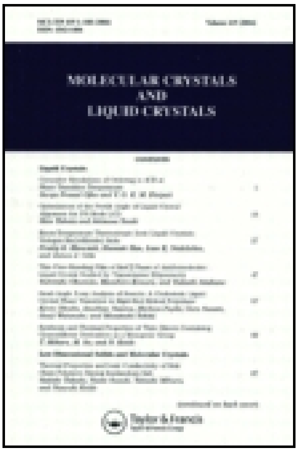

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New Ground States in Mixed-Metal MX-Chains

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New Ground States in Mixed-Metal MX-Chains

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We argue theoretically that a new state, namely, no halogen displacements around Pd ions and, consequently, their trivalent states with finite magnitudes of spin, will be realized by modest inclusion of Ni ions in Pd-Ni mixed-metal MX-chains. This state is peculiar to such mixed-metal systems, because it is never found as a ground state for homo-metal chains of Pd. Moreover, from the theoretical viewpoint, strong electron-lattice interaction and strong electron-electron Coulombic repulsion are mixed up to give a very interesting example for the study of both. Here we particularly discuss the following two points, based on Hartree-Fock (HF) calculations applied to a extended Peierls-Hubbard model. One is the dependence of the metal valencies on the mixing ratio. The obtained dependence is well consistent with the IR spectra, which shows the disappearance of charge disproportionation in the presence of 30%-Ni ions. Another theoretical result is on the relative position between the two metal bands. It has been assumed in the previous calculations that the two centers of the gravity of them were located at the same position. In this study, we show that the main conclusion survives even if they are apart from each other by a moderate energy.

Keywords CDW; Mott-Insulator; Metal-Mixing; MX-chain.

1 INTRODUCTION

The quasi-one-dimensional halogen(X)-bridged metal(M) complexes (so called MX chains) have been attracting much attention from both theoretical and experimental sides, because of the realization of essentially distinct two ground states, namely, a charge-density-wave (CDW) state accompanying halogen-sublattice dimerization and a Mott-insulator one with no halogen displacement, as the ground states of Pt or Pd compounds and Ni ones, respectively. So far this correspondence of the phase to the metal kind has no exception although some Pd compounds of which the optical gap energies are rather small are considered to be close to the CDW-'Mott-insulator' boundary. In this sense, the ground states of pure MX-chains was believed to be already well clarified.

However, very recently, mixed-metal MX-chains, of which the chemical formulas are expressed as $Ni_{(1-x)}Pd_x(chxn)_2Br_3$, have been newly synthesized to give a good opportunity for re-examining the ground-state properties. What is the most important aspect there is that a strong electron-lattice (e-l) interaction and a strong electron-electron interaction are forced to be directly competing with each other. In fact, the existence of a new state resulting from such a competition has been claimed for more than 50% of Ni concentrations from both experimental and theoretical sides. [1–8] This state is nothing but a combination of complete suppression of the halogen displacements around not only the Ni-sites but also the Pd-sites and trivalent states accompanying spins on both the metal sites. Since there has been no Pd^{3+} state found as a ground state for homo-metal Pd compounds, this state is considered to be new and typical to mixed-metal systems.

Following the above-mentioned previous result, in this article we first show the overall development of the electronic properties as a consequence of Ni-ion inclusion. In particular, we focus on the metal valencies, which is directly related to the IR absorption spectra. Next, we focus on the effect of band-center misfitting, which means that the Pd and Ni bands relatively shift from each other. The result of the latter assures that the simplified assumption used so far, namely, the coincidence of the centers of gravity of the two bands, is now justified.

2 MODEL and METHOD

We use an extended Peierls-Hubbard model whose Hamiltonian is

$$\begin{aligned} H &= -\sum_{l\sigma} t_0 (C^{\dagger}_{l+1\sigma} C_{l\sigma} + h.c.) + \sum_{l} \Delta_l n_l + \sum_{l} U_l n_{l\alpha} n_{l\beta} \\ &\quad + V \sum_{(l,l')} n_l n_{l'} - S \sum_{l} (Q_{l+1} - Q_l) n_l + \frac{S}{2} \sum_{l} Q_l^2 \quad , \qquad (1) \end{aligned}$$

where the creation and annihilation operators are related to the outermost d_{z^2} orbitals of Pd or Ni, and Q_l is the dimensionless displacement of l th halogen ion from each midpoint. The number operators, $n_{l\alpha}$ and $n_{l\beta}$, are those for the metal sites with spin up and down, respectively, and n_l means $n_{l\alpha} + n_{l\beta}$. Depending on the metal kind, the on-site Coulombic energy U_l and the site energy Δ_l take different values, which are 5.0 and 1.0 for U(Ni) and U(Pd), in unit of t_0, respectively, and Δ(Ni) -Δ(Pd) depends on the cases. The other parameters, namely, the electron transfer energy t_0, the Coulombic energy between nearest-neighbor metal sites V, and the e-l interaction energy S, are set to be constant for simplicity. They are 0.2 and 0.5 for S and V, respectively.

We calculate the valence and a lattice-related quantity, focusing on its change resulting from the Ni-site increase. We here perform sufficient sampling over a large number of metal-site distributions, to give statistically converged values. In more detail, we generate many random distributions of large-U and small-U sites, corresponding to Ni and Pd sites, respectively. This assumptions for randomness is motivated by the fact that no metal-site order was detected by X-ray analyses. We next find the minimum-energy lattice configuration for each distribution, to average them with equal statistical weight.

3 RESULTS

In Figure1, we show distributions of charge density, i.e., $< n_l - 1 >$, for different Ni concentrations. As seen clearly, the two-peak structure at low Ni concentrations in (a) gradually changes to a single-peak one. It is most remarkable that the distribution with 30%-concentration is almost regarded as a single peak. This feature is also seen in the experimental spectra of IR absorption. [5] There the N-H mode in the metal-surrounding ligand is a good measure of the metal valencies. We think that the present result explains the concentration dependency of the experimental result.

We show one more figure in Figure 2, where the Q_l-distribution at 50%-concentration of Ni is plotted for different Δ(Ni)-Δ(Pd). It should be here remarked that Δ(Ni) -Δ(Pd)=-2 corresponds to the condition that the centers of gravity of the two bands coincide with each other. As easily seen, the distribution tends to expand with lower positions of the Ni band This comes from the charge transfer from Pd to Ni and the lattice deformations caused thereby. However, those magnitudes are still regarded as rather small for these moderate degrees of band misfitting, because the magnitude of the uniform dimerization for the pure Pd case is as large as 0.8.

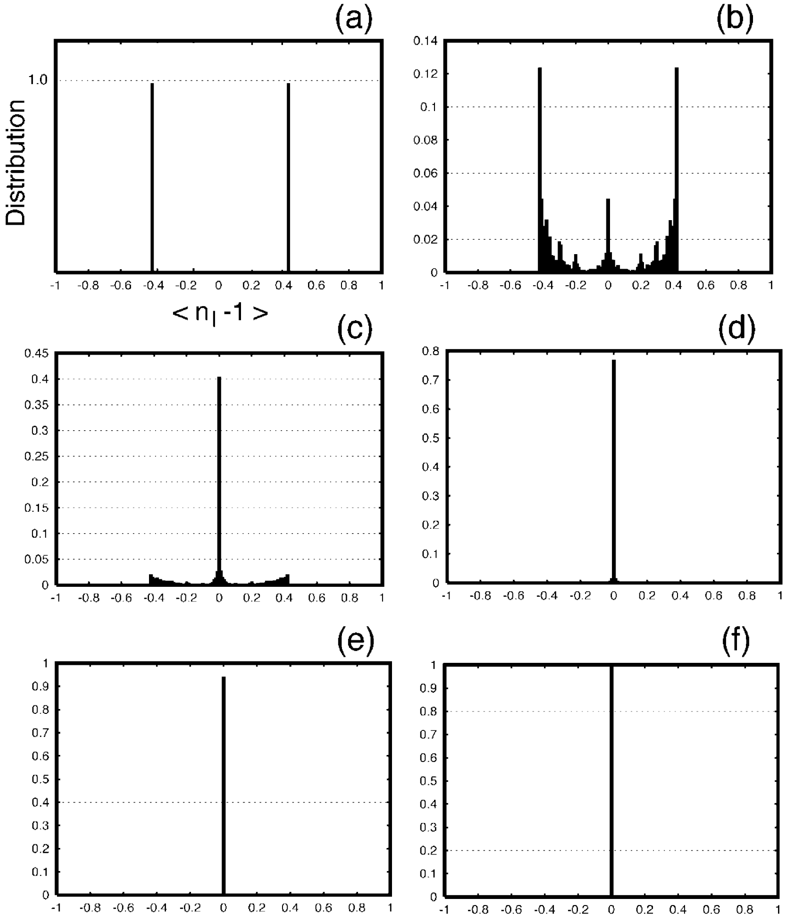

FIGURE 1. The charge distributions for different Ni-concentrations. (a). Zero %. (b). 10%. (c). 20%. (d). 30%. (e). 40%. (f). 100%.

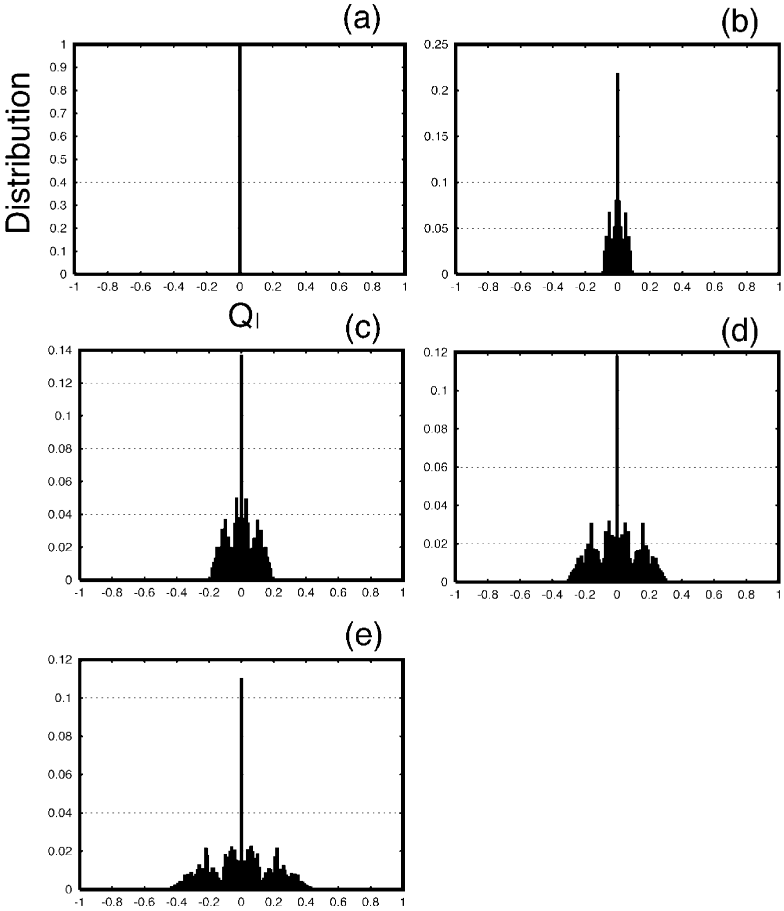

FIGURE 2. The Q_l distributions for different values of Δ(Ni) - Δ(Pd). They are -2.0, -2.2, -2.4, -2.6, and -2.8, for (a), (b), (c), (d), and (e), respectively. The Ni concentration is 50% for all the figures. The amplitude of the uniform dimerization in the pure Pd case is about 0.8.

4 CONCLUSION

We have investigated the dependence of the metal valencies on the metal-mixing ratio. The obtained results, namely, the valency distributions calculated by the HF method, are well consistent with the observed IR spectra. Furthermore, we have also studied the band-misfitting effect that was not treated explicitly in the precious studies, to show that the main conclusion seems to survive even with the effect.

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