Comment on "Origin of Giant Optical Nonlinearity in Charge-Transfer-Mott Insulators: A New Paradigm for Nonlinear Optics"

Zhang [1] has proposed a novel mechanism for the giant optical nonlinearities in linear chain nickel halides (Ni-X) [2] and the cuprate Sr_2CuO_3 [3]. We show that Zhang's theory is inapplicable to these systems and, also, some of his numerical results are finite size artifacts. Zhang's extended Hubbard Hamiltonian for Ni-X contains a site energy dependent term $\Delta \sum_{i,\sigma}(-1)^i n_{i,\sigma}$. Zhang chose the Ni atoms to occupy the odd sites in his exact diagonalization of $N = 8$ sites, such that the site energy of Ni is *lower* than that of X. There is then a competition between the on-site correlation U_{Ni} (which prefers Ni^{3+}) and Δ (which prefers Ni^{2+}), and, near the interface, the nonlinear coefficient γ is huge for $\Delta < \Delta_c(U)$ and zero for $\Delta > \Delta_c(U)$ (see Fig. 1 of [1]). Based on earlier estimates of U and the *magnitude* of Δ, Zhang claims that Ni-X lie very close to the interface.

Within Zhang's Hamiltonian, the charge-transfer (CT) gap $E_{\mathrm{CT}} \simeq (U_{\mathrm{Ni}} - U_X) + V - 2\Delta$, which is in contradiction to *all* earlier theoretical work [4], within which $E_{\mathrm{CT}} \simeq (U_{\mathrm{Ni}} - U_X) + V + 2\Delta$. The conventional models [4] are consistent with the Okamoto *et al.* parametrization of Δ from experiments: Between Ni-Cl and Ni-Br, the former has both larger Δ and larger E_{CT} [5]. Zhang's choice of the *same* sign of Δ as in Ref. [5] is incorrect, as larger Δ for Ni-Cl [5] would now predict a *smaller* E_{CT}. Zhang's error originates from the negative site energies on the Ni sites. With parametrization consistent with the observed trends in E_{CT} in Ni-X [4], there is no competition between U_{Ni} and Δ, and, hence, no enhanced γ.

In addition to Zhang's model being inappropriate for Ni-X, there are serious errors in Zhang's analysis of the model. The sudden drop in γ by orders of magnitude to zero (see Fig. 1 of [1]) is a consequence of a crossover of the ground state from total spin $S = 0$ to $S = 1$, a finite size effect. It is well known that the ground state of a *finite* undistorted non-half-filled periodic ring with $4n$ electrons is $S = 1$. With $U_{\mathrm{Ni}} \neq U_X$ and $V > 0$, this occurs at nonzero Δ. Zhang must have used a numerical approach that conserves total S_z and not total S. In Fig. 1(a), we have plotted $\Delta E = E(S_z = 1) - E(S_z = 0)$ for the parameters of Zhang's Fig. 1. In all cases, ΔE vanishes at *exactly* the same Δ_c as in [1]. Using a method that conserves total S, we have confirmed that, for $\Delta < \Delta_c$, $E(S = 0) = E(S_z = 0)$, while for $\Delta > \Delta_c$, $E(S = 0) > E(S_z = 0)$. With specifically $N = 8$ and 12 electrons, the $S = 1$ ground state is not coupled to excited states by the current operator, and this is the reason for the sharp drop in γ in [1]. We have confirmed that the spin crossover does not occur for $N = 12$ with 18 electrons. The true Δ_c that defines the Ni^{3+}-Ni^{2+} interface is larger. In Fig. 1(b), we have plotted E_{CT} as well as the matrix element $\hat{J}_{01}$ of the current operator between the lowest $S = 0$ state and the $S = 0$ one-photon state for the $N = 8$ periodic ring, using the site energies in [1]. $\hat{J}_{01}$ is symmetric about the true Δ_c indicating a nearly symmetric behavior of γ even with Zhang's parametrization.

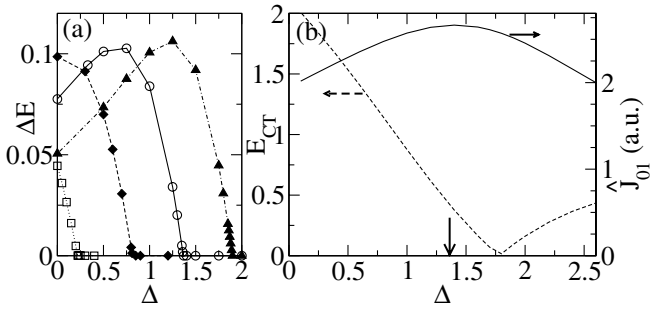

FIG. 1. (a) Energy difference between the lowest $S_z = 1$ and $S_z = 0$ states of the $N = 8$ periodic ring for, from left to right, $U_{\mathrm{Ni}} = 2, 3, 4$, and 5, with other parameters the same as in Fig. 1 of [1]. (b) E_{CT} and the matrix element of the current operator $\hat{J}$ for $S = 0$ and $U_{\mathrm{Ni}} = 4$. The arrow indicates the Δ where spin crossover occurs.

In conclusion, (i) Zhang's site energies for Ni-X are incorrect, (ii) his determination of Δ_c is incorrect, and (iii) the calculated behavior of γ for $\Delta > \Delta_c$ in [1] is a finite size artifact. Finally, the giant increase in γ near $\Delta_c(U)$ [1] is largely due to decreasing E_{CT} rather than increasing $\hat{J}_{01}$. This does not permit device application, as losses due to absorption would be large.

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