LEGIBILITY NOTICE

A major purpose of the Technical Information Center is to provide the broadest dissemination possible of information contained in DOE's Research and Development Reports to business, industry, the academic community, and federal, state and local governments.

Although a small portion of this report is not reproducible, it is being made available to expedite the availability of information on the research discussed herein.

LA-UR -89-3336

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

LA-UR--89-3336

DE90 002438

TITLE MX CHAINS: 1-D ANALOG OF CuO PLANES?

AUTHOR(S) J. Tinka Gammel
I. Batistic
A. R. Bishop
E. Y. Loh, Jr.
S. Mazumdar

SUBMITTED TO Proceedings of the International Conference on Highly Correlated Electron Systems, Santa Fe, NM, Sept. 11-15, 1989

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MX CHAINS: 1-D ANALOG OF CuO PLANES?

J. Tinka Gammel, I. Batistic, A.R. Bishop, E.Y. Loh, Jr., and S. Marianer

Theoretical Division and Center for Non-Linear Studies,
Los Alamos National Laboratory, Los Alamos, NM

ABSTRACT

We study a two-band Peierls-Hubbard model for halogen-bridged mixed-valence transition metal linear chain complexes (MX chains). We include electron-electron correlations (both Hubbard and PPP like expressions) using several techniques including calculations in the zero-hopping limit, exact diagonalization of small systems, mean field approximation, and a Gutzwiller like Ansatz for quantum phonons. The adiabatic optical absorption and phonon spectra for both photo excited and doping induced defects (kinks, polarons, bipolarons, and excitons) are discussed. A long period phase which occurs even at commensurate filling for certain parameter values may be related to twinning. The effect of including the electron-phonon in addition to the electron-electron interaction on the polaron/bipolaron (pairing) competition is especially interesting when this class of compounds is viewed as a 1-D analog of high temperature superconductors.

INTRODUCTION

Halogen-bridged transition-metal linear chain complexes (MX chains) have been of interest to chemists for many decades as dyes and strongly dichroic materials [1]. However they have only recently begun to receive detailed consideration in the physics community [2-5]. A typical crystal of this material consists of an array of linear chains of alternating metal (M) and halogen (X) atoms; with ligands attached to the metals, and possibly counterions between the chains to give charge neutrality. A typical chain is shown schematically in Fig 1. The potential importance of MX chains arises because of:

(*i*) The increasing appreciation of strong, competing electron-electron and electron-phonon interactions in low-dimensional materials and the consequent need to expand many-body techniques. The MX materials offer a rapidly expanding, near single-crystal, class of quasi-1-D systems which can be "tuned" (by chemistry, pressure, doping, etc.) between various ground state extremes: from strong charge-disproportionation and large lattice distortion ($\sim$ 15% distortion in PtCl chains) to weak charge-density-wave and small lattice distortion ($\sim$ 5% distortion in PtI chains), to magnetic and undistorted (a recently synthesized NiBr chain [6]);

(*ii*) The opportunity to probe doping- and photo-induced local defect states (polarons, bipolarons, kinks, excitons) and their interactions in controlled environments and the same large range of ground states; and

(*iii*) The similarities between models and theoretical issues in these materials and the recently discovered high temperature oxide superconductors, as well as the BaPbBiO compounds. The MX materials are also closely connected conceptually with mixed-stack charge-transfer salts and organic conductors.

Focusing on the similarity of the MX chains to the oxide superconductors, we note that they both can be described by a 3/4-filled, two-band tight-binding Peierls-Hubbard model; though 1-d for the MX compounds and 2-d for the oxide superconductors. Intrinsic defects in both these materials are thought to be "polaronic" obtained via doping or photoexcitation. The electron hole asymmetry has been experimentally observed in MX compounds [5], and is perhaps important to superconductivity (see the contribution to this volume by J. Hirsch). The model described below manifests long period ("superlattice") phases, possibly observed in recent experimental measurements on the MX compounds [5], which may be related to twinning or real space pairing in the oxide superconductors.

The MX class, then, is important in its own right, but also as a 1-d testing ground for concepts and many body electronic structure techniques in strongly interacting (both electron-electron and electron-phonon), electronic materials.

THE MODEL

Focusing on the metal d_{z^2} and halogen p_z orbitals and including only near neighbor interactions, we use the following two-band model for the isolated MX chain [3]:

$$H = \sum_{l,\sigma}\{(-t_0+\alpha\Delta_l)(c_{l,\sigma}{}^{\dagger}c_{l+1,\sigma} + c_{l+1,\sigma}{}^{\dagger}c_{l,\sigma}) + [(-1)^l e_0 - \beta_l(\Delta_l + \Delta_{l-1})]c_{l,\sigma}^{\dagger}c_{l,\sigma}\}$$
$$+ \sum_l U_l n_{l\uparrow} n_{l\downarrow} + V\sum_l n_l n_{l+1} + V_{MM}\sum_{l\ even} n_l n_{l+2}$$
$$+ \frac{1}{2}K\sum_l \Delta_l^2 + \frac{1}{2}K_{MM}\sum_l(\Delta_{2l} + \Delta_{2l+1})^2 + \frac{1}{2}\sum_l \frac{p_l^2}{M_l}$$

which includes as parameters the difference between metal and halogen electron affinities ($2e_0 = \epsilon_M - \epsilon_X$), electron hopping ($t_0$), on-site ($\beta_M, \beta_X$) and inter-site ($\alpha$) electron-phonon coupling, on-site (U_M, U_X) and intersite (V, V_{MM}) electron-electron repulsion, and finally effective metal-halogen (K) and metal-metal (K_{MM}) springs to model the elements of the structure not explicitly included. M atoms sit on even sites, X atoms on odd sites. $\Delta_l = u_{l+1} - u_l$ and p_l are the lattice distortion and momentum. For the discussion here we set $V_{MM} = 0$. We have also constrained the sum of the displacements to be zero (renormalizing t_0). We have chosen not to include a halogen-halogen though there is no conceptual difficulty in including it. The model parameters are shown schematically in Fig. 1. At stochiometry there are 6 electrons per MX unit, or 3/4-filling. We expect this model to be applicable to many systems. To insure approximation independent results we have used a number of theoretical techniques in our investigation [3], including Hartree-Fock approximation, perturbation theory (both weak and strong coupling), exact diagonalization of small systems, quantum Monte-Carlo methods, adiabatic molecular dynamics techniques to investigate photoexcitation, and variational approaches to investigate quantum phonons. We focus here on the mean-field, (static) adiabatic results, and note that quantum phonon corrections are not important for the heavy atoms considered here. We have checked our mean field code against the exact results obtained using a Lanczos diagonalization procedure on 12 sites [3] and find essentially no difference for small to intermediate correlations.

GROUND STATES

The values of K_{MM} and β_X do not affect the CDW ground state, and we have set $K_{MM} = 0$, $\beta_M = \beta_X = beta$, and $U_M = U_X = U$ in the ensuing discussion of the ground states, to reduce the number of parameters and to explore the possibility of a BOW phase.

A. Long Period

While Peierls' theorem guarantees that a commensurate distortion is lower in energy than no distortion in one-dimensional e-p coupled systems, it does not rule out the possibility that another distortion will be even lower in energy. The β term drives a long period phase at exactly commensurate filling [4]. Consider the trivial zero-hopping limit ($t_0 = \alpha = 0$) where the electronic Hamiltonian is site-diagonal and the eigenstates are fully described by their site occupancy. The period 4 phase is then:

$$\cdots NMN\ M\ NMN\ M\ \cdots\ =\ \cdots 202\ 2\ 202\ 2\ \cdots$$

First consider $U' = V' = 0$. It is easily seen that the lowest energy state for small e_0 phase separates into two regions, one of which has all the sites fully occupied and one of which has all the sites empty:

$$2\ 2\ 2\ \cdots\cdots\cdots\ 2\ 2\ 20\cdots 0\ .$$

The hopping drives the competing period 4 phase. A roughly period 10 distortion, lower in energy than the period 4 phase, is shown in Fig. 2. Long range Coulomb effects clearly also disfavor such long period phases. In Ref. 4 we investigate this phase using an unscreened Coulomb interaction plus an on-site exchange, treating the hopping t_0 in perturbation theory. Defining at 3/4-filling the period 4α states C_α and C''_α:

$$C_\alpha:\quad \underbrace{2\ 2\ 2\ \cdots\cdots\cdots\ 2\ 2\ 2}_{3\alpha\ \text{sites}}\ \underbrace{0\cdots 0}_{\alpha\ \text{sites}}\ ,$$

$$C''_\alpha:\quad \underbrace{2\ 2\ \cdots\cdots\ 2\ 2}_{2\alpha\ \text{sites}}\ \underbrace{1\ 1\ \cdots\cdots\ 1\ 1}_{2\alpha\ \text{sites}}\ ,$$

we find that for small t_0 and fixed strength of the electron-electron correlations there is a sequence of transitions through the states $C_1, C_2, C_3, \ldots, C''_\alpha, C''_{\alpha+1}, \ldots, C''_\infty$ as β is increased. Recent STM data indicates that this long period phase may be realized experimentally [5]. We speculate that this tendency toward charge-clumping may be related to twinning (superlattice discommensurations), or real space (bipolaronic) pairing in the 2 d extension of our model. For the rest of the discussion we restrict the ground state to be in the period 4 phase.

B. Period 1

In the ground state in the absence of e-e correlations, this problem can be analyzed analytically. The resulting phase diagram is rather featureless: for positive δ the lowest energy period 4 phase is nearly always a charge-density-wave on the M sites (CDW) [3]. (We label the states by the M behavior in analogy with the one-band model notation [2].) This is in agreement with the fact that all known MX materials with structural distortion are in the CDW phase, and demonstrates one important difference between the two-band model and one-band models [2], where the BOW phase is found for a substantial range of parameter values. It also implies there can never be an exact mapping to a one band model.

We have mapped out the phase diagram as a function of U and V numerically. We find [3] (for $K_{MM} = 0$) for small U that the system has a CDW with decreasing magnitude as U is increased, but for intermediate U the system switches over to a BOW, again with decreasing magnitude, and finally a SDW phase develops. The Hubbard V term lowers the transition from CDW to SDW [3].

EXCITATIONS AND ASSOCIATED OPTICAL ABSORPTIONS

We have studied polarons, bipolarons, kinks, and polarexcitons in the CDW phase numerically [3]. We focus here on the results for static polarons. We stress that this model has no electron-hole symmetry even in the absence of correlations, and this is reflected in the fact that the electron and hole defects have slightly different absorptions. This asymmetry is not present in the one-band model [2], again emphasizing the necessity of using the full two-band model. We have investigated the parameter dependence of the optical absorption spectra for polarons at $U = 0$. Three distinct intragap absorptions are observed, which are historically labeled as the C, A, and B bands (in order of increasing energy). For small Δ the C peak is at lower energy and has larger amplitude than at large Δ. The B peak is lost at small Δ. The electron polaron is insensitive to ϵ_0 and δ_M, whereas the hole polaron absorptions are quite sensitive.

We have investigated the dependence of the optical absorption spectra on K_{MM} and U_M. We have scaled the parameters when including $U_{M,X}$ to keep the uniform structure bands and distortion constant; in keeping with the interpretation of the $U_{M,X} = 0$ parameters as the effective mean field values. Decreasing K_{MM} from infinity tends to move the B absorption to the gap edge and the A and C absorptions to the gap center, and a BOW roughly following the derivative of the CDW amplitude develops. U_X has little effect, and U_M effectively increases the polaron A gap state absorption energy. The Hubbard V first delocalizes the defect in the CDW phase, then drives the SDW phase where the defect is again localized.

The spectrum in Fig. 3 agrees fairly well with the experimentally measured spectrum for $[Pt(en)_2][Pt(en)_2Cl_2](ClO_4)_4$ ($en = NH_2CH_2CH_2NH_2$) [5]. The parameters were derived by fitting

the known uniform structural and band structure data: $\Delta = .38$Å, $E_{IVCT} = 2.5 - 3.0$eV, $E_{Pt^{IV}} - E_{Cl} = 4.7$eV; yielding for the dimensionless parameters modeling PtCl $t_0 = .5$, $\alpha = .5$, $\epsilon_0 = .3$, $\beta_M = .03$, $K = .54$, and $\Delta = .58$. As we expect the ligands to strongly constrain the metal-metal distance, we used $K_{MM} = \infty$. The defect peak locations were then calculated and compared with experiment: yielding good agreement. Experimentally observed Raman resonances are observed at 1.3-1.4 and 1.9-2.1 eV enhancing a 263 cm^{-1} mode, 1.4-1.7 and 2.2-2.5 eV enhancing a 287 cm^{-1} mode, and 1.7-1.9 eV enhancing a 272 cm^{-1} mode, with a peak at .4 eV observed in infrared absorption [5]. The IVCT edge is at 2.5 eV. We identify these peaks as the A and B peaks of the electron polaron; the A and B peaks of the hole polaron; a bipolaron absorption; and a polaron C absorption, respectively. We stress that this identification means that the separate absorptions for the electron and hole polaron are seen in the resonance Raman studies [5]. The excess charge density for these defects is shown in Fig 4. Note that the hole defect is more delocalized.

ACKNOWLEDGEMENTS

We would like to thank D. Baeriswyl, D.K. Campbell, R. Donohoe, R. Martin, S.R. Phillpot, J. Reichl, B. Swanson, and S.M. Weber-Milbrodt for useful discussions. This work was supported by the US DOE.

REFERENCES

1. M.B. Robin and P. Day, in H.J. Emeleus (ed.), "Advances in Inorganic Chemistry and Radiochemistry", Vol. 10, Academic Press, New York, 1967, p. 247; P. Day, in H.J. Keller (ed.), "Low Dimensional Cooperative Phenomena", Plenum Press, New York, 1974, p. 191; H.J. Keller, in J.S. Miller (ed.), "Extended Linear Chain Compounds", Vol. 1, Plenum Press, New York, 1982, p. 357.
2. K. Nasu, J. Phys. Soc. Japan, 50 (1981) 235; 52 (1983) 3865; 53 (1984) 302; 53 (1984) 427; 54 (1985) 1933; J. Luminescence, 38 (1987) 90. K. Nasu and Y. Toyozawa, J. Phys. Soc. Japan, 51 (1982) 2098; 51 (1982) 3111. A. Mishima and K. Nasu, Synthetic Metals, 29 (1989) F175 and unpublished. Y. Ichinose, Solid State Commun., 50 (1984) 137. Y. Onodera, J. Phys. Soc. Japan, 56 (1987) 250. S. Kurita, M. Haruki, and K. Miyagawa, J. Phys. Soc. Japan, 57 (1988) 1789; S. Kurita and M. Haruki, Synthetic Metals, 29 (1989) F129; L. Degiorgi, P. Wachter, M. Haruki, and S. Kurita, *ibid*, F137. A. Painelli and A. Girlando, Synthetic Metals, 29 (1989) F181. D. Baeriswyl and A.R. Bishop, Physica Scripta, T19 (1987) 239; J. Phys. C: Solid State Phys., 21 (1988) 339. S.D. Conradson et al., Solid State Commun., 65 (1988) 723.

3. A. Bishop, J.T. Gammel, and S. Phillpot, Synthetic metals, 29, F151 (1989); J.T. Gammel, S.M. Weber-Milbrot, E.Y. Loh, Jr., and A.R. Bishop, Synthetic Metals, 29 (1989) F161. J. Tinka Gammel, A.R. Bishop, and S.R. Phillpot, unpublished. J. Tinka Gammel, A.R. Bishop, I. Batistic, E.Y. Loh, Jr., S. Marianer, S.M. Weber-Milbrodt, and Jakob Reichl, unpublished. A.R. Bishop, J. Tinka Gammel, E.Y. Loh, Jr., S.R. Phillpot, and S.M. Weber-Milbrodt, to be published in the Proceedings of the NATO Advanced Research Workshop on Interacting Electrons in Reduced Dimensions, Torino, Italy, Oct. 3-7, 1988 (Plenum).
4. I. Batistic et al, to be published.
5. R. Donohoe et al., to be published.
6. K. Toriumi et. al., J. Amer. Chem Soc., 111 (1989) 2341.

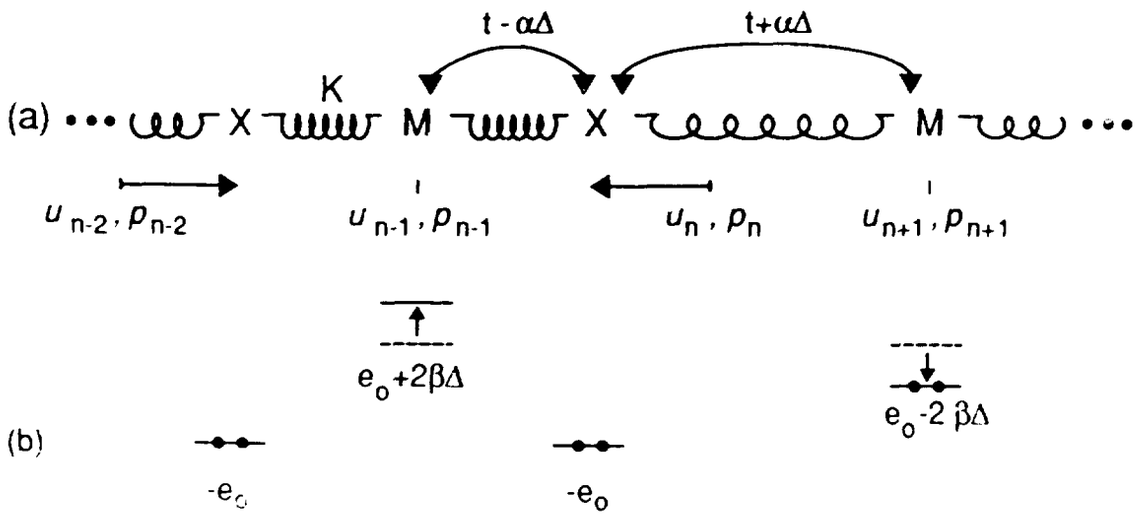
FIGURES

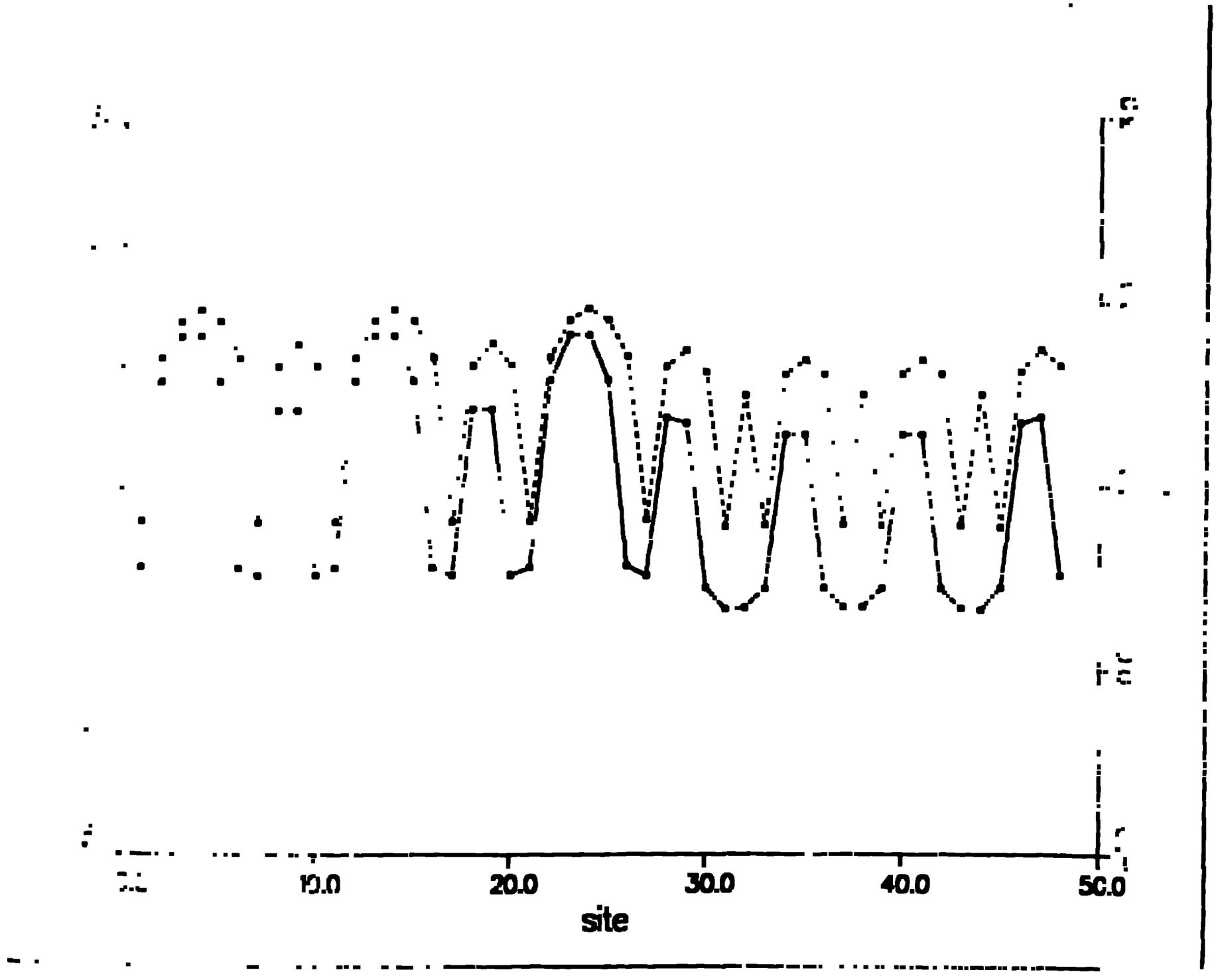
Fig. 1: (a) Schematic of the MX chain showing the model parameters and a CDW distortion; (b) the corresponding $t_0 = \alpha = 0$ energy levels.

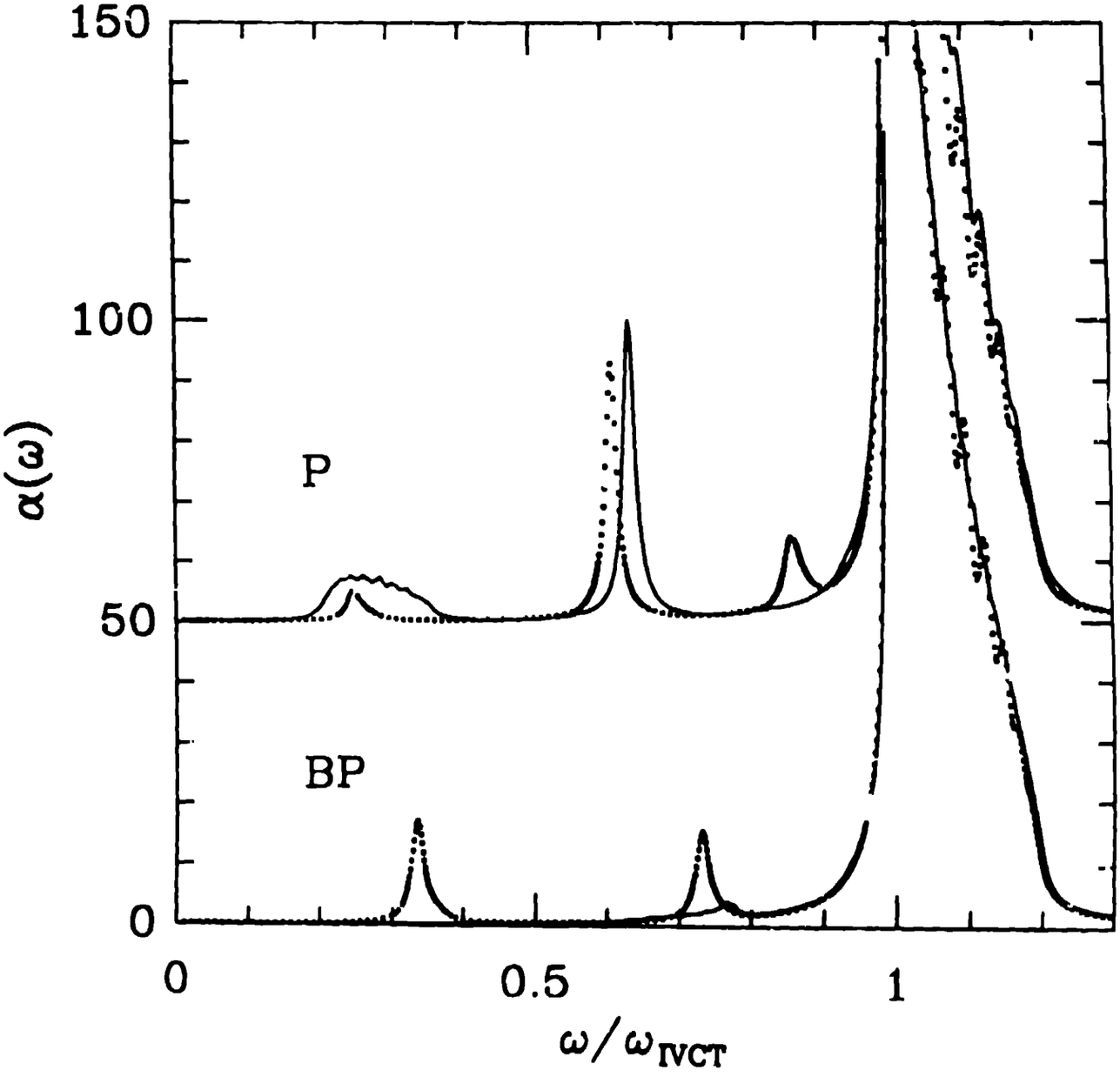
Fig. 2: A long period distortion of roughly period 10. Shown are the lattice distortion (solid) and charge density (dotted). Parameter values are $t_0 = 1.$, $\alpha = 0$, $e_0 = .5$, $\beta_{M,X} = .7$, and $\Delta = .5$.

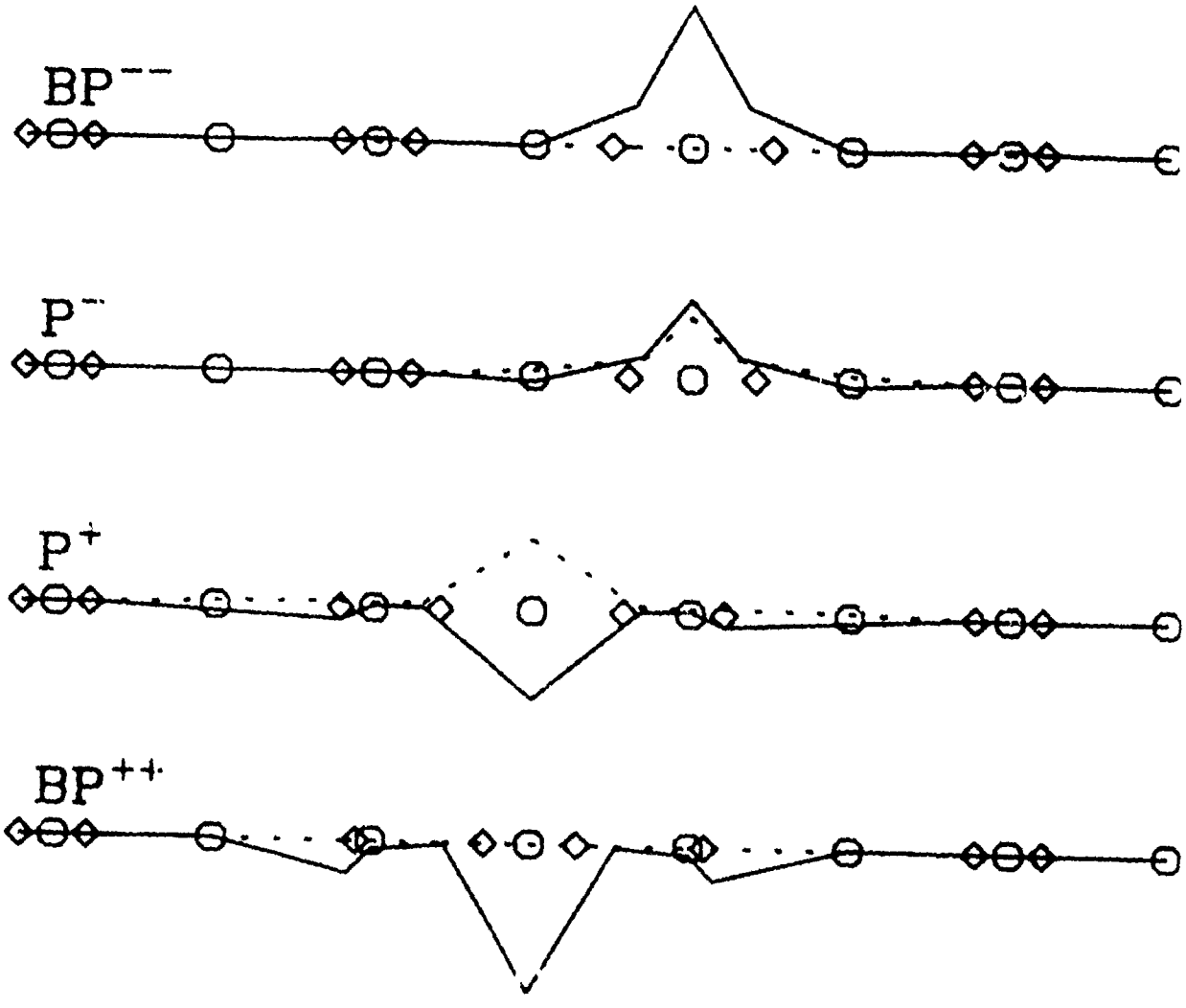
Fig. 3: The optical absorption spectra, with the IVCT scaled to 1, for the hole (solid) and electron (dotted) polaron and bipolaron with PtCl parameters. Note the electron-hole asymmetry.

Fig. 4: The lattice positions of the metal (circle) and halogen (diamond), excess charge density (solid), and excess spin density (dotted) for the defects of Fig. 3, stressing the electron-hole asymmetry.


t - αΔ
t+αΔ
K
(a)
X
M
X
M
u_{n-2}, p_{n-2}
u_{n-1}, p_{n-1}
u_n, p_n
u_{n+1}, p_{n+1}
$e_o+2\beta\Delta$
$e_o-2\beta\Delta$
(b)
$-e_o$
$-e_o$


10.0
20.0
30.0
40.0
50.0
site


150
100
50
0
α(ω)
P
BP
0
0.5
1
ω/ω_IVCT


BP⁻⁻
P⁻
P⁺
BP⁺⁺