Compressibility and High-Pressure Electrical Resistivity of One-Dimensional Phthalocyanine Conductors: The Relationship with d-π Charge Transfer

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COMPRESSIBILITY AND HIGH-PRESSURE ELECTRICAL RESISTIVITY OF ONE-DIMENSIONAL PHTHALOCYANINE CONDUCTORS: THE RELATIONSHIP WITH d-π CHARGE TRANSFER

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Abstract   Powder X-ray diffraction patterns of one-dimensional phthalocyanine conductors (phthalocyaninato)-nickel hexafluoroarsenate, $NiPc(AsF_6)_{0.5}$ and (phthalocyaninato)-cobalt hexafluoroarsenate, $CoPc(AsF_6)_{0.5}$, were measured under high pressure. The crystal symmetries of the both compounds were maintained in the pressure range of 0-3.5 GPa. In both compounds, the compressibility along the chain axis is larger than that along the interchain axis. The compressibility of $NiPc(AsF_6)_{0.5}$ below 0.5 GPa is unusually larger than that of $CoPc(AsF_6)_{0.5}$. The relation between the lattice contraction along the chain axis and the pressure-induced d-π charge transfer (metal-ligand charge transfer) is discussed based on a simple ligand field theory.

The enhancement of the electrical resistivity was observed at about 0.5 GPa in $NiPc(AsF_6)_{0.5}$. This enhancement is consistent with the suggestion by the analysis of the pressure-dependent plasmon absorption. This resistivity change is attributed to the Anderson localization accompanying the metal-ligand charge transfer.

Keywords: phthalocyanine, one-dimensional conductor, high pressure, X-ray diffraction, electrical conductivity

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INTRODUCTION

We have reported the high-pressure absorption spectra of the powdered samples of phthalocyanine conductors, $MPc(AsF_6)_{0.5}$ (M=Ni, and Co).[1,2] In these compounds, the vibrational modes in infrared region, plasmon absorption in near-infrared region, and interband transition in visible region show reversible systematic changes upon high pressure. We interpreted this phenomenon as follows: the high pressure induces a change of the charge distribution from the metal (M) to the macrocycle (Pc), which is named a metal-ligand charge transfer (or d-π charge transfer). The phthalocyanine conductors are the double chain systems which consists of π-band produced by the a_{1u}-orbital of the macrocycle and d-band by the $3d_{z^2}$-orbital of the transition metal ion. In these compounds the positive holes are doped into this π-band at ambient pressure.[3,4] The valence can be formally described as $M^{2+}Pc^{1.5-}(AsF_6^{1-})_{0.5}$. When the pressure is applied to these compounds, these π-holes begin to move from the π-band to the d-band at *ca.* 0.5 GPa in $NiPc(AsF_6)_{0.5}$ and *ca.* 1.1 GPa in $CoPc(AsF_6)_{0.5}$. These charge transfer continuously evolves up to *ca.* 7 GPa. In this pressure range the valence can be written as $M^{(2-\delta)+}Pc^{(1.5+\delta)-}(AsF_6^{1-})^{0.5}$ ($0<\delta<0.5$). Probably the metal-ligand charge transfer is fully achieved above 7 GPa, and the formal valence is expressed as $M^{1.5+}Pc^{2-}(AsF_6^{1-})_{0.5}$. The compressibility of the unit cell provides a basic information to understand the mechanism of this phenomenon. In this paper, we will present the pressure-dependent lattice constants of $NiPc(AsF_6)_{0.5}$ and $CoPc(AsF_6)_{0.5}$ determined by powder X-ray diffraction patterns.

$NiPc(AsF_6)_{0.5}$ is metallic around the room temperature at ambient pressure.[3] However, the pressure dependent optical experiment suggests that it changes into a nonmetallic state above 0.5 GPa at which the d-π charge transfer begins to occur. Above 0.5 GPa the d-hole density increases whereas the π-hole density decreases due to the evolution of the metal-ligand charge transfer, as the external pressure is increased. From the standpoint of this simple band-filling process, the appearance of the nonmetallic phase is unusual. To confirm this phenomenon more directly, we measured the pressure and temperature dependencies of the electrical resistivity of $NiPc(AsF_6)_{0.5}$.

EXPERIMENTAL

The finely powdered nickel phthalocyanine (NiPc) and cobalt phthalo-cyanine (CoPc) (Tokyo Kasei Co. Ltd.) were sublimed in vacuum (*ca.* 10^{-4} Pa) for three times. The radical salts of NiPc and CoPc were prepared by the method of electrochemical crystallization at 120 ± 2 °C under Ar atmosphere. 1-Chloronaphthalene used as the solvent of electrochemical crystallization was refluxed with CaH_2 and purified by vacuum distillation. The concentration of the electrolyte (tetrabuthyl-ammonium hexafluoroarsenate) and MPc (M = Ni and Co) was 2.5×10^{-3} and 3×10^{-4} mol/l, respectively. The crystals were grown after about two weeks with a galvanostatic mode of 2~4 μA.

The X-ray diffraction patterns of $NiPc(AsF_6)_{0.5}$ were measured on the MAX80 at the beam line of BL13B in the Photon Factory Facility of KEK. The high pressure was applied using a cubic-anvil type pressure apparatus, in which the pressure cell made of pyrophyllite is formed into a 8 mm cube. The sample container made of the mixture of boron nitride and epoxy resin is formed into a 3mm diameter cylinder. The finely powdered sample was tightly filled in a 2 mm diameter $\times$ 1 mm height cylindrical space. The diffraction pattern was recorded at $2\theta = 4°$ with an energy dispersion method. The diffraction lines of NaCl were used to determine the inner pressure according to Decker's scale. The details of the experimental procedure is described in ref.5. The X-ray diffraction patterns of $CoPc(AsF_6)_{0.5}$ were measured with an angle dispersion method using a diamond anvil cell of a Basset type at the beam line BL-6B in the Photon Factory Facility of KEK. The X-ray beam is collimated into 0.3 mm in diameter, and the diffraction was detected by the imaging plate. The diffraction from the silver plate was used to determine the distance between the sample and imaging plate. The details of the experimental procedure is described in ref.6. Pressure in the diamond anvil cell was determined by a conventional ruby-fluorescence method using a microphotometric method. The homogeneity of pressure in the pressure cell was checked by observing the fluorescence from the several

different places in the sample space. The lattice constants were determined by the least square method.

The high-pressure electrical resistivity of the $NiPc(AsF_6)_{0.5}$ single crystal was measured by means of a four probe method using a clamped piston cylinder made of BeCu alloy. Idemitsu Daphne oil #7373 was used as a pressure medium. The pressure in the cell was monitored with the resistance change of a manganin wire. The thermoelectric power of $NiPc(AsF_6)_{0.5}$ was measured along the conducting axis by the method of Chaikin and Kwak.[7] An ESR measurement was performed using a conventional X-band spectrometer (Brukur ESP-300E) equipped with a continuous-helium-flow cryostat (Oxford ESR 900).

X-RAY DIFFRACTION UNDER HIGH PRESSURE

The crystal of $CoPc(AsF_6)_{0.5}$ belongs to a tetragonal system, the lattice parameters being a = 14.234 Å, c = 6.296 Å, and Z = 2.[8] The molecules on a 4-fold axis are stacked exactly in the metal-over-metal overlapping mode. AsF_6^- is displaced by 0.6 Å from the molecular sheet of CoPc and has not a three-dimensional order. The crystal of $NiPc(AsF_6)_{0.5}$ belongs to an orthorhombic system, the lattice parameters being a = 14.015 Å, b = 28.485 Å, c = 6.466 Å, and Z = 4.[3] The unit cell contains four molecules, and has a pseudo-tetragonal symmetry. In this molecular column NiPc is stacked nearly in the metal-over-metal overlapping mode. More strictly, NiPc is alternately displaced by ± 0.21 Å to the direction of b-axis from the axis (0.5, 0.25, z), so that they are stacked in a zigzag way. The neighboring molecules are related to each other by a glide plane. The structural difference from $CoPc(AsF_6)_{0.5}$ is very small, so the crystal structure is approximately described by a tetragonal symmetry.

All the diffraction lines showed the continuous high-angle shift with increasing the pressure, and any anomaly such as a disappearance or splitting of some diffraction lines was not observed in all pressure region. These results mean that the crystal symmetry is maintained in all pressure region, although the d-π charge transfers of $CoPc(AsF_6)_{0.5}$ and $NiPc(AsF_6)_{0.5}$ occur at 1.1 GPa and 0.5 GPa, respectively. This structural aspect is consistent with the high-pressure infrared spectra in both

compounds.[2] The X-ray diffraction patterns are indexed based on the single-crystal data obtained by the four-circle diffractometer. Since $CoPc(AsF_6)_{0.5}$ has a high symmetry, we could select more than 10 diffraction lines which do not overlapp with other lines and thus uniquely be indexed. However, the same procedure was very difficult in $NiPc(AsF_6)_{0.5}$, because the lattice parameters of a and $b/2$ are very close to each other and, for example, (200) and (040), and (141) and (221) could not be separated from each other. We thus analyzed the X-ray diffraction lines of $NiPc(AsF_6)_{0.5}$ assuming a tetragonal system. Since the estimated lattice constant a of $NiPc(AsF_6)_{0.5}$ is the average value of a and $b/2$, the standard deviations of a-axis is naturally larger than the c-axis. These results are listed in Table 1.

TABLE 1 Pressure dependence of the lattice constants of $NiPc(AsF_6)_{0.5}$ and $CoPc(AsF_6)_{0.6}$.

	$NiPc(AsF_6)_{0.5}$		$CoPc(AsF_6)_{0.5}$	
P (GPa)	a,b	c	a,b	c
0	14.129(1)	6.466(3)	14.236(1)	6.302(1)
0.1	14.07(2)	6.410(3)		
0.5	13.70(3)	6.272(5)		
0.9			13.997(2)	6.176(1)
1.0	13.58(2)	6.168(6)		
1.4	13.46(3)	6.098(8)		
1.5			13.823(2)	6.074(1)
2.0			13.729(3)	5.992(2)
2.2	13.32(4)	6.00(1)		
3.0	13.23(5)	5.92(2)		
3.1			13.612(3)	5.900(2)
3.6	13.16(6)	5.86(2)		
4.1	13.11(6)	5.82(2)		

Figure 1 shows the pressure dependence of the lattice parameters of $NiPc(AsF_6)_{0.5}$ and $CoPc(AsF_6)_{0.5}$. The lattice parameters of $CoPc(AsF_6)_{0.5}$ decreases linearly up to 2 GPa, which is a similar behavior as other organic conductors such as

β-(BEDT-TTF)$_2$I$_3$[9], (TMTSF)$_2$PF$_6$ [10], and TTF-TCNQ[11]. The compressibility ($dlog(x)/dP$) of each axis was calculated to be -0.018 for a- and b-axes and -0.023 for c-axis. In quasi-one-dimensional conductors, the compressibility along the stacking axis is largest: -0.047 for the b-axis of TTF-TCNQ[11] and -0.046 for the a-axis of (TMTSF)$_2$PF$_6$.[10] Compared with these compounds, CoPc(AsF$_6$)$_{0.5}$ is rather hard along the stacking axis. The pressure dependence of NiPc(AsF$_6$)$_{0.5}$ is very different from CoPc(AsF$_6$)$_{0.5}$ although they are nearly isostructural. In the pressure region of 0-0.5 GPa, the compressibilities are -0.058 for a- and b-axes and -0.060 for c-axis, which are much larger than those of CoPc(AsF$_6$)$_{0.5}$. The compressibilities, -0.017 for a- and b-axes and -0.026 for c-axis, in the region of 0.5-2.0 GPa, are almost the same as those of CoPc(AsF$_6$)$_{0.5}$. In the region higher than 2 GPa, the compressibility in all directions tends to level off in the same way as CoPc(AsF$_6$)$_{0.5}$. These results mean that NiPc(AsF$_6$)$_{0.5}$ is unusually soft in all directions in low-pressure region and may suggest a structural phase transition at 0.5 GPa. However, we do not have any indication of a structural phase transition. More detailed single crystal
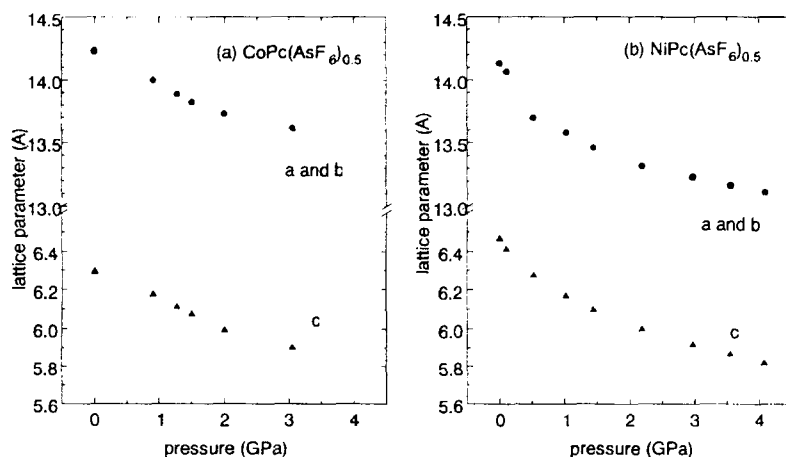

FIGURE 1   Pressure dependence of the lattice constants of (a)
CoPc(AsF$_6$)$_{0.5}$ and (b) NiPc(AsF$_6$)$_{0.5}$.

experiment is necessary to elucidate the origin of the change of this compressibility.

Since the pressure below 10 GPa makes little effect to the covalent bond within the molecule, M-N distance within the phthalocyanine molecule will not change

under the pressure below 10 GPa. The contraction along the a- or b-axes makes the molecular columns closer, but the inter-chain interaction probably does not increase so much, since the π-conjugation in Pc is terminated by hydrogen atoms. On the other hand, the contraction along the c-axis directly shorten the metal-metal distance. Consequently, the hydrostatic pressure gives the same effect as the uniaxial stress along the c-axis. The environment of the metal ion is the octahedral coordination elongated along the c-axis as shown in Fig. 2a. As the external pressure increases, only the metal-metal distance is shortened: Ni-N=2.00 Å, Ni-Ni=3.23 Å at ambient pressure and Ni-N=2.00 Å, Ni-Ni=2.91 Å at 4.1 GPa. This geometrical change makes a big influence on the $3d_{z^2}$-orbital
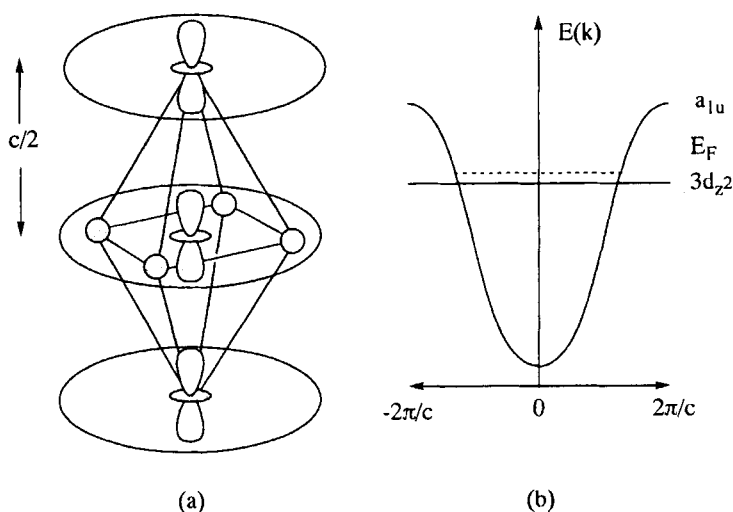

(a)   (b)

FIGURE 2   (a) Elongated octahedron around the metal ion of metalo-phthalocyanine. The metal ions are represented by the $3d_{z^2}$-orbital and the four nickel atoms coordinating to the central metal are represented by the hatched circle. The large open circles schematically express the molecular plane of phthalocyanine. (b) Band structure of $MPc(AsF_6)_{0.5}$ near the Fermi level (E_F). The a_{1u}-band is spread over the macrocycle, while the $3d_{z^2}$-band is localized at the central metal. They are not hybridized because of the orthogonality of the orbital symmetry.

of Co^{2+} and Ni^{2+} and pushes up the orbital energy of $3d_{z^2}$ according to the ligand field theory. The band structure of NiPcI was calculated by Kutzler and Ellis.[12] Their schematic picture of the a_{1u} and $3d_{z^2}$ bands are reproduced in Fig. 2b.[13]   If the $3d_{z^2}$-

orbital is located near the Fermi level of the a_{1u}-band, the electrons in $3d_z2$-orbital will flow into the vacant state of the a_{1u}-band, and result in the change of the charge distribution.

Let us compare with the neutral-ionic phase transition in tetrathiafulvalen-p-chloranil (TTF-CA), in which the degree of charge transfer discontinuously changes from 0.40 to 0.60 at 1 GPa.[14] The Madelung energy gain was thought to be the driving force of this first order phase transition. Later on, however, it was found that the lattice dimerization was accompanied by this phase transition.[15] So the electron-phonon interaction such as the spin-Peierls instability is involved in the mechanism of this phase transition. Contrary to this phenomenon, the charge transfer in $NiPc(AsF_6)_{0.5}$ and $CoPc(AsF_6)_{0.5}$ continuously changes.[2] The lattice dimerization is not accompanied by this d-π charge transfer according to the high-pressure vibrational spectra which is sensitive to the lattice dimerization. Taking into account of this continuous change and non-existence of the symmetry breakdown, it seems to be reasonable that the selective contraction of the M-M distance is the origin of this pressure-induced charge transfer.

Let us examine the pressure dependence of the transfer integral between adjacent phthalocyanine molecules. The transfer integral t is estimated from the following equation[16],

$$ t = \frac{\varepsilon_0 \pi \hbar^2 \rho \omega_p^2}{4(\frac{z}{v_c})e^2 d^2 \sin^2(\pi\rho / 2)} $$

where ω_p is the plasma frequency, $\rho=0.5$ degree of oxidation of the molecule, $z=1$ number of the hole per a unit cell, v_c the volume of the unit cell, d intermolecular distance. The transfer integral is estimated at 0.30 eV for $\omega_p=7170$ cm^{-1},[2] $d=3.233$ Å, and $v_c=1307.3$ Å at ambient pressure, while it increases to 0.32 eV for $\omega_p=7535$ cm^{-1},[2] $d=3.136$ Å, and $v_c=1176.3$ Å at 0.5 GPa. The transfer integral increases at the rate of $d\ln(t)/dP=1.3$ % per kbar, which is comparable with the corresponding value 2-3 % of TTF-TCNQ.[17]

PRESSURE-DEPENDENT ELECTRICAL RESISTIVITY OF NiPc(AsF$_6$)$_{0.5}$

Before going to the high-pressure properties, we briefly describe the electronic properties of NiPc(AsF$_6$)$_{0.5}$ at ambient pressure. As we reported before there was a notable sample dependence in the ESR linewidth of NiPc(AsF$_6$)$_{0.5}$.[3] The linewidth of the recently synthesized samples is distributed in the range of 1-30 G, the major component being 5-7 G. This linewidth has been interpreted to corresponds to the small amount of Ni(3+): the larger the linewidth the higher the concentration of Ni(3+).[3] The linewidth of 5-7 G means that the concentration of Ni(3+) is very small. We could not observe a big difference in the resistivity of T>100 K region in these samples having a different ESR linewidth. No difference was observed in the thermoelectric power in whole temperature region. We have not succeeded yet to obtain the low-temperature electrical resistivity of NiPc(AsF$_6$)$_{0.5}$, since it always shows a resistivity jump below 100 K at ambient pressure. In many samples of NiPc(AsF$_6$)$_{0.5}$, the resistivity minimum is observed at 100-170 K depending upon the sample.[18] However, the thermoelectric power is not affected by the resistivity jump and gives a reproducible result as shown in Fig. 3. It has a positive value
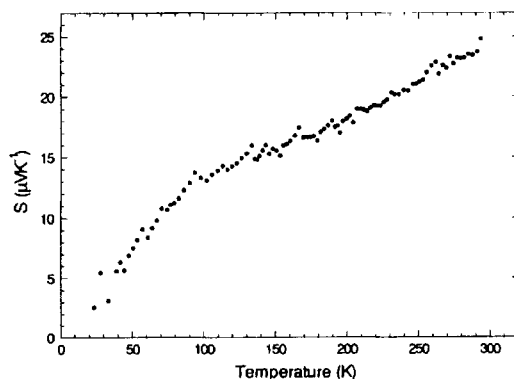

FIGURE 3   Thermoelectric power of NiPc(AsF$_6$)$_{0.5}$.

S= +25 μVK at room temperature and keeps positive value throughout the temperature range 10-300 K. This behavior is consistent with a simple consideration of the 3/4-filled band. The thermoelectric power linearly decreases down to *ca.* 90 K

without exhibiting any anomaly around 150 K where the resistivity minimum was observed. According to the one-dimentional tight-binding model, the thermoelectric power S is given by the following equation[19],

$$S = \frac{2\pi^2 k_B \cos(\pi\rho / 2)}{3e(4t)\sin^2(\pi\rho / 2)} T$$

where $\rho=0.5$ is the degree of oxidation of NiPc. The bandwidth $4t = 1.3$ eV is estimated from the slope of the high-temperature region, $S/T = 0.0632$ μV K^{-2}. This bandwidth agrees well with the value of 1.2 eV obtained from the analysis of the optical reflectivity spectrum.[3] The thermoelectric power changes the slope at 90 K, below which the slope gives the bandwidth value of 4t = 0.6 eV. Since no anomaly was observed in the magnetic susceptibility and ESR at 90 K, this may be related to the phonon drag. This thermoelectric power indicates that $NiPc(AsF_6)_{0.5}$ seems to be metallic down to at least 20 K.
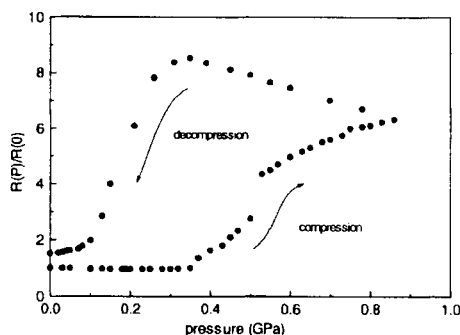

FIGURE 4   Normalized electrical resistance of $NiPc(AsF_6)_{0.5}$ single crystal against the external pressure.

The pressure dependence of the resistance is shown in Fig. 4. The resistance first decreases continuously and increases around 0.5 GPa up to 0.9 GPa. As the pressure is released, the resistivity reverts to the original value showing a large hysteresis. The pressure, 0.5 GPa, at which the samples showed the resistivity enhancement, coincides with the   pressure where the metal-ligand charge transfer occurs. The same pressure-induced resistivity enhancement was observed for different three crystals. The temperature dependences of the electrical resistivity at 0, 0.3, 0.5, and 1.0 GPa

were shown in Fig. 5. On lowering the temperature above 150 K, the resistivity decreases at 0 and 0.3 GPa, while the slope against the temperature becomes very small at 0.5 GPa and it becomes almost temperature independent at 1.0 GPa. This resuls clearly indicates that the high pressure induces the nonmetallic phase, and supports the suggestion by the high-pressure optical spectrum of $NiPc(AsF_6)_{0.5}$.

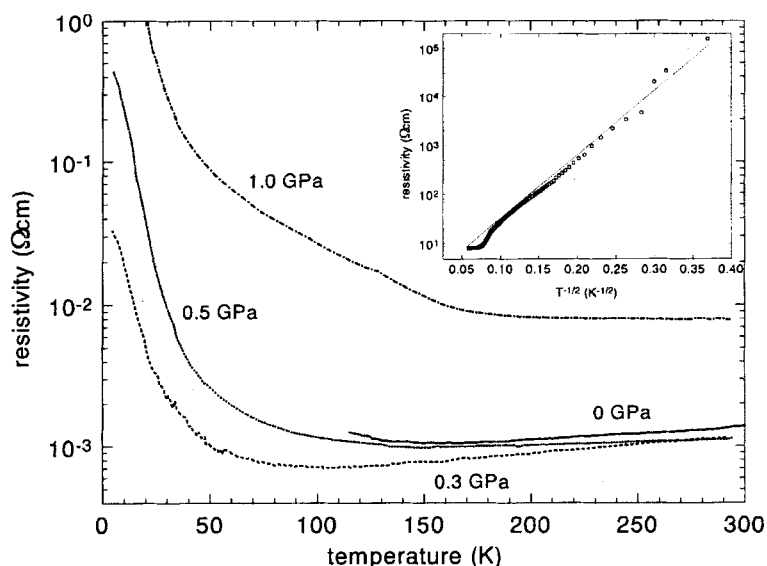
FIGURE 5   Temperature dependence of the electrical resistivity of a $NiPc(AsF_6)_{0.5}$ single crystal at 0, 0.3, 0.5, and 1.0 GPa. The inset shows the logarithmic plot of 1.0 GPa resistivity against $T^{-1/2}$. The solid line shows the best-fit curve assuming the one-dimensional variable range hopping model, $R = R_0 \exp\{(T_0/T)^{1/2}\}$, where $R_0 = 25$ Ωcm and $T_0 = 933$ K.

Let us discuss about the origin of the nonmetallic phase. Generally the metallic state of pseudo-one-dimensional conductors is stabilized by high pressure due to the increase of the interchain interaction. As mentioned in the preceding section, the X-ray diffraction shows that the high pressure *does not* bring about a large structural change. A small lattice distortion such as a dimerization or tetramerization sometimes causes the metal-insulator transition. However, the infrared spectra does not show any indication of the vibronic mode, which is a very sensitive probe of the lattice distortion such as the tetramerization of the phthalocyanine molecule.[2] These results

indicate that this nonmetallic state is not ascribed to the structural phase transition such as a Peierls transition. As we mentioned before, the metal-ligand charge transfer begins to occur at 0.5 GPa. According to the optical experiment, Ni $3d_{Z^2}$-band has a very narrow bandwidth.[2] Therefore, the d-hole (Ni^{3+}), which is produced by the metal-ligand charge transfer, would be localized in the Ni chain. These localized positive holes will distribute to mininize the repulsive energy between them and will make a d-hole superlattice along the c-axis, if the long range Coulomb force is not screened at all. For example, the periodic unit of the superlattice will be given by $2c/n$, where $n(=N_h/N)$ is a fraction of the d-hole site (N_h) among the Ni sites (N). When the concentration of d-holes is low enough, the above periodicity will not be complete and the distribution will become nearly random, since the distances between d-holes are long enough. On the other hand, the π-holes seem to be more delocalized under high pressure due to the increase of the bandwidth. If we take into account the localized d-holes in the Ni-chain, Ni^{3+} will produce a random electrostatic potential. This random potential will make a big influence on the itinerant π-holes in the one-dimensional macrocycle chain and will make them localized. Probably the nonmetallic state above 0.5 GPa is the localized state due to the mechanism of the Anderson localization. This interpretation is consistent with the low-temperature behavior of the electrical resistivity at 1.0 GPa, which is well expressed by the one-dimensional variable range hopping model.

As the pressure is increased above 1 GPa, the degree of the metal-ligand charge transfer increases and thus the d-hole concentration increases. To minimize the electrostatic repulsion, the d-holes might make a periodic lattice. Therefore this material might be metallic again, if this d-hole lattice is produced before all the π-holes change into d-holes. We measured the high-pressure electrical resistivity of the powdered sample of $NiPc(AsF_6)_{0.5}$. As shown in Fig. 6, the resistivity steeply decreased due to the decrease of the contact resistance between the powder particles, gently decreased from 3 GPa to 7.4 GPa, and reverted to the original value with a hysteresis. At 7.1 GPa, the optical experiment suggests that all of the π-holes seem to move into the d-band.[2] If the d-holes are still localized, $NiPc(AsF_6)_{0.5}$ will become an insulator and should show an upturn in the resistivity curve. At this pressure,

therefore, the d-holes are probably delocalized and contribute to the electrical conductivity. Further study in the high-pressure region is interesting.
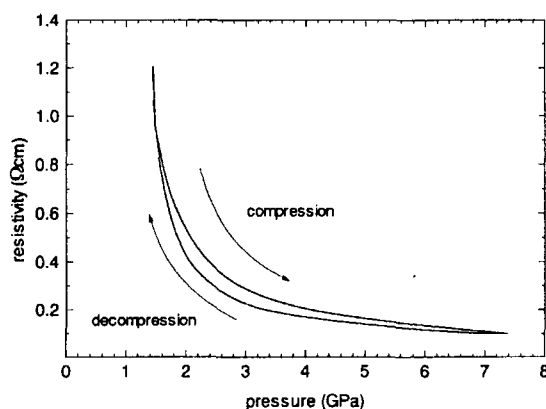

FIGURE 6   Pressure dependence of the room-temperature electrical resistivity of the powdered sample of $NiPc(AsF_6)_{0.5}$.

DEDICATION

This paper is dedicated to Professor Yusei Maruyama and Professor Fumio Ogura on the occasion of their retirement from the positions of the Professor of Innstitute for Molecular Science (Y.M.) and of the Professor of Hiroshima University (F.O.) who have made great scientific contributions to the field of organic conductors.

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