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Enhanced effects of local moment–carrier couplings in the high-purity alloys Cu_xM_{1-x}(phthalocyanine)I ($M=H_2$ or Ni)

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Utilizing techniques for synthesizing very pure M(pc), (pc=phthalocyanine), we prepared alloys of the type Cu_xM_{1-x}(pc)I, $M=H_2$ or Ni to examine the interaction between the conduction electrons and the local moments associated with the $S=\frac{1}{2}$ Cu^{II} metal ions embedded in the macrocycle center. The effects of the local moments, which include large decreases in conductivity and large positive magnetoconductivities, are greatly enhanced in these purer materials. Introduction of 5% Cu(pc) reduces the conductivity by a factor of 3. This same alloy shows a positive magnetoconductivity with a relative increase in conductivity of tenfold; this effect is four times greater than that observed in $Cu_{0.05}Ni_{0.95}$(pc)I made from commercially available material. Magnetic studies including susceptibility and electron paramagnetic resonance confirm that the two spin systems are strongly coupled. A magnetic susceptibility fit to a Curie-Weiss expression yields a Weiss constant, $|\theta|$, that increases linearly with x, the Cu content. The slope of $|\theta|$ is explained in the companion paper by Martin and Phillips [Phys. Rev. B **60**, 530 (1999)]. [S0163-1829(99)04521-X]

INTRODUCTION

Quasi-one-dimensional (q1D) conductors are of great interest because they display such features as charge-density waves (CDW's), spin-density waves (SDW's), and anion ordering, that can lead to unusual phase transitions and magnetic properties.[1–4] The interaction of local moments with conduction electrons, which gives rise to such characteristic phenomena as the Kondo effect in three-dimensional metals, has not been studied as extensively in one-dimensional systems.[5–13] We have been examining this phenomenon within a family of q1D conductors based on the macrocycle phthalocyanine (pc), the molecular metals $[M(\mathrm{pc})]^{0.33+}(\mathrm{I}_3^-)_{0.33}$. Substitution of a paramagnetic metal ion such as Cu^{II} ($S=1/2$) into pc leads to a unique situation wherein the itinerant carriers associated with the macrocycle and the local moments associated with the metal ion coexist on the *same* molecule, and thus, the *same* q1D stack. This may be contrasted with the system of $(\mathrm{perylene})_2M(mnt)_2$, $M=$Pd or Pt, which forms a family of q1D molecular conductors where the conduction electrons are associated with the perylene stack while the local moments are associated with the $M(mnt)_2$ stack.[11,12]

Magnetic susceptibility measurements of Cu(pc)I, and of the alloys Cu_xNi_{1-x}(pc)I, and Cu(tatbp)I (tatbp=triazatetrabenzoporphyrin) have shown a Curie-Weiss component due to the presence of Cu^{II} local moments and a Pauli term from the conduction electrons associated with the pc ring.[5,6,14] However, EPR studies showed only one signal from these two spin systems, which demonstrates that the Cu^{II} local moments are exchange coupled to the conduction electrons. The spin-exchange coupling between a local moment and the carriers in a metal is described schematically by the Hamiltonian term[15]

$$H_{s-d}=2J_{e-d}\mathbf{S_d}\cdot\mathbf{s_e}, \tag{1}$$

where $\mathbf{S_d}$ represents the local moment spin, $\mathbf{s_e}$ is the carrier spin, and J_{e-d} represents the coupling between them. Studies of the Cu_xNi_{1-x}(pc)I alloys further showed that the coupling of the local moments and the itinerant carriers leads to carrier-mediated Cu-Cu exchange interactions along the one-dimensional stacks of the form[16]

$$H=\sum_{i,j} J(i,j)\mathbf{S_i}\cdot\mathbf{S_j}. \tag{2}$$

This indirect interaction was found to be substantially stronger than the direct Cu-Cu exchange coupling between neighbors along a stack.[17]

The Cu^{II} local moments in these materials strongly suppress the conductivity through spin-flip scattering; the maximum conductivity decreases with increasing levels of Cu and the temperature at which the maximum conductivity occurs increases.[5–7,14] However, for small values of x, these materials show large increases in conductivity upon application of a magnetic field (positive magnetoconductivity),[7] because the field freezes the local spins thereby decreasing the spin-flip scattering of the carriers by the Cu(II) local moments. At low temperatures and high Cu concentrations, there is a frequency effect in the conductivity that manifests itself as a sharp enhancement in the microwave conductivity at 16.8 GHz as compared to that seen in the four-probe measurements (27 Hz). This appears to reflect a novel carrier and local moment relaxation mechanism that results from the carrier-mediated Cu-Cu coupling.[6–8,14]

We have recently found that the purity of the M(pc) precursors dramatically affects the low-temperature charge-transport properties of the M(pc)I materials, with the conductivity maximum of H_2(pc)I and Ni(pc)I at low temperature being improved from the previously reported value of five times greater than that at room temperature[18,19] to ~30-fold or more.[20–22] Therefore, we have used these high-purity materials to examine the effects that local moments have on the intrinsic charge-transport and magnetic properties of these q1D conductors by using the high-purity $M(\mathrm{pc})$ parent materials to prepare and study the $\mathrm{Cu}_x\mathrm{H}_{2(1-x)}(\mathrm{pc})\mathrm{I}$ alloys and to reexamine the $\mathrm{Cu}_x\mathrm{Ni}_{1-x}(\mathrm{pc})\mathrm{I}$ alloys. The nature of the local moment-itinerant spin coupling in the newly prepared alloy systems, $\mathrm{Cu}_x\mathrm{H}_{2(1-x)}(\mathrm{pc})\mathrm{I}$ and $\mathrm{Cu}_x\mathrm{Ni}_{1-x}(\mathrm{pc})\mathrm{I}$ is explained in a companion paper by Martin and Phillips[23] in which they extract a value for the carrier-mediated exchange interaction.

EXPERIMENTAL

Synthesis of $Cu_xM_{1-x}(pc)I$*,* $M=H_2$ *and Ni.* High-purity $\mathrm{H}_2(\mathrm{pc})$ and Ni(pc) were prepared as reported earlier;[20] high-purity Cu(pc) was prepared similarly.[21] Dark-green crystals of $\mathrm{Cu}_xM_{1-x}(\mathrm{pc})\mathrm{I}$, $M=\mathrm{H}_2$ and Ni, at the desired composition were prepared as described before.[6] For $M=\mathrm{H}_2$, alloys of the ratios $x=0.01$, 0.02, 0.05, 0.10, 0.25, 0.35, 0.50, 0.75, 0.90, and 1.0 were prepared. Because studies have already been done on the $\mathrm{Cu}_x\mathrm{Ni}_{1-x}(\mathrm{pc})\mathrm{I}$ system, fewer alloys were prepared from the high-purity parent materials: $x=0.05$, 0.25, 0.50, and 0.75. Previous studies on $M_x\mathrm{Ni}_{1-x}(\mathrm{pc})\mathrm{I}$ alloys, where $M=\mathrm{Cu}$ or Co, demonstrated that the $M(\mathrm{pc})$ to iodine ratio is indeed unity, that the M:Ni ratio is the same as that of the starting material $M_x\mathrm{Ni}_{1-x}(\mathrm{pc})$, and that the $M(\mathrm{pc})$ units are homogeneously distributed throughout the crystals.[6,24] The $\mathrm{Cu}_xM_{1-x}(\mathrm{pc})\mathrm{I}$, $M=\mathrm{H}_2$, and Ni alloys prepared here behave similarly, as described in detail elsewhere.[21]

Conductivity measurements. Single crystals were mounted on graphite fibers with a locally prepared palladium paste. Measurements of the four-probe ac (27 Hz) conductivity along the stacking axis were performed as described[20,21] at temperatures between 300 and 1.85 K and magnetic fields of 5 T. Room-temperature conductivities ranged from 150 to 700 $\Omega^{-1}\,\mathrm{cm}^{-1}$ for these alloys. The microwave conductivity and magnetoconductivity data at 16.8 GHz were obtained utilizing a cavity perturbation technique,[25] with the capability of application of a transverse magnetic field of up to 10 T.

Magnetic measurements. EPR and magnetic-susceptibility measurements were performed as described.[20,21] The susceptibility data for the $\mathrm{Cu}_x\mathrm{H}_{2(1-x)}(\mathrm{pc})\mathrm{I}$ and $\mathrm{Cu}_x\mathrm{Ni}_{1-x}(\mathrm{pc})\mathrm{I}$ alloys were initially fit to a Curie-Weiss susceptibility law associated with the $\mathrm{Cu}^{\mathrm{II}}$ $(S=\frac{1}{2})$ local moments plus a term for the temperature-independent Pauli paramagnetism of the carriers,

$$\chi=\chi_P+\frac{C}{T-\theta}. \tag{3}$$

Previous studies on Cu(pc)I and Cu(tatbp)I, show that the susceptibility does not follow the above equation down to the lowest available temperature (2 K),[5,6,14,17] and thus, the susceptibility fits for large x were done over a truncated temperature range of 50–8 or 10 K to emphasize the contribution from the Curie-Weiss term. However, as x decreases, the contribution of this term decreases proportionately ($C\propto x$), and so does the temperature at which deviation from Curie-Weiss behavior is observed. Thus, we extended the fits down to lower temperatures for decreasing x. Plots of $1/\chi$ vs T were used to aid in determining the low-temperature cutoff for the fits. Variation of the high-temperature limit for the fit did not significantly alter the fit parameters. The results of the fits to Eq. (3) are given in Tables I and II along with the temperature range of the fit. We also fit the susceptibility data over the same temperatures to the following equation:[26,27]

$$\chi=\frac{\chi_P}{(1-\theta/T)}+\frac{C}{(T-\theta)}, \tag{4}$$

which self-consistently takes into account the coupling between the local moments and the conduction electrons. The parameters derived from the two equations were indistinguishable.

TABLE I. Composition and magnetic susceptibility data for $\mathrm{Cu}_x\mathrm{H}_{2(1-x)}(\mathrm{pc})\mathrm{I}$ alloys.

x	x_{meas}[a]	C_{calc} (emu K/mol)	C_{meas}[b] (emu K/mol)	θ (K)	Temp. range (K)
0.02		0.008 18	0.0094(8)	−1.2(6)	300–5
0.05	0.06(1)	0.020 45	0.020(4)	−1.0(1)	300–5
0.10	0.14(6)	0.040 9	0.0410(3)	−1.42(5)	300–5
0.25	0.23(6)	0.102 25	0.102(3)	−1.8(3)	300–8
0.35	0.42(4)	0.143 15	0.1465(6)	−2.25(7)	300–8
0.50	0.52(5)	0.204 5	0.193(1)	−2.62(5)	300–8
0.75		0.306 75	0.320(3)	−3.5(2)	300–14
0.90	1.04(4)	0.368 1	0.367(3)	−3.7(1)	300–14
1.00	1.07(3)	0.409	0.386(1)	−3.86(6)	300–14

[a] Values determined by EDAX measurements on single crystals.

[b] Curie constant determined by fit of susceptibility data to $\chi_M=C/(T-\theta)+\chi_P$, Eq. (3).

RESULTS AND DISCUSSION

Four-probe conductivity. To appreciate the effects of incorporating paramagnetic $\mathrm{Cu}^{\mathrm{II}}(\mathrm{pc})$ units into a partially oxidized $M(\mathrm{pc})$ stack, $M=\mathrm{H}_2$ or Ni, we first recall the conductivity of high-purity $\mathrm{H}_2(\mathrm{pc})\mathrm{I}$ and Ni(pc)I; as the data for Ni(pc)I is similar, we show only that for $\mathrm{H}_2(\mathrm{pc})\mathrm{I}$ in Fig. 1. The room-temperature conductivities for high-purity $\mathrm{H}_2(\mathrm{pc})\mathrm{I}$ and Ni(pc)I are similar to earlier values, with $\sigma(RT)\approx 500\,\Omega^{-1}\,\mathrm{cm}^{-1}$.[18,19,28–30] As the temperature is lowered

TABLE II. Composition and magnetic susceptibility data for $\mathrm{Cu}_x\mathrm{Ni}_{1-x}(\mathrm{pc})\mathrm{I}$ alloys.

x	x_{meas}[a]	C_{calc} (emu K/mol)	C_{meas}[b] (emu K/mol)	θ (K)	Temp. range (K)
0.05	0.036(9)	0.020 45	0.0294(9)	−1.6(2)	300–5
0.25	0.020(1)	0.102 25	0.121(2)	−2.0(1)	300–8
0.50	0.49(5)	0.204 5	0.203(1)	−2.14(6)	300–8
0.75	0.74(4)	0.306 75	0.307(3)	−2.96(1)	300–14
1.00	1.07(3)	0.409	0.392(1)	−4.20(6)	300–14

[a] Values determined by EDAX measurements on single crystals.

[b] Curie constant determined by fit of susceptibility data to $\chi_M=C/(T-\theta)+\chi_P$, Eq. (3).

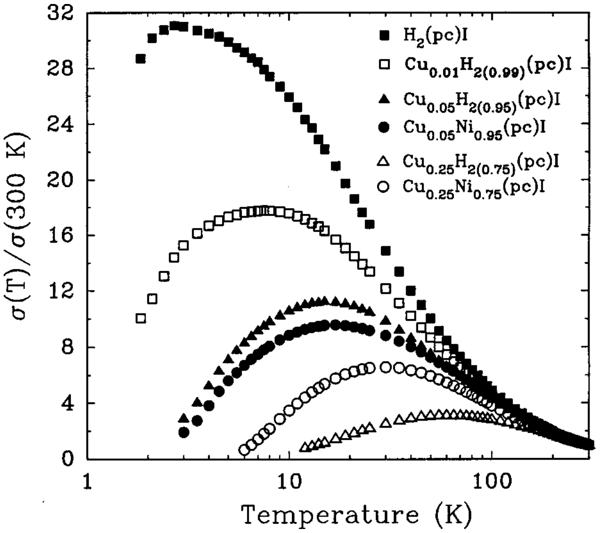

FIG. 1. Temperature dependence of the normalized single-crystal conductivity of $Cu_xH_{2(1-x)}(pc)I$, $x=0$, 0.01, 0.05, 0.25, and $Cu_xNi_{1-x}(pc)I$, $x=0.05$ and 0.25.

from 300 K, the conductivities of these two high-purity compounds increase in a metallic fashion with decreasing temperature over the temperature range 300–$\sim$3 K, where they reach a maximum, and then slightly (10–40 %) decrease upon further cooling to 1.9 K.[20] At the conductivity maximum, $T_{\max}\sim 3\,K$, the absolute conductivity is $\sim 1-2 \times 10^4\,\Omega^{-1}\,cm^{-1}$, representing an increase in conductivity over that at room temperature of $\sigma_{rel}^{\max}=\sigma(T_{\max})/\sigma(300\,K) \approx 30$. In contrast, earlier studies on $H_2(pc)I$ and Ni(pc)I gave values of $\sigma_{rel}^{\max}\approx 2-7$ and $T_{\max}\approx 15-25\,K$.[18,19,29–33]

Plots of the temperature dependence of the normalized conductivity data for the two series of alloys $Cu_xM_{1-x}(pc)I$, $M=H_2$ and Ni, are also presented in Fig. 1. The two alloy systems behave similarly. For each composition with $x>0$, the maximum conductivity is reduced from that of the $x=0$ compound and the maximum occurs at a higher $T_{\max}$; below $T_{\max}$ the conductivity for the $x>0$ alloys rapidly tends toward zero with further cooling. The value of $\sigma_{rel}^{\max}$ decreases sharply upon addition of Cu ($x\sim 0.1-0.2$) and $T_{\max}$ shifts correspondingly to higher temperatures (Fig. 2). Indeed, incorporation of only 1% Cu^{II} into Ni(pc)I or $H_2(pc)I$ causes a twofold decrease in $\sigma_{rel}^{\max}$, and 5% incorporation decreases $\sigma_{rel}^{\max}$ from $\sim$30 down to $\sim$10. The importance of this is emphasized when it is noted that the effective dilution in a 1 D metal is far greater than in an isotropic 3 D metal because of the reduced dimensionality. Thus, for a 1% doping level ($x=10^{-2}$) in one dimension, a carrier travels on average $\sim$100 lattice sites before encountering a dopant molecule, whereas in a 3D isotropic material, a much lower doping level of $x=10^{-4}\%$ ($x=10^{-6}$) would give the same average first-encounter distance. As x is increased beyond $\sim$0.10–0.2, $\sigma_{rel}^{\max}$ and $T_{\max}$ become weakly dependent on x with plateau values of $\sigma_{rel}^{\max}\sim 2.5-5$ and $T_{\max}\sim 60-80\,K$ (Fig. 2, inset).

The high-purity M(pc)I conductors and their $Cu_xM_{1-x}(pc)I$, $M=H_2$ or Ni, alloys show much higher conductivities for $x<0.25$ than reported in previous studies on $Cu_xNi_{1-x}(pc)I$ alloys, and the effects of addition of Cu^{II} displayed in Figs. 1 and 2 are far more dramatic than seen before. Addition of 5% Cu into the Ni(pc)I lattice led to a decrease from $\sigma_{rel}^{\max}\sim 5$ to $\sim$4 in the alloy prepared from multiply sublimed, commercially available material.[18,19,22] In general, for $x\geqslant 0.25$, the values of $\sigma_{rel}^{\max}$ in the $Cu_xH_{2(1-x)}(pc)I$ and $Cu_xNi_{1-x}(pc)I$ alloys are similar to those previously reported for the $Cu_xNi_{1-x}(pc)I$ alloys which, however, did vary somewhat in different reports.[5,22,34] The general agreement at larger values of x is not surprising because the present data show that $\sigma_{rel}^{\max}$ is roughly independent of the concentration of any impurities for $x\geqslant 0.25$.

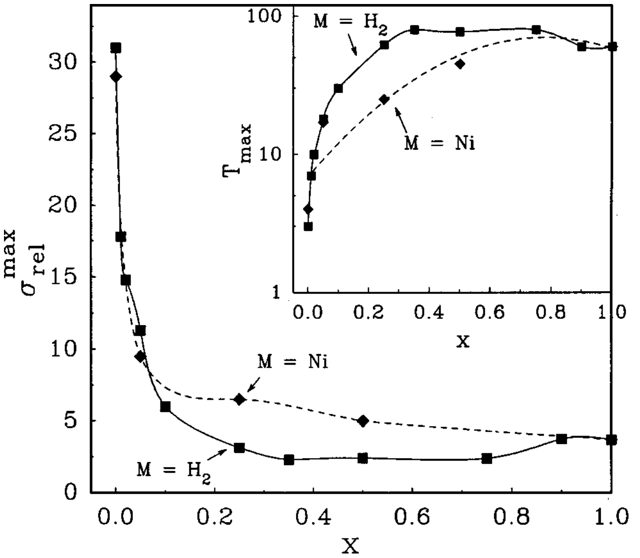

FIG. 2. Plot of $\sigma_{rel}^{\max}$ for both alloy systems, $Cu_xM_{1-x}(pc)I$, $M=H_2$ and Ni, versus Cu content, x. Inset: Plot of $T_{\max}$ versus Cu content x.

More careful examination of the composition-dependence of $\sigma_{rel}^{\max}$ and $T_{\max}$ in the plateau region, $0.25\lesssim x\lesssim 0.8$ (Fig. 2), shows modest quantitative differences for the two alloy systems that can be attributed to scattering from the random potential created by the random occupancy of metal-ion sites along a molecular stack. Thus, $\sigma_{rel}^{\max}\approx 2.5$ for the $Cu_{0.5}H_{2(0.5)}(pc)I$ alloy is one-half that of the $Cu_{0.5}H_{2(0.5)}(pc)I$ alloy, and $T_{\max}$ is $\sim$2 times greater, Fig. 2, inset. Moreover, as x increases from 0.8 to 1.0 in the $Cu_xH_{2(1-x)}(pc)I$ alloys, the conductivity improves slightly, as reflected in a small increase in $\sigma_{rel}^{\max}$ and a small decrease in $T_{\max}$. These results are counter to expectation if scattering of the itinerant carriers is dominated by interaction with the local moments; instead they reflect the existence of a second scattering mechanism in the $Cu_xH_{2(1-x)}(pc)I$ alloys. This is confirmed in other studies on a wide range of $Ni_xH_{2(1-x)}(pc)I$ and $Ni_xZn_{1-x}(pc)I$ alloys, which show that the difference in the π orbital energies of adjacent M(pc) and M'(pc) units in a conducting stack causes scattering of the carriers;[35] this may be denoted "potential" scattering in contrast to the spin-flip scattering from the Cu^{II} local moments.

Microwave conductivity. Our earlier work shows that microwave conductivity and magnetoconductivity measurements can be used to examine the role of spin-flip scattering of the itinerant carriers by the local moments in $Cu_xH_{2(1-x)}(pc)I$ and $Cu_xNi_{1-x}(pc)I$ alloys. Figure 3 shows the 16.8 GHz microwave conductivity measurements of a set of $Cu_xH_{2(1-x)}(pc)I$ alloys. For $20\,K\lesssim T\lesssim 300\,K$, these

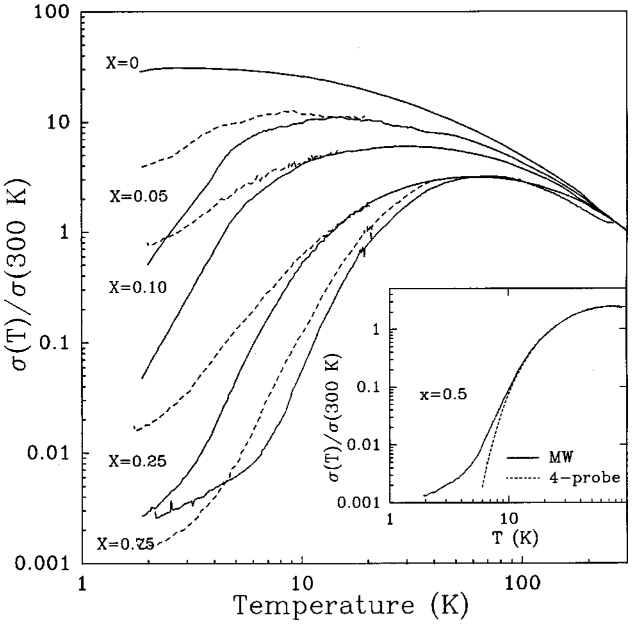

FIG. 3. Normalized microwave conductivity (16.8 GHz) as a function of temperatures for $Cu_xH_{2(1-x)}$(pc)I at H=0 T (symbols) and $H=10$ T (lines). $X=0$ (○), 0.05 (▽), 0.10 (□), 0.25 (△), and 0.75 (◇). Inset: Temperature dependence of the normalized four-probe (— — —) and microwave (——) conductivity for $Cu_{0.5}H_{2(0.5)}$(pc)I.

curves have the same general shape as the corresponding four-probe data of Fig. 1, and they exhibit the same decrease in $\sigma_{\rm rel}^{\rm max}$ and increase in $T_{\rm max}$ with increasing x. An expanded comparison of the 27 Hz and 16.8 GHz data for $Cu_{0.5}H_{2(0.5)}$(pc)I, $x=0.50$ is shown in Fig. 3, inset. In this case the normalized curves agree well down to 10 K. At low temperatures, the microwave conductivity levels off at some temperature T_P depending on x and approaches a temperature-independent value; in the case of $x=0.50$, this plateau value is 1000 times less than that at room temperature. The deviation between the four-probe and microwave conductivity has been observed previously in Cu_xNi_{1-x}(pc)I alloys and is attributed to a type of frequency-dependent carrier relaxation associated with the Cu(pc) local moments.[6–8,14] Thus, observation of this same frequency dependence in the $Cu_xH_{2(1-x)}$(pc)I alloys confirms that the spin-flip scattering mechanism here is similar to that observed in the previously studied Cu_xNi_{1-x}(pc)I alloys.

Magnetoconductivity. To confirm that the decrease of $\sigma_{\rm rel}^{\rm max}$ with increasing x in the $Cu_xH_{2(1-x)}$(pc)I and Cu_xNi_{1-x}(pc)I alloys results from spin-flip scattering by $S=\frac{1}{2}$ Cu^{II} ions, we measured the effect of an applied magnetic field on the four-probe conductivity. Materials with spin-flip scattering typically exhibit increases in their conductivities upon application of a magnetic field.[7,15,36,37] This occurs because the field largely quenches the spin degrees of freedom, which reduces the probability of a spin-flip scattering event, and thereby, decreases the effect of the coupling between the local moments and the itinerant carriers. As a control, we prepared the $Ni_{0.25}H_{2(0.75)}$(pc)I alloy because the N^{II} ion has no local moments. Figure 4 shows the four-probe magnetoconductivities of the $Ni_{0.25}H_{2(0.75)}$(pc)I and $Cu_{0.25}H_{2(0.75)}$(pc)I alloys plotted as the fractional increase in the conductivity induced by the application of a field: $\Delta\sigma(H)=[\sigma(H)-\sigma(0)]/\sigma(0)$. Neither alloy shows an effect in a 5 T field for $T\geqslant 20$ K. As T decreases, the magnetoconductivity of the $Cu_{0.25}H_{2(0.75)}$(pc)I alloy in this field rises to $\Delta\sigma=0.6$ at $T=3$ K, then decreases to 0.45 with further cooling to the lowest temperature available, $T=1.9$ K. In contrast, for the $Ni_{0.25}H_{2(0.75)}$(pc)I alloy, $\Delta\sigma$ becomes negative as T is lowered and is small, with $\Delta\sigma(5\ {\rm T})\sim -0.04$ at $T\approx 4$ K. This latter behavior parallels that of ordinary metals.[38] With further cooling, a small positive $\Delta\sigma$ is imposed on the weak negative curve; this likely reflects residual paramagnetic impurities. Thus, the large, positive magnetoconductivity exemplified by the $Cu_{0.25}H_{2(0.75)}$(pc)I alloy confirms the importance of spin-flip scattering in the charge-transport properties of the $Cu_xH_{2(1-x)}$(pc)I and Cu_xNi_{1-x}(pc)I alloy systems.

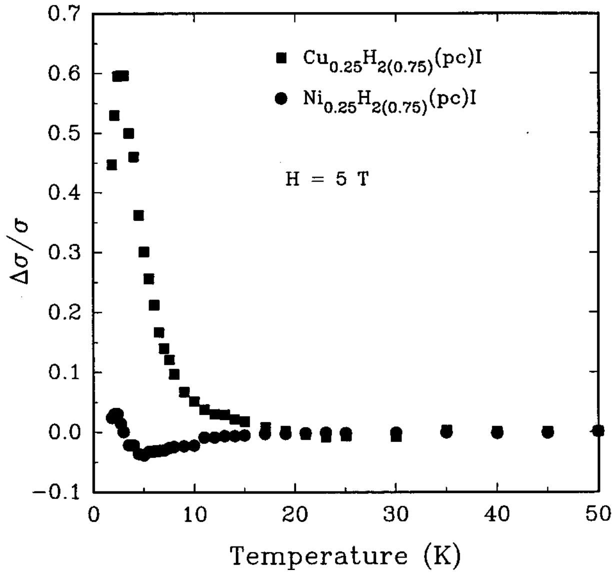

FIG. 4. Comparison of magnetoconductivity, $\Delta\sigma/\sigma$, of $Cu_{0.25}H_{2(0.75)}$(pc)I and $Ni_{0.25}H_{2(0.75)}$(pc)I for $T=50-1.9$ K and $H=5$ T.

Figure 3 also shows the normalized microwave conductivity for a series of $Cu_xH_{2(1-x)}$(pc)I alloys in the presence of a 10 T field. For $x<0.50$, at the fields and temperatures available, the conductivity in the applied field always is greater than the zero-field conductivity. For $x\geqslant 0.50$, the magnetoconductivity is positive in the temperature range $T_P\lesssim T\lesssim T_{\rm max}$, but below T_P the magnetoconductivity becomes negative as shown for $Cu_xH_{2(1-x)}$(pc)I, $x=0.75$ in Fig. 3.

Although the general characteristics of the microwave magnetoconductivity of the Cu_xM_{1-x}(pc)I, $M=H_2$ and Ni, alloys are very similar to those observed previously for the Cu_xNi_{1-x}(pc)I alloys,[7,22] the magnitude of the magnetoconductivity is much greater in the newly prepared materials especially for small values of x. For example, direct comparison of the data for Cu_xNi_{1-x}(pc)I, $x=0.05$ shows that at ~2 K the increase in conductivity in a 10 T field is remarkably large and over four times greater in the new alloys: $\Delta\sigma/\sigma=8$ vs $\Delta\sigma/\sigma=1.7$.[7,22] This may be compared with $\Delta\sigma/\sigma=-0.05$ for the corresponding diamagnetic alloy $Ni_xH_{2(1-x)}$(pc)I, $x=0.05$.[35] At higher concentrations of Cu, $x\gtrsim 0.25$, the new materials show larger field-dependent ef-

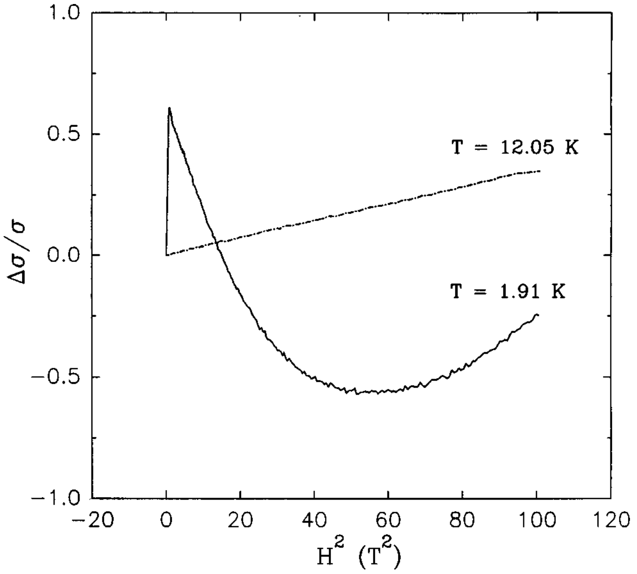

FIG. 5. Magnetoconductivity $\Delta\sigma/\sigma$ of $\mathrm{Cu}_{0.5}\mathrm{H}_{2(0.5)}$(pc)I as a function of H^2 at $T=12.05$ and 1.91 K.

fects as well, but these increases are not as pronounced as those found for low values of x.

At temperatures $T_p<T<T_{\max}$ the magnetoconductivity of both high-purity $\mathrm{Cu}_x M_{1-x}$(pc)I alloys increase linearly with H^2,[7,15] as shown for $T=12$ K in Fig. 5 for $\mathrm{Cu}_{0.5}(\mathrm{H}_2)_{0.5}$(pc)I for which $T_P\approx 4.5$ K. However, for $T\lesssim T_P$ the magnetoconductivity of this material has a complicated field dependence (Fig. 5). Similar behavior was reported for the $\mathrm{Cu}_x\mathrm{Ni}_{1-x}$(pc)I alloys.[7,22] Full analysis of the unusual magnetoconductivity observed in the $\mathrm{Cu}_x M_{1-x}$(pc)I, $M=\mathrm{H}_2$ and Ni, alloys will be presented in a separate paper.[39]

Magnetic properties. EPR measurements confirm that the conduction electrons and the local moments are tightly coupled in both the $\mathrm{Cu}_x\mathrm{H}_{2(1-x)}$(pc)I and $\mathrm{Cu}_x\mathrm{Ni}_{1-x}$(pc)I alloys. Both systems exhibit spin coupling between the $\mathrm{Cu}^{\mathrm{II}}$ local moments ($g_\parallel=2.18$ and $g_\perp=2.05$) and the π conduction electrons ($g=2.0$) that leads to a single EPR signal with axial symmetry and $g_\parallel>g_\perp$. The observed g values are susceptibility-weighted averages of those for the two spin systems. Thus, (i) at any temperature both $g_\parallel$ and $g_\perp$ increase with increasing Cu(pc) content, and (ii) both $g_\parallel$ and $g_\perp$ increase in value with decreasing temperature and appear to approach the g values for isolated Cu(pc), $g_\parallel=2.18$ and $g_\perp=2.05$. The latter follows because the $\mathrm{Cu}^{\mathrm{II}}$ spins have a Curie-Weiss susceptibility that increases at low temperature, whereas the conduction electrons have a roughly temperature-independent Pauli susceptibility.

Earlier X-band EPR studies on the $\mathrm{Cu}_x\mathrm{Ni}_{1-x}$(pc)I alloys reported large increases in the parallel linewidth below 10 K and increases of $g_\parallel$ to values even greater than 2.8.[6] EPR measurements on $\mathrm{Cu}_x\mathrm{Ni}_{1-x}$(pc)I, $x=0.50$, show similar behavior; as T is lowered from 4.2 to 2 K, $g_\parallel$ increases from $\sim$2.17 to $\sim$2.3 and the linewidth increases twofold, Fig. 6. In a surprising contrast, the g values for the $\mathrm{Cu}_x\mathrm{H}_{2(1-x)}$(pc)I, $x=0.25$, 0.35, and 0.50, alloys remain at the Cu(pc) limit for $2\leqslant T\leqslant 4.2$ K, and the linewidths do not increase.

Susceptibility measurements provide a measure of the strength of the coupling of the $\mathrm{Cu}^{\mathrm{II}}$ local moments to the conduction electrons. The high-temperature susceptibility for a metal doped with paramagnetic metal ions can be described as the sum of two terms [Eqs. (3),(4)]: a temperature-independent Eq. (3) or nearly independent Eq. (4) contribution from the conduction electrons, and the Curie-Weiss term, representing the contribution from the local moments. We fit the susceptibility data as described in the experimental section. The Curie constant C depends linearly on the Cu(pc) fraction in both the $\mathrm{Cu}_x M_{1-x}$(pc)I, $M=\mathrm{H}_2$ and Ni alloys, and the slope C^0 agrees well with the expected value, $C^0=\mathrm{N}g^2\mu_B S(S+1)/3k_B$ [Tables I and II]; a small residual term as $x\rightarrow 0$ reflects the presence of powder defects and residual magnetic impurities in the parent compound.[40] Mean-field theory for local moments in an insulator predicts that the absolute value of θ, the Weiss constant, varies linearly from 0 as x increases and an indirect coupling of the local moments through the conduction electrons can be described in terms of a Weiss constant θ that is a simple, linear function of x, with $|\theta|\rightarrow 0$ as $x\rightarrow 0$. The absolute value of θ does vary approximately linearly with x with a slope of $\approx$3 K, but with a nonzero intercept at $x=0$ (Fig. 7); this behavior is similar to that previously seen for $\mathrm{Cu}_x\mathrm{Ni}_{1-x}$(pc)I alloys. The intercept, $\theta_{\mathrm{res}}\sim 1$ K is attributed to the powder defects and residual magnetic impurities in the parent compounds.[40] The susceptibility data is analyzed by Martin and Phillips in terms of the 1D exchange between local Cu spins and itinerant carriers.[23]

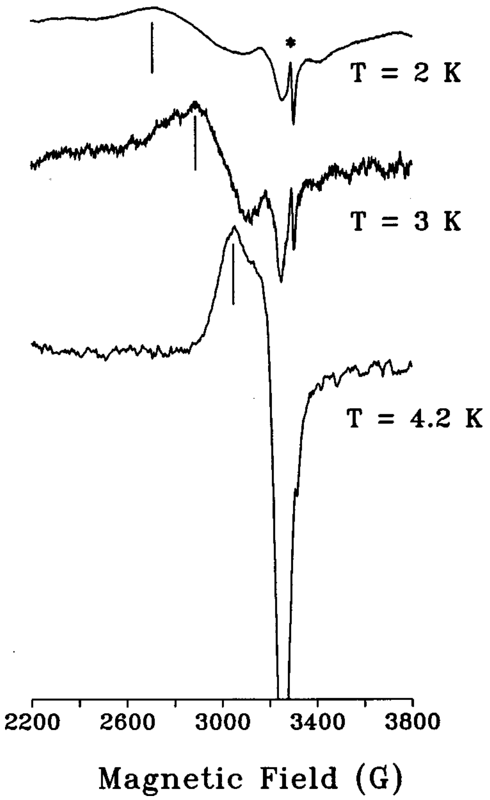

FIG. 6. Powder EPR spectra of $\mathrm{Cu}_{0.5}\mathrm{Ni}_{0.5}$(pc)I taken at 9.5 GHz ($X$ band).

SUMMARY

The $\mathrm{Cu}_x M_{1-x}$(pc)I, $M=\mathrm{H}_2$ and Ni, conductors represent a unique system with which to examine the interactions of

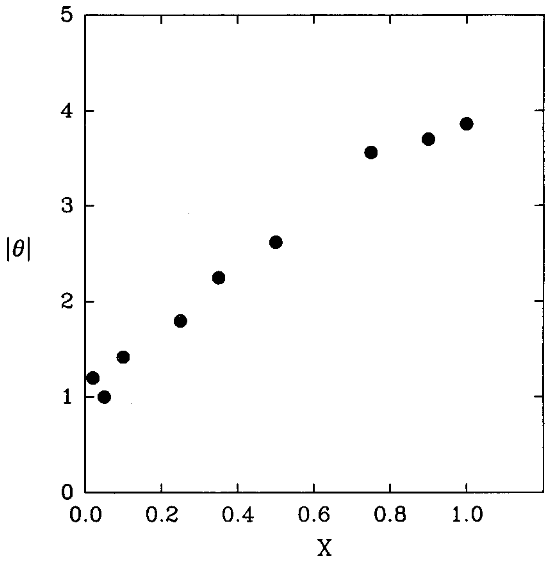

FIG. 7. Absolute value of θ, the Weiss constant, for the $Cu_xH_{2(1-x)}$(pc)I alloys as a function of Cu content x.

itinerant carriers with local moments embedded within the stack of a q1D conductor. Recent improvements in materials preparation of the diamagnetic hosts[20] have resulted in unprecedented conductivities of $1-2\times10^4\,\Omega^{-1}\,\mathrm{cm}^{-1}$ at $T \sim 4$ K for H_2(pc)I and Ni(pc)I. These values are ~30 greater than those at room temperature, and appear to represent the *intrinsic*, low-temperature charge-transport behavior. The introduction of low levels of paramagnetic Cu(pc) dopant ($x \leqslant 0.05$) into both H_2(pc)I and Ni(pc)I to give the Cu_xM_{1-x}(pc)I, $M=H_2$ and Ni, alloys leads to substantially larger effects on the conductivity than observed earlier for Cu_xNi_{1-x}(pc)I alloys prepared from purified, commercially available material,[6,7,22,34] as represented by $\sigma_{\mathrm{rel}}^{\mathrm{max}}$ and T_{max} (Fig. 2). Because of the quasi-one-dimensionality of our systems, this dopant level of 5% is equivalent to a dopant level of $\sim 10^{-3}$% in an isotropic three-dimensional metal. Therefore, these q1D materials are in the dilute limit where the widely studied Kondo effect is operative in 3D metals.[15]

The small quantitative differences in the values of $\sigma_{\mathrm{rel}}^{\mathrm{max}}$ and T_{max} at intermediate values of x in the Cu_xM_{1-x}(pc)I, $M=H_2$ and Ni, alloys are attributed to a second scattering mechanism due to differences in the energy of the Homo π orbital of various M(pc) molecules based on studies of $Ni_xH_{2(1-x)}$(pc)I and Ni_xZn_{1-x}(pc)I alloys.

The availability of high-purity and highly conducting materials has permitted us to discover quite remarkable magnetoconductivities in the materials with low x. For the Cu_xM_{1-x}(pc)I, $M=H_2$ and Ni alloys studied here, when $x=0.05$, the relative increase in conductivity upon application of a 5 T magnetic field is $\Delta\sigma/\sigma$, ~10 fold, more than four times greater than in the $Cu_{0.05}Ni_{0.95}$(pc)I material prepared from commercial Cu(pc) and Ni(pc). These values are very large compared to those observed for most 3D Kondo systems, but are of the same order of magnitude as $(LaCe)B_6$ with 1.2% atomic percent Ce.[36,37]

Analysis of the linear dependence of $|\theta|$ on x by Martin and Philips[23] leads to a value for carrier-mediated exchange interaction, $|J_{e-d}|\approx 240-370$ K [Eq. (1)]. This constitutes the first determination of the carrier-mediated exchange coupling for a molecular conductor like Cu_xNi_{1-x}(pc)I.[41]

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[40] Likely candidates for the residual magnetic impurities are trace quantities of $\mathrm{Cu}^{\mathrm{II}}$ and π-type free radicals.

[41] In addition, as a first step in achieving a deeper insight into the characteristics of the composition dependence of the susceptibility, classical Monte Carlo calculations have been performed on a model for the Cu_xM_{1-x}(pc)I that involves an array of magnetic moments on an isolated one-dimensional chain, surrounded by a free-electron gas representative of the conduction electrons; Q. Shen, D. E. Ellis, Y. Lee, W. P. Halperin, J. A. Thompson, and B. M. Hoffman, J. Magn. Magn. Mater. **152**, 139 (1996).