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Nickel phthalocyanine iodide: A highly-one-dimensional low-temperature molecular metal

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The conductivity of the linear-chain molecular-metal phthalocyanatonickel(II)iodide [Ni(pc)I] remains metallic down to ~ 30 K, goes through a weak maximum, and then levels off to a high asymptotic ($T \rightarrow 0$) value that varies from $\frac{1}{2}$ to 2 times the value at room temperature ($\sim 500\ \Omega^{-1}\,\text{cm}^{-1}$). The full characterization of this compound, reported here, includes a thermoelectric power linearly proportional to T, a Pauli-like static and EPR magnetic susceptibility, and single-crystal reflectivity spectra exhibiting a plasma edge for light polarized parallel to the conducting axis. The results confirm that this compound possesses all the characteristics of molecular metal that retains a metallic band structure down to a temperature below 2 K. However, Ni(pc)I does not possess any strong interstack interactions of the type necessary to suppress a Peierls metal-nonmetal transition via an increase in the dimensionality, and should be classified as one of the most one-dimensional molecular metals studied to date. A structurally imposed weakening of the interstack Coulomb interactions, coupled with weak random potentials from structurally disordered triiodide chains, is apparently sufficient to suppress the three-dimensional transition normally associated with the tendency of an anisotropic conductor to undergo a Peierls distortion.

I. INTRODUCTION

In a variety of linear-chain molecular conductors, it has been found that the metallic state is destroyed by the onset of a three-dimensional metal-nonmetal transition driven by the Peierls instability of a one-dimensional metal.[1] Although the electronic band structure in these materials is highly anisotropic, there nevertheless exist sufficient Coulombic interchain interactions to support such a transition.[2] When the interchain interaction is increased, as in molecular crystals such as tetramethyltetraselenafulvalenium salts, $(\text{TNTSeF})_2X$, which exhibit strong chalcogen-mediated interstack interactions,[3] these compounds may exhibit novel low-temperature phases ranging from spin-density-wave ground states[4] to ambient-pressure superconductivity.[5] Such materials are no longer quasi one dimensional, and a Peierls instability is suppressed by the chalcogen-mediated interstack interactions.[6] Indeed, in materials such as tetrathiafulvalene-bis-cis-(1,2-perfluoromethylethylene-1,2-dithiolato salts) $(\text{BEDT-TTF})_2X$ electronic coupling perpendicular to the stacking axis may be stronger than the interactions along that axis,[7] and thus the system more accurately described as a quasi-two-dimensional molecular metal.

Recently, we have shown that the conductivity of the molecular metal phthalocyanatonickel(II)iodide [Ni(pc)I] (Refs. 8—10) remains metallic down to ~ 30 K, goes through a weak maximum, and then levels off to a high asymptotic ($T \rightarrow 0$) value that varies from $\frac{1}{2}$ to 2 times the value at room temperature.[11] The full characterization of this compound, reported here, including thermoelectric power, magnetic susceptibility, EPR, and single-crystal reflectivity, confirms that this compound possesses all the characteristics of a molecular metal that retains a metallic band structure down to a temperature below 2 K. However, Ni(pc)I does not possess any chalcogen-mediated nor, indeed, any apparent strong interstack interactions of the type necessary to suppress a

Peierls metal-nonmetal transition via an increase in the dimensionality. Instead, the present results indicate that the size and electronic structure of the molecular subunits lead to highly-one-dimensional interactions along stacks with a large effective spatial segregation. The resultant weakening of the interstack Coulomb interactions coupled with the weak random potentials of the structurally disordered tri-iodide chains is sufficient to suppress the three-dimensional transition normally associated with tendency of an anisotropic conductor to undergo a Peierls distortion. Thus, Ni(pc)I should be classified as one of the most one-dimensional molecular metals studied to date.

II. EXPERIMENTAL DETAILS

A. Preparation of Ni(pc)I

Ni(pc)I was purchased from Eastman Kodak and sublimed prior to use. Iodine was obtained from Mallinckrodt and used without further purification. Batches of shiny green needles of Ni(pc)I were grown using procedures previously outlined.[10] A routine check of stoichiometry (Micro-Tech Laboratories, Inc.) across a number of batches prepared under different conditions gave the composition Ni(pc)$I_{1.00(3)}$. This supports the conclusion from thermodynamic studies that Ni(pc)$I_{1.0}$ is a line phase,[12] and there are no crystalline materials having iodine stoichiometries slightly greater than 1.0, such as the superstoichiometric, bic(tetrathiatetracene) tri-iodides, $TTT_2I_{3+\delta}$.[13]

B. Single-crystal polarized reflectivity spectra

Room-temperature single-crystal polarized reflectivity spectra were recorded for Ni(pc)$I_{1.0}$, both along the highly conducting crystal axis and perpendicular to it, using a microspectrophotometer consisting of a Carl-Zeiss double monochromator, tungsten and xenon lamps as sources, a microscope with quartz or reflecting lenses, and a detecting system utilizing a photomultiplier tube (Hamamatsu TV Co., Ltd. F928) and PbS or InSb ir detectors (Santa Barbara Research Center). The monochromatic light was polarized using an MgFe polarizer. Absolute reflectivities were calibrated using a SiC-crystal standard. The reflectance spectra were recorded between 2.5 and 25 kK; the small crystal dimensions ($1\times0.03\times0.03$ mm^3), as well as surface features, preclude lower energy measurements.

C. Charge-transport measurements

Crystals were mounted with great care on silvered graphite fibers as described previously. Measurements at temperatures between 400 and 20 K employed an ac apparatus described earlier,[14] a frequency of 27 Hz, and a crystal sampling current of 10 μA. However, no differences were observed for frequency variations from 10 Hz to 3 KHz. Ohmicity was verified in the crystal current range of 1 μA to 10 mA. Contact integrity was confirmed by the lead-interchange technique. The lock-in phase was monitored over the full temperature range and found to vary less than 2° (the detection limit). The temperature variation was achieved by placing the sample in a cold gas stream (N_2 or He). Data for temperatures below 20 K were recorded with the sample mounted in an S.H.E. Corporation dilution refrigerator. The magnetoresistivity was measured transverse to the conducting axis up to a 50-kG field at 4.2 K.

Thermoelectric-power (TEP) measurements along the highly conducting axis between 20 and 300 K were obtained using an apparatus described previously.[15] Temperature variability was accomplished by placing the copper thermal block in an Air Products LTD-3 Helitran. A slow, sinusoidal thermal-cycling technique was used with a maximum temperature gradient across the sample of 0.5 K.

D. Electron-paramagnetic-resonance measurements

EPR spectra at about 9 GHz were obtained on a modified Varian Associates E-4 spectrometer interfaced to a 9-in. magnet (Varian Associates model no. 2500). EPR-intensity measurements were obtained from numerical double integrations performed on a Fabritek model 1074 instrument computer. Absolute EPR intensities absorption at room temperature of a known amount of 2,2-phenyl-1-picrylhydrazine (DPPH, $g=2.0036$ and $n=0.89$ spins per molecule).[16] Temperatures above 4.2 K were obtained with an Air Products LTD-3 Helitran. Systematic errors that might be introduced by, say, variation in spectrometer sensitivity caused by cooling of the quartz insert and/or cavity, were avoided by comparing the integrated signal strength of Ni(pc)I with that of the DPPH reference at the same temperature. The temperature range 2.1—4.2 K was accessed by placing the sample in liquid helium and varying the vapor pressure above the liquid.

E. Magnetic-susceptibility measurements

Static magnetic susceptibilities were measured from 1.7 to 300 K using a S.H.E. Corporation model VTS-10 superconducting quantum-interference device (SQUID) susceptometer. The standard Si-Al alloy "bucket" supplied with the instrument exhibited a background signal $\sim$20 times larger than the signal for a typical sample of Ni(pc)I. Therefore, buckets made of high-purity Spectrosil quartz (Thermal American, Inc.) were employed. The background was run over the full temperature range just prior to running the sample, and then checked at a few temperatures after the sample was run. The instrument calibration was routinely checked with $HgCo(SCN)_4$ as a standard and found to match the reported value[17] to within 0.2%. Although field-dependence studies showed no significant deviations up to 50 kG at various temperatures, the measurements were routinely done at 5 or 15 kG. Sample sizes varied from 15 to 40 mg, with $\sim$30 mg being the average size.

III. RESULTS

A. Single-crystal polarized reflectivity measurements

The polarized room-temperature reflectance spectra of Ni(pc)I are shown in Fig. 1. With the electric field vector oriented perpendicular to the highly conducting chain ($\hat{c}$

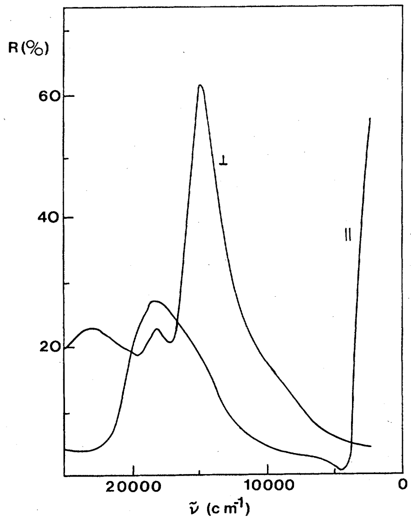

FIG. 1. Room-temperature polarized reflectance spectrum of a single crystal of Ni(pc)I. The perpendicular (⊥) orientation has the electric field polarized perpendicular to the highly conducting stacking axis, while the parallel (||) orientation has the electric field polarized along the stack axis.

axis) direction, peaks are observed at 23, 18, and 15 kK; these are readily assigned to the inplane $\pi_g^* \leftarrow \pi_u$ transitions of the phthalocyanine π system.[18] At low frequency the reflectivity is quite small and exhibits no features attributable to intraband transitions. In the spectrum taken with light polarized parallel to the axis of conductivity, there is a strong peak at 18.5 kK, which can be assigned to a $\sigma_u^* \leftarrow \sigma_g$ transition to the tri-iodide chain.[19] More importantly, the infrared region is characterized by a particularly sharp plasma edge beginning at $\sim$4.5 kK. The occurrence of this feature in parallel polarization and its absence in perpendicular polarization confirms the picture of this material as a quasi-one-dimensional conductor, with conduction along the Ni(pc) stacks.

The dielectric response function $\epsilon(\omega)$ for a Drude metal (ignoring interband transitions) is given by the expression[20]

$$\epsilon(\omega)=\epsilon_{\rm core}-\frac{\omega_p^2}{\omega^2-i\omega/\tau}\equiv\epsilon_1+i\epsilon_2 \ , \qquad (1)$$

where

$$\omega_p^2=\frac{4\pi Ne^2}{m^*} \ , \qquad (2)$$

$\epsilon_{\rm core}$ is the residual dielectric constant at high frequency arising from core polarizability, τ is the electronic relaxation time, ω_p is the plasma frequency,

$$N=(2-\rho)/[(\hat{a}\times\hat{b}\times\hat{c})/2]$$

is the conduction-band electron density, and m^* is the anisotropic optical effective mass. The reflectance is given in terms of the real and imaginary parts of ϵ by[21]

$$R=\frac{1+|\epsilon|-[2(|\epsilon|+\epsilon_1)]^{1/2}}{1+|\epsilon|+[2(|\epsilon|+\epsilon_1)]^{1/2}} \ , \qquad (3)$$

where

$$|\epsilon|=(\epsilon_1^2+\epsilon_2^2)^{1/2} \ .$$

Fitting the parallel polarized data in Fig. 1 to Eq. (3) yields the parameters $\omega_p=5042$ cm^{-1} (0.625 eV), $\tau=6.84\times10^{-15}$ sec, and $\epsilon_{\rm core}=2.04$. Values derived in recent reflectance measurements employing pressed pellets are in surprisingly good agreement with these results.[22]

Band-structure and transport parameters may be calculated from these reflectance parameters. The effective carrier mass is obtained from Eq. (2), using $N=2.6\times10^{21}$ cm^{-3} calculated from the x-ray data: $m^*=9.3m_e$, where m_e is the free-electron mass. The one-dimensional tight-binding bandwidth $4t$ is evaluated from the expression[23]

$$t=(\omega_p\hbar)^2/16ne^2a^2\sin(\rho\pi/2) \ , \qquad (4)$$

where $n=1.63\times10^{-21}$ cm^{-3} is the volume density of molecules and $a=3.24$ Å is the lattice spacing along the highly conducting, crystallographic $\hat{c}$ axis: $4t=0.84$ eV.

The optical dc conductivity $\sigma_{\rm opt}$ can also be obtained from the fit parameters of Eq. (3) via the expression[20]

$$\sigma_{\rm opt}=\omega_p^2\tau/4\pi \ . \qquad (5)$$

The calculated value of $\sigma_{\rm opt}=550$ Ω^{-1}cm^{-1} compares very well with the experimental four-probe—conductivity values of $\sim$550 Ω^{-1}cm^{-1} (*vide infra*),[10] suggesting that the same scattering process dominates the optical as well as the dc conductivities. Further evidence for this is gained by comparing the electron-phonon interaction at dc and optical frequencies. Hopfield has obtained an expression for the total phonon scattering rate at optical frequencies,[24]

$$\tau^{-1}=\lambda_1(2\pi k_B/\hbar)(T+T_\Theta) \ , \qquad (6)$$

where λ_1 is a dimensionless electron-phonon—coupling constant and T_Θ is the Debye temperature. For $T>T_\Theta$ (as is usually the case at room temperature), this becomes

$$\lambda_1=\hbar/2\pi k_B T\tau \ . \qquad (7)$$

For Ni(pc)I at room temperature, this equation gives $\lambda_1=0.6$, comparable to that reported for tetrathiafulvalenium tetracyanoquinodimethane (TTF-TCNQ) (Ref. 25) ($\lambda_1=1.3$). In both cases, λ_1 is larger than typical values for "good" metals such as copper ($\lambda_1=0.1$) and sodium ($\lambda_1=0.11$),[20] suggesting that the charge carriers in Ni(pc)I (and TTF-TCNQ) are coupled rather strongly to the lattice.

An alternative expression for the electron-phonon coupling, which includes lifetime terms arising from impurities or surface scattering, involves the temperature variation of the dc resistivity ρ,[24]

$$\lambda_2=(\hbar\omega_p^2/2\pi k_B)(\partial\rho/\partial T) \ . \qquad (8)$$

The parameter λ_2 can be evaluated using a value of 9.0×10^{-6} Ω cm/K for $\partial\rho/\partial T$ (calculated from the fit of the resistivity[26]); the result is $\lambda_2=1.0$. The close agreement between λ_1 and λ_2 argues that, for room temperature at least, carrier scattering in Ni(pc)I is dominated by phonon contributions, with only a small term resulting from impurity and surface scattering. This is reasonable, since a short mean free path caused by strong phonon scattering would prevent the carriers from reaching impurities or the surface between scattering events. A complete exploration of this issue would require the temperature dependence of the reflectivity.

B. Ni(pc)I charge transport

A typical four-probe conductivity measurement on a single crystal of Ni(pc)I is shown in Fig. 2(a). As reported previously,[10] the room-temperature conductivity of Ni(pc)I is high, $\sigma \sim 550\ \Omega^{-1}\,\text{cm}^{-1}$. The conductivity shows a metallic rise ($d\sigma/dT<0$) throughout the entire temperature region displayed (390—20 K), without any sign of the metal-insulator transition. The resistivity ($\rho = 1/\sigma$) has been fitted, using a standard nonlinear least-squares routine,[27] to the expression

$$\rho(T)=\rho_0+\rho_1 T^{\gamma}\ , \tag{9}$$

resulting in $\rho_0=(3.2\pm0.2)\times10^{-4}\ \Omega\,\text{cm}$, $\rho_1=(8.9\pm0.2)\times10^{-8}\ \Omega\,\text{cm/K}^{\gamma}$, and $\gamma=1.72\pm0.04$ ($\chi^2=9\times10^{-11}$). The value of 1.7 for γ is larger than the value of unity expected for simple metals,[20] yet is it slightly lower than the values typically found in other organic molecular metals (2.0—3.0),[28] as well as in the previous reports on Ni(pc)I ($\gamma=1.90\pm0.02$).[10] Other samples of Ni(pc)I, measured over a more limited temperature range, show large variations in ρ_0 and ρ_1, but only modest variations in γ (1.65—1.75).

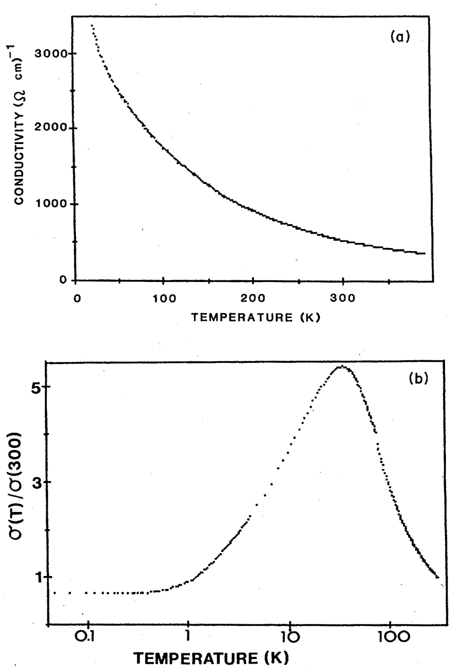

FIG. 2. (a) Temperature dependence of the needle-axis ($\hat{c}$ axis) conductivity of a Ni(pc)I crystal taken between 20 and 300 K. (b) Temperature dependence of the single-crystal needle-axis conductivity emphasizing the low-temperature behavior; the conductivity has been normalized to an ambient temperature value of about 450 $\Omega^{-1}\text{cm}^{-1}$.

Further investigation at lower temperatures in a dilution refrigerator was prompted by the absence of any phase transition in the conductivity down to 20 K. The conductivity, displayed in Fig. 2(b), is metallic upon cooling from room temperature, reaching a gentle maximum at $T_m \sim 20$—30 K with $\sigma(T_m)\sim 3000$—5000 $\Omega^{-1}\,\text{cm}^{-1}$. Both T_m and the relative conductivity vary somewhat from sample to sample; this variability, along with the monotonic increase of σ down to 20 K in Fig. 2(a), suggests that the maximum may not be fully intrinsic, but instead may result from residual stresses in the mount as well as from variations in crystal quality. Upon further cooling, the conductivity decreases gradually and then levels off. A high asymptotic ($T\to0$) conductivity (i.e., $d\sigma/dT=0$), varying with sample from 0.5 to 2 times the value at room temperatures, is fully achieved below about 1.5 K and persists down to 50 mK, the lowest attainable temperature, with no evidence of superconductivity.

In order to explore the nature of the observed conductivity maximum, transverse magnetoresistance measurements on Ni(pc)I were performed at 4.2 K. There is only a modest positive effect, $\Delta\rho/\rho\sim5\%$, in a 50-kG field. Although this measurement is only a preliminary to a complete temperature- and field-dependent study, it is instructive to compare this observation with results for other molecular conductors showing similar conductivity temperature dependencies. Systems such as N-ethylmorpholium-tetraselenafulvalenium tetracyanoquinodimethane[29] (HMTSeF-TCNQ) and some $(\text{TMTSeF})_2X$ salts[3] show large positive effects, $\Delta\rho/\rho>100\%$, below this conductivity maximum, with a high degree of anisotropy, indicative of a dimensionality crossover from a one-dimensional band structure to a two- [$(\text{TMTSeF})_2X$] or three- (HMTSeF-TCNQ) dimensional Fermi surface. Perhaps the most revealing comparison, however, is with $\text{TTT}_2\text{I}_{3+\delta}$.[30] Although a conductivity transition occurs at $\sim$100 K, there is no detectable magnetoresistance above 22 K. Below 22 K, a moderately large positive isotropic magnetoresistance has been observed ($\Delta\rho/\rho\sim13\%$ at $T=4.2$ K and $H=50$ kG).

Thermoelectric-power measurements[31] are useful in determining the sign of the predominant charge carriers as well as providing band parameters, and are very sensitive to any phenomenon causing a change in the density of states at the Fermi level. The temperature dependence of the Seebeck coefficient for a typical sample of Ni(pc)I is shown in Fig. 3. That S is positive throughout the entire temperature range 10—300 K, confirms the assignment of holes as the predominant charge carriers and the phthalocyanine stack as the conduction pathway. The temperature dependence exhibits two distinct linear regions, one between 300 and 60 K, and one between 60 and 9 K. This behavior is similar to that observed in the metallic range of the $(\text{TMTSeF})_2\text{ClO}_4$ thermoelectric-power temperature dependence.[32] These data show that there is no major change in the density of states at the Fermi energy, and, in particular, they give no indication that Ni(pc)I undergoes a metal-nonmetal transition within the range explored, $9\lesssim T\lesssim300$ K, thus indicating that the material is indeed metallic down to temperatures of at least 9 K. This, in turn, suggests that the peak in the electrical con-

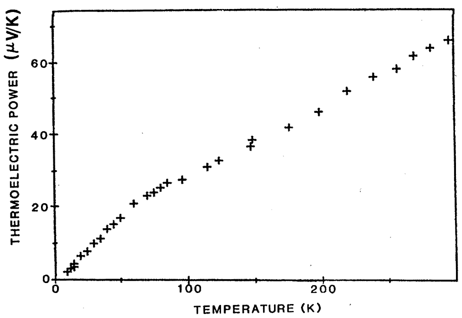

FIG. 3. Temperature dependence of the needle-axis thermoelectric power(s) of a Ni(pc)I crystal taken between 10 and 300 K.

ductivity at about 20—30 K is extrinsic, perhaps the consequence of residual stress in the crystal mount. The origin of the "bump" at 60 K is unknown, although it might be attributable to a phonon drag contribution to the thermopower.[33]

The high-temperature segment of the thermopower data does not exhibit the zero intercept expected for a metal; rather, the intercept ranges from 5 to 10 μV/K. Although no explanation exists for the source of this effect, it appears to be a general phenomenon in conductors containing I_3^- units, such as the various metallic M(pc)I species and $TTT_2I_{3+\delta}$.[13,30] However, when the thermopower plots do exhibit two segments (such as in Fig. 3), the low-temperature segment generally intercepts at zero.

Within the confines of the tight-binding band model, the thermoelectric power of a one-dimensional metal is given by[34]

$$S=-\{[\pi^2k_B^2\cos(\pi\nu/2)]/6\,|\,e\,|\,t\sin^2(\pi\nu/2)\}T\ , \quad (10)$$

where t is the transfer integral ($4t$ is the bandwidth), k_B is Boltzmann's constant, e is the electronic charge, and $\nu=2-\rho$ is the number of conduction electrons per site (ρ is the degree of oxidation). A linear least-squares analysis of the data in Fig. 3 for the temperature region $60<T<300$ K gives a value of $t=0.22(1)$ eV for the transfer integral, and thus a bandwidth of 0.88 eV. This result agrees well with the value of 0.84 eV obtained from the room-temperature optical reflectivity. The slope of the low-temperature segment in Fig. 3 ($10<T<60$ K) corresponds to a value $t=0.11(1)$ eV, and thus a bandwidth of 0.44 eV.

C. Ni(pc)I magnetic susceptibility

The static magnetic susceptibility of a typical polycrystalline sample of Ni(pc)I, measured between 1.7 and 300 K, can be fitted by adding a Curie-Weiss—law contribution[35] to a Pauli term,

$$\chi(T)=\chi_p+c'/(T-\Theta)\ . \quad (11)$$

The temperature-independent Pauli paramagnetism is found to be $\chi_p=1.93\times10^{-4}$ emu/mol, in excellent agreement with that recently reported,[22] and also with the value of 2.01×10^{-4} emu/mol obtained from EPR integrations (*vide infra*). The "impurity level" is found to vary from $\sim1\%$ to $\sim5\%$ depending on the sample used, and has been found to be introduced by subjecting the material to vacuum during the measurement itself. Presumably the impurity moments are formed on the surface as a result of loss of molecular iodine.

The difficulties associated with measurements of static susceptibility led us to perform absolute measurements of spin susceptibility by EPR integrations on a number of polycrystalline samples (6—10 mg). The room-temperature result, $\chi^s=(2.01\pm0.15)\times10^{-4}$ emu/mol (equivalent to 0.16 ± 0.01 spins per macrocycle at room temperature when $S=\frac{1}{2}$ and $g=2$), is in excellent agreement with the SQUID measurements. Results at lower temperatures confirm that χ^s is very nearly temperature independent down to 2 K: Numerical values at 77 K and $\chi^s=2.34(20)\times10^{-4}$ (average of four samples), and at 4.2 K and $\chi^s=2.7\times10^{-4}$ emu/mol (one sample), suggest, if anything, a modest ($<15\%$) rise.

Because the EPR results at 4.2 K give no indication of a Curie tail, χ^s was further measured between 4.2 and 2.1 K, Fig. 4, and was found to remain virtually temperature independent. The absence of any observable curvature in the low temperature plot of χ^s clearly shows that Ni(pc)I exhibits a Pauli-like susceptibility from 300 to well below 2 K. In general, when a highly conducting quasi-one-dimensional material exhibits a conductivity maximum upon cooling, the susceptibility is strongly temperature dependent below the maximum, behavior which manifests the opening of a gap at the Fermi surface. In contrast, for Ni(pc)I, the magnetic susceptibility, like the thermoelectric power, suggests that the density of states at the Fermi level remains metallic well below 2 K.

The Pauli paramagnetic susceptibility can be used to obtain a value for the bandwidth at absolute zero. The expression in the one-dimensional tight-binding band theory for the transfer integral t is[36]

$$t=N\beta^2/\chi_p\pi\sin(\pi\rho/2)\ , \quad (12)$$

where β is the Bohr magneton, N is Avogadro's number, and ρ is the degree of oxidation. Using the value of 1.93×10^{-4} emu/mol for χ_p and $\frac{1}{3}$ for ρ yields $t=0.11(4)$ eV, corresponding to a bandwidth of 0.44 eV, which agrees well with the value calculated from the low-

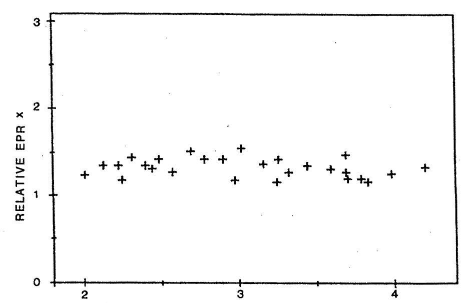

FIG. 4. Temperature dependence of the EPR magnetic susceptibility of a polycrystalline sample of Ni(pc)I between 4.2 and 2.1 K. The χ value is plotted relative to the value of 298 K.

temperature slope of the thermopower, and is in acceptable agreement with the optical measurements.

IV. EPR LINEWIDTH

In studies of molecular conductors, measurements of the carrier-spin EPR linewidths, and their temperature variation, gives information on the dimensionality of the charge-transport process[37] and of the occurrences of phase transitions.[38] The room-temperature linewidth of Ni(pc)I is rather small and quite anisotropic (Fig. 5). Upon cooling to ~ 60 K, the width diminishes in proportion to the resistivity, as expected for a contribution from phonon scattering; by 60 K the signal is almost isotropic in width and is quite narrow, less than 1 G. The linewidth is essentially temperature independent between 60 and 2 K.

The onset of metal-metal or metal-nonmetal transitions is commonly accompanied by a change in the temperature dependence of the EPR linewidth in the region of the phase transition.[38] Although a number of different effects have been observed in molecular metals, the linewidth typically decreases significantly below and/or in the region of the conductivity maximum. For example, the linewidth of TTT_2I_3 is roughly linear with T between 30 and 300 K;[13,30] however, in a small region (<10 K) around the conductivity maximum at ~ 105 K, the slope increases dramatically. Thus, the constant low-temperature ($T<60$ K) EPR linewidth of the Ni(pc)I carrier spins argues strongly against associating the conductivity maximum with a phase transition.

In most cases, observation of narrow conduction-electron spin resonances can be attributed to a weakening of the efficiency of the spin-orbit-induced relaxation in one dimension. Weger and co-workers have shown that

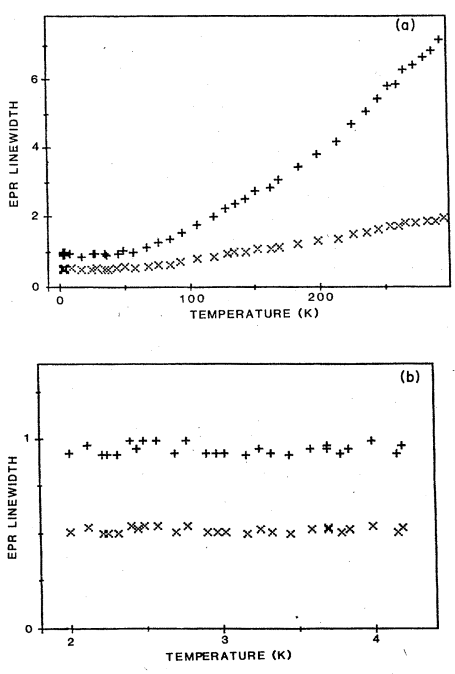

FIG. 5. Temperature dependence of the parallel (+) and perpendicular ($\times$) EPR linewidth for Ni(pc)I in the region (a) 300–2 K, and (b) 4.2–2 K.

deviations from one-dimensional behavior in the Elliot formulation of the linewidth leads to the relationship[39]

$$\Gamma \alpha \mid t_{\perp} \mid^2 ,$$

where $t_{\perp}$ is a measure of the interstack interactions and is thus a good gauge of the dimensional character of the system. By this criterion, Ni(pc)I appears to be a very good approximation to a one-dimensional metal.

V. DISCUSSION

Ni(pc)I behaves as a molecular metal without any apparent transition to a nonmetallic state down to 50 mK. In particular, the thermoelectric-power and magnetic-susceptibility measurements show that the band structure remains essentially metallic down to 2 K, and the conductivity remains high as $T \to 0$. Although a conductivity maximum is observed at $T \lesssim 30$ K, even this must represent, to a substantial degree, the effects of crystal variability and/or stress in the crystal amount.

The physical properties of highly conducting molecular crystals are usually dominated by strong unidimensional interactions within the conducting columnar stacks of planar molecules.[40] Concomitantly, the vast majority of organic molecular metals also exhibit a metal-nonmetal transition, usually the Peierls transition, resulting from the inherent instability of a partially filled one-dimensional band. Only a few molecular metals other than Ni(pc)I have been observed to retain a high-ambient-pressure electrical conductivity down to the lowest available temperatures.[7–11,32,41–47] These other compounds, listed in Table I, are all based on derivatives of organic chalcogens, in which a low-temperature conducting state can be stabilized by strong two- or three-dimensional, chalcogen-mediated, interstack interactions.

The molecular metal Ni(pc)I is the first molecular crystal that behaves as a metal down to the lowest available temperature, 50 mK, yet contains neither chalcogen-mediated, nor any other apparent, pathway for strong interstack interactions. Indeed, the very narrow EPR linewidth and relatively weak magnetoresistance suggest that the material is highly one dimensional. Despite this, the charge-transport properties of Ni(pc)I are quite similar to those of the more multidimensional $(TMTSeF)_2ClO_4$ system.[49] These two materials are the only documented systems to date in which, at ambient pressure, the temperature dependence of the thermoelectric power and the magnetic susceptibility show no apparent change as the material passes through a maximum in the four-probe conductivity. Since both the thermoelectric power and susceptibility directly probe the density of states at the Fermi level, these results argue that in neither compound does the density of states change through the conductivity maximum, contrary to expectation if the conductivity maximum corresponds to the opening of a Peierls gap at the Fermi surface. This conclusion is not surprising for $(TMTSeF)_2ClO_4$, since the interstack interactions in terms of the transfer integral are strong and, in fact, lead to the onset of superconductivity at 1.4 K.[32] However, in the highly-one-dimensional Ni(pc)I, the maintenance of a metallic band structure

TABLE I. Charge-transport parameters of low-temperature molecular metals. (RT denotes room temperature.)

Compound	σ(RT) (Ω^{-1}cm^{-1})	T_m[a] (K)	T_b[b] (K)	$\sigma(T_b)/\sigma$(RT)	Reference
Ni(pc)I	500	25–35	0.1	0.5–2	10
HMTSeF-TCNQ	2000	35	1.1	0.5	42
HMTSeF-TNAP	2000	47	1.5	0.1–1	43
DEDMTSeF-TCNQ	500	55	20	~1	44
$(TMTSeF)_2X$					
$X = ClO_4^-$	1000	5.5	0.8	c	32
$X = NO_3^-$	800	12	4.2	~5	48
$TTT\text{-}I_{1.6}$	700–1500	100	4.2	1.4	43
$(TSeT)_2X$					
$X = Cl^-$	700	27	4.2	0.5–1.2	46
$X = Br^-$	1000	35	4.2	~1	47
$X = I^{-1}$	1500	35	0.1	0.5–1.5	41
$(BEDT\text{-}TTF)_2ClO_4$	250	16	1.4	35	7

[a]Temperature of conductivity maximum.
[b]Lowest temperature attained.
[c]Superconducting transition at 1.4 K.

down to at least 2 K is very surprising.

Disorder in the tri-iodide lattice probably makes a major contribution to the suppression of the three-dimensional Peierls transition by interfering with the already weak interstack Coulombic interactions. A phthalocyanine stack is surrounded by four tri-iodide chains, each of which is ordered, but the chains are disordered with respect to one other via a translation along the stacking axis. A given chain can be positioned with respect to a neighboring Ni(pc) stack in one of three ways; thus, there are 27 possible arrangements of nearest-neighbor tri-iodide chains around a given phthalocyanine stack. In order for the Coulomb potentials to most effectively couple the one-dimensional ordered states on two adjacent phthalocyanine stacks, the tri-iodide environment surrounding the stacks must be identical. Statistically, this occurs in one out of every 243 phthalocyanine stacks; in the other arrangements the Ni(pc) stacks experience different potentials which modulate the Coulombic coupling and, therefore, interfere with the three-dimensional ordering process.

In general, this type of disorder is not enough to suppress the Peierls transition; for example, TTT_2I_3 exhibits an analogous disorder in the tri-iodide superlattice,[13] yet shows a Peierls transition at ~100 K. However, in Ni(pc)I the interstack interactions must be unusually weak. The conducting stacks of most molecular metals, such as TTF-TCNQ, $(TMTSeF)_2X$, and TTT_2I_3, are composed of molecules that are roughly rectangular in shape.[40] In the solid state these units pack in a manner such that the interstack separations along at least one edge of the molecular (usually the "longer" side of the rectangle) are relatively small, and thus short interstack distances are found between a number of atoms on each molecule in the adjacent stacks. Furthermore, these molecules contain heteroatoms in the periphery along the edge closest to the adjacent stacks, and these favor strong interstack interactions. For example, in TTT_2I_3, the shortest interstack contact is between sulfur atoms at a distance of 3.37 Å.[13] The Ni(pc) units, on the other hand, do not pack in a manner favoring short interchain distances between more than one or two atoms on the periphery of each unit in adjacent stacks. Furthermore, these peripheral atoms are all C—H units, and the packing must accommodate the accompanying hydrogen atom. Thus, whereas non-hydrogen interchain distances in most organic molecular metal systems are 3.2–3.34 Å, the closest non-hydrogen contact between stacks in Ni(pc)I is 3.70 Å in the plane of any given Ni(pc) unit, and 3.61 Å between a given molecule in a stack and its neighbors either one unit up ($\hat{c}/2$) or down in the adjacent stack. These distances are indeed too long to expect any appreciable direct interactions between stacks.

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