Ab Initio Calculation of the Dimerization in the Halogen-Bridged Transition-Metal Linear-Chain Compound $Pt_2Br_6(NH_3)_4$

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All-electron local-density-approximation electronic-structure calculations show how the ligand structure of a neutral halogen-bridged transition-metal linear-chain compound, $Pt_2Br_6(NH_3)_4$, modifies the electronic structure to reduce it to an effective one-dimensional system. The dimerization and opening of the band gap is then understood on the basis of a conventional two-band Su-Schrieffer-Heeger model for isolated chains. Despite the strong $pd\sigma$ coupling between the Pt $d_{3z^2-r^2}$ and Br p_z orbitals along the chains, the system will not dimerize in the absence of the ligand structure.

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The *MX* materials, which are halogen-bridged transition-metal linear-chain compounds, provide an important testing ground for low-dimensional strongly correlated materials. In particular: (i) They exhibit low dimensionality, mixed valence, and strong electron-electron and electron-phonon interactions. (ii) They have competing charge-density, spin-density, and other ground states, which are sensitive to tuning by chemical substitutions, pressure, or doping [1-5]. (iii) The similarities in their physics to the high-temperature superconducting compounds have stimulated intense studies by several groups [4-8]. (iv) By chemical or photodoping, carriers can be introduced into the system producing interesting nonlinear excitations such as polarons, kinks, and excitons [7,8]. They also have possible technological applications because of their strong optical dichroism and their potential as nonlinear optical materials.

In this Letter we present the first complete all-electron full-potential local-density-approximation (LDA) electronic-structure calculations of an *MX* chain material. These calculations provide a detailed understanding of the electronic structure of the PtBr *MX* chain $Pt_2Br_6(NH_3)_4$ and demonstrate an *intricate* interplay between crystal structure and electronic structure. In particular, the ligands surrounding the chainlike structures play a crucial role in determining the electronic properties: *With the ligands present* the electronic states near the Fermi energy consist of a single one-dimensional hybridized Pt-Br band. Within the LDA approximation we can then explain the observed dimerization via a conventional Peierls mechanism caused by one-dimensional Fermi-surface nesting. *Without the ligands* our calculations show the presence of nonbonding Pt orbitals at the Fermi energy that prevent dimerization. Thus, our calculations explain why, in the presence of the ligands, the two-band Su-Schrieffer-Heeger (SSH) model [9] currently used to describe the *MX* systems [7,8] works so well, and provides first-principles values for the model's parameters. Finally, in addition to their effect on dimerization, the Br ligands also strengthen the material by bonding neighboring chains together along one direction; hence, while the important electronic structure near the Fermi energy that controls the electronic properties of this material is one dimensional, the chemical bonding is such that the material is better described as a set of strongly bonded planes with a relatively weak interplane bonding through the ammonia molecules.

In a related class of π-conjugated polymers, polyacetylene, there is much discussion over the role of electron-electron correlations and electron-phonon interactions on the observed dimerization and other properties [10]. In the PtBr *MX* chains, which are dominated by strong $pd\sigma$ coupling between rather delocalized Pt $5d$ and Br $4p$ orbitals, some model calculations [6] have indicated that correlations may play a less important role than is the case for π-conjugated polymers. Although LDA calculations cannot, of course, answer this type of question, the correlations that are included in the LDA exchange-correlation potential seem to be sufficient to give a reasonably good prediction for the experimentally observed PtBr-chain dimerization of 0.22 Å, which is much larger in amplitude than that of polyacetylene (0.02–0.03 Å).

The crystal structures of the *MX* materials share certain features. In particular, they all form in linear chains with alternating transition-metal atoms (M=Ni, Pd, or Pt) and halogen atoms (X=Cl, Br, or I) along a chain. Different kinds of complex ligand structures can surround the chains, and the whole matrix forms a three-dimensional crystal with the chains aligned parallel to each other. Some *MX* compounds have all the chains electrically neutral, while others have negatively charged counterions between the positively charged chains [3]. This work looks at a neutral chain, even though most of the recent data are for charged chains [11].

A simplified unit cell consists of two *MX* units, arranged such that two neighboring *X* atoms move closer to one of the *M* atoms. This dimerization can be schematically represented by $\ldots M(\mathrm{II})\ldots XM(\mathrm{IV})X\ldots M(\mathrm{II})\ldots XM(\mathrm{IV})X\ldots$ Because of the strong electronegativity of the neighboring X atoms, the dimerization causes an alternation of the valence character of the transition-metal atoms between (formally) two (II) and four (IV); of course, the real change in valence is expected to be only partial.

We have studied the MX system with the fewest number of atoms per unit cell, viz., $\mathrm{Pt_2Br_6(NH_3)_4}$. Figure 1 shows the overall structure of a single PtBr chain. The experimental x-ray data for the crystal structure, which has not been able to distinguish between the two valence states of the Pt atoms, give the result that the Pt atoms form a body-centered orthorhombic structure with lattice parameters $a=8.23$ Å, $b=7.76$ Å, and $c=5.55$ Å. In this calculation we have ordered the dimerized chains in order to minimize the number of atoms in the unit cell. This leads to a Bravais lattice with basis vectors $(a/2,-b/2,c/2)$, $(a/2,b/2,c/2)$, and $(0,0,2c)$. This structure is monoclinic with twice the number of atoms as the undimerized structure. Because the same ligand structure surrounds the Pt atoms irrespective of valence, we have assumed that the chain ordering is unimportant.

All calculations presented in this paper used an all-electron scalar-relativistic linear-muffin-tin-orbital (LMTO) method [12], which requires no shape approximations for either the potential or the charge density. The exchange-correlation potential and energy use the von Barth-Hedin parametrization [13]. The core electrons are allowed to relax and the irreducible Brillouin zone (IBZ) integration uses Gaussian sampling (for 16 **k** points/IBZ the total energy is converged to within 1 mRy).

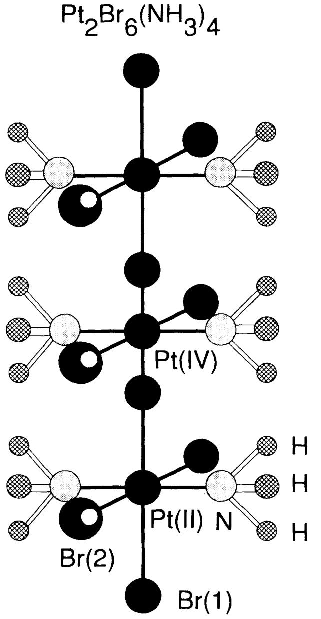

FIG. 1. Geometry of a single $\mathrm{Pt_2Br_6(NH_3)_4}$ neutral linear chain. The lattice distortion moves two of the neighboring Br atoms on the chain closer to one of the Pt atoms, which causes an alternation of the valence character of the Pt atoms, formally two (II) and four (IV), due to the strong electronegativity of the Br atoms.

We have computed the PtBr electronic structure both with and without some of the ligands. We found that *all the ligands were necessary* to generate the insulating dimerized ground state with the large lattice distortion that is observed experimentally. The calculated band gap is about 1.15 eV, compared to the 1.5 eV experimental band gap found for the charged PtBr chains [11]. As expected, the strong coupling between the Pt $d_{3z^2-r^2}$ and the Br p_z orbitals that point along the chain dominates the Pt-Br bonding in the chains. Also, the bands above and below the gap have a strong Pt(II) and Pt(IV) character, respectively, consistent with conventional notions of an "intervalence charge-transfer gap." Figure 2 shows the LDA calculated total energy as a function of dimerization. The dimerization ζ is defined as the ratio of the off-center distance of the Br atom away from its symmetric position (midway between the Pt atoms) to the Pt-Pt distance. The minimum of the total energy occurs at a dimerization of 4% which is close to the values of 4.8% and 5.2% found experimentally [2,3]. The curvature of the total energy versus lattice dimerization at the minimum energy provides an estimate for the effective phonon energy of a Raman-active breathing mode. A simple harmonic oscillator model then gives a phonon frequency of 22.8 meV, compared to the values of 21.7 and 21.5 meV found experimentally for neutral and charged chains, respectively [3,4]. This agreement with the fre-

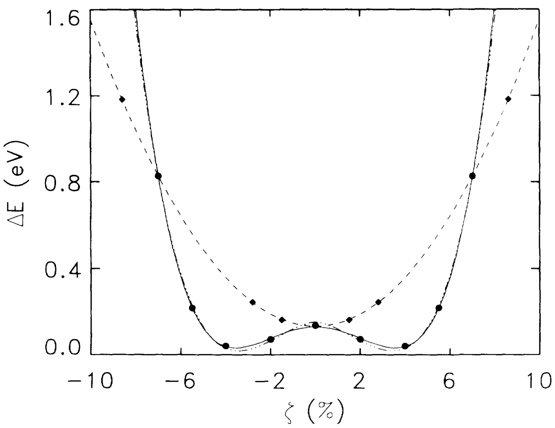

FIG. 2. LDA total energy of PtBr as a function of dimerization ratio ζ (in %). The full curve is for the real structure, the dashed curve is for the structure without the $\mathrm{NH_3}$ ligand, and the dot-dashed curve is for the Hamiltonian Eq. (1) using the calculated parameters. This clearly shows that the ligands are essential for the formation of the dimerized state. The dimerization energy is 0.1 eV [15]. A simple harmonic-oscillator-model fit to the curvature of the LDA total energy gives a breathing mode of 22.8 meV in agreement with Raman data.

quency of the Raman breathing mode is a strong confirmation of the correctness of our electronic structure calculations.

To analyze the mechanism of the lattice distortion and the origin of the band gap we have folded down the relevant band structure in terms of a two-band single-chain SSH model that is currently used to describe the electronic structure of defects in the charged MX chains [8,14]. In this model, both the hopping parameter and the on-site energy levels depend linearly on the degree of dimerization through the electron-phonon couplings α and β. Only a single $d_{3z^2-r^2}$ orbital on the Pt sites and a single p_z orbital on the Br sites along the chain are considered important. All the other orbitals and ligand structure are assumed to play a passive role, and are implicitly included in the elastic energy of the model (see $K^{(j)}$ below). On-site and nearest-neighbor Hubbard terms can be added as needed for a more explicit treatment of electron-electron correlation. The two-band SSH Hamiltonian with a minimum number of parameters is given by

$$\begin{aligned} H=\sum_{l\sigma}\{&(-t_0+\alpha\Delta_l)(c^{\dagger}_{l\sigma}c_{l+1\sigma}+\text{H.c.})\\ &+[(-1)^l e_0-\beta_l(\Delta_l+\Delta_{l-1})]c^{\dagger}_{l\sigma}c_{l\sigma}\}\\ &+\sum_{l,j=0,1}K^{(j)}\Delta_l^{2(1+j)}. \end{aligned} \qquad (1)$$

Here M and X occupy even and odd sites, respectively, and α, $\beta_{2l}=\beta_M$, and $\beta_{2l+1}=\beta_X$ are electron-phonon parameters that couple the atomic positions to the electronic structure through $\Delta_l=x_{l+1}-x_l$, where x_l is the deviation of the atoms from their positions in the symmetric structure. The zero of energy is chosen to be midway between the metal- and halogen-atom on-site levels for the undimerized structure. The M-X spring coefficients $K^{(0)}$ and $K^{(1)}$ model all other aspects of the electronic and ligand structure that are not included in the simple electronic Hamiltonian.

We have performed a least-squares fit of the bands for the Hamiltonian given by Eq. (1) to the four LDA bands that have the most Pt $d_{3z^2-r^2}$ and Br p_z character along the chain direction (ΓZ). In Fig. 3 the fitted model bands are superimposed on top of the LDA bands for the ground-state (4% dimerization) bands. The fit provides values for e_0, t_0, α, and β_M (we have neglected β_X to minimize the number of parameters). Although this set can be calculated for each separate dimerization, a more accurate procedure is to perform a simultaneous global fit with only one set of parameters to the bands for each of the different dimerizations we used, and to compare these parameters to those obtained from individual fits to the LDA bands for each dimerization. We have found that the parameters of the individual least-squares fits differ at most by 3% from the respective global-fit parameters except for β_M which is relatively small and has scattered values. An error-correlation matrix for the fit shows that the least-squares fit is less sensitive to β_M. The calculated parameters and the spring coefficients are used to obtain the total energy of the model as a function of the dimerization; this compares nicely with the LDA total energy (see Fig. 3). We have found that the widely used quadratic approximation to the elastic energy is only valid for small dimerizations ($\leq 2\%$) and that a quartic term is *necessary* for large dimerizations. Here the spring coefficients are found to be $K^{(0)}=0.74$ eV/Å^2 and $K^{(1)}=12.05$ eV/Å^4.

The results of the fit, which provide the electron-phonon coupling constants, are given in Table I. The last two columns, labeled "Emp. (1)" and "Emp. (2)," give two recent empirical fits to various experimental data [8,14]. In addition to the size of the band gap and the dimerization, the second empirical fit uses the experimental Raman and infrared frequencies. A comparison of these two fits gives some feeling for the sensitivity of the model parameters to the input experimental data (namely, that the deviations for the on-site energies and the β values are significantly large). As shown in Table I, our *a priori* LDA predictions for the parameters of the model are more consistent with the second empirical fit, which uses more experimental data than the first.

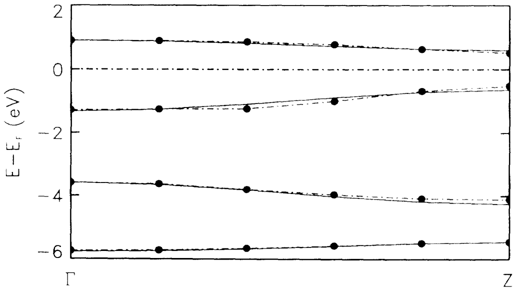

FIG. 3. Least-squares fit of the two-band Su-Schrieffer-Heeger Hamiltonian bands (full curves) to the LDA Pt$d_{3z^2-r^2}$ and Br p_z bands (dot-dashed curves). The LDA band gap is 1.15 eV compared to 1.28 eV obtained from the model.

TABLE I. Two-band Su-Schrieffer-Heeger model parameters as obtained from the fit to the LDA results and to experimental data (last two columns). The errors are obtained from the error-correlation matrix, i.e., the errors in the parameters correspond to the shifts of the parameters which would change the square root of the least-squares deviation of the band energies by 13.6 meV.

	Fit to LDA	Emp. (1)[a]	Emp. (2)[b]
$2e_0$ (eV)	2.32 ± 0.03	1.0	2.4
t_0 (eV)	1.50 ± 0.02	1.3	1.4
α (eV/Å)	2.4 ± 0.2	2.2	1.9
β_M (eV/Å)	0.3 ± 0.2	0.2	0.8

[a] Empirical values for the charged PtBr system from Ref. [7].
[b] Empirical values for the charged PtBr system from Ref. [14].

For the undimerized case, we have done calculations both with and without the ammonia ligand structure. We have found that the important one-dimensional bands near the Fermi energy, which were modeled by the two-band SSH model, are very similar to each other for these two cases; this suggests that the ammonia ligands play almost no role in determining the conducting properties of these important bands. Instead, their main role seems to be to *remove* from the Fermi energy the nonbonding d orbitals that point in the direction of the ammonia ligands. Once this is done, the Peierls mechanism is effective in producing a dimerized ground state. We have found that the case of PtBr without ammonia ligands *does not dimerize* (i.e., the lowest total energy is for the the undimerized structure; see Fig. 2). To show that the interchain coupling is unimportant, we have also done calculations without the ammonia ligands for the undimerized band structure for a lattice expanded by 15% perpendicular to the chain direction. The flat nonbonding d bands near the Fermi surface were nearly identical to those for the unexpanded case and the Pt $d_{3z^2-r^2}$ and Br p_z bands remained unchanged. This indicates that these nonbonding orbitals primarily point toward the positions that would normally be occupied by the ammonia ligands. In the real structure the ammonia-ligand lone-pair orbitals and the Pt$(d_{x^2-y^2},s)$ nonbonding orbitals form bonding molecular orbitals and move away from Fermi energy.

In conclusion, we have found that the LDA correctly predicts dimerization for the MX chain compound $Pt_2Br_6(NH_3)_4$. With the ligands present the one-dimensional bands at the Fermi energy, which have an approximately nearest-neighbor form (with only small deviations from the expected cosine k dependence along the chain), dominate the physics of this system and allow the Peierls mechanism to be effective in causing a dimerized ground state. A SSH model is able to provide an excellent fit to the LDA bands and total energy. Detailed electronic-structure calculations were needed to show that the reason the SSH model works for the MX chains is actually quite subtle, since it depends on the ligand structures to remove all the nonbonding orbitals away from the Fermi energy region. Finally, we find it remarkable that all of the atoms (particularly the ammonia molecules) of the experimental system are *necessary* for lattice dimerization to occur.

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[1] H. J. Keller, in *Extended Linear Chain Compounds*, edited by J. S. Miller (Plenum, New York, 1982), Vol. 1, p. 357.

[2] R. J. H. Clark and R. E. Hester, in *Infrared and Raman Spectroscopy* (Wiley Heyden, New York, 1984), Vol. 11, p. 95.

[3] H. J. Keller *et al.*, Acta Crystallogr. **37**, 674 (1981).

[4] L. Degiorgi *et al.*, Phys. Rev. B **40**, 3285 (1989).

[5] R. J. Donohoe *et al.*, Solid State Commun. **71**, 49 (1989), and references therein; M. Tanaka *et al.*, Chem. Phys. **91**, 257 (1984).

[6] S. M. Weber-Milbrodt *et al.*, Phys. Rev. B **45**, 6435 (1992).

[7] D. Baeriswyl and A. R. Bishop, J. Phys. C **21**, 339 (1988).

[8] J. T. Gammel *et al.*, Phys. Rev. B **45**, 6408 (1992), and references therein.

[9] W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. B **22**, 2099 (1980).

[10] See references and discussion in D. Baeriswyl, D. K. Campbell, and S. Mazumdar, in *Conducting Polymers*, edited by H. Kiess (Springer, Heidelberg, 1992); M. Takahashi and J. Paldus, Int. J. Quantum Chem. **28**, 459 (1985); S. Suhai, Phys. Rev. B **27**, 3506 (1983); G. König and G. Stollhoff, Phys. Rev. Lett. **65**, 1239 (1990); M. Springborg *et al.*, Phys. Rev. B **44**, 12 713 (1991); see also the discussion in J. L. Brĕdas and A. J. Heeger, Phys. Rev. Lett. **63**, 2534 (1987).

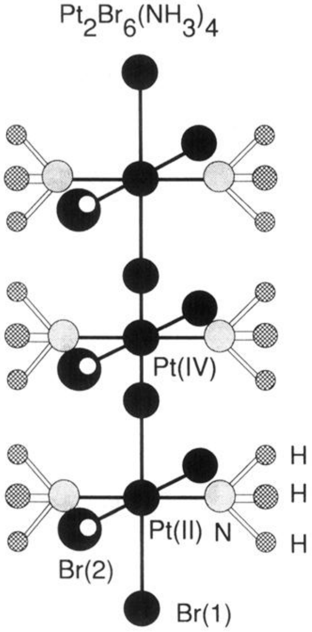
[11] Very little is known experimentally about the neutral MX chains, because (at the present time) it is difficult to make large enough samples for most measurements [B. Swanson (private conversation)]. However, the neutral and the charged systems have sufficiently close available electronic properties that comparisons between our predictions for neutral PtBr and experimental results for charged PtBr are appropriate.

[12] J. M. Wills (unpublished); M. Springborg and O. K. Andersen, J. Chem. Phys. **87**, 7125 (1987).

[13] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1988).

[14] X. Z. Huang *et al.* (unpublished).

[15] At zero dimerization the total energy, including the core electrons, for $Pt_2Br_6(NH_3)_4$ is $E_0 = -1433891.587$ eV/(unit cell).



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