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CONF-880669-9

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--88-2508

DE88 014404

TITLE: LMTO ELECTRONIC BAND-STRUCTURE CALCULATIONS FOR LINEAR PT-BR CHAINS

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SUBMITTED TO: Submitted for international COnference on Science and Technology of Synthetic Metals, June 26-July 2, 1988, in Santa Fe, NM. The proceedings will be published in several issues of the journal, Synthetic Metals.

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# LMTO ELECTRONIC BAND-STRUCTURE CALCULATIONS FOR LINEAR PT-Br CHAINS

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## ABSTRACT

Self-consistent first-principles Linear Muffin-Tin Orbital (LMTO) scalar-relativistic and Dirac-relativistic electronic band structure calculations are presented for linear Pt-Br chains (without any ligand structure) embedded in a three-dimensional crystal with empty atomic spheres added to isolate the chains. These calculations are a first step towards a complete a priori calculation of the electronic structure of the halogen-bridged linear platinum chain compound  $\text{Pt}_2\text{Br}_6(\text{NH}_3)_4$ , an MX chain compound (M = transition metal and X = halogen atoms).

## INTRODUCTION

Linear platinum chain compounds are of great interest because of their low dimensionality, mixed-valence character, strong electron-electron and electron-phonon interactions, competing ground states, and the large overlap in physics with the high-temperature superconductors[1]. They exhibit interesting nonlinear excitations such as polarons and solitons and by tuning with chemical substitutions and pressure their charge density (or dimerized) ground states can be pushed towards a more metallic limit that removes their mixed-valent character. Interest in possible commercial applications for this class of materials is usually based on their strong optical dichroism.

Most of these effects are driven by the electronic structure of these materials, which, because of the very open crystalline structures and the tendency towards the formation of localized electronic states, is unfortunately difficult to calculate by conventional a priori solid-state methods. To date only tight-binding methods that are fit to experiment have been used[2-3]. In an attempt to try a first-principles method on this class of materials we have started with some simple model calculations where we have isolated ligand-free Pt-Br chains in a hypothetical three-dimensional geometry. Our ultimate goal is to understand the (geometrically) simplest of the MX systems, viz.  $\text{Pt}_2\text{Br}_6(\text{NH}_3)_4$ , which has neutral chains (that avoid the complications of long-range Madelung and other electrostatic effects) in a

body-centered orthorhombic unit cell[4]. The alternating Pt and Br chain structure parallel to the z-axis has two Br ligands at a distance of +/- 2.445 Å along the x-axis and two NH<sub>3</sub> molecules at a distance of +/- 2.066 Å (Pt-N distance) along the y-axis around each Pt atom. Thus each Pt atom in this PtBr<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub> molecular fragment formally has a valence of two, Pt<sup>II</sup>, since each Br is expected to remove one electron.

The simplest possible chain structure is the symmetric case, indicated schematically by ...M...X...M...X...M...X..., where each Br (X) atom is equidistant from its neighboring Pt<sup>III</sup> (M) atoms. The real PtBr<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub> compound actually has a dimerization that consists of moving each Br atom off center in a staggered fashion by 10.4 % (relative to the symmetric Pt-Br distance of 2.77625 Å) to give a pattern of ...M..X-M-X...M...X-M-X... and so on. The Pt-Pt distance along the chain is 5.5525 Å and the two Pt-Br distances are 2.485 Å and 3.068 Å. In effect, we have a X-M-X molecular fragment that alternates with more isolated M atoms. Each Pt atom in the X-M-X fragments then formally has a valence of four, which gives rise to the alternating Pt valence along the chain: Pt<sup>II</sup>—Pt<sup>IV</sup>—Pt<sup>II</sup>—Pt<sup>IV</sup>. Adding the other chains completes the three-dimensional crystal structure. In both the real and model systems each chain has four nearest-neighbor chains. They differ in their interchain distances and the alignment of the Pt atoms between the chains.

## METHOD

All of the calculations use the Linear Muffin-Tin Orbital (LMTO) band structure method[5-6], including the combined correction terms, with a von Barth-Hedin local-density exchange-correlation potential[7]. Self-consistency was achieved using 75 k points in the irreducible part of the Brillouin zone. Three different types of calculations were done: both semi-relativistic and full (Dirac) relativistic calculations were done for the symmetric structure (Br midway between the Pt atoms) and semi-relativistic calculations for the dimerized structure. For all of these calculations a tetragonal unit cell was chosen such that the Pt-Br chains form a square lattice. In between these chains are chains of empty spheres to fill space and isolate the Pt-Br chains. For the symmetric structure the cell dimensions are chosen so that the Pt-Pt distance (the c-axis dimension) is the same as for the real material (5.5525 Å) and is also equal to the a and b axis dimensions. The 8 atomic positions (in units of a, the a-axis length) were chosen as: Pt at (1/2,1/2,0), Br at (1/2,1/2,1/2), and empty spheres at (0,0,0), (1/2,0,0), (0,1/2,0), (0,0,1/2), (1/2,0,1/2), and (0,1/2,1/2). For the dimerized structure the unit cell doubles along the c axis to 16 atomic spheres in the unit cell and the Br atoms and associated empty spheres move up or down by the required 10.4 %.

## RESULTS

The semi-relativistic bands along and perpendicular to the chains for the symmetric case are shown in Fig. 1. A Br p<sub>z</sub> band lies lowest in energy, followed by the Br p<sub>x</sub> and p<sub>y</sub> bands (degenerate along the chain), and finally the 5 Pt d bands. This band ordering differs from the tight-binding fits to the optical data in Ref. 10, where the Br p<sub>x</sub>—p<sub>y</sub> and p<sub>z</sub> band ordering is

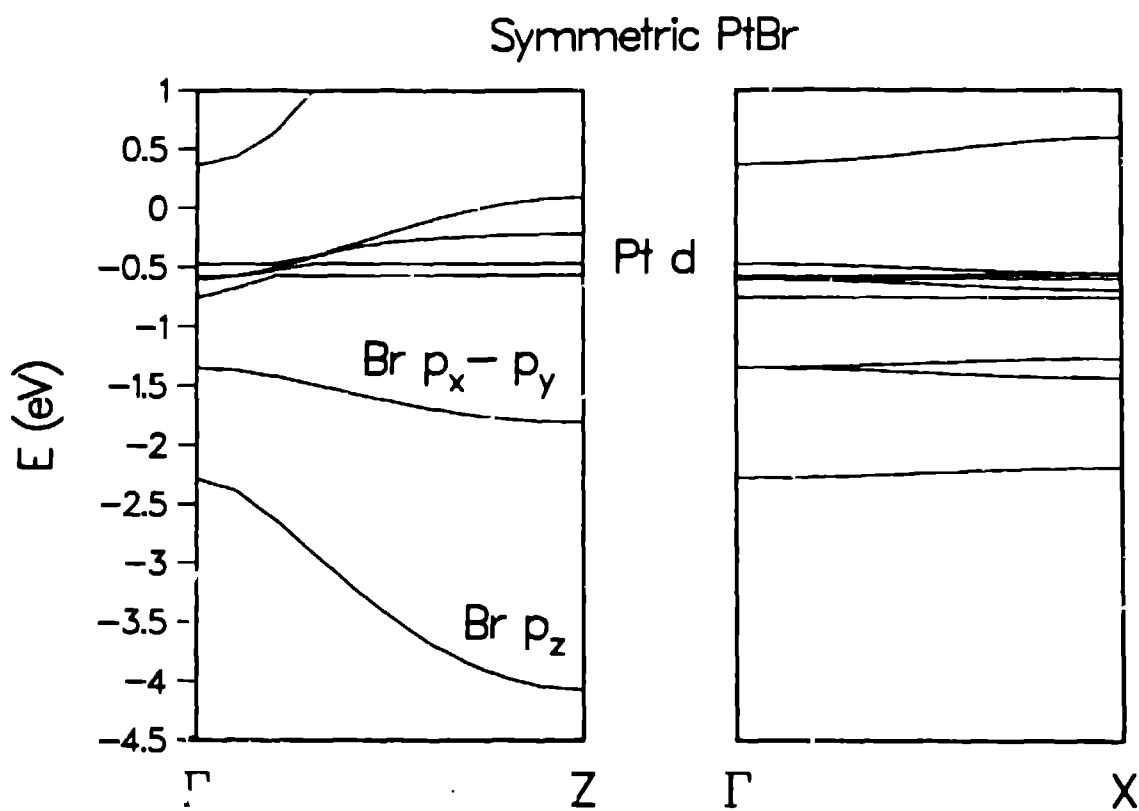


Fig. 1. Bands along the chains ( $\Gamma$  to  $Z$ ) and perpendicular to the chains ( $\Gamma$  to  $X$ ) for symmetric PtBr (Br atoms midway between Pt atoms). The Fermi energy is at zero.

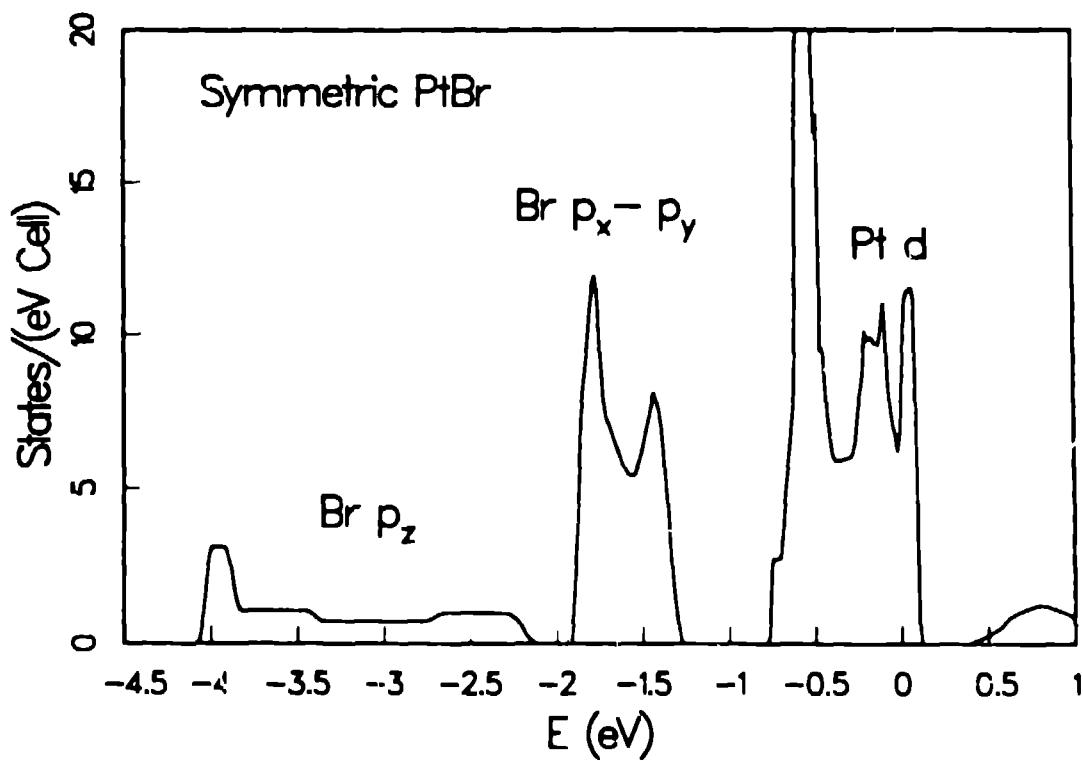


Fig. 2. Total density of states (DOS) for symmetric PtBr. The Fermi energy is at zero.

reversed. Besides ligand effects this discrepancy is probably a consequence of expected strong electronic relaxation[9], which could easily change relative band ordering when empirically fitting experimental results to an independent-electron model. The band filling also differs since the Fermi energy cuts the top of the Pt d bands in our model calculations, leaving a hole band containing one electron (there are 5 Br electrons and 10 Pt electrons per atom; each band contains two electrons from the spin degeneracy). In  $\text{Pt}_2\text{Br}_6(\text{NH}_3)_4$  the two ligand Br atoms around each Pt atom pull off two additional electrons per Pt atom, moving the Fermi energy closer to the middle of the Pt d band and probably causing a stronger Pt-Br hybridization that will increase the band widths. It also means that our dimerized case will formally have  $\text{Pt}^0$  and  $\text{Pt}^{II}$  valences, but we will ignore this distinction and continue to refer to these valences as  $\text{Pt}^{II}$  and  $\text{Pt}^{IV}$  to avoid confusion with the description for the real compound.

The symmetric case d-bands have two bands with dispersion along the chain axis and the two other flat d bands (the  $d_{xy}$  and  $d_{x^2-y^2}$  bands). It is difficult to follow these bands due to a near degeneracy about a third of the way from the  $\Gamma$  to the Z point. The  $d_{z^2}$  band is lowest in energy at the zone center but is actually only the second highest band at the zone boundary (with a bandwidth of about 0.5 eV). The highest band at the zone boundary (but second highest at the zone center) really consists of a pair of two degenerate bands: the  $d_{xz}$  and  $d_{yz}$  bands (with a bandwidth of about 0.7 eV). Their surprisingly large dispersion is probably due to the missing ligand structure, which allows them to hybridize as strongly as possible with the Br atoms along the chain. In more realistic situations, for example, in extended Debye-Hückel tight-binding calculations[4] for symmetric  $[\text{Pt}(\text{NH}_3)_4\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{+4}$ , this dispersion is not seen and the relative Pt d band ordering is also different. This suggests that the ligand side structure does more than just change the band filling; it also changes the electronic structure along the chain through indirect symmetry and hybridization effects.

The symmetric case electronic structure is also shown as a density of states (DOS) in Fig. 2 in order to more easily compare to the dimerized case (Fig. 3), where the DOS form is particularly useful due to the doubling and very complicated nature of the dimerized bands. (Note that we have clipped off the highest peaks in all the DOS plots.) The dimerized electronic structure can be viewed as electronic molecular states of the X-M-X fragment (M =  $\text{Pt}^{IV}$ ) that tunnel through the isolated  $\text{Pt}^{II}$  atoms. All of the bands that are present in the symmetric case are also present for the dimerized case and have approximately the same energy position relative to the Fermi energy. However, their band width is greatly reduced due to the large distance between the X-M-X and X clusters that the electrons must tunnel through to form bands. A second set of bands that arise from the doubling of the unit cell are lower in energy and belong to the X-M-X cluster; an analysis of their wave functions shows strong Br-Pt<sup>IV</sup> hybridization. The original and hybridized Br p bands are well separated in Fig. 3 since the band dispersion is less than the band separation. For the Pt d bands this is not the case and most of the bands overlap each other. The one exception is a pair of flat Pt<sup>IV</sup>  $d_{xy}$  and  $d_{x^2-y^2}$  bands that are pulled below the d band complex. The spiky structure near -0.5 eV is similarly due to the  $\text{Pt}^{II}$   $d_{xy}$  and  $d_{x^2-y^2}$  bands. If we ignore their

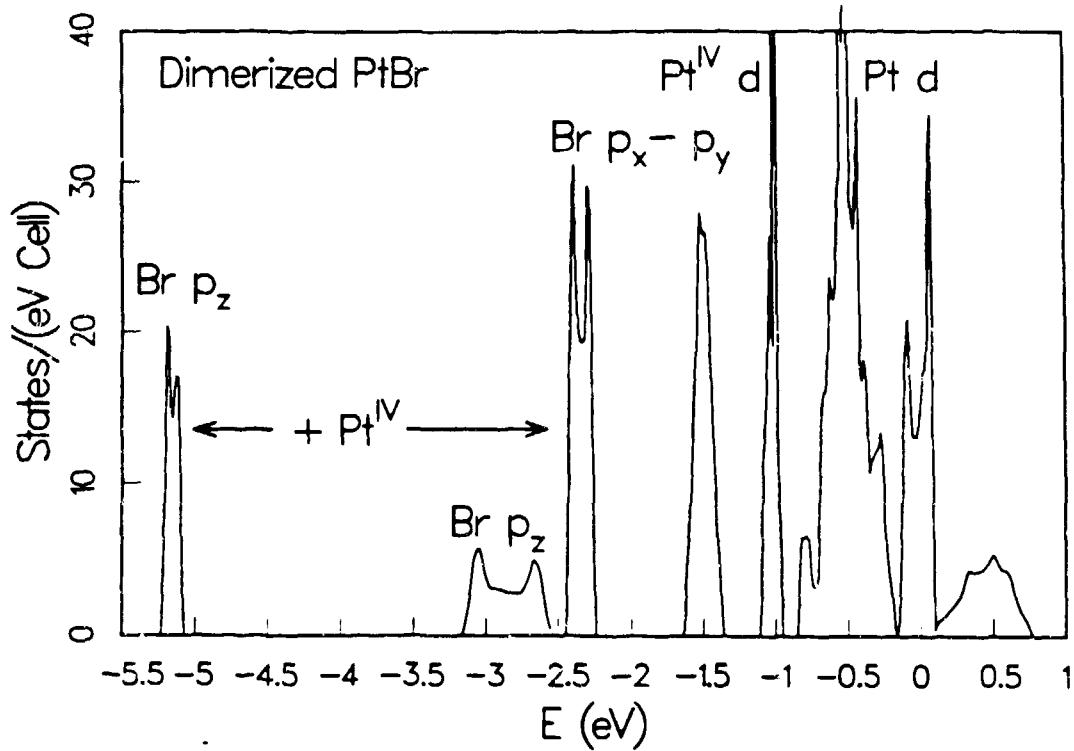


Fig. 3. Total density of states (DOS) for dimerized PtBr. The Fermi energy is at zero.

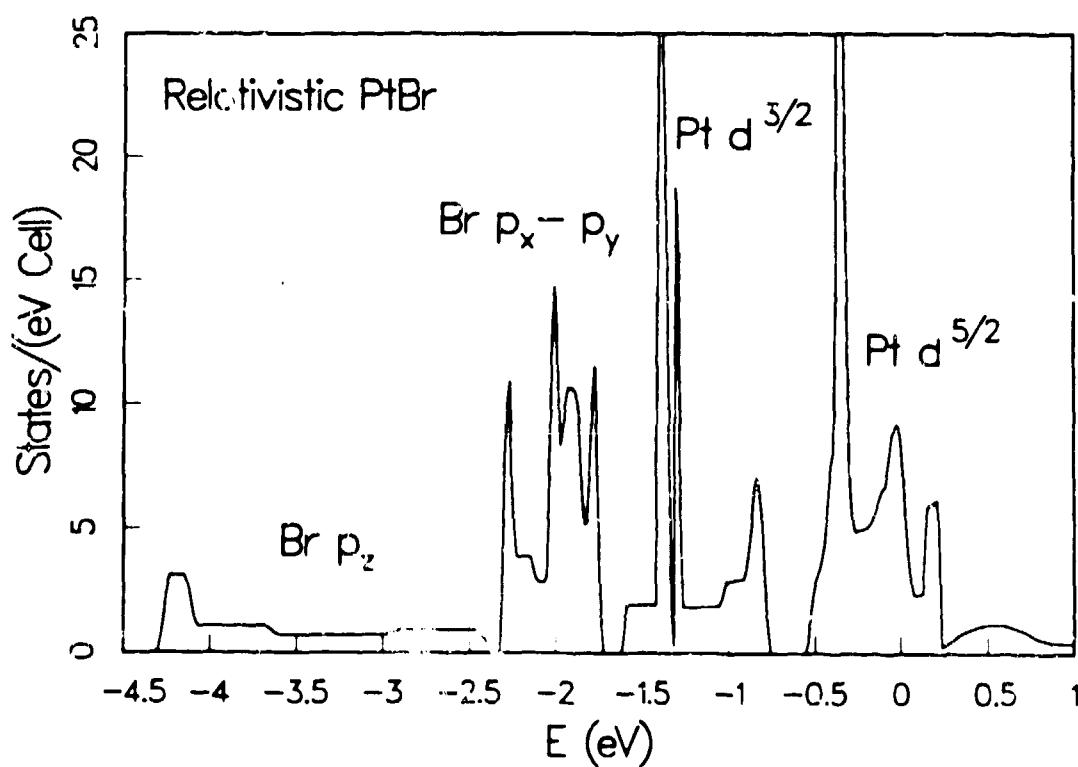


Fig. 4. Total density of states (DOS) for Dirac relativistic calculations of symmetric PtBr. The Fermi energy is at zero.

the d-band complex upwards in energy) is: Pt<sup>IV</sup>  $d_{z^2}$ ; Pt<sup>IV</sup>  $d_{xy}$  and  $d_{x^2-y^2}$ ; Pt<sup>II</sup>  $d_{z^2}$ ; and Pt<sup>II</sup>  $d_{xy}$  and  $d_{x^2-y^2}$ . As discussed above, ligand structure will probably change this band ordering. Finally, the Pt<sup>IV</sup> s states in the X-M-X complex have been lowered in energy due to the additional Br hybridization and now sit just above the top of the Pt d complex.

Because of their high Z-number, Pt can be expected to exhibit relativistic effects. To a first approximation these may be handled by using a semi-relativistic approach, which may be viewed as a j-weighted or j-averaged relativistic calculation[8]. This takes care of effects involving charge redistribution and the approximately correct energy-band placement. Also, because the normal non-relativistic orbital angular momentum and spin angular momentum quantum numbers ( $\ell$  and  $s$ ) remain good quantum numbers in this formalism and because relativistic effects are only significant deep in the core of the atoms and are negligible in the outer parts of the atoms where bonding occurs, except for a modified numerical integration in the atomic cores this approach has the advantage of allowing the normal non-relativistic formalism to be used. Only the symmetry breaking spin-orbit terms are neglected. To explore the spin-orbit effects we have made Dirac-relativistic calculations for the Pt-Br symmetric case. The resulting DOS is shown in Fig. 4 and indicates a 1 eV Pt d band spin-orbit splitting. Because this is larger than the d-band widths, the DOS shows two well defined Pt d  $j=3/2$  and  $j=5/2$  peaks. The lower  $j=3/2$  component then comes very close to the top of the Br  $p_x$  and  $p_y$  bands, greatly enhancing their hybridization with the Pt d states. Thus, besides the direct splitting of the d bands, other parts of the electronic structure are also indirectly modified by the Pt spin-orbit interaction, which suggests that a full (and computationally expensive) relativistic calculation is required if the electronic structures of the Pt MX and MMX systems are to be quantitatively explained. It also suggests that relativistic selection rules should be used in place of the normal non-relativistic dipole selection rules for assigning optical transitions.

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