

replacement of axial ligands is accompanied by substantial changes in the bonding between iron and macrocyclic ligands. Upon replacement of the axial ligands  $PR_3$  by  $P(OR)_3$ , there must be both an increase in  $p \rightarrow Fe \pi$  donation to compensate for the  $Fe \rightarrow P(OR)_3$  back-bonding and a significant decrease in  $p \rightarrow Fe \sigma$  donation to diminish  $n_x^2-y^2$ . This mechanism explains trend d and is consistent with trend b. The macrocyclic ligands appear to be able to modify their  $\sigma$ - and  $\pi$ -bonding characteristics to suit the requirements of the axial ligands.

Small differences in axial bond lengths might equally explain trend d as in the case for the carbonyl hemochromes.<sup>11</sup> Although X-ray structural data are not available for the present complexes, the electronic spectra of  $Fe(TPP)L_2$  suggest the larger  $n_x^2$  in  $Fe(TPP)(PR_3)_2$ .<sup>15</sup> A similar situation may be expected in  $FePcL_2$ .

Our results support the existence of an "electron sink"<sup>2</sup> or an "electron buffer"<sup>13</sup> capability of macrocyclic ligands such as porphyrins and phthalocyanine, proposed previously. Such behavior may be responsible in part for the diverse functions in which metalloporphyrins participate in biological systems.

**Registry No.**  $Fe(TPP)(PEt_3)_2$ , 89165-45-7;  $Fe(TPP)(PBu_3)_2$ , 89165-46-8;  $Fe(TPP)[P(OMe)_3]_2$ , 89165-47-9;  $Fe(TPP)[P(OEt)_3]_2$ , 89165-48-0;  $Fe(TPP)[P(OBu)_3]_2$ , 89165-49-1;  $FePc(PEt_3)_2$ , 89165-50-4;  $FePc(PBu_3)_2$ , 61005-30-9;  $FePc[P(OEt)_3]_2$ , 55925-78-5;  $Fe(TPP)Cl$ , 16456-81-8;  $FePc$ , 132-16-1.

(15) The larger red shift observed results from the stronger interaction between the phosphorus  $3p_z$  and porphyrin  $e_g(\pi^*)$ , which suggests a stronger interaction between the phosphorus  $3p_z$  and iron  $3d_x^2$ .

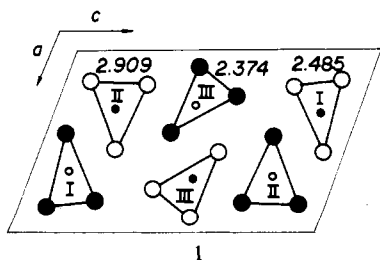
Contribution from the Department of Chemistry,  
North Carolina State University,  
Raleigh, North Carolina 27650,  
and Laboratoire de Physicochimie des Solides,  
Université de Nantes, 44072 Nantes Cedex, France

### Characterization of the Charge Density Waves in $NbSe_3$ by Band Electronic Structure

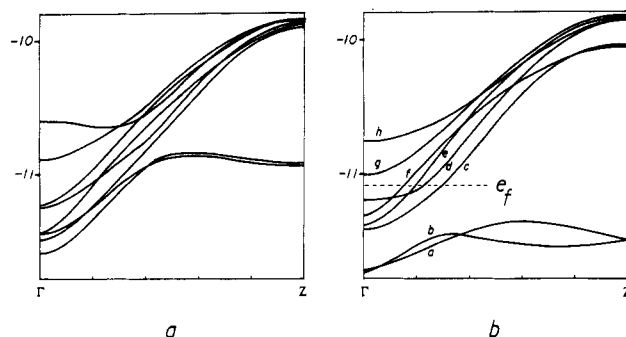
Myung-Hwan Whangbo\*<sup>1a</sup> and Pascal Gressier<sup>1b</sup>

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$NbSe_3$  is made up of trigonal-prismatic chains that are parallel to the monoclinic  $b$  axis.<sup>2</sup> As shown by the projected view along the  $b$  axis in **1**, each unit cell contains three different



pairs of  $NbSe_3$  chains, hereafter referred to as type I, II, and III chains.  $NbSe_3$  exhibits spectacular resistivity anomalies associated with two charge density waves (CDW's).<sup>3</sup> The



**Figure 1.** d-Block band structures of  $NbSe_3$  along the chain direction  $\Gamma \rightarrow Z$ , where  $\Gamma = (0, 0, 0)$  and  $Z = (0, 0.5, 0)$  in fractions of the reciprocal vectors  $a^*$ ,  $b^*$ , and  $c^*$  (band orbital energies in eV): (a) for a unit cell containing six identical, ideal chains (Se-Se distances of an ideal chain taken to be the average values of the corresponding values of type I and III chains); (b) for a real unit cell **1** containing three nonequivalent pairs of chains.

**Table I.** Exponents  $\xi_\mu$  and Valence-Shell Ionization Potential  $H_{\mu\mu}$  for Slater Type Atomic Orbitals  $\chi_{\mu a, b}$

$\chi_\mu$	$\xi_\mu$	$\xi_\mu'$	$H_{\mu\mu}$ , eV
Nb 5s	1.9 <sup>c</sup>		-10.1
Nb 5p	1.85		-6.86
Nb 4d	4.08 (0.6401)	1.64 (0.5516)	-12.1
Se 4s	2.44 <sup>d</sup>		-20.5 <sup>e</sup>
Se 4p	2.07		-14.4

<sup>a</sup> The d orbitals of Nb are given as a linear combination of two Slater type orbitals, and each is followed by the weighting coefficient in parentheses. <sup>b</sup> A modified Wolfsberg-Helmholz formula was used to calculate  $H_{\mu\mu}$ .<sup>9</sup> <sup>c</sup> Reference 10. <sup>d</sup> Reference 11. <sup>e</sup> Reference 12.

wave vectors of these CDW's are  $q_1 = (0, 0.243b^*, 0)$  at 144 K and  $q_2 = (0.5a^*, 0.263b^*, 0.5c^*)$  at 59 K.<sup>4</sup> Thus, the vector component along the chain direction (i.e.,  $q_{1b} = 0.243b^*$  and  $q_{2b} = 0.263b^*$ ) suggests nearly one-fourth-filled bands for both CDW's.

On the basis of the difference in the Se-Se distance (1), Wilson proposed an oxidation formalism of  $(Nb^{5+} + 3Se^{2-})$  for type II chains.<sup>5</sup> Given the oxidation formalism of  $(Se^{2-} + Se_2^{2-})$  for the selenium atoms of type I and II chains, therefore, there remain two d electrons per unit cell to distribute among the niobium ions of the four type I and II chains. According to this model, each type I or III chain has a nearly one-fourth-filled d-block band while each type II chain has an empty d-block band. Thus, CDW's appear only in type I and III chains, and type II chains are insulating and diamagnetic.

In order to check Wilson's model, Devreux has recently carried out a <sup>93</sup>Nb NMR study of  $NbSe_3$ .<sup>6</sup> Wilson's model led to the expectation that the NMR spectrum of  $NbSe_3$

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**Table II.** Character of the d-Block Bands of NbSe<sub>3</sub> at the Fermi Level

band	% contribn <sup>a</sup>		
	chain I	chain II	chain III
c	76.9 (61.9)	20.6 (11.9)	2.7 (0.9)
d	9.0 (4.6)	20.0 (7.9)	71.0 (51.6)
e	15.8 (7.3)	10.2 (3.3)	74.0 (53.7)
f	83.5 (62.2)	6.6 (4.4)	9.9 (7.0)

<sup>a</sup> Numbers without parentheses refer to overall chain contribution, and those in parentheses to metal contribution.

should show the absence of Knight shift for one Nb line and the effects of the CDW's on the quadrupolar structure for the other two Nb lines. Contrary to this expectation, Devreux found no diamagnetic chains in NbSe<sub>3</sub>. The chains not affected by the CDW's are found to have the largest Knight shift and the largest quadrupolar interaction. Thus, these chains are characterized by a small density of states at the Fermi level. On the basis of the band structure of Hoffmann et al.,<sup>7</sup> Devreux suggested that two of the six low-lying d-block bands (see Figure 1a) should be lowered to be completely filled and the remaining four bands should accommodate two electrons to provide four roughly one-fourth-filled bands. In this model, the two lowered bands were thought to be the d bands of type II chains.

Concerning the nature of type II chains, Wilson's model is not compatible with that of Devreux. In addition, the NbSe<sub>3</sub> band structure of Hoffmann et al. is based upon a unit cell constructed from six identical, ideal NbSe<sub>3</sub> chains. In resolving the apparent discrepancy between Wilson's and Devreux's models, we felt it necessary to reexamine the band structure of NbSe<sub>3</sub> by allowing the presence of three nonequivalent pairs of chains in a unit cell. Results of our tight-binding band calculations<sup>8</sup> are described in the following. The parameters of our calculations are given in Table I.

Figure 1a shows the d-block band structure of NbSe<sub>3</sub> with an ideal unit cell containing six identical chains, and Figure 1b that of NbSe<sub>3</sub> with a real unit cell containing three nonequivalent pairs of chains. With all the bands lying below the

d-block bands completely occupied, six electrons are left over to fill the d-block bands of Figure 1. The most striking difference between the band structures of parts a and b of Figure 1 is that two of the six low-lying d-block bands of Figure 1a are lowered upon introducing the presence of three nonequivalent pairs of chains. Thus, in Figure 1b, bands a and b are completely occupied while bands c-f each become roughly one-fourth filled. This is in complete agreement with Devreux's suggestion.<sup>6</sup>

Population analysis of band orbitals shows that the completely filled bands a and b of Figure 1b have small type II chain character. Throughout  $\Gamma \rightarrow Z$ , overall type II chain contribution is less than 35% and type II niobium contribution is less than 10%. It is the empty bands g and h of Figure 1b that have strong type II chain character. For example, overall type II chain contribution is about 80% and type II niobium contribution is about 60% near the zone center. This finding is consistent with Wilson's model.<sup>5</sup>

Table II summarizes the population analysis for bands c-f at the Fermi level.<sup>13</sup> In terms of both the overall chain and the niobium contribution, we observe the following: (a) Bands d and e have mainly type III chain character, while bands c and f type I chain character. (b) At the Fermi level of bands c-f, type II chain character is small but nonvanishing. The latter finding is consistent with Devreux's observation concerning the Nb line unaffected by the CDW's.<sup>6</sup> Note from Figure 1b that the  $2k_f$  values of d and e are very similar and lie in between the corresponding values of c and f. The vector component  $q_{1b}$  of the high-temperature CDW is smaller than  $q_{2b}$  of the low-temperature CDW, while the sum ( $q_{1b} + q_{2b}$ ) is close to  $0.5b^*$ .<sup>4</sup> These observations can be reproduced from Figure 1b if we consider that  $q_1$  is associated with d and/or e, and  $q_2$  with c. Then the high- and low-temperature CDW's occur primarily in type III and I chains, respectively. This is in agreement with Wilson's conclusion<sup>5</sup> based upon the vector components of  $q_1$  and  $q_2$  perpendicular to the chain axis.

In essence, the present band structure is consistent with Wilson's model and Devreux's <sup>93</sup>Nb NMR study. Type II chain character at the Fermi level is nonvanishing but small.

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**Registry No.** NbSe<sub>3</sub>, 12034-78-5.

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