

## Electronic structure of substoichiometric carbides and nitrides of zirconium and niobium

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The electronic structures of  $ZrC_x$ ,  $ZrN_x$ ,  $NbC_x$ , and  $NbN_x$  for several concentrations  $x$  were investigated by means of the Korringa-Kohn-Rostoker coherent-potential approximation and the Korringa-Kohn-Rostoker Green's-function methods. The influence of vacancies on the electronic structure of these compounds is quite similar to the case of substoichiometric carbides and nitrides of  $3d$  metals: near the minimum in the density of states between the nonmetal  $p$  and the metal  $d$  subbands additional "vacancy peaks" appear, and (except for  $ZrC_x$ ) the Fermi energy is lowered. It is argued that similar properties may be expected for other  $d$ - and  $f$ -metal carbides, pnictides, and chalcogenides.

### INTRODUCTION

In a recent paper<sup>1</sup> we have presented Korringa-Kohn-Rostoker coherent-potential-approximation (KKR-CPA) calculations of carbides and nitrides of titanium and vanadium with vacancies on the nonmetal sublattice. In the present work we apply the same formalism to the carbides and nitrides of the  $4d$  metals zirconium and niobium. Since all these compounds have many properties in common, and several questions concerning the theoretical treatment of substoichiometry have already been discussed in our previous work,<sup>1-3</sup> we refer the reader to these papers for details.

### FORMALISM AND COMPUTATIONAL DETAILS

The Korringa-Kohn-Rostoker coherent-potential-approximation (KKR-CPA) method for pseudobinary alloys is discussed in detail by Klima *et al.*<sup>2</sup> and by Marksteiner *et al.*<sup>1</sup> For a compound  $MX_x$ , where  $M$  denotes a metal,  $X$  a nonmetal, and  $x$  the concentration of atoms  $X$  on the nonmetal sublattice, the total density of states (DOS)  $g(E)$  is defined as the sum of "component densities of states:"

$$g(E) = xg_1^X(E) + (1-x)g_1^{\text{vac}}(E) + g_2^M(E). \quad (1)$$

The only input parameters are the potentials, the lattice constants, and the concentrations  $x$ . The  $M$  and  $X$  potentials were taken from self-consistent augmented plane wave (APW) calculations.<sup>4-6</sup> The vacancy potentials were constructed, in analogy to our previous work on  $VC_x$  and  $VN_x$ , by a superposition of free  $M^{0.75+}$  and  $X^-$  ions placed on the respective lattice sites of an ordered super-

structure  $M_4X_3\Box_x$  ( $\Box_x$  denoting a vacancy), the anions being stabilized by Watson spheres.<sup>7</sup>

The lattice constants for the carbides were taken from Rudy,<sup>8</sup> those for  $ZrN_x$  from Christensen and Fregerslev,<sup>9</sup> and those for  $NbN_x$  from Brauer and Kirner.<sup>10</sup>

The concentrations  $x$  were chosen to cover the whole range of existence of these compounds in the NaCl phase, as reported by Landesman *et al.*<sup>11</sup> For some concentrations ordered superstructures have been observed ( $Nb_6C_5, Nb_4N_3$ ).<sup>11</sup> These concentrations were also taken into account. The details of the CPA calculations, especially the Brillouin zone integration, are completely analogous to those of Ref. 1.

### RESULTS AND DISCUSSION

The total densities of states of the compounds investigated are shown in Figs. 1-4. The main contributions to the local partial densities of states are shown in Figs. 5-8. The Fermi energy is indicated as a dashed line, all figures are labeled by the respective concentration  $x$ , Figs. 1-4 also by the respective lattice constant  $a$ . In Figs. 5-8 the left-hand column shows the metal  $t_{2g}$ -like density of states as a solid line and the metal  $e_g$ -like density of states as a dotted line. In the center column the nonmetal (solid line) and the metal (dotted line)  $t_{1u}$ -( $p$ -like) local partial DOS are shown, and in the right-hand column the vacancy  $a_{1g}$ - ( $s$ -like, solid line) and  $t_{1u}$ - ( $p$ -like, dotted line) local partial DOS. In Figs. 5-8, the first entry in the right-hand column refers to a single vacancy in an otherwise perfect (stoichiometric) host.

Practically all the effects of substoichiometry on the electronic structure observed in the  $3d$  metal carbides and nitrides occur also in the case of the corresponding  $4d$

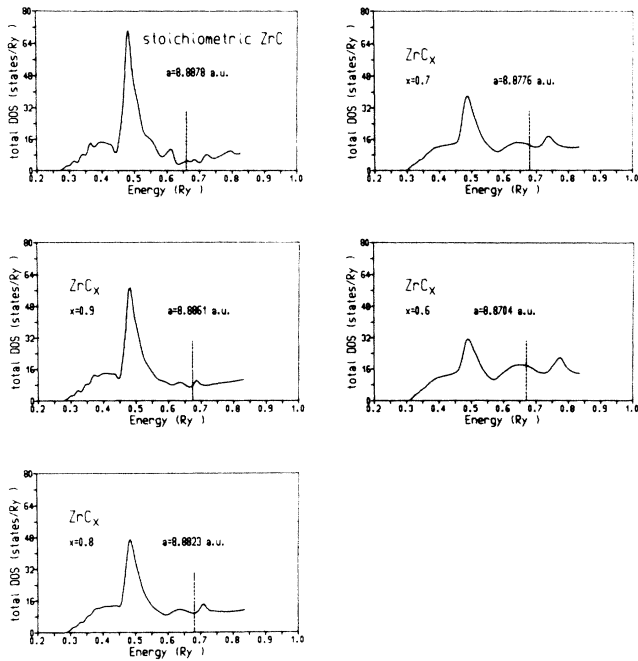


FIG. 1. Total density of states for  $ZrC_x$ ; concentration and lattice parameter are indicated in each case.

metal compounds. Besides a general smoothing of the peak structure and a considerable loss of intensity of the nonmetal  $p$  peaks there appear additional peaks (“vacancy peaks”) near the minimum of the density of states between the nonmetal  $p$  and the metal  $d$  subband. There is also an increase of the metal  $e_g$ -like DOS in this energy region. The  $s$ -like vacancy peak, which corresponds to a virtual bound state (see Ref. 2) is very sharp in the case of

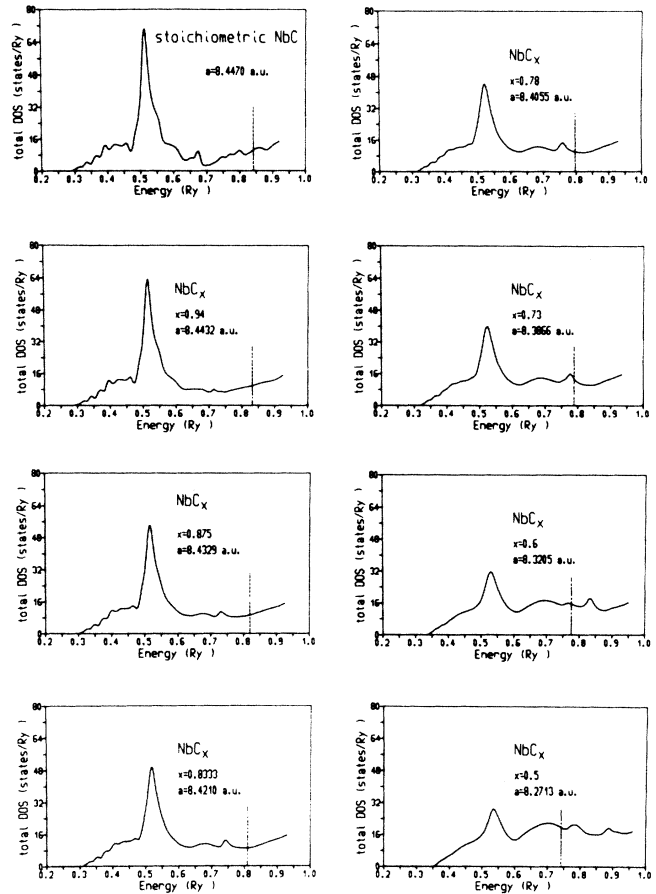


FIG. 3. Total density of states for  $NbC_x$ ; concentration and lattice parameter are indicated in each case.

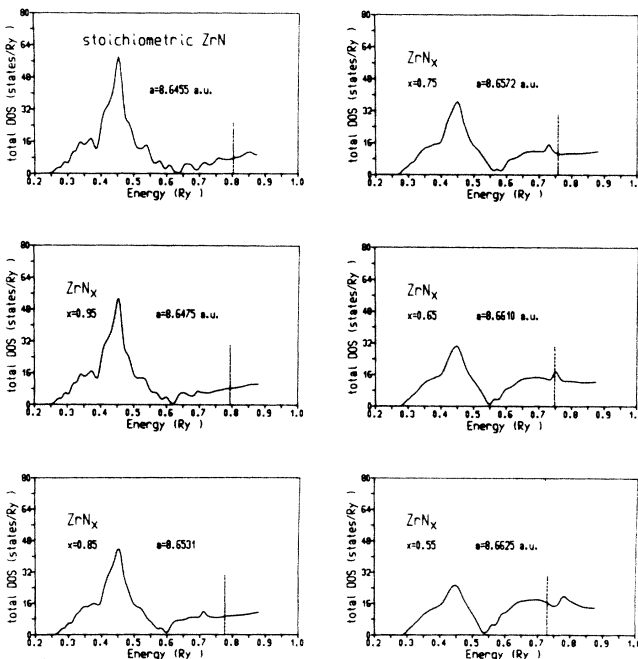


FIG. 2. Total density of states for  $ZrN_x$ ; concentration and lattice parameter are indicated in each case.

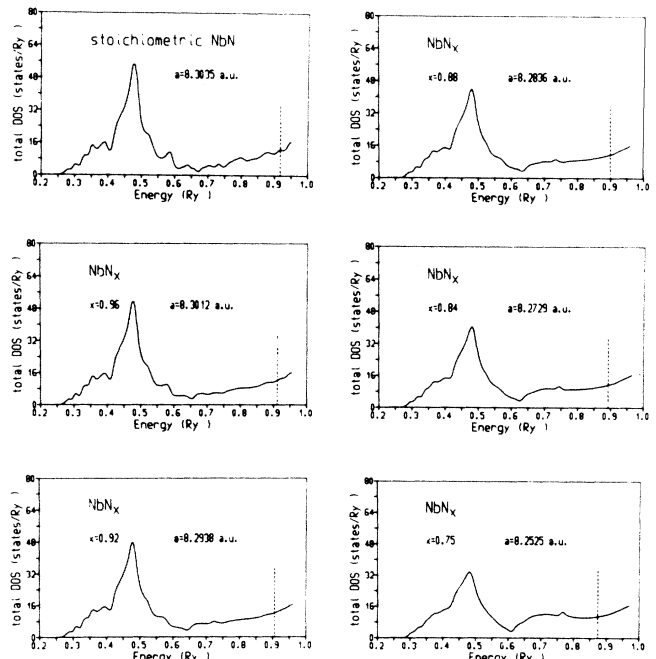


FIG. 4. Total density of states for  $NbN_x$ ; concentration and lattice parameter are indicated in each case.

a single vacancy, and is continually broadened with increasing vacancy concentration until it is split into two separate peaks. The positions of the nonmetal  $p$  and the metal  $d$  subbands are affected very little by the vacancies, the vacancy peaks themselves are constantly shifted to higher energies with increasing vacancy concentration.

In the  $4d$  metal carbides and nitrides the nonmetal  $p$  peaks are sharper and rather more intense than in the corresponding  $3d$  metal compounds. In contrast to the  $3d$  metal compounds, where there are only very weak and diffuse metal  $p$  peaks, there are also considerable metal  $p$  contributions. In the substoichiometric cases metal  $p$  con-

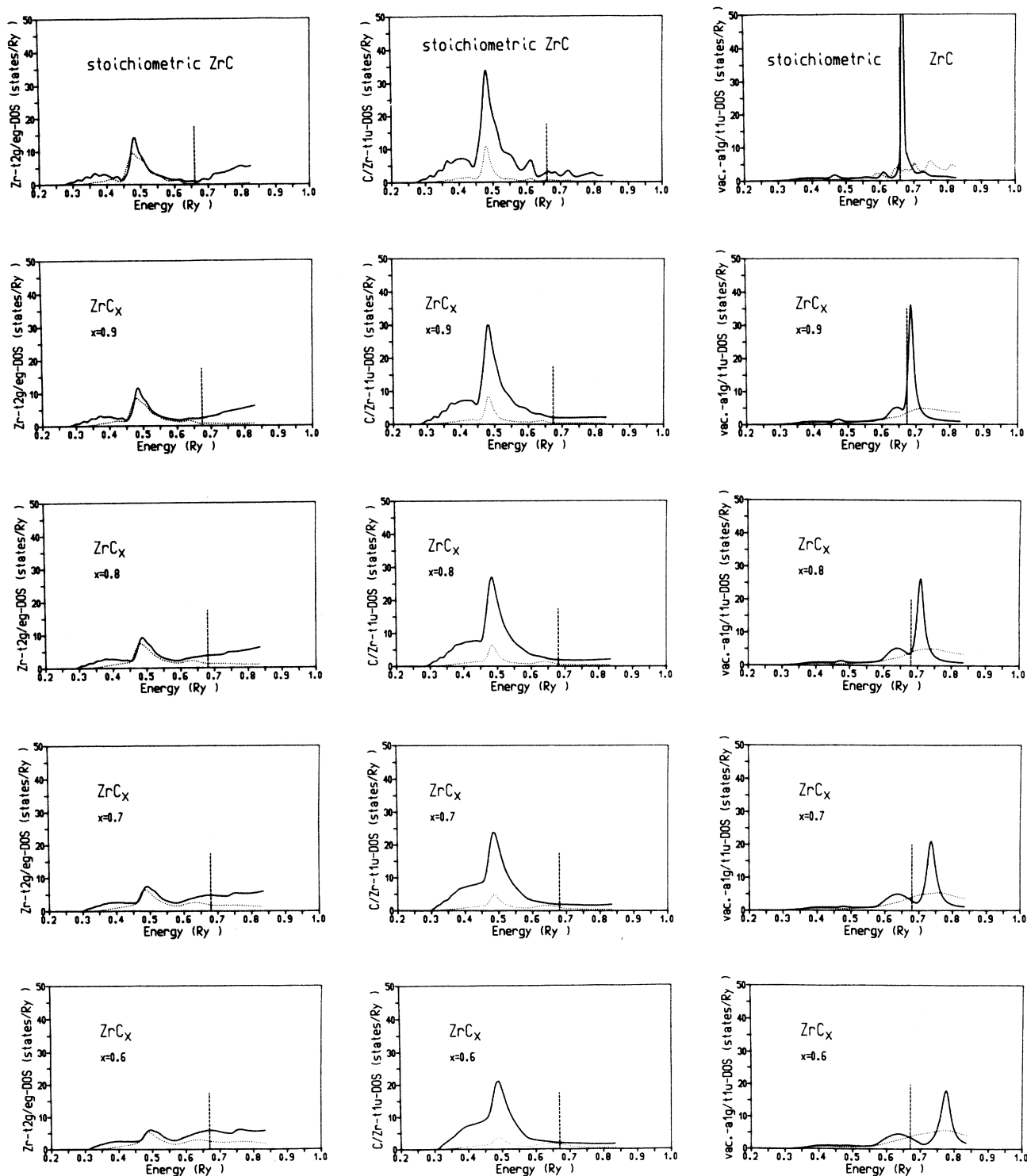


FIG. 5. Partial densities of states for  $ZrC_x$ : left column,  $t_{2g}$ -like (solid line) and  $e_g$ -like (dotted line) metal partial DOS; center column,  $t_{1u}$ -like nonmetal (solid line) and metal (dotted line) partial DOS; right column,  $a_{1g}$ -like (solid line) and  $t_{1u}$ -like (dotted line) vacancy partial DOS.

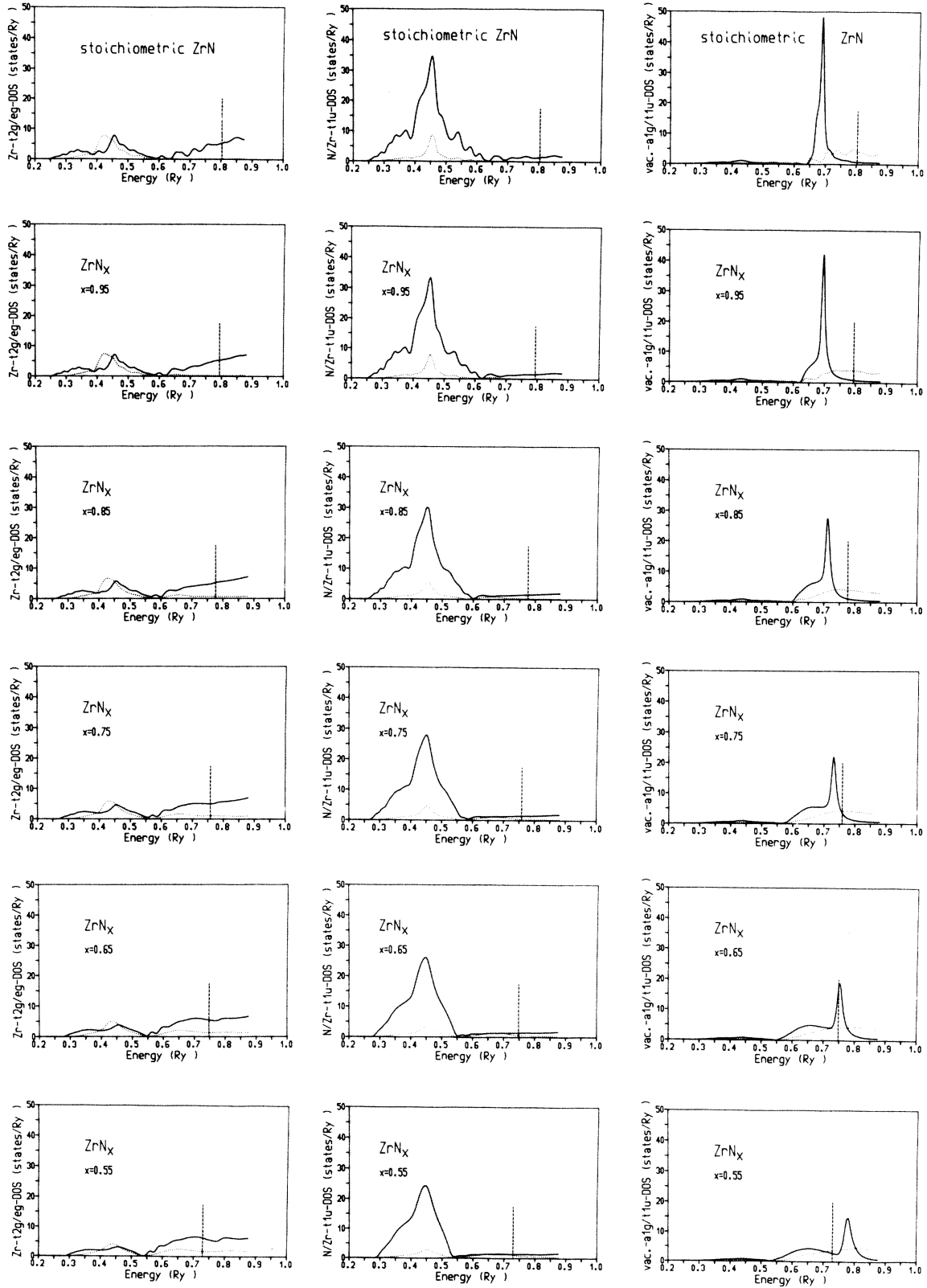


FIG. 6. Partial densities of states for  $\text{ZrN}_x$ : left column,  $t_{2g}$ -like (solid line) and  $e_g$ -like (dotted line) metal partial DOS; center column,  $t_{1u}$ -like nonmetal (solid line) and metal (dotted line) partial DOS; right column,  $a_{1g}$ -like (solid line) and  $t_{1u}$ -like (dotted line) vacancy partial DOS.

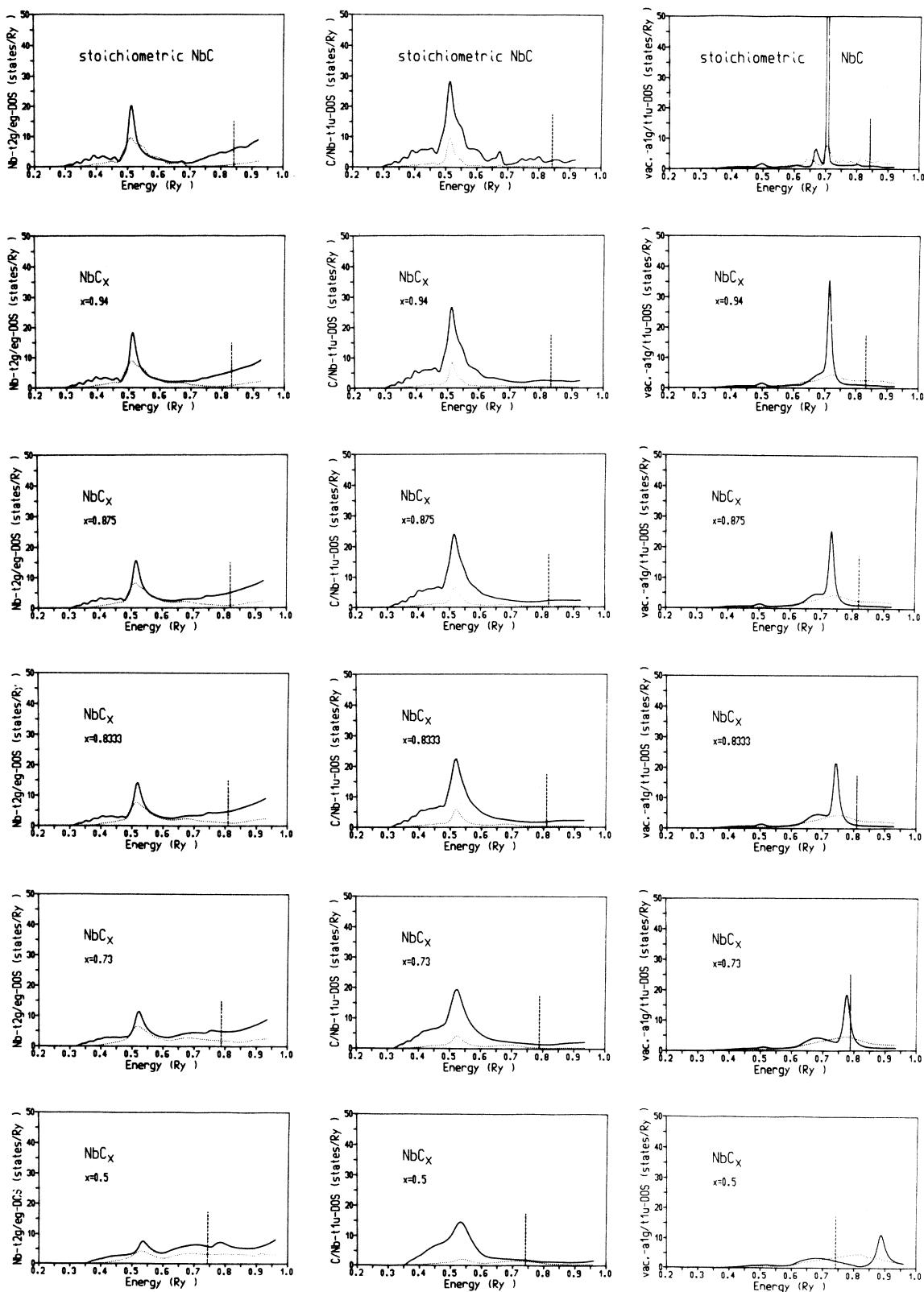


FIG. 7. Partial densities of states for  $\text{NbC}_x$ : left column,  $t_{2g}$ -like (solid line) and  $e_g$ -like (dotted line) metal partial DOS; center column,  $1t_{1u}$ -like nonmetal (solid line) and metal (dotted line) partial DOS; right column,  $a_{1g}$ -like (solid line) and  $t_{2u}$ -like (dotted line) vacancy partial DOS.

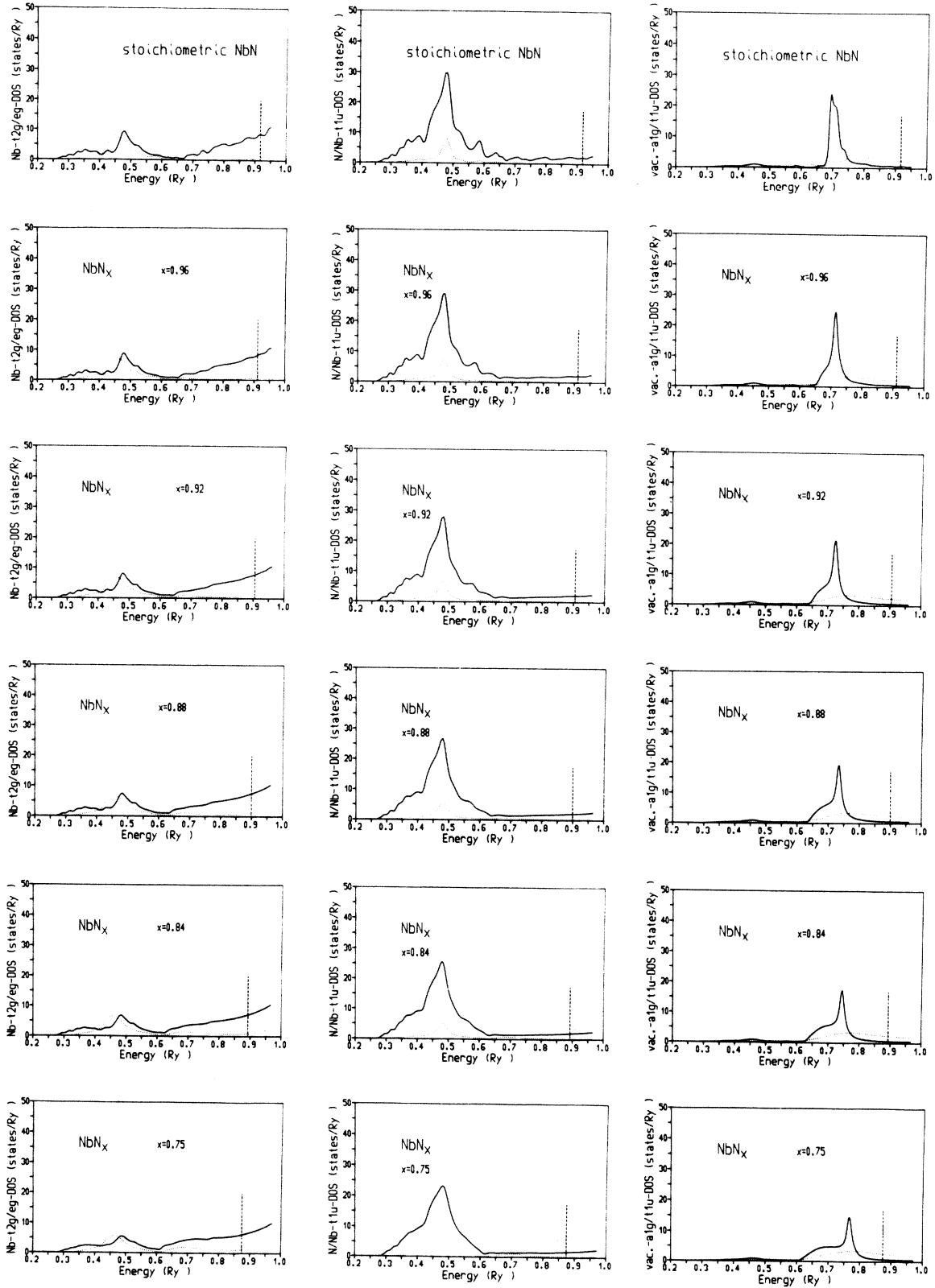


FIG. 8. Partial densities of states for  $\text{NbN}_x$ : left column,  $t_{2g}$ -like (solid line) and  $e_g$ -like (dotted line) metal partial DOS; center column,  $t_{1u}$ -like nonmetal (solid line) and metal (dotted line) partial DOS; right column,  $a_{1g}$ -like (solid line) and  $t_{1u}$ -like (dotted line) vacancy partial DOS.

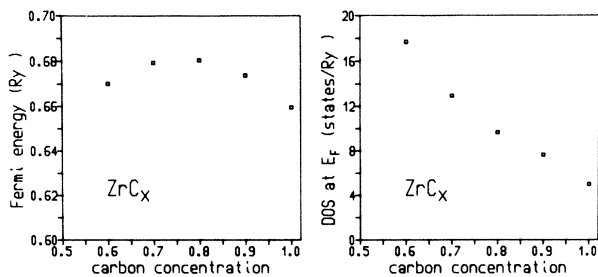


FIG. 9. Fermi energy and density of states at the Fermi energy for  $ZrC_x$  versus concentration  $x$ .

tributions can also be seen, albeit not very distinctly, in the energy region of the vacancy peaks. These metal  $p$  states play an important role in the interpretation of  $x$ -ray photoemission spectroscopy (XPS) spectra.<sup>12</sup> The fact that the metal  $e_g$  and metal  $p$  states are particularly affected by the introduction of vacancies can be interpreted by geometrical considerations, since these states point directly to the nearest neighbor on the nonmetal sublattice. In terms of a tight-binding description these vacancy-induced states can be interpreted as nonbonding states building up in the gap between bonding and antibonding states. The metal  $t_{2g}$  DOS shows a slight kink near the position of the vacancy  $p$ -like peak. This may be interpreted as a metal  $t_{2g}$  metal  $t_{2g}$  interaction across the vacancy, where these states have  $p$  symmetry at the vacancy site.

The electronic structure of substoichiometric transition-metal carbides and nitrides has been investigated experimentally by a number of techniques (see, e.g., Porte *et al.*<sup>13</sup> and references therein). Several spectroscopic methods, in particular photoelectron spectroscopy, give information about the density of states. In a forthcoming paper<sup>12</sup> we shall present a comparison between calculated XPS spectra based on this work and on Ref. 1 and XPS measurements.<sup>13–18</sup> The calculated spectra reproduce very well the positions of the peaks (except for the usual deviations due to the local-density approximation) and, with properly included cross sections, also their shapes and intensities. It seems, however, that the intensities of the vacancy-induced peaks are generally overestimated by KKR-CPA theory, which makes the agreement slightly worse for high-vacancy concentrations.

The Fermi energy with respect to the muffin-tin zero

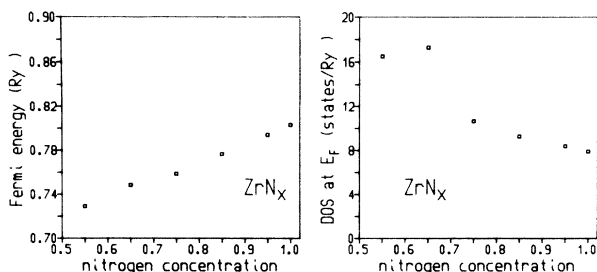


FIG. 10. Fermi energy and density of states at the Fermi energy for  $ZrN_x$  versus concentration  $x$ .

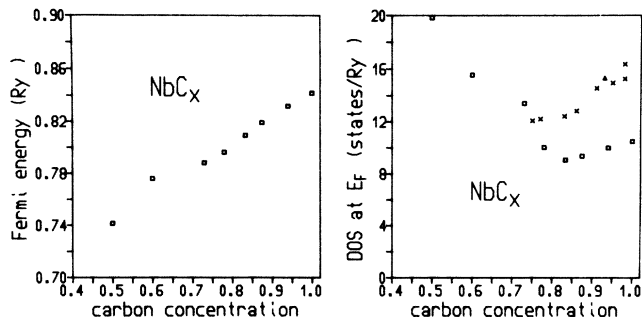


FIG. 11. Fermi energy and density of states at the Fermi energy for  $NbC_x$  versus concentration  $x$ . Experimental values of  $g(E_F)$  from Ref. 24 (triangle) and Ref. 25 (crosses).

and the density of states at the Fermi energy for  $ZrC_x$ ,  $ZrN_x$ ,  $NbC_x$ , and  $NbN_x$ , as a function of concentration  $x$  are shown in Figs. 9–12. Contrary to the results of the linear combination of atomic orbitals—coherent-potential approximation (LCAO-CPA) method,<sup>19,20</sup> the Fermi energy is generally lowered by the introduction of vacancies. This is not true for  $ZrC_x$ , where the Fermi energy does not vary much with the vacancy concentration, and is, up to a certain value of  $x$ , even increased. A very similar behavior was found in the  $3d$  metal carbides and nitrides. This is a direct consequence of the presence of vacancy-induced states. The LCAO-CPA method,<sup>19,20</sup> which detects no such states, predicts an upward shift of  $E_F$ . According to our results, there are more states present to accommodate the same number of electrons, consequently  $E_F$  is lowered. In the case of  $TiC_x$  and  $ZrC_x$ , most of the vacancy-induced states are found above  $E_F$ , so they cannot affect the position of the Fermi energy very much. It should be noted, however, that since we overestimate the intensity of the vacancy-induced peaks we also overestimate the downward shift of  $E_F$ . Recent  $x$ -ray emission spectroscopy (XES) measurements on substoichiometric  $TiN_x$  (Ref. 21) clearly show a vacancy-induced Ti  $p$ -like peak and a slight downward shift of  $E_F$ . Calculated XES spectra based on the KKR-CPA DOS of Ref. 1 again show too high an intensity of the vacancy-induced peak and a larger downward shift of  $E_F$ . The case of  $TiN_x$  may be expected to be typical for other transition-metal carbides and nitrides. Most likely these discrepancies are due to the fact that our calculations are based on self-

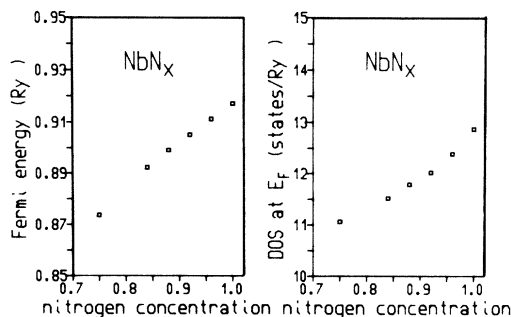


FIG. 12. Fermi energy and density of states at the Fermi energy for  $NbN_x$  versus concentration  $x$ .

consistent potentials for the stoichiometric binary compounds, but are not self-consistent with respect to the charge density of the nonstoichiometric systems, and probably also to local displacements and short-range-order effects. A detailed discussion of these points is given in Ref. 12. For not too high vacancy concentrations ( $x \geq 0.8$ ), however, the agreement between theory and XPS and XES experiments is really excellent. Also, angle-integrated ultraviolet photoemission spectroscopy (UPS) spectra of substoichiometric  $ZrN_x$  ( $x = 0.82$ ) at photon energies of 40.8 eV (Ref. 18) and 50 eV (Ref. 22) clearly show vacancy-induced peaks at energy positions in accordance with theory. Moreover, UPS intensities cannot be calculated theoretically in such a straightforward manner as in the x-ray regime, so no direct quantitative comparison is made.

The density of states at the Fermi energy is correlated to a number of observables, most simply to the linear coefficient of specific heat  $\gamma$ . However, most of the compounds investigated in this paper are high  $T_c$  superconductors. This makes the experimental determination of  $\gamma$  extremely difficult. In the case of nearly stoichiometric NbN, measurements of the specific heat above  $T_c$  with extrapolation to 0 K (Ref. 23) and measurements in a high magnetic field to suppress superconductivity<sup>24</sup> yield considerably different results. The  $\gamma$  value of Geibel *et al.*<sup>23</sup> obtained by the first method for  $NbN_{0.97}$  (2.1 mJ/mol K<sup>2</sup>) agrees fairly well with our value for  $NbN_{0.96}$  (2.14 mJ/mol K<sup>2</sup>). There are some more  $\gamma$  values published for the compounds investigated here,<sup>25</sup> but only in the case of  $NbC_x$  there are enough data available to show a clear trend of the concentration dependence of  $\gamma$ . In Fig. 11 the experimental values of  $g(E_F)$  of  $NbC_x$  are shown together with the theoretical results, assuming that the relation

$$\gamma = \frac{1}{3} \pi^2 k_B^2 g(E_F) \quad (2)$$

holds. The agreement is reasonable, considering that Eq. (2) neglects electron-phonon enhancement. Moreover, most of the experiments were performed about 20 years ago on rather ill-defined samples.

### CONCLUSION

In this work and in previous papers<sup>1-3,26</sup> we have investigated the influence of substoichiometry on the car-

bides and nitrides of Ti, V, Zr, Nb, and Mo. Although the densities of states of these compounds may differ considerably in several details (e.g., the width and positions of the various bands, the position of the Fermi level due to the different number of electrons per unit cell, etc.) they all have one feature in common: There is a nonmetal  $p$  subband separated by a deep minimum from a metal  $d$  subband. Introduction of vacancies in the nonmetal sublattice invariably leads to a building up of new states in this minimum. Theoretical and experimental evidence of these vacancy states is by now overwhelming. In our opinion the controversy between the LCAO-CPA method, which detects no such states,<sup>19,20</sup> and the KKR-CPA method is by now settled in favor of the latter.

Because of the remarkably similar behavior of all these compounds it may be expected that such vacancy states occur in many other substoichiometric systems. Carbon vacancies have been reported for a wide range of concentrations in  $ThC_x$ ,  $UC_x$ ,  $NpC_x$ ,  $PuC_x$ .<sup>11</sup> In many transition metal, rare earth, and actinide carbides, pnictides (UN, UAs, USb, UBi, CeN, CeAs), and chalcogenides (YS, US, USe, UTe) vacancies probably influence profoundly the electronic structure. Even in systems with two metallic components not crystallizing in the NaCl structure which, however, do have two subbands (e.g., Fe-Al, Co-Al, Ni-Al) substoichiometry occurs. For the Fe-Al system vacancy calculations have been reported recently.<sup>27</sup>

Probably substoichiometry is a far more common property of compounds and alloys than has been up to now experimentally determined. From our results it may be inferred that in most systems where substoichiometry occurs the vacancies profoundly change the electronic structure. Any theoretical model that ignores effects of substoichiometry, or treats them in an oversimplified way (such as rigid-band model) will lead to a misleading description of the electronic structure of such systems.

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