

Induced spin moments in quasi-one-dimensional halogen-bridged mixed metal complexes of nickel and palladium

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Spin susceptibility χ obtained by electron spin resonance in quasi-one-dimensional halogen-bridged mixed metal complexes $\text{Ni}_{1-x}\text{Pd}_x(\text{cyclohexandiamine})_2\text{Br}_3$ ($0 \leq x \leq 1$) shows a crossover from Curie-like to weakly temperature-dependent behaviors above around 200 K. The values of χ show a clear enhancement from the linear summation of susceptibilities of Ni and Pd fractions of pure cases, without enhancement of Curie-spin concentration, providing strong evidence for the conversion of nonmagnetic Pd^{2+} - Pd^{4+} states into magnetic Pd^{3+} states in mixed metal chains. [S0163-1829(99)11735-1]

Much attention has been paid to quasi-one-dimensional halogen-bridged mixed-valence metal complexes because of their interesting physical properties due to their quasi-one-dimensional structures, such as charge-density-wave (CDW) states, spin-density-wave (SDW) states, etc.¹⁻⁵ Theoretically, the quasi-one-dimensional halogen-bridged mixed-valence metal complexes are regarded as typical cases of the Peierls-Hubbard system.⁴

Among these compounds, $M(\text{chxn})_2\text{Br}_3$ ($M = \text{Ni}, \text{Pd}$; $\text{chxn} = 1R, 2R$ -cyclohexandiamine) have been shown to be either in a magnetic SDW (Ni^{3+}) state for the Ni case or in a nonmagnetic CDW (Pd^{2+} - Pd^{4+}) state for the Pd case. This difference depends on the relative magnitude of on-site Coulomb interaction (U) to the electron-phonon interaction (S), i.e., $U > S$ in the Ni complexes and vice versa.^{6,7} Recently the mixed metal complexes $\text{Ni}_{1-x}\text{Pd}_x(\text{chxn})_2\text{Br}_3$ ($0 \leq x \leq 1$) have been successfully synthesized to study the competition between the SDW and CDW states.^{8,9} Various kinds of measurements including room temperature electron spin resonance (ESR) have been applied. The IR, resonance Raman, and x-ray photoelectronic spectroscopy (XPS) showed that the Pd^{2+} - Pd^{4+} mixed-valence states are influenced and approaching the Pd^{3+} states with the increase of the Ni^{3+} components. ESR signals showed monotonic decrease of the linewidth as the value of x increases. There has been, however, no evidence for induced magnetic moments of Pd^{3+} .

In this paper, we report on direct detection of the induced spin moments of Pd^{3+} in the mixed metal chains through the study of the variation of the temperature-dependent ESR spin susceptibility with the mixing ratio. Preliminary results at room temperature have been briefly reported.¹⁰ The observed temperature-dependent spin susceptibilities of the whole x region show clear enhancements from the linear summation of the susceptibilities of Ni and Pd fractions of pure cases, without enhancement of Curie-spin concentration, providing strong evidence that Pd converts from nonmagnetic CDW states of pure Pd chains into a Pd^{3+} state in mixed metal chains. The results are consistent with the recent theoretical study of the present system by Iwano, who has shown the conversion of CDW states into Pd^{3+} states due to the com-

petition between the CDW and SDW states in mixed metal chains, based on the Peierls-Hubbard model.¹¹ Additional experimental evidence for the conversion into a Pd^{3+} state is provided from the observed dependence of the ESR linewidth and g values on the mixing ratio, as discussed below.

Samples of the mixed metal complexes $\text{Ni}_{1-x}\text{Pd}_x(\text{chxn})_2\text{Br}_3$ ($0 \leq x \leq 1$) were prepared by the electrochemical oxidation method as described elsewhere.⁸ ESR measurements were performed on polycrystalline samples by using a Bruker E500 X-band spectrometer equipped with a gas-flow type cryostat (Oxford ESR-900). The spin susceptibility was obtained by integrating the first derivative ESR signal twice. The absolute magnitudes of the susceptibility and g value were calibrated using crystals of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and diphenylpicrylhydrazyl (DPPH) as a standard, respectively.

Temperature dependence of the spin susceptibility χ of the present complexes showed Curie-like behavior at low temperatures, and weakly temperature-dependent behavior for higher temperatures for all the x values examined, as shown in Fig. 1. The results for $x=0$ and 1, that is, pure Ni and Pd cases, were consistent with those reported previously by Okamoto *et al.*⁷ The small amount of spins in the pure Pd case may be ascribed to thermally excited solitons or chain defects. In the pure Ni case, weakly temperature-dependent χ for higher temperature is interpreted as a Bonner-Fisher type susceptibility of the Heisenberg antiferromagnetic (AF) chain. The exchange interaction $J = 2700 \pm 500$ K was obtained for the pure Ni case by fitting the present data to the theoretical curve of χ by Bonner and Fisher.¹² On the other hand, the qualitatively similar behavior of the susceptibility at higher temperatures of the mixed system may suggest the occurrence of an AF chain due to Ni^{3+} at first sight. The measurements of the absolute value of χ , however, reveal a striking feature of the present system.

Figure 2 shows the palladium concentration dependence of χ at 300 K on the mixing ratio for the whole x region. The error bar of χ is mainly due to the broad ESR linewidth, in particular, in the Ni-rich region, that causes a certain ambiguity in the integrated value of ESR intensity. χ retains nearly the same magnitude as x increases from $x=0$ of the

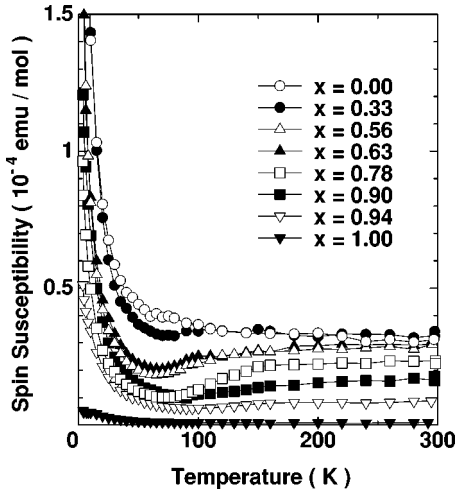


FIG. 1. Temperature dependence of spin susceptibilities of $\text{Ni}_{1-x}\text{Pd}_x(\text{chxn})_2\text{Br}_3$ ($0 \leq x \leq 1$).

pure Ni case up to around $x \sim 0.6$ then it monotonically drops to the value of $x=1$ of the pure Pd case. This shows that χ exhibits a clear enhancement from the linear summation of the susceptibilities of Ni and Pd fractions of pure cases, which is shown by a dotted line. A similar situation occurs for χ at temperatures above around 200 K. Since χ at higher temperatures should reflect the intrinsic magnetic property of the chains, the observed enhancement indicates that the magnetic states of mixed chains are significantly modified as compared with pure cases.

Ni and Pd ions in these materials are believed to be randomly distributed.⁸ Generally speaking, the enhancement may occur from two possibilities. The first possibility is that the enhanced fraction is due to the induced moments, Pd^{3+} in the Pd region, which may be reasonably correlated with the results of optical and XPS measurements. As pointed out in the preceding paragraph, these measurements show that the $\text{Pd}^{2+}\text{-Pd}^{4+}$ mixed-valence states are approaching the Pd^{3+} states with increasing Ni^{3+} components. The second possibility is the modification of the Ni^{3+} chain by the introduction of nonmagnetic Pd^{2+} or Pd^{4+} sites if they are isolated, or $\text{Pd}^{2+}\text{-Pd}^{4+}$ segments for the Pd-rich side. This would bring about scission of the chain, which may more or

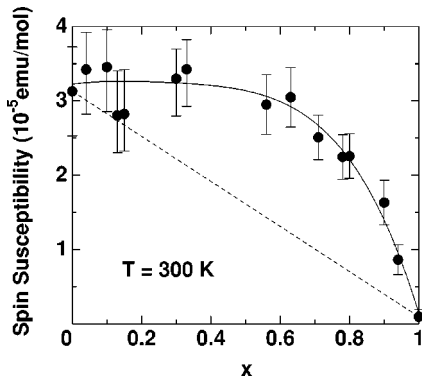


FIG. 2. Palladium concentration dependence of spin susceptibility at room temperature for $\text{Ni}_{1-x}\text{Pd}_x(\text{chxn})_2\text{Br}_3$ ($0 \leq x \leq 1$). The dashed line shows the linear summation of the susceptibilities of Ni and Pd fractions of pure cases. The solid line is a guide for the eye.

TABLE I. Comparison of observed Curie-spin concentration N_C (%) of $\text{Ni}_{1-x}\text{Pd}_x(\text{chxn})_2\text{Br}_3$ in the Ni-rich region ($x \leq 0.3$) with theoretically expected value $x/(2-x)$ in the case of nonmagnetic impurities in Heisenberg antiferromagnetic chains for $x \ll 1$.

x	N_C	$x/(2-x)$
0.00	0.34%	0.00%
0.04	0.18%	2.04%
0.10	0.15%	5.26%
0.15	0.27%	8.11%
0.30	0.22%	17.65%

less result in the enhancement of the susceptibility due to the suppression of antiferromagnetic spin correlation at a given temperature. This possibility, however, may be excluded by the observed x dependence of Curie-spin concentration as discussed below. Thus the x dependence of χ indicates that Pd becomes Pd^{3+} up to around $x \sim 0.6$, then the nonmagnetic $\text{Pd}^{2+}\text{-Pd}^{4+}$ fraction increases as x increases, and finally all Pd becomes $\text{Pd}^{2+}\text{-Pd}^{4+}$ in the pure Pd chain, except for a small number of Pd^{3+} spins associated with thermally excited solitons or chain defects. In other words, the experimental results indicate that the CDW state of $\text{Pd}^{2+}\text{-Pd}^{4+}$ is drastically suppressed by the replacement of Pd sites by Ni sites and it is almost destroyed when the Ni concentration becomes about 40%.

According to the recent theoretical study by Iwano,¹¹ this conversion may be caused by the effect that the Hubbard U at Ni sites is larger compared with the electron-phonon interaction. The effect of the random mixing of Ni and Pd in the one-dimensional chain was treated by using a Peierls-Hubbard model and a mean-field approximation. The theoretical results have shown that the 50% concentration of Ni sites is enough to destroy the order of the CDW, which is consistent with the present experimental results.

The above discussion may be further supported by the fact that the Pd fraction in the Ni-rich side, i.e., $x \ll 1$, does not simply act as nonmagnetic impurities for Ni chains. As pointed out above, Curie spins are observed at low temperatures for the whole x region (Fig. 1). The Curie component at low temperatures may be ascribed to the free spins associated with the defect site of the chain, such as chain ends. Table I shows the number of the Curie spins, N_C , estimated from the susceptibility data at low temperatures for $x \leq 0.3$. As is also shown in Table I, these values are much smaller than the theoretically expected values $x/(2-x)$ in the case of nonmagnetic impurities in Heisenberg AF chains for $x \ll 1$, which is the probability of the odd spin segments.^{13,14} It should be pointed out also that the theoretical value increases as x , while the observed Curie spins rather decrease as x increases. Thus the Pd substitution does not simply cut the magnetic chain and the substituted Pd atoms rather act as magnetic ions, that is, Pd^{3+} . This would be consistent with the observation that the room temperature susceptibility remains constant by Pd substitution of Ni chains up to around $x \sim 0.6$.

Thus, the present results strongly suggest the first possibility of the induced spin moments due to Pd^{3+} sites. Induced Pd^{3+} spins are not isolated and they may be interacting rather strongly to give the weakly temperature-dependent

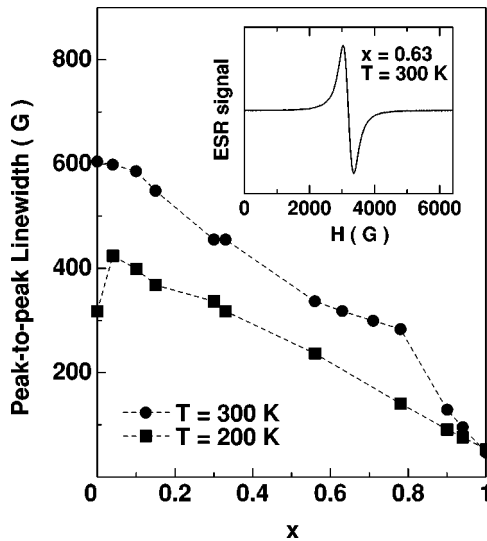


FIG. 3. Palladium concentration dependence of peak-to-peak ESR linewidth of $\text{Ni}_{1-x}\text{Pd}_x(\text{chxn})_2\text{Br}_3$ ($0 \leq x \leq 1$) at 200 and 300 K. Inset: ESR signal of $\text{Ni}_{1-x}\text{Pd}_x(\text{chxn})_2\text{Br}_3$ ($x=0.63$) at 300 K.

spin susceptibility close to those of AF chains for higher temperatures, as observed. From the temperature dependence of spin susceptibility, it may be considered that the contribution of induced Pd^{3+} spins to the susceptibility is comparable to that from Ni^{3+} chains. In this connection, it would be an interesting problem to obtain theoretically the spin susceptibility of the mixed chains by estimating the exchange interactions between Pd^{3+} - Ni^{3+} and Pd^{3+} - Pd^{3+} spin sites.

The behavior of the linewidth also indicates the participation of Pd^{3+} sites in the ESR signal. Figure 3 shows the x dependence of the peak-to-peak linewidth at 300 K and 200 K. Linewidth monotonically decreases as x increases. The linewidth of the Pd^{3+} region seems to be narrower than that of Ni^{3+} chains. These Ni^{3+} and the Pd^{3+} region may be strongly exchange coupled, because there is only a single amalgamated resonance line for the whole concentration range. An example of ESR signal for $x=0.63$ is shown in the inset of Fig. 3. Exchange-narrowed dipolar width H_d^2/H_{ex} is excluded as the origin of linewidth because it is estimated to the order of 10^{-2} G, using the dipolar field H_d of several hundred gauss obtained from the lattice parameters and the exchange field H_{ex} of 1.9×10^7 G using $J=2700$ K. This value is much smaller than the observed value even when the exchange narrowing of the AF chain may give a width broader than H_d^2/H_{ex} due to one-dimensional spin diffusion.¹⁵

Rather large temperature dependence of the linewidth of the Ni-pure case is consistent with the previous report by Okamoto *et al.*, who assigned the origin of the large temperature dependence of linewidth to that of the spin-lattice relaxation times due to spin-orbit coupling, that is, the modulation of crystal fields.⁷ In this case, the relaxation time may become longer as Δg becomes smaller.¹⁶ The principal g values of pure cases have been reported as $g_{\parallel}=2.021$, $g_{\perp}=2.171$ for Ni, $g_{\parallel}=2.006$, and $g_{\perp}=2.112$ for Pd, respectively. This suggests the decrease of the linewidth as the contribution of the Pd^{3+} signal increases, which is consistent with the observed decrease of the width as x , the Pd fraction,

increases. This interpretation is further supported by the monotonic decrease of g values as x increases, which has been previously reported⁸ and also confirmed in the present case using single crystalline samples. The obtained g_{\perp} values are, for example, $g_{\perp}=2.156$ and 2.135 , for $x=0.60$ and 0.94 , respectively, that falls between the g_{\perp} values of pure cases.

Thus the above discussion of the x dependence of χ , ΔH , and g values clearly indicates the generation of Pd^{3+} in the present mixed metal chain. This conclusion is consistent with the optical and XPS measurements.^{8,9} More recently, x-ray scattering experiments of the present system also supported this conclusion.¹⁷ Strong diffuse scattering, reflecting the CDW order, was not observed for x below about 0.7 , which means that most of the transition metal ions including Pd ions have a valence of $+3$ in these samples.

The observed x dependence of χ , ΔH , and g values, in particular, χ , should contain information about the concentration of Pd^{3+} sites and their exchange interactions which is not known at present. Also, whether the Pd^{3+} spin sites are spatially frozen or fluctuating in the Pd-rich side may be an interesting problem. In this connection, it should be pointed out that χ tends to drop at lower temperatures for $T=100$ – 200 K, which becomes more prominent for the larger x values, as seen from Fig. 1. One possible explanation for this behavior would be the conversion of Pd^{3+} sites into CDW states at lower temperatures for the Pd-rich side. Such a possibility might be related to the thermal excitation of solitons at higher temperatures in the CDW chain, suggested in the pure Pd case.⁷ The existence of the soliton excitation is also discussed in the theoretical treatment of a mixed chain by Iwano.¹¹ The relevance of the excitations to the observed behavior of χ is left open for further experimental and theoretical studies of the present system, which could serve as a prototype system to study the interplay between CDW and SDW states and hence the understanding of the nature of the individual states also.

In summary, the induced spin moments due to Pd^{3+} spins in halogen-bridged mixed metal complexes $\text{Ni}_{1-x}\text{Pd}_x(\text{chxn})_2\text{Br}_3$ ($0 \leq x \leq 1$) have been clarified by ESR. At low temperatures, the Curie-spin concentration does not increase as x increases. This result cannot be explained by the model of Heisenberg antiferromagnetic (AF) chains with nonmagnetic impurities and indicates the existence of Pd^{3+} spins around Ni^{3+} ions. At high temperatures, the spin susceptibilities χ showed the clear enhancement from the summation of the susceptibilities of Ni and Pd fraction of pure cases and the existence of induced moments due to Pd^{3+} spins. The CDW state is drastically suppressed as Ni concentration increases and it is almost destroyed when Ni concentration is about 40%. The induced Pd^{3+} spins and Ni^{3+} spins are strongly exchange coupled due to the existence of a single amalgamated resonance line of the ESR spectra. These magnetic behaviors agree well with the recent theoretical study of the present mixed metal system by Iwano using the Peierls-Hubbard model to treat the competition between CDW and SDW states.

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