

COHERENT-POTENTIAL-APPROXIMATION CALCULATIONS  
OF THE ELECTRONIC PROPERTIES OF THE SUBSTOICHIOMETRIC  
REFRACTORY MONOCARBIDES  $\text{NbC}_x$ ,  $\text{TaC}_x$  AND  $\text{HfC}_x$

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1. Introduction

The carbides are well-known for their great hardness and high melting temperatures (see Toth 1971, for a review), properties often ascribed to strong covalent-like bonding in these materials. Even though this type of bonding is usually associated with non-metallic materials, nearly stoichiometric carbides are often good metallic conductors, and in fact several of them with 9 valence electrons per molecule (e.g.  $\text{NbC}$  and  $\text{TaC}$ ) superconduct with transition temperatures  $T_c \sim 11$  K. Here we will discuss recent theoretical work that we have done regarding the electronic structure of three carbide systems:  $\text{NbC}_x$ ,  $\text{TaC}_x$  and  $\text{HfC}_x$ ,  $x \leq 1.0$ . We have used the coherent-potential-approximation (CPA) in a linear-combination-of-atomic-orbitals (LCAO) basis to study the effects due to carbon vacancies ( $x < 1.0$ ). Further details of this work may be found in Klein, *et al* (1980).

2. APW calculations and the LCAO Hamiltonian

Self-consistent augmented-plane-wave (APW) calculations were done for all three rocksalt structure stoichiometric carbides ( $x = 1.0$ ) following procedures reviewed by Mattheiss *et al* (1968). Relativistic effects, neglecting spin-orbit coupling were included, as well as "soft-core" corrections. Local exchange approximations ( $X\alpha$ ) were used in all cases.

An LCAO Hamiltonian was determined by fitting to the APW energy bands for each compound following the method of Slater and Koster (1954). We have used a basis set of 13 wave functions:  $s$ ,  $p$  and  $d$  functions for the transition metal (TM), and  $s$  and  $p$  functions for C. A total of 51 interaction integrals, up to 2nd neighbors of the same atom-type were included. The overlap matrix was set equal to unity. The non-linear least squares fitting procedure used 164 APW energy values corresponding to at least nine bands for each  $\bar{k}$ -point on a 20  $\bar{k}$ -point mesh. The rms fitting accuracy was  $\sim 10$  mRyd for bands near the Fermi energy,  $E_F$ . Somewhat larger fitting errors occurred for the low valence or higher conduction bands. The LCAO fit reproduced the APW energy bands, densities-of-states and Fermi surfaces very well.

3. CPA theory

The LCAO-CPA approach that we used follows the theory developed by Faulkner (1976) extended by us to include both  $s$  and  $p$  orbitals in the LCAO basis set of the vacancy atom (C). In this method complex energy-dependent but  $\bar{k}$ -independent self-energies  $\sigma_s^x$  and  $\sigma_p^x$  are introduced into an effective Hamiltonian corresponding to randomly distributed carbon vacancies of concentration  $1-x$ . The CPA constraint is used to formulate a self-consistency condition for  $\sigma_s^x$  and  $\sigma_p^x$  in terms of the complex Green's function,  $g^x$ , for each  $x$ . Iterating to convergence yields  $g^x$ , the self-energies, densities-of-states and Bloch spectral functions.

4. Charge transfer and Fermi level motion for  $x < 1.0$

The APW results for  $x = 1.0$  indicate significant charge transfer  $\text{TM} \rightarrow \text{C}$  during the SC cycles. This has been verified by the LCAO results which show an  $\sim 5$  electron population for carbon (see Table 1), one more than its valence, in all three compounds at stoichiometry. This charge transfer indicates strong ionic-covalent TM-C bonding and

Table 1  
Fermi energy,  $E_F$ , total densities-of-states,  $n(E_F)$ ,  
and electrons per unit cell,  $N^{TM}$  and  $N^C$

	$E_F$ (Ry)	$n(E_F)$ (states/Ryd/cell)	$N^{TM}$ (electrons)	$N^C$ (electrons)
NbC <sub>1.0</sub>	0.877	8.33	3.97	5.03
NbC <sub>0.9</sub>	0.905	9.74	4.11	4.49
NbC <sub>0.8</sub>	0.922	12.89	4.25	3.95
NbC <sub>0.7</sub>	0.930	15.21	4.38	3.42
TaC <sub>1.0</sub>	0.901	7.67	4.00	5.00
TaC <sub>0.9</sub>	0.933	9.27	4.15	4.45
TaC <sub>0.8</sub>	0.953	11.44	4.28	3.92
TaC <sub>0.7</sub>	0.963	13.50	4.40	3.40
HfC <sub>1.0</sub>	0.701	4.55	2.91	5.09
HfC <sub>0.9</sub>	0.791	4.48	2.99	4.61
HfC <sub>0.8</sub>	0.848	7.38	3.12	4.08
HfC <sub>0.7</sub>	0.886	9.53	3.25	3.55

accounts, qualitatively, for the extreme hardness and high melting temperatures of these materials.

The CPA results given in Table 1 show that  $E_F$  moves to higher energy as the number of carbon vacancies increases. This is a sensible result once one realizes the influence of the charge transfer. At stoichiometry 5 carbon states/atom are occupied; and when a carbon atom is removed, 4 electrons leave the system with five holes and one electron transferred back to the TM. This transferred electron must fill an empty TM state above the old  $E_F$ , and hence  $E_F$  is shifted to higher energy. These kinds of ideas lead to a generalized rigid-band type of picture for  $AB_x$  compounds, with  $E_F(x)$  dependent on charge transfer in the system. Three cases are possible: (1) charge transfer is  $A \rightarrow B$ , (2)  $B \rightarrow A$ , or (2) no charge transfer. These three cases correspond to  $E_F(x)$  moving up, down, or staying constant, respectively, with decreasing  $x$ . The carbides are an example of case (1), while  $PdH_x$  is an example of case (2) (Papaconstantopoulos *et al* 1978).

### 5. Densities-of-states

Figure 1 shows the densities-of-states,  $n(E)$ , for NbC<sub>1.0</sub> and NbC<sub>0.8</sub>, and Table 1 gives some numerical results for all of the carbides we have studied. The energy dependence of  $n(E)$  for TaC<sub>*x*</sub> is very similar to NbC<sub>*x*</sub>; while HfC<sub>*x*</sub> differs by having its  $E_F(1.0)$  fall at a minimum in  $n(E)$  (corresponding to  $E \sim 0.7$  Ryd in Fig. 1). The fact that  $E_F$  moves to higher energy as  $x$  decreases causes  $n(E_F)$  to increase with the number of carbon vacancies in all cases.

### 6. Fermi surfaces, phonon anomalies and superconductivity

Klein *et al* (1976) and Gupta and Freeman (1976) have shown that the 5th band stoichiometric Fermi surfaces of NbC and TaC are jungle-gyms having relatively flat parallel arms ("nesting") which leads to enhanced electron-phonon scattering. They showed that these Fermi surface features and the resultant resonant scattering could be related to the observed phonon anomalies in these materials (Smith and Gläser 1970, Smith 1972). Phonon anomalies have not been found experimentally for HfC, and the theoretical nesting features are absent in this material. In addition, it has been found experimentally that the phonon anomalies tend to disappear with increasing numbers of carbon vacancies.

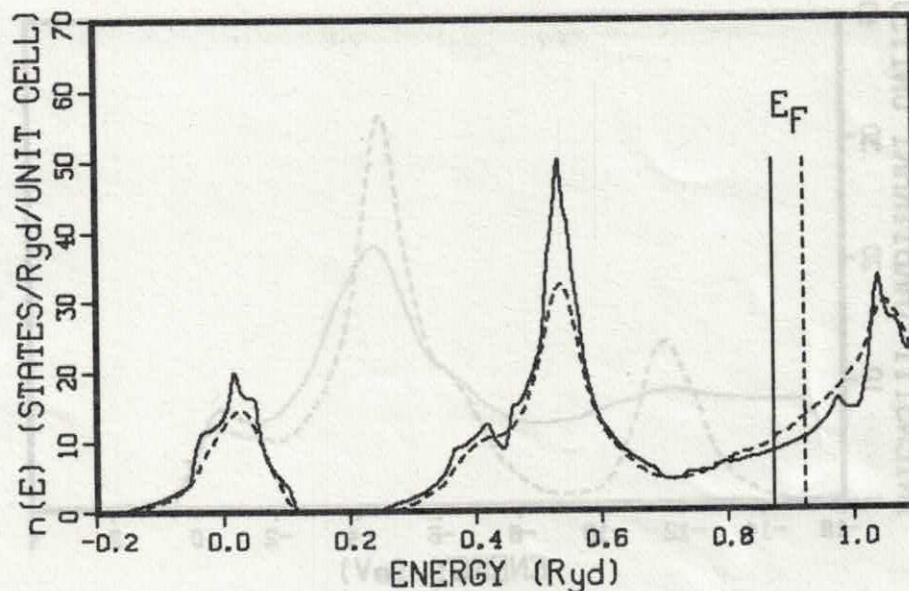


Figure 1. Calculated density-of-states,  $n(E)$ , for  $\text{NbC}_{1.0}$  (solid lines), and  $\text{NbC}_{0.8}$  (dashed lines).

We have used our LCAO-CPA results to calculate the effects of substoichiometry on the Fermi surfaces by calculating the Bloch spectral functions for different values of  $x$  (Klein *et al* 1980). We have found that the "nested" Fermi surfaces of  $\text{NbC}_x$  and  $\text{TaC}_x$  become smeared with decreasing  $x$  (see Klein *et al* 1980 for pictorial representations). Although we have not as yet done quantitative calculations using the Fermi surface lifetime or smearing effects, the fact that the "nesting" features are largely destroyed by the carbon vacancies correlates well with the disappearance of the phonon anomalies.

Finally we note that we believe that the strong electron lifetime effects induced by the carbon vacancies will also be important for explaining the monotonic decrease of the superconducting transition temperature,  $T_c$ , with decreasing  $x$ . Straightforward applications of rigid-band types of arguments (neglecting lifetime effects) for estimating  $T_c(x)$  have not been successful in this regard, due to the increase of  $n(E_F)$  with decreasing  $x$ .

### 7. Photoelectron spectra

We have calculated broadened total densities-of-states to compare with measured photoelectron spectra of the carbides. Figure 2 shows a comparison of theoretical and experimental results for  $\text{NbC}_{1.0}$ . The agreement is quite good. Klein *et al* (1980) show additional theoretical spectra for the other carbides, as well as the expected changes in the spectra as a function of  $x$ . The predicted  $x$ -dependent peak shifts and heights should be observable experimentally on well characterized samples.

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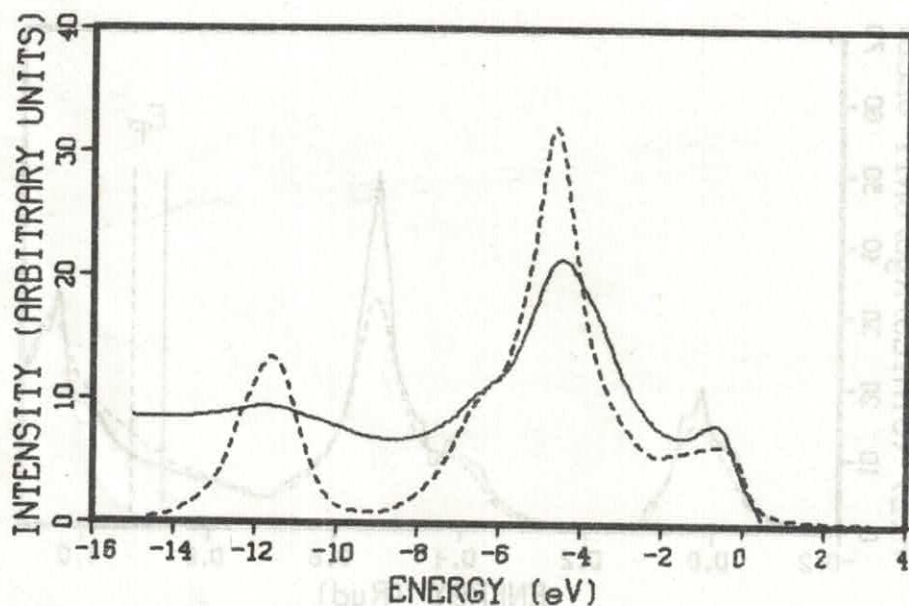


Figure 2. Calculated gaussian-broadened (0.5 eV FWHM) total density-of-states of  $\text{NbC}_{1.0}$  (dashed line); and measured photoelectron spectrum (solid line) of Weaver and Schmidt (1980).  $E_F$  corresponds to 0.0 on the abscissa.

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