.226(2)	14.234(2)
c	6.466(3)	6.435(2)	6.414(1)	6.296(2)
Z	4	4	2	2

involves two conducting columns with a metal-over-metal stack, half of the unit cell being almost same as the unit cell of $CoPc(AsF_6)_{0.5}$. Therefore the structure of $CoPc(AsF_6)_{0.5}$ is nearly isostructural to $NiPc(AsF_6)_{0.5}$, which is the reason for the formation of the mixed crystal system in a wide range of x.

ESR PROPERTIES

Figure 1 shows well-resolved anisotropic hyperfine structures of $Co_{0.01}Ni_{0.99}Pc(AsF_6)_{0.5}$ at 3.5 K (H//c) and 3.2 K (H $\perp$ c). 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 angular dependence of the g values at 3.2 K is consistent with the characteristic crystal structure that the molecules are aligned perpendicular to the c-axis of the crystal. This result clearly shows that the doped CoPc is relevantly substituted in the alloy. Hyperfine structure is interpreted according to the Hamiltonian involving the electron and nuclear spins in the field of axial symmetry [14], which is used to analyze the ESR signal of the magnetically diluted CoPc [15]. The anisotropic g values and hyperfine constants A and B are shown in (Table 2) 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-$Co_{0.001}Zn_{0.999}Pc$. This is because the local environment of the Co^{2+} ion doped in $NiPc(AsF_6)_{0.5}$ resembles that in β-NiPc [15].

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 $NiPc^{0.5+}$. The ESR signal ascribed to $CoPc^+$ is

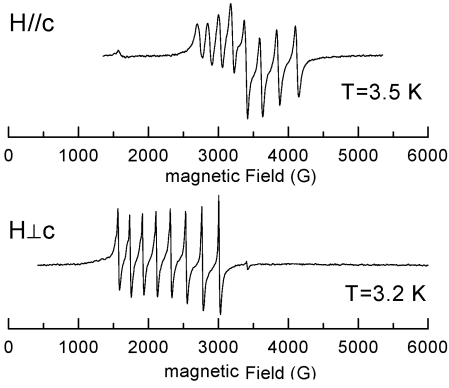

FIGURE 1 Hyperfine structure of $Co_{0.01}Ni_{0.99}Pc(AsF_6)_{0.5}$.

TABLE 2 Anisotropic g Values and Hyperfine Constants

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]These data are taken from Ref.15.

not found in this alloy. This result is consistent with the fact that the oxidation potential of NiPc is lower than that of CoPc. The very similar hyperfine signals were observed in the mixed crystals with $x = 0.005$, 0.014, 0.02, and 0.05. The signal of $Co_{0.09}Ni_{0.91}Pc(AsF_6)_{0.5}$ is nearly a single peak with the linewidth of *ca.* 500 G. No ESR signal was observed in the alloy with $x > 0.1$. It should be noted that the magnetic impurity in this alloy is well characterized.

RAMAN SPECTRUM

The Raman spectra of these compounds provide another experimental evidence for the formation of the mixed crystal in a whole range of x. The He-Ne laser (633 nm) excited Raman spectrum of $Co_xNi_{1-x}Pc(AsF_6)_{0.5}$ in (a, a) polarization was simply a superposition of those of $CoPc(AsF_6)_{0.5}$ and $NiPc(AsF_6)_{0.5}$. However, the spectrum in (c, c) polarization showed new peaks at 368 cm^{-1} and 736 cm^{-1}, which were observed neither in $CoPc(AsF_6)_{0.5}$ nor $NiPc(AsF_6)_{0.5}$ but found in all mixed crystal system. It is surprising that these Raman bands are observable even in a dilute alloy

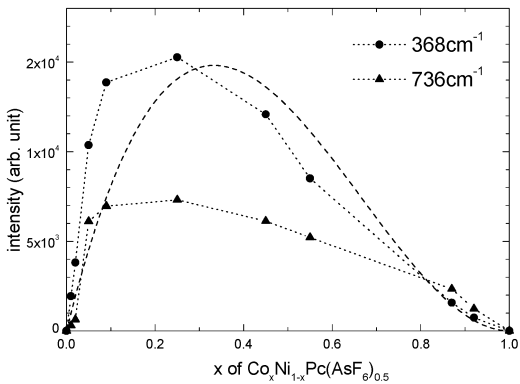

FIGURE 2 Intensity of the new Raman bands which appears only in mixed crystals. The dotted line is the function $x(1-x)^2$ (see text).

$Co_{0.01}Ni_{0.99}Pc(AsF_6)_{0.5}$. These Raman bands were strongly suppressed when the Ar^+ laser (514 nm) was employed. The resonance effect can explain the appearance of the second harmonic band at 736 cm^{-1}, strong excitation-energy dependence, and high sensitivity to the introduction of CoPc in $NiPc(AsF_6)_{0.5}$. The 368 cm^{-1} band is tentatively assigned to the a_{1g} breathing mode of NiPc [16,17]. Since the 368 cm^{-1} band appears only in (c,c) polarization, we consider that the excited state formed in the mixed crystals is associated with the charge-transfer excited state between the 3d orbitals of Co^{2+} and Ni^{2+}. This excited state can be formed only in the mixed crystals. The probability to find NiPc and CoPc in the neighboring position in $Co_xNi_{1-x}Pc(AsF_6)_{0.5}$ is $x(1-x)$. Therefore the Raman intensity of 368 cm^{-1} band of NiPc is expected to be proportional to $x(1-x)^2$, which qualitatively reproduces the x dependence of the Raman intensity. This result also strongly indicates the formation of the mixed crystal in a wide range of x.

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