EFFECT OF METALLIC VACANCIES ON THE ELECTRONIC STRUCTURE OF NIOBIUM NITRIDE

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The effect of metallic vacancies on the density of states in niobium nitride is examined. Calculations were carried out using the recursion and coherent-potential methods for NbN and Nb_{0.75}N. The recursion density of states in nonstoichiometric niobium nitride is obtained for parallel and antiparallel arrangement of the metallic vacancies. It is found that the formation of such vacancies leads to the formation of an electronic spectrum of additional (in comparison with the complete compound) states in the high-energy part of the hybrid metal—nonmetal region. The changes in the density of states of Nb_{0.75}N in relation to the degree of ordering in the metallic sublattice are also examined.

It is well-known [1] that niobium nitride solidifies in an NaCl-type lattice. A typical feature of this compound is that its crystal structure is retained even in the case of large deviations from the stoichiometric composition toward the side of a shortage of both the metal atoms and the nitrogen atoms. This stability of the crystal structure is typical of cubic nitrides of d-metals [1, 2]. Certain nitrides can contain up to 25% vacancies with respect to the metal [2]. In titanium, zirconium, and hafnium nitrides with the maximum number of defects with respect to the metal, the metal—dielectric transition takes place [2].

Theoretical investigations of the electronic structure of the nitrides Ti_{0.75}N, Zr_{0.75}N, and Hf_{0.75}N were carried out in [3] by the LTMO band method. In [4, 5], electronic spectra of Zr_xN and Ti_xN were produced by the coherent-potential (CP) method. As far as the authors know, no investigations have been carried out into the density of the electronic states (DS) of the compound Nb_xN (at x differing from 1.0). Taking into account these considerations, it is interesting to examine the effect of vacancies with respect to the metal in niobium nitride on the DS (using Nb_{0.75}N as an example). In this work, we produced the DS of structures of Nb_{0.75}N with ordered and disordered distribution of metallic vacancies.

The densities of states of the compounds Nb_4N and Nb_3N_4 were produced by the nonorthogonal recursion method [6]. The basis functions were represented by atom-like orbitals of s- and p-symmetry, centered on N-nodes, and orbitals of d-symmetry centered on Nb-nodes. The DS were constructed by the terminator method [6], using 11 pairs of recursion coefficients for each of the 9 basis orbitals. The crystal structure of Nb_4N_4 and Nb_3N_4 was modeled by translation of a tetragonal elementary cell with 16 atoms in three directions with spacings a, a, and 2a (where a is the lattice spacing). Using this elementary cell, it was possible to model both the complete lattice of the NaCl type and the defective lattice of Nb_3N_4 with parallel and antiparallel distribution of vacancies with respect to the metal. The possibility of two variants of the distribution of vacancies in the M_xX_3 and M_2X_4 structures (where M is a transition metal, and X = C, N, O) was indicated in [8]. Calculations of the DS were carried out for a spherical cluster that included 2500 atoms. The value of the DS for the disordered compound Nb_{0.75}N was obtained by the coherent-potential method [4].

Figure 1 shows DS curves of the complete niobium nitride obtained by the recursion method and the coherent potential method. The recursion DS is in good agreement with the DS obtained by the CP method with respect to both the shape and the position of the peaks. The electronic spectrum of niobium nitride is typical of the compounds of d-metals with an NaCl type structure: it consists of two bands — a low-energy band of the M−X interaction, and a high-energy band of the M−M interaction. Figure 2 shows DS of the nitride Nb_{0.75}N obtained by these methods. According to Fig. 3, in both the ordered and disordered structures, vacancies with respect to the metal cause the formation of vacancy states (which are not found in the complete phase) in the electronic spectrum in the high-energy part of the band of the M−X interactions. Similar
Fig. 1. Complete DS of the nitride $\text{Nb}_{1.075}N$ produced by the recursion (1) and coherent-potential (2) methods. In this and other figures, the DS is presented in units of electrons/(elementary cell-ryd). $E_F$ is the Fermi level.

Fig. 2. Complete DS of the structure of $\text{Nb}_{0.75}N$ with antiparallel (1) and parallel (2) distribution of vacancies, produced by the recursion (1, 2) and coherent potential (3) methods.

Fig. 3. Schema of atomic structures corresponding to the parallel (a) and antiparallel (b) vacancy distribution.

Fig. 4. Partial DS of nitrogen, produced by the coherent-potential (a) and recursion (b, c) methods: b) antiparallel vacancy distribution for atoms with one (1) and two (2) adjacent vacancies; c) parallel distribution of vacancies for atoms with three adjacent vacancies (3) and atoms whose nearest environment does not contain any vacancies (4).

effects were also observed in examining other nitrides defective with respect to the metal [3-5]. However, in contrast to the results of studies [4, 5], the data obtained in this work show that the band of the M–N interaction in $\text{Nb}_{0.75}N$ is not separated from the metallic band by an energy gap. Analysis of the data in [4, 5] and in this work indicates that the formation of an energy gap at the minimum of the DS depends on the nature of the overlapping of these bands. The extent of this overlapping is smallest for $\text{ZrN}$ and, consequently, an energy gap forms in the DS of the nitride $\text{Zr}_{0.75}N$ that separates these bands and converts this compound to a dielectric. According to Fig. 3, the vacancy states are almost completely represented by states of the nonmetal with p-symmetry. This is due to the fact that the formation of metallic vacancies in niobium nitride is accompa-