LA-UR--89-16

DE89 006551

Received by US 11
FEB 06 1989

TITLE A TWO BAND MODEL FOR HALOGEN-BRIDGED TRANSITION METAL LINEAR
CHAIN COMPLEXES

AUTHOR(S) A. R. Bishop
J. Tinka Gammel
E. Y. Loh, Jr.
*S.R. Phillpot
**S. M. Weber-Milbrodt

SUBMITTED TO Plenum, NY

*Materials Science Division
Argonne National Laboratory
Argonne, IL

**Physikalisches Institut
Universität Bayreuth
West Germany

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 its employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, product, or process disclosed, or represents that it would necessarily accept any liability for damages resulting therefrom. This report is the property of the United States Government. It and its contents are not to be distributed outside the United States Government (and its agencies).

In compliance with this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the copyrighted form of this contribution, and to allow others to reproduce it for government purposes.

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 National Laboratory
Los Alamos, New Mexico 87545

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

A TWO BAND MODEL FOR HALOGEN-BRIDGED TRANSITION METAL LINEAR CHAIN COMPLEXES.

A.R. Bishop, J. Tinka Gammel, E.Y. Loh, Jr.,

Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM;

S.R. Phillpot,

Materials Science Division, Argonne National Laboratory, Argonne, IL;

S.M. Weber-Milbrodt,

Physikalisches Institut, Universität Bayreuth, W. Germany.

INTRODUCTION

Halogen-bridged transition-metal complexes 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 [2-8]. Their potential importance 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 (in contrast to, e.g., polyacetylene), 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 (e.g., $\sim 20\%$ distortion in PtCl) to weak charge-density wave and small lattice distortion (e.g., $\sim 5\%$ distortion in PtI), to magnetic and undistorted (e.g., NiBr);
- (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 oxide superconductors [3]. The MX materials are also closely connected conceptually with mixed stack charge-transfer salts [9].

The MX class, then, is important in its own right, but also as a template for concepts and electronic structure techniques in strongly interacting (both electron-electron and electron-phonon (e-p)), low dimensional electronic materials.

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.

THE MODEL

Focusing on a single orbital per site and including only nearest neighbor interactions, we use the following two-band model for the isolated MX chain [8]:

$$\begin{aligned}
 H = \sum_{l,\sigma} \{ & (-t_0 + \alpha\Delta_l)(c_{l,\sigma}^\dagger c_{l+1,\sigma} + c_{l+1,\sigma}^\dagger c_{l,\sigma}) + [(-1)^l \epsilon_0 - \beta_l(\Delta_l + \Delta_{l-1})] c_{l,\sigma}^\dagger c_{l,\sigma} \} \\
 & + \sum_l U_l n_{l\uparrow} n_{l\downarrow} + V \sum_l n_l n_{l+1} + V_{MM} \sum_{l \text{ even}} n_l n_{l+2} \\
 & + \frac{K}{2} \sum_l \Delta_l^2 + \frac{K_{MM}}{2} \sum_l (\Delta_{2l} + \Delta_{2l+1})^2 + \frac{1}{2} \sum_l \frac{\hat{p}_l^2}{M_l}
 \end{aligned}$$

with $\beta_l = [\beta_X, \beta_M]$, $U_l = [U_X, U_M]$, relative coordinates $\Delta_l := \hat{u}_{l+1} - u_l$, momenta $\hat{p}_l$, and displacements from uniform lattice spacing u_l . For the discussion here we set $V = V_{MM} = 0$. We have also constrained the sum of the displacements to be zero. This is not necessary, but omitting this constraint just renormalizes t_0 , and the parameter to compare with experiment is the renormalized one. The model parameters are shown schematically in Fig. 1. At stoichiometry there are 6 electrons per MX unit, and the model has 3/4-filling. We estimate for the dimensionless parameters modeling PtCl in the absence of e-e correlations [8]: $t_0 = 5$, $\alpha = 5$, $\epsilon_0 = .6$, $\beta_M = 3$, $\beta_X = -1.5$, and $K = 1$. As we have previously discussed [8], if e-e correlations are not too strong, mean-field approximation agrees rather well with exact results, and these numbers should be interpreted as the effective mean field values. For large ϵ_0 this model can be related to the one-band model developed by Baeriswyl and Bishop [3], giving an effective β/α of 3.2. Note that the effective parameters are such that the ground state is always in the CDW part of the one-band phase diagram. As we expect the ligands to strongly constrain the metal-metal distance, we have taken $K_{MM} \rightarrow \infty$ when discussing the defects. The values of K_{MM} and β_X do not affect the CDW ground state, and we have set $\beta_X = \beta_M = \beta$ and $K_{MM} = 0$ in the ensuing discussion of the ground states, to reduce the number of parameters and to explore the possibility of a BOW phase. In the discussion of the excitation spectrum below we discuss values

for the Hubbard terms. Since we expect this model to be applicable to many other systems it is interesting to explore the full parameter space.

GROUND STATES

A. Long Period

While Peierls' theorem [10] 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. For this model with $K_{MM} = 0$, the β term drives a long period phase. To see this consider the trivial zero-hopping limit ($t_0 = \alpha = 0$) where the electronic Hamiltonian is site-diagonal. First consider no electron-electron correlations. The lowest energy state phase separates into two regions, one of which has all the sites fully occupied and one of which has all the sites empty. Long range Coulomb effects clearly disfavor long period phases. From our numerical studies we find that this "clumped" long period phase occupies a significant portion of the phase diagram. This phase is not observed experimentally though the inferred parameters for PtCl are in the nominally long period regime. We are currently investigating [11] how inclusion of (site dependent) short- and long-range correlations, allowing β to have a site dependence, quantum phonons, etc., will shift the phase boundary and whether the β term in conjunction with some of these additional interactions can drive "twins" or discommensurations, i.e., long period patterns intermediate between clumping and period 4. Preliminary results indicate that such superlattice orderings are nearby metastable states. For the rest of the discussion we restrict the ground state to be in the experimentally relevant period 4 phase.

Fig. 2: Lattice distortion amplitude as a function of U from the various approaches. The metastable amplitude of the BOW or CDW in the other phase regime is shown as dotted. The circles are the results from the QPVA.

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 β the lowest energy period 4 phase is nearly always a charge-density-wave on the M sites (CDW) [3]. (There is a bond-order-wave on the X sites, but we label the states by the M behavior in analogy with the one-band model notation [3].) 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 [2-7], where the BOW phase is found for a substantial range of parameter values. Using perturbation, Hartree-Fock, and Lanczos exact diagonalization techniques to treat e-e correlations, and treating the phonons in adiabatic approximation, we have mapped out the phase diagram for small β and moderately small to large ϵ_0 . (We avoid large β as it drives the long period phase discussed above.) We also set $U_X = U_M = U$. We find [8] for small U that the system has a CDW and for intermediate U the system has a BOW. Since Hartree-Fock contributes in the CDW, explicit correlation corrections are not so striking. This is in contrast to the BOW where, as in polyacetylene [12], Hartree-Fock level terms vanish and exact treatment of the e-e correlations is essential. Fig. 2 shows the amplitude of the CDW or BOW phase as a function of U . We have used a (Gutzwiller-like) variational approach (QPVA) [13], to investigate the effects of quantum phonons. We found [8] that for small values of U , the QPVA always yields a lower bound than the exact diagonalization of the electronic part of our model in combination with a classical treatment of the phonon degrees of freedom (EDCP), which can also be interpreted in terms of a variational Ansatz [13]. The quality of the QPVA, compared to the EDCP bound, increases with ϵ_0 . In addition, the relative distance between the two bounds decreases with growing ϵ_0 . For reasonably small values of the Hubbard U a CDW-state exists with decreasing amplitude as a function of U , also shown in Fig. 2 (circles). Quantum effects have dramatically reduced the CDW amplitude. The influence of quantum fluctuations contained in the QPVA removes the BOW phase, found above in our adiabatic treatment, in the parameter regime under consideration; experimentally no MX material with a BOW phase is observed.

EXCITATIONS AND ASSOCIATED OPTICAL ABSORPTIONS

The cases of one and two added or subtracted electrons on a 100 site ring (polarons, bipolarons, and kink pairs) and zero or one added or subtracted electron on a 98 site ring (neutral and charged kinks) in the CDW phase were studied. Photoexcitations were also studied. When the MM distance was allowed to vary, the CDW distortion for the various cases was accompanied by a localized BOW distortion, which followed roughly the derivative of the CDW distortion (similar to including acoustic and optic phonons in polyacetylene models). This model has no electron-hole symmetry even in the absence of correlations, and this was reflected in the fact that the electron and hole defects had slightly different absorptions. This asymmetry is not present in the one-band model [3]. In Fig. 3 we show the optical absorption spectra for the polarons discussed above. We note that increasing β sharply decreases the width of the polaron toward the valence-trapped limit [3], whereas increasing ϵ_0 has little effect.

Fig. 4 shows the bipolaron and and Fig. 5 the kink spectra. As might be expected, bipolarons are narrower and deeper than the corresponding polarons, and have associated localized electronic states deeper in the gap. Both the electron polaron

Fig. 3 (left): The optical absorption spectra for a hole (solid) and electron (dotted) polaron in the absence of e-e correlations with $t_0 = 0.5$, $\alpha = 0.5$, $\epsilon_0 = 0.6$, $\beta_M = 0.3$, $\beta_X = -0.15$, $K = 1$, and $K_{MM} = \infty$; and the electron-polaron with $K_{MM} = 0$ is also shown (dashed). The lines have been Lorentzian broadened and the inter-valence charge transfer (IVCT) has been scaled to 1.

Fig. 4 (right): The optical absorption spectra for a hole (solid) and electron (dotted) bipolaron with the same parameters as for Fig. 3.

and bipolaron are at least as stable as two appropriately charged kinks; their relative stability increases with increasing J , but decreases with increasing ϵ_0 . Note however that the relative stability of polarons versus kinks or bipolarons is sensitive to U [3].

Fig. 5 (left): The optical absorption spectra for a hole (solid) and electron (dotted) kink with the same parameters as for Fig. 3.

Fig. 6 (right): The optical absorption spectra for an electron polaron with $U = 0$ (dotted) and $U = 2$ (solid) and other parameters the same as for Fig. 3.

absorption has been scaled to 1.0. U_V has little effect, and U_M decreases the IVCT, or effectively increases the polaron gap state energies. We have checked our mean field code against the exact results obtained using a Lanczos diagonalization procedure on 12 sites and find essentially no difference for these parameters values. The spectrum in Fig. 6 with $U = .2$ agrees fairly well with the experimentally measured spectrum for PtCl [14].

ACKNOWLEDGEMENTS

We would like to thank S. Mazumdar and D.K. Campbell for useful discussions. We are happy to acknowledge the Centers for Materials Science and Nonlinear Studies for computational support at Los Alamos National Laboratory, the Computational Sciences Division of the US DOE for computational support at the NMFEC at Livermore, and the Höchstleistungsrechenzentrum (HLRZ) for computational support at the KFA Jülich, W. Germany. Work of SRP supported by U.S. Department of Energy B.E.S.-Materials Science under Contract W-31-109-Eng-38. We would also like to thank LANL for supporting non-defense basic research.

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, Proceedings of ICSM '88, to appear in Synthetic Metals and unpublished.
3. D. Baeriswyl and A.R. Bishop, Physica Scripta, **T12** (1987) 239; J. Phys. C: Solid State Phys., **21** (1988) 339.
4. Y. Ichinose, Solid State Commun., **50** (1984) 137.
5. Y. Onodera, J. Phys. Soc. Japan, **56** (1987) 250.
6. S. Kurita, M. Haruki, and K. Miyagawa, J. Phys. Soc. Japan, **57** (1988) 1789; S. Kurita and M. Haruki, Proceedings of ICSM '88, to appear in Synthetic Metals.
7. S.D. Conradson et al., Solid State Commun., **65** (1988) 723; B.I. Swanson and S.D. Conradson, Proceedings of ICSM '88, to appear in Synthetic Metals.
8. A. Bishop, J.T. Gammel, and S. Phillpot, Proceedings of ICSM '88, to appear in Synthetic Metals; J.T. Gammel, S.M. Weber-Milbrot, E.Y. Loh, Jr., and A.R. Bishop, Proceedings of ICSM '88, to appear in Synthetic Metals.
9. A. Painelli and A. Girlando, Proceedings of ICSM '88, to appear in Synthetic Metals.
10. R.E. Peierls, "Quantum Theory of Solids", Clarendon, Oxford, 1955, p. 108.
11. I. Batistic et. al, to be published.
12. D. Baeriswyl and K. Maki, Phys. Rev. B, **31** (1985) 6633.
13. S. Weber and H. Büttner, J. Phys. C: Solid State Phys., **17**, 1984, L337-L344; S. Weber and H. Büttner, Solid State Comm., **56**, 1985, 395-398; S. Weber, thesis (Dissertation), Univ. Bayreuth (1985); S. M. Weber-Milbrodt and H. Büttner, to be submitted (1988).
14. R. Donohoe, D. Tait, and B.I. Swanson, private communication.