New Low-Dimensional Molecular Metals: Single-Crystal Electrical Conductivity of Nickel Phthalocyanine Iodide

Abstract. *Single crystals of* $NiPcI_{1.0}$ *(Pc = phthalocyanine), which are composed of one-dimensional stacks of* $(NiPc)^{+0.33}$ *molecules and chains of* I_3^- *molecules, exhibit metallic electrical conductivity in the stacking direction. At room temperature the mean free path of the carrier is 3.3 to 8.2 angstroms.*

Because of their highly anisotropic and sometimes spectacular electrical, magnetic, and optical characteristics, molecular materials with strongly one-dimensional interactions are of great current interest to chemists and physicists (*1-4*). As part of our efforts to obtain a better understanding of, and chemical control over, the fundamental properties of such materials, we recently synthesized an extensive new class of highly conductive molecular solids, containing stacks of metallophthalocyanine (MPc) molecules (Fig. 1A) (*5*). These were made by a preparative procedure which utilizes iodine oxidation to produce lattices composed of one-dimensional arrays of planar donor molecules (in this case MPc units) with fractionally occupied electronic valence shells ("partial oxidation" or "mixed valence") and chains of polyiodide counterions (*5-11*). The general structural pattern of such lattices is shown schematically in Fig. 1B.

Our initial studies of the partially oxidized phthalocyanines revealed a greater chemical flexibility in terms of metal-ion constituents and range of stoichiometries than in any previously reported class of conductive molecular materials. The electrical conductivities of pressed microcrystalline powder samples were comparable to those of other molecular metals (*1-4*), and we predicted that single-crystal conductivities would be metal-like in the MPc stacking direction. We report here the synthesis and physical properties of single crystals of one member of this new series of highly conductive compounds: $NiPcI_{1.0}$. Our earlier predictions (*5*) about such materials have been confirmed. At room temperature the mobilities of the individual charge carriers in $NiPcI_{1.0}$, expressed as the mean free path, are comparable to or greater than those of any previously known stacked molecular conductor (*1-4*) and the temperature dependence of the electrical conductivity is indeed metallic.

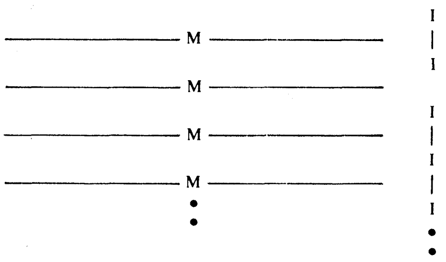

Fig. 1. (A) The molecular structure of a metal phthalocyanine. (B) Schematic representation of the crystal structure of $NiPcI_{1.0}$ and similar materials. This view is perpendicular to the stacking direction.

We prepared needlelike crystals of $NiPcI_{1.0}$, exhibiting a silver-gold metallic luster in reflection, by slowly diffusing together solutions of I_2 and sublimed NiPc (*10*). The resonance Raman spectrum of the crystals with 5145-Å Ar^+ excitation exhibits the characteristic symmetric stretching fundamentals of I_3^- at a frequency $\nu = 107\ cm^{-1}$ along with the expected $n\nu$ ($n = 2, 3, 4, 5 \ldots$) overtone progression (*5, 6, 11*). These data confirm the partially oxidized formulation $NiPc(I_3^-)_{0.33}$ (Fig. 1B). Single-crystal electron paramagnetic resonance studies of $NiPcI_{1.0}$ provide evidence that the partial oxidation is predominantly ligand-centered rather than metal ion-centered (*10*). Further metrical details of the crystal structure, based on single-crystal x-ray diffraction and diffuse scattering measurements, will be presented elsewhere (*10*).

Figure 2 presents typical electrical conductivity data, $\sigma_{\|}(T)$ [four-probe, phase-locked, 27-Hz a-c apparatus (*12*)], for $NiPcI_{1.0}$ along the NiPc stacking direction (crystallographic *c*-axis). At room temperature, conductivities in the range 250 to 650 $ohm^{-1}\ cm^{-1}$ are observed. These values are comparable to those for the "organic metal" tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) (*1-4, 13*). However, because of the very large cross-sectional area of the NiPc molecules, when comparing $NiPcI_{1.0}$ to other materials, it is important to consider the properties of the individual charge carriers (*8*). Within the framework of one-electron band theory (*3, 14*), the conductivity can be related to λ, the mean free path of a carrier along the stacking direction (the average distance traveled between scattering events) and to A, the cross-sectional area per conducting stack, by the equation

$$\sigma_{\|} = \frac{2e^2\lambda}{\pi\hbar A} \tag{1}$$

where e is the electronic charge and $\hbar$ is Planck's constant divided by 2π. For $NiPcI_{1.0}$ at room temperature, we find λ to be in the range 3.3 to 8.2 Å or 1.0 to 2.3 intermolecular spacings. This result can be compared to values for other highly conductive stacked molecular systems of 2.1 to 2.8 spacings for TTT_2I_3 (TTT = tetrathiatetracene) (*15*), 1.6 to 2.5 spacings for HMTSF-TCNQ (HMTSF = hexamethylenetetraselenafulvalenium) (*16*), 0.4 to 0.6 spacing for TTF-TCNQ (*13*), ~ 0.6 spacing for $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$ (*2*), ~ 0.15 spacing for Qn $(TCNQ)_2$ (Qn = quinolinium) (*17*), and ~ 0.06 spacing for the related macrocyclic system Ni(octamethyltetrabenzporphyrin)$I_{1.0}$ (*8, 9*). The mean free path for the most highly conductive $NiPcI_{1.0}$ crystals, however, is less than that in nickel metal, ~ 60 Å or about 24 interatomic spacings (*18*).

Figure 2 shows that as the temperature is decreased from ambient values the conductivity is metallic, increasing with decreasing temperature until a maximum is reached at a temperature $T_m \approx 90°K$ which varies somewhat from crystal to crystal. At T_m calculated values of λ are in the range 4 to 9 spacings which may be compared with a λ of 10 to 15 spacings for TTF-TCNQ at its temperature of maximum conductivity (60°K). For

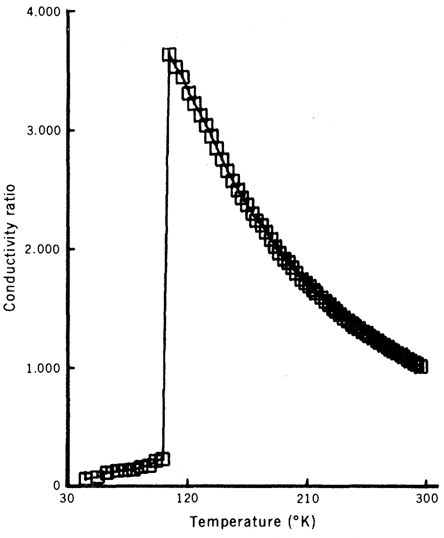

Fig. 2. Plot of the conductivity ratio, $\sigma_{\|}(T)/\sigma_{\|}(295°K)$, versus temperature T for a typical crystal of $NiPcI_{1.0}$ in which $\sigma_{\|}(295°K)$ is 350 $ohm^{-1}\ cm^{-1}$.

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$T > T_m$ there is no hysteresis in the conductivity-temperature curves, and $\sigma_{\|}(T)$ obeys the relationship (*1, 3, 15, 16*)

$$1/\sigma_{\|}(T) = a + bT^{\gamma} \tag{2}$$

where a and b are constants. For all crystals examined, a least-squares fitting to Eq. 2 yields $\gamma = 1.9 \pm 0.1$, and a plot of $\log\{1 - [\sigma(295°\mathrm{K})/\sigma(T)]\}$ versus T yields a superimposable family of curves; this result has been shown to provide assurance of the reliability of the measurements and of a well-defined scattering mechanism (*15*). The value of γ obtained is distinctly different from the value $\gamma = 1$ found for simple metals and is similar to that found for several other molecular metals, 2.0 to 2.4 (*15, 16*).

Upon cooling below T_m the conductivity abruptly decreases and then continues to slowly decrease with further cooling (Fig. 2). This behavior suggests that a Peierls transition (*1-4*) or a first-order phase transition is taking place. Raman spectral studies down to 4°K do indicate that the lattice charge distribution, that is, the average degree of partial oxidation of NiPc, remains unaltered through this transition. Pronounced hysteresis in d-c conductivity observed upon passage through T_m is suggestive of contributions from stress at the contacts, and microwave conductivity studies in collaboration with T. Poehler suggest that the transition occurs at lower temperatures in unstressed crystals.

Thus, the temperature dependence of the conductivity of $\mathrm{NiPcI}_{1.0}$ is metal-like, and the mean free path at room temperature compares favorably with that of the most highly conductive materials composed of molecular stacks. This study and related work (*8*) confirm the idea that the partial oxidation of metallomacrocyclic systems is a chemically versatile synthetic route to a wide array of new molecular metals.

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Periodicity and Chaos in Coupled Nonlinear Oscillators

Abstract. *A system of coupled tunnel diode relaxation oscillators shows a variety of complex periodic states as the external voltage is varied. The existence of chaotic or nonperiodic states is more dependent on the nature of the coupling than on the number of degrees of freedom. A simple but accurate numerical model shows many of the phenomena observed experimentally.*

Nonlinear models of physical and biological systems sometimes show nonperiodic time evolution even though they involve only a few degrees of freedom (dynamical variables) (*1*). This phenomenon has been noted in models of fluid motion (*2*), populations (*3*), physiological control systems (*4*), ion motion in electric and magnetic fields (*5*), and geomagnetism (*6*). A number of investigators have suggested that the onset of turbulence in fluids and the behavior of other complicated systems might be understandable in terms of models having far fewer variables than the systems they represent (*7*). However, this hypothesis has proved exceedingly hard to test because of the difficulty of using experimental data to generate or test models in systems with many degrees of freedom. In response to a suggestion by R. Landauer, we have studied a system of coupled electronic relaxation oscillators (*8*) which has particular advantages for efforts to understand the conditions under which a dissipative dynamical system can exhibit nonperiodic behavior.

For a certain type of coupling (see below), we find experimentally that a two- or three-oscillator system frequently has an apparently erratic time dependence. However, phase space diagrams and high-resolution frequency spectra of the diode voltages show convincingly that there is usually a single time (often quite long as compared to the natural frequencies of oscillation) over which the oscillators are periodic. We observe numerous transitions between different dynamical regimes as the (time-independent) applied voltage is varied. Using a simple mathematical model of the experiment, we have made accurate numerical computations which are in agreement with these experimental observations. Furthermore, a second coupling scheme transforms the system into one that does show regimes with intrinsic broadband noise and trajectories uniformly filling a region of the phase space.

The systems we have studied consist of tunnel diode relaxation oscillators which are resistively coupled, as shown in Fig. 1A. The tunnel diodes (TD_1 and TD_2) (1N3720) are hysteretic devices with the following properties. As the diode current increases, the voltage across it remains low (less than 0.15 V) until the current exceeds 22 mA, when the voltage rises suddenly to about 0.55 V. If the current now declines, the voltage hardly changes until the current reaches 3 mA, at which point the voltage drops essentially to zero. A tunnel diode in series with a d-c voltage source and inductor will oscillate spontaneously if the d-c load line intersects only the negative resistance region of the current-voltage characteristic. The frequency of oscillation is determined roughly by the ratio of resistance to inductance of the circuit. The voltage wave form is essentially rectangular (Fig. 1B), whereas the current is composed of exponential curves.

Several of these oscillators, with different natural frequencies, may be coupled together in different ways. The resistor R (Fig. 1A) provides such a coupling, because the voltage applied to one oscillator depends on the current being drawn by the others. Alternately (or in addition), a cross resistor R_c joining the two diodes directly may be used. In this case the current through a diode depends not only on the current through its inductor but also on the relative values of the voltages V_1 and V_2.