

Electronic Characteristics of Quasi-2D Metalochloronitrides: Na_xHfNCl ($T_c=25$ K)

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Abstract. Local density functional results are presented for the electron-doped metalochloronitrides $A_x\text{ZrNCl}$ and $A_x\text{HfNCl}$, $A=\text{Li}$ or Na , which superconduct up to 25K. The alkali non-stoichiometry is treated in a virtual crystal approximation. The electronic structure is strongly two dimensional, especially in the conduction band region occupied by the carriers, because the states are formed from the in-plane orbitals d_{xy} , $d_{x^2-y^2}$ of the metal ion and the p_x , p_y orbitals of the N ion. We predict a change of behavior at a doping level of $x=0.3$.

INTRODUCTION

High temperature superconductivity (HTS) in the layered cuprates continues to puzzle even after a dozen years of intense scrutiny. Even outside of the class of HTSs, however, the appearance of high T_c (in the pre-cuprates sense) also is baffling. The highest T_c is achieved in the fullerenes, with $T_c=40$ K reported, [1] which are three dimensional (3D) materials with, however, a great deal of zero dimensional (cluster) character. $T_c \sim 35$ K is achieved in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$, also a 3D system, with only some flat portions of Fermi surface to bring in questions of low dimensionality. There is not yet any clear theoretical accounting for the magnitude of T_c in these two systems [2,3] although some phonon modes in the fullerenes are strongly coupled to the conduction electrons. The A15 superconductors (T_c up to 23 K) present a class in which the relatively high value of T_c is understood in terms of strong electron-phonon coupling and a high density of states (DOS) $[N(E_F)]$ at the Fermi level E_F . [4]

A new, 2D material has recently been added to the list of (non-HTS) superconductors with unusually high T_c . Yamanaka *et al.* [5] discovered superconductivity up to 12 K in Li-doped ZrNCl , and up to 25.5 K in Na-doped HfNCl . [6] Shamoto *et al.* [7,8] have reproduced the superconductivity and determined the crystal structure of superconducting materials using synchrotron X-ray diffraction data. We provide here the first calculation of the electronic structure of this system, considering in particular variation with doping level.

DESCRIPTION OF CALCULATIONS

Electronic Structure Methods

We have applied the local density approximation [9] using two methods: the linearized augmented plane wave (LAPW) method [10] for the bands and density of states (DOS) that we show, and the plane wave ultrasoft pseudopotential method [11] for the phonon frequencies. Both methods produced essentially the same band structures.

To account for the doping we have used a virtual crystal treatment. For example, for x fractional occupancy of a site by Na (ten core electrons and one valence electron), that site is fully occupied by a nucleus of charge $10+x$ with the corresponding number of electrons. As expected, Na is ionized with the electrons going into bands that are primarily metal d bands, so the virtual crystal treatment should be reasonable. We will find that it is important to treat this charge self-consistently, because non-rigid-band behavior appears not far from the region of immediate interest.

Structure

We have used the structures of Shamoto *et al.* [7,8] for these materials. Because a Cl-HfN-HfN-Cl slab is only weakly coupled to its neighboring slabs, we expect that the stacking sequence (for example, whether hexagonal or rhombohedral) is not important, and indeed that was found to be the case. One such structure is shown in Fig. 1, and the slab structure is the same for Hf and Zr, with only the stacking sequence varying with doping. [12]

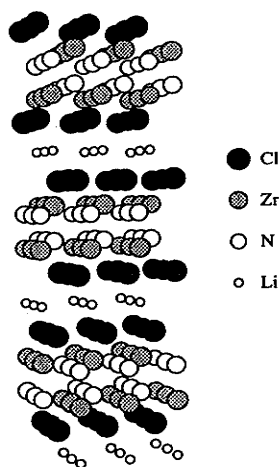


FIGURE 1. Rhombohedral structure of Li_xZrNCl determined by Shamoto *et al.* [7,8] The stacking along c can change with doping, but the basic slab structure structure is unchanged with doping. Li sites are only fractionally occupied

DISCUSSION OF RESULTS

The band structures are strongly two dimensional, so we discuss only the in-plane dispersion here. The undoped compounds have a band gap of 1.7-1.8 eV, between valence bands that are $2p$ states of Cl and N, and conduction states that are mostly Hf or Zr. Thus the formal ionic description $(\text{Hf,Zn})^{4+}\text{N}^{3-}\text{Cl}^-$ is reasonable, but obscures the strong metal-N hybridization.

In Fig. 2 the band structure of $\text{Na}_{0.25}\text{HfNCl}$ is shown along the hexagonal symmetry directions. Only a single band is occupied by the doped carriers, and the band structure is very similar to that of the undoped compound, *i.e.* a rigid band picture is good. The projected DOS of Fig. 3 illustrates several things: (1) the occupied band is a hybridized planar band of Hf $d_{xy}, d_{x^2-y^2}$ and N p_x, p_y character; (2) Hf d_{xz}, d_{yz} and N p_x character do not appear until the band flattening 0.3

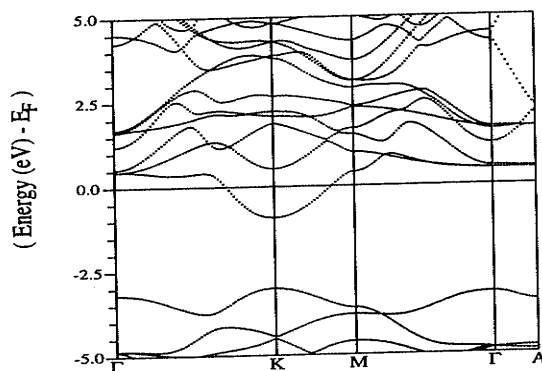


FIGURE 2. Plot along symmetry lines of the band structure of $\text{Na}_{0.25}\text{HfNCl}$. Points are $\Gamma = (0,0,0)$, $K = (2/3, 1/3, 0)$, $M = (1/2, 0, 0)$, $A = (0, 0, 1/2)$, in units of the hexagonal reciprocal lattice vectors. The lack of dispersion along Γ -A of the lower conduction bands reflects the strong 2D character of the important conduction band.

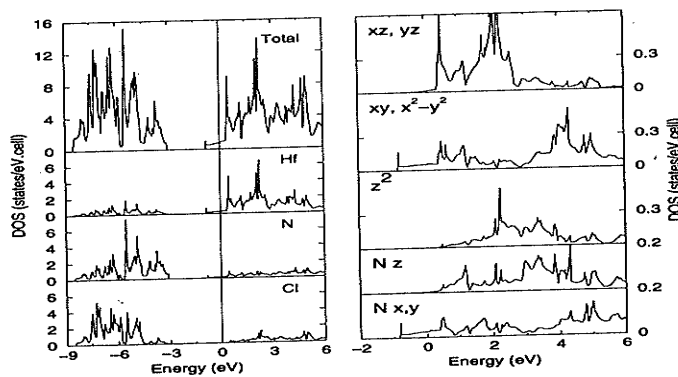


FIGURE 3. Atom (left panel) and orbital (right panel) projected DOS for $\text{Na}_{0.25}\text{HfNCl}$. In the right panel only the conduction bands are pictured.

eV above E_F in Fig. 2; (3) the Hf d_{z^2} character is higher still. This behavior is completely different from what Woodward and Vogt [13] calculated for a bilayer structure reported by Juza and collaborators, [14] in which two Hf ions are bonded across the bilayer, rather than the Hf-N bonding across the bilayer as in the structure determined by Shamoto. Thus electrons are not doped into a very flat band, which almost certainly would be strongly correlated, but rather into a broad band with a light mass $m^* \approx 0.6m$.

The other material parameters we obtain (for $x=0.25$) are

- Fermi velocity $v_F = 3 \times 10^7$ cm/s
- Drude plasma energy $\Omega_p = [4\pi e^2 N(E_F)v_{F,x}^2]^{1/2} = 1.5$ eV
- Gap $2\Delta \approx 3.5 k_B T_c \approx 7.5$ meV
- Coherence length $\xi = \frac{\hbar v_F}{\pi\Delta} \approx 180$ Å
- London penetration depth $\Lambda = \frac{c}{\Omega_p} = 1300$ Å
- $\kappa = \Lambda/\xi = 7 \rightarrow$ Type II superconductor.

In Fig. 4 we present the Fermi surface for $x=0.25$ doping level. It consists of threefold distorted circles at the zone corner (K) points. There are two inequivalent such points, each with mean radius $k_F = \frac{2}{9}\frac{\pi}{a}$. On-Fermi-surface scattering processes will be dominated by (1) small $Q \leq 2k_F$ intraband scattering, and (2) large $Q \sim K$ interband scattering. [Note that the vector connecting two neighboring zone corners K is also the vector K.]

We have calculated the frequencies of the three fully symmetric (A_{1g}) Raman active vibrational modes of pristine ZrNCl and HfNCl at the zone center, corresponding to modulation of the internal coordinates $z_{Zr/Hf}, z_N, z_{Cl}$. The frequencies are 586, 334, and 202 cm^{-1} and 604, 368, and 191 cm^{-1} respectively for the two compounds. The highest frequency is almost pure N motion.

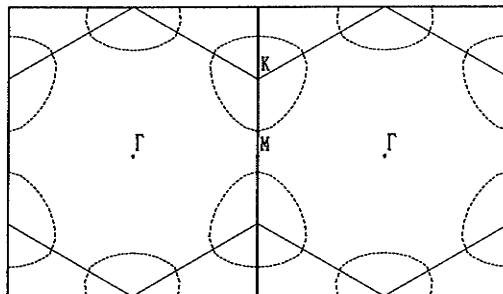


FIGURE 4. Plot of the distorted circular Fermi surface of $Na_{0.25}HfNCl$ shown in two hexagonal Brillouin zones. The surface is centered at the zone corner point K; since there are two such inequivalent points, there are two Fermi surfaces.

DOPING

As these systems are studied further, the question of the effect of doping will be very important. We have performed virtual crystal calculations for several doping levels, with results for $x = 0.25$, 0.35 and 0.45 shown in Figure 5. There are continuous rigid-band-like changes up to just above $x = 0.30$, above which bands with different character (specifically, out of plane orbitals) begin to become occupied. At this point in doping the properties should show a change in slope (plotted versus x). At $x=0.35$ E_F coincides with a band that is very flat band along Γ -K and has a small mass along Γ -M as well, *i.e.* a peak in the density of states. This range of doping should prove very interesting, and whether T_c rises or falls will reveal important characteristics of the pairing mechanism.

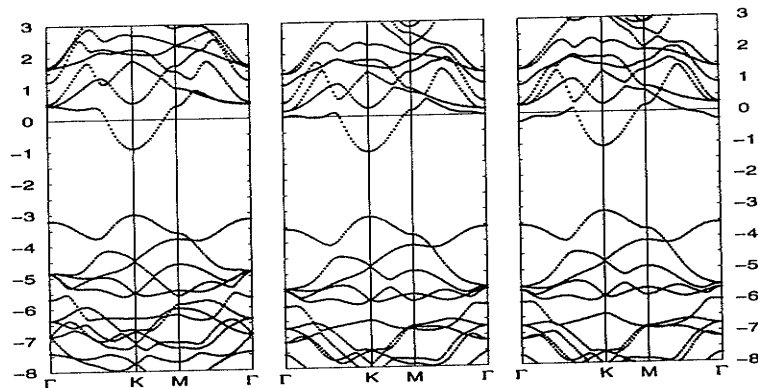


FIGURE 5. Band structure plots of Na_xHfNCl , for $x=0.25$, 0.35 , and 0.45 (left to right). Around $x=0.35$ the Fermi level enters a region where the bands have different character, and already the conduction band dispersion is visibly non-rigid-like. At $x=0.45$ there is a large Fermi surface centered at Γ as well as the ones at K.

SUMMARY AND ACKNOWLEDGMENTS

It is surprising that such low mass, low DOS materials such as those described here can superconduct up to 25 K. Since there is no indication, experimentally or theoretically, of strong correlation effects in the range of doping reported by the superconductors, a possible candidate for pairing mechanism could be phononic. Given the 2D character and the strong nesting that might introduce characteristics of 1D behavior, purely electronic pairing mechanisms should also be considered. Given the apparent extreme two dimensionality of the crystal, it will be important to establish that coherent supercurrent actually will flow perpendicular to the layers.

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