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NEW LOW-DIMENSIONAL MOLECULAR METALS: SINGLE CRYSTAL ELECTRICAL--ETC(U)
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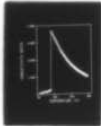
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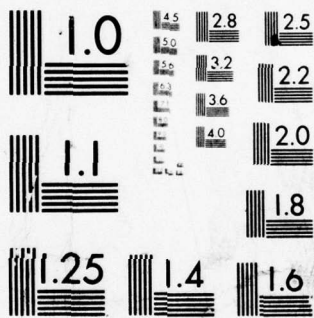
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Single Crystal Electrical Conductivity of Nickel Phthalocyanine Iodide,

by

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C.J. / Schramm,
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B.M. / Hoffman
T.J. / Marks

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NEW LOW-DIMENSIONAL MOLECULAR METALS: SINGLE CRYSTAL
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Abstract

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

The highly anisotropic and sometimes spectacular electrical, magnetic, and optical characteristics of molecular materials with strongly one-dimensional interactions have made them of great current interest to chemists and physicists (1-5). 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 (Figure 1A) (6). These were made via a preparative procedure which utilizes iodine oxidation to afford 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 (6-13). The general structural pattern of such lattices is schematized in Figure 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. Electrical conductivities of pressed microcrystalline powder samples were comparable to those of other "molecular metals" (1-5), and we predicted that single crystal conductivities would be metal-like in the MPc stacking direction. We here report the synthesis and physical properties of single crystals of one member of this new series of highly conductive compounds: $\text{NiPcI}_{1.0}$. The earlier predictions about such materials

are confirmed: At room temperature the mobilities of the individual charge carriers in $\text{NiPcI}_{1.0}$, expressed as the mean free path, are comparable to or greater than any previously known stacked molecular conductor (1-5) and the temperature dependence of the electrical conductivity is indeed metallic.

Needle-like crystals of $\text{NiPcI}_{1.0}$, exhibiting a silver-gold metallic lustre in reflection, were prepared by slowly diffusing together solutions of I_2 and sublimed NiPc (12). The resonance Raman spectrum of the crystals with 5145 \AA Ar^+ excitation exhibits the characteristic symmetric stretching fundamentals of I_3^- at $\nu = 107 \text{ cm}^{-1}$ along with the expected $n\nu$ ($n = 2, 3, 4, 5, \dots$) overtone progression (6, 7, 14). These data confirm the partially oxidized formulation $\text{NiPc}(\text{I}_3^-)_{\frac{1}{3}}$ shown in Figure 1b. Single crystal electron paramagnetic resonance studies of $\text{NiPcI}_{1.0}$ provide evidence that the partial oxidation is predominantly ligand-centered, rather than metal-ion centered (12). Further metrical details of the crystal structure, provided by single crystal X-ray diffraction and diffuse scattering measurements, will be presented elsewhere (12).

Figure 2 presents typical electrical conductivity data, $\sigma_{||}(T)$, data (four-probe, phase-locked 27 Hz. ac apparatus (15)) for $\text{NiPcI}_{1.0}$ along the NiPc stacking direction (crystallographic c -axis). At room temperature, conductivities in the range $250\text{-}650 \text{ ohm}^{-1} \text{ cm}^{-1}$ are observed. These values are comparable to those for the well known "organic metal" TTF-TCNQ (1-5, 16). However, because of the very large cross-sectional area of the NiPc molecules, when

comparing $\text{NiPcI}_{1.0}$ to other materials, it is important to consider the properties of the individual charge carriers (10). Within the framework of one-electron band theory (3, 17), the conductivity can be related to λ , the mean free path of a carrier along the stacking direction (the average distance travelled between scattering events) and to A , the cross-sectional area per conducting stack, by the equation

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

For $\text{NiPcI}_{1.0}$ at room temperature, we find values for λ to be in the range 3.3-8.2 Å or 1.0-2.3 intermolecular spacings. This result can be compared to values in other highly conductive stacked molecular systems of 2.1-2.8 spacings for TTT_2I_3 (18), 1.6-2.5 spacings for HMTSF-TCNQ (19), 0.4-0.6 spacings for TTF-TCNQ (16), ~0.6 spacings for $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3} \cdot 3\text{H}_2\text{O}$ (2) ~ 0.15 spacings for Qn (TCNQ)₂ (20) and ~0.06 spacings for the related macrocyclic system Ni(octamethyltetrabenzporphyrin)I_{1.0} (10, 11). The mean free path for the most highly conductive $\text{NiPcI}_{1.0}$ crystals still, however, is less than that in Ni metal, ca. 60 Å or ca. 26 interatomic spacings (21).

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 $T_m \approx 90^\circ\text{K}$ which varies somewhat from crystal to crystal. At the maximum, calculated values of λ are in the range 4-9 spacings which may be compared with λ of 10-15 spacings for TTF-TCNQ at its temperature of maximum conductivity (60°K).

For $T > T_m$ there is no hysteresis in the conduc-

tivity- temperature curves and $\sigma_{||}(T)$ obeys the relationship (1, 3, 18, 19)

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

For all crystals examined, a least-squares fitting to equation (2) yields $\gamma = 1.9 \pm 0.1$ and a plot of $\log[1 - (\sigma(295\text{ K})/\sigma(T))]$ versus T yields a superimposable family of curves; this has been shown to provide assurance of the reliability of the measurements and of a well-defined scattering mechanism (18). 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 - 2.4 (18, 19).

Upon cooling below T_m the conductivity abruptly decreases and then continues to slowly decrease with further cooling (Figure 2). This behavior suggests an interpretation in terms of a Peierls transition (1-5) or a first-order phase transition. Raman spectral studies down to 4°K do indicate that the lattice charge distribution, i. e., the average degree of NiPc partial oxidation, remains unaltered through this transition. Pronounced hysteresis in dc conductivity observed upon passage through T_m is suggestive of contributions from stress at the contacts, and indeed microwave conductivity studies in collaboration with Prof. T. Poehler suggest that the transition is at lower temperatures in unstressed crystals.

Thus, the temperature dependence of the conductivity of $\text{NiPcI}_{1.0}$ is metal-like and the room temperature mean free path compares favorably with that of the most highly conductive materials composed of molecular stacks. On a broader plane, this study and related

work (10) confirm the idea that the partial oxidation of metallomacrocycles is a chemically versatile synthetic route to a wide array of new molecular metals.

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References and Notes

1. H. J. Keller, ed., "Chemistry and Physics of One-dimensional Metals," Plenum Press, New York, 1977.
2. J.S. Miller and A.J. Epstein, Prog. Inorg. Chem., 20, 1 (1976).
3. A.J. Berlinsky, Contemp. Phys., 17, 331 (1976).
4. Z.G. Soos and D.J. Klein in "Molecular Associations," R. Foster, ed., Academic Press, New York, 1975, Chapter 1.
5. W.D. Metz, Science, 190, 450 (1975).
6. J.L. Peterson, C.J. Schramm, B.M. Hoffman, and T.J. Marks, J. Amer. Chem. Soc., 99, 286 (1977).
7. T.J. Marks, Ann. N.Y. Acad. Sci., in press.
8. A. Gleizes, T.J. Marks, and J.A. Ibers, J. Amer. Chem. Soc., 97, 3545 (1975).
9. M.A. Cowie A. Gleizes, G.W. Grynkewich, D.W. Kalina, M.S. McClure, R.P. Scaringe, R.C. Teitelbaum, S.L. Ruby, J.A. Ibers, C.R. Kannewurf, and T.J. Marks, submitted for publication.
10. T.E. Phillips and B.M. Hoffman, J. Amer. Chem. Soc., 99, 7734(1977).
11. T.E. Phillips, R.P. Scaringe, B.M. Hoffman, and J.A. Ibers, manuscript in preparation.
12. C.J. Schramm, R.P. Scaringe, D.R. Stojakovic, B.M. Hoffman, T.J. Marks, and J.A. Ibers, manuscript in preparation.
13. T.J. Marks, D.F. Webster, S.L. Ruby, and S. Schultz, J. Chem. Soc., Chem. Comm., 444 (1976).

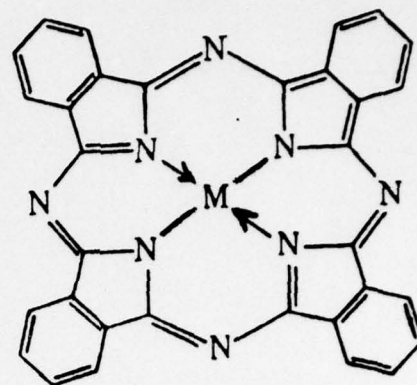
14. D.W. Kalina, D.R. Stojakovic, R.C. Teitelbaum, and T.J. Marks, manuscript in preparation.
15. T.E. Phillips, J.R. Anderson, and B.M. Hoffman, manuscript in preparation. Measurements were made with the precautions suggested in, D.E. Schafer, F. Wudl, G.A. Thomas, J.P. Ferraris, and D.O. Cowan, Solid State Commun., 14, 347 (1974).
16. G.A. Thomas, et. al., Phys. Rev., B, 13, 5105 (1976).
17. N.F. Mott and E.A. Davis, "Electronic Processes in Noncrystalline Materials," Clarendon Press, Oxford, 1971.
18. L.C. Isett and E.A. Perez-Albuerne, Solid State Commun., 21, 433 (1977).
TTT = tetrathiotetracene.
19. A.N. Bloch, D.O. Cowan, K. Beckgaard, R.E. Pyle, R.H. Bands, and T.O. Poehler, Phys. Rev. Lett., 34, 1561 (1975).
20. V. Walatka, Jr., and J.H. Perlstein, Mol. Cryst. Liq. Cryst., 15, 269 (1971). Qn = quinolinium.
21. CRC Handbook of Chemistry and Physics, 58th ed., CRC Press, Inc., Cleveland, 1977, p. F-170.
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Figure Captions

Fig. 1A. The molecular structure of a metal phthalocyanine. B. Schematic representation of the crystal structure of $\text{NiPcI}_{1.0}$ and similar materials. The view is perpendicular to the stacking direction.

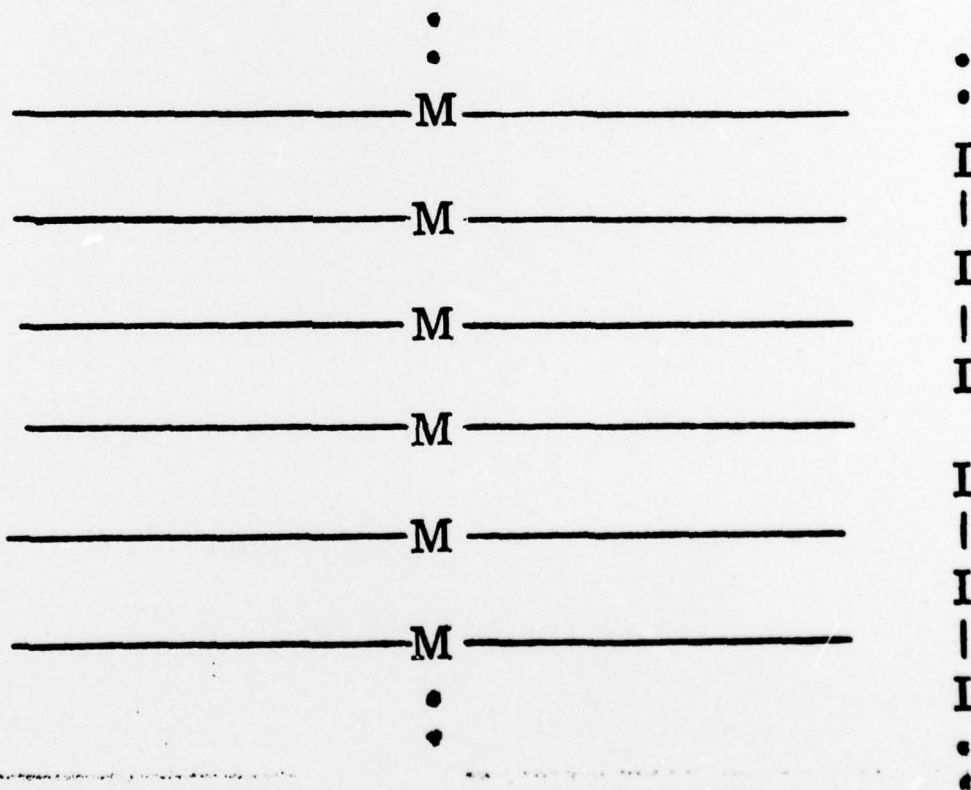
Fig. 2. Plot of the conductivity ratio, $\sigma_{||}(T)/\sigma_{||}(295\text{K})$, versus temperature for a typical crystal of $\text{NiPcI}_{1.0}$ in which $\sigma_{||}(295\text{K}) = 350 (\Omega \text{ cm})^{-1}$.

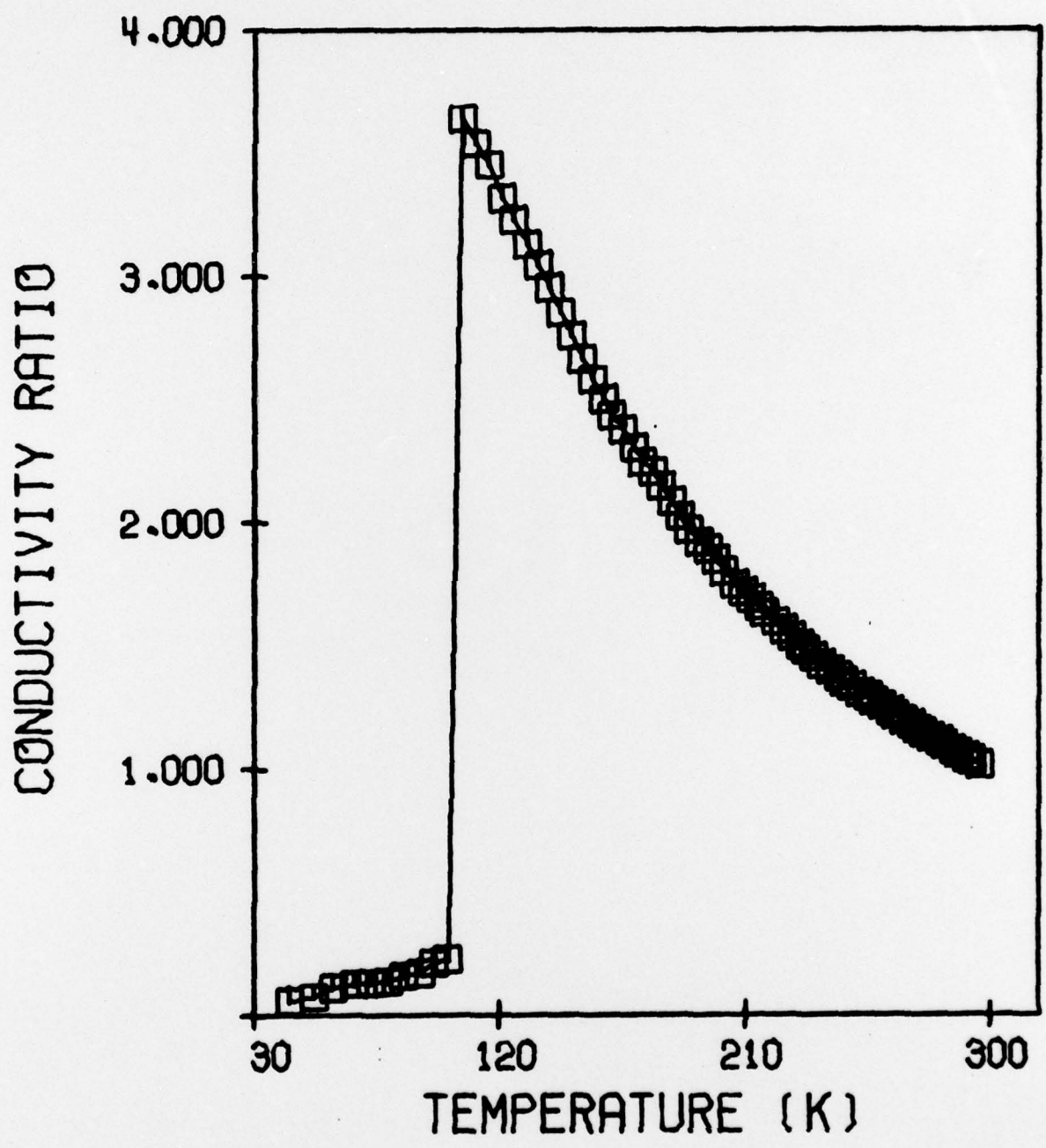
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