DENSITY OF STATES OF SUBSTOICHIOMETRIC TiN$_{1-x}$*)

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The electronic states of substoichiometric TiN$_{1-x}$ are studied by the CPA method and both the partial and total densities of states (DOS) are calculated. The results reveal that with increasing vacancy concentration $x$ the Fermi level $E_F$ moves to higher energies and the DOS at $E_F$, $g(E_F)$, increases linearly. The calculated L$_{II,III}$ X-ray spectra of Ti compare well with experiment.

1. INTRODUCTION

The transition metal carbides and nitrides have most interesting physical and chemical properties [1]. They possess extremely high melting temperatures, the extreme hardness and good corrosion resistance, what makes them technically important. Another remarkable property of these materials is the wide region of homogeneity i.e. they exist in an equilibrium state with a large fraction of nonmetal sites empty. All physical properties depend drastically on the stoichiometry of the sample, e.g. the melting temperature, paramagnetic susceptibility, specific heat, optical properties etc. The last three quantities measure more or less directly the DOS and give the simplest test of the calculated single particle DOS.

The calculation of the DOS of a substoichiometric crystal poses a problem which cannot be solved exactly so far and various approximations have been proposed, e.g. rigid band model (RB) and virtual crystal approximation [2]. The coherent potential approximation was suggested by the author to deal with the similar problem of DOS in substoichiometric TiC$_{1-x}$ [3] and the same approach is described concisely below as applied to the TiN$_{1-x}$. The reader should consult [3] for details of theoretical formulation.

2. THE PERFECT CRYSTAL

The band structure of stoichiometric TiN was carefully calculated by Neckel et al. [4]. According to this calculation the energies of 4s and 4p titanium states lie fairly high and can be left out of the tight binding set describing the lowest valence bands, similarly the nitrogen 2s states contribute virtually only to the TiN 2s-band, which lies fairly below the rest of the valence bands. Hence in view of the subsequent CPA

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*) Work supported by the Research Institute for Powder Metallurgy, Šumperk, Czechoslovakia.

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calculation we may simplify the tight binding Hamiltonian of TiN as follows

\[ H = \sum_{n} \sum_{p_a} \langle n p_a | \varepsilon_{p_a}^N(n) | n p_a \rangle + \sum_{\vec{n}} \sum_{d_a} \langle \vec{n} d_a | \varepsilon_{d_a}^{Ti}(\vec{n}) | \vec{n} d_a \rangle + \]

\[ + \sum_{n,\vec{n}} \sum_{\alpha,\beta} t(n, \vec{n}) \langle \vec{n} d_{\alpha} \rangle \langle \vec{n}\' d_{\beta} \rangle + \]

\[ + \sum_{\vec{n}=\vec{n}'} \sum_{\alpha,\beta} \langle \vec{n} d_{\alpha} \rangle \langle \vec{n}' d_{\beta} \rangle + \sum_{n,\vec{n}} \sum_{\alpha,\beta} \sum_{n',\vec{n}'} \langle n p_a | t(n, n') | n' p_{\beta} \rangle \]  

where \( |n p_{\alpha}\rangle, \alpha = 1, 2, 3 \) and \( |\vec{n} d_{\alpha}\rangle, \alpha = 1, \ldots, 5 \) represent the Löwdin orthogonalized orbitals made of the atomic \( |2p_{\alpha}\rangle \) nitrogen resp. \( |3d_{\alpha}\rangle \) titanium states and \( n \) resp. \( \vec{n} \) label the nitrogen resp. metal lattice points (TiN crystalizes in the rock salt structure). The first two terms correspond to the diagonal part of the Hamiltonian, the next three are Ti-N, Ti-Ti and N-N interactions, respectively. The values of the matrix elements \( \varepsilon_{p_a}^N, \varepsilon_{d_a}^{Ti} \) and \( t \) were taken directly from [4].

3. THE SUBSTOICHIOMETRIC CRYSTAL OF TiN\(_{1-x}\)

The recent neutron diffraction study [5] shows that the vacancies in the TiN\(_{1-x}\) are limited only to the non-metal lattice while the Ti sublattice is stoichiometric. The further analysis of these experiments [6] also reveals the presence of some short range order, and under the special circumstances and for \( x = 0.61 \) even the long range order appears. These effects have to be neglected in the simple application of the CPA method and the nitrogen sublattice is simply treated as a random alloy of the vacancies and nitrogen atoms.

The vacancies are dealt with as usually by putting the vacancy selfenergy \( \varepsilon'(n) = + \infty \) (see [3]). Then the hopping integrals onto the vacancy site are irrelevant and can be taken the same as in a perfect crystal (the diagonal disorder).

In the CPA one replaces the configurational average of a single particle Green’s function by the Green’s function \( \hat{G} \) calculated from a periodic effective Hamiltonian \( \hat{H}_{eff} \). One gets \( \hat{H}_{eff} \) simply by replacing the diagonal part of a random Hamiltonian by a complex selfenergy \( \Sigma \), i.e. in our case by replacing \( \varepsilon_{p_{\alpha}} \) by \( \Sigma_{p_{\alpha}} = \Delta \sigma_{p_{\alpha}} + \varepsilon_{p_{\alpha}} \), while \( \Sigma_{d_{\alpha}} = \varepsilon_{d_{\alpha}}^{Ti} \) or \( \Delta \sigma_{d_{\alpha}} = 0 \) (the metal lattice is not random).

The selfenergy \( \Delta \sigma_{p_{\alpha}} \) satisfies the Soven’s equation, which in this case has a simple form (see [3, 7])

\[ \Delta \sigma_{p_{\alpha}} = -x |f_{p_{\alpha}}| \]  

where \( x \) is a vacancy concentration and \( f_{p_{\alpha}} \) is the trace of a \( p_{\alpha} \)-projection of the Green’s function \( \hat{G} \)

\[ f_{p_{\alpha}}(E) = \frac{1}{N} \text{Tr} \left( \hat{N}_{p_{\alpha}} \hat{G}(E + i\delta) \hat{N}_{p_{\alpha}} \right) = \langle 0 p_{\alpha} | \hat{G}(E + i\delta) | 0 p_{\alpha} \rangle, \quad \alpha = 1, 2, 3 \]  

where \( N \) is the number of unit cells in a sample, \( \delta \) is a positive infinitesimal and \( \hat{N}_{p_{\alpha}} = \)  