ON THE QUALITATIVE THEORY OF SHOCKLEY SURFACE STATES OF THE (111) FACE OF NbC AND THE NATURE OF BONDING IN THIS COMPOUND

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Qualitative theory of Shockley surface states is applied to the analysis of the (111) surface of the niobium carbide crystal. The existence of Shockley states is predicted in two hybridizational gaps. One of (p, t_{2g}) character lies just below the Fermi energy and the other of (e_g, t_{2g}) character is at higher energies. The relation between Shockley states and bonding is discussed. A strong (p, t_{2g}) covalent component of the metal-nonmetal bond is found.

The surface electronic structure and especially Shockley surface states[1] of niobium carbide and related compounds have not yet been studied theoretically with the exception of TiO and VO (ref.[2,3]). Therefore such an investigation for the (111) surface of NbC has been undertaken using the so-called qualitative theory of Shockley states[4-8] which deals with the following questions: *1*) whether the surface of a particular solid can exhibit Shockley states (dangling bonds), *2*) which type of bonding is responsible for their appearance.

This qualitative theory consists of two basic tools: *a*) surface projections combined with symmetry arguments (*i.e.* the projected surface energy band structure – surface projection – is obtained by projecting volume states from the 3-dimensional Brillouin zone onto the 2-dimensional surface Brillouin zone) and *b*) general rules for the existence of Shockley states. These rules are closely related to the theory of chemical bonding. Items *a*) and *b*) have been explained in detail in refs[4-8].

The qualitative theory is based on the use of the so-called Shockley model[1,6,9] of the crystal surface, which appears[6,9] to be sufficient for a qualitative description of Shockley surface states. Naturally, a quantitative treatment should include also the effects of self-consistency, both electronical and geometrical.

The analysis performed here is based on self-consistent APW volume state energy bands of NbC as obtained by Schwarz (refs[10-13]). The nature of bonding in the transition metal compounds has been the subject of dispute for some time[13-15]. Our results focus on the covalency aspect and closely resemble the model proposed in ref.[18].

THEORETICAL

Shockley Surface States and Chemical Bonding. According to general rules[4,5], a Shockley state with a particular value of $\boldsymbol{k}_{\parallel}$ (in the surface Brillouin zone) can appear on the surface of a solid only for energies lying in a certain hybridizational gap (HG) of the energy spectrum. Such a HG arises if, with hydridization neglected, two bands of volume states cross, *i.e.* if in the HG formation two dispersion curves $E^0(\boldsymbol{k})$, each of definite character (*e.g.* *s*, *p* or *d*), play a dominant role. These curves correspond to mutually non-interacting Bloch functions based on different types of orbitals (*s*, *p*, *d*) located on the same or different types of atoms (Nb or C in our case). Hence, the HG appears due to *non-crossing rule*[26]. Sometimes the term strong hybridization is used and it is understood that all other cases lead to weak (or no) hybridization[27]. An illustrative example of the above definition of a HG is found in Results. The gaps which are not HG are nonhybridizational (NHG) by definition. They cannot contain any Shockley states.

The important point is that the qualitative theory relates[4,5,28] (strong) hybridization with the chemical term strong covalency. Therefore, when (strong) hybridization is found, the bonding of the solid contains a covalent component. Here the notion of the covalent bond is generalized[4,5] as compared with its classical chemical meaning which corresponds to situations where the HG exists for the whole Brillouin zone (*e.g.* Si). Hence the generalization is such that it includes also systems sometimes called electron deficient in which there are less valence electrons per atom available than neighbouring atoms to bind. As a consequence the bond bears to a certain degree a resonant (mesomeric) character. Naturally, its strength depends on the occupation of the states which are bonding or antibonding with regard to the respective hybridization (HG), as well as on the number of such states, *i.e.* on the extent of the HG existence condition in $\boldsymbol{k}$-space. The strength reaches the maximum for E_F falling into this HG.

To summarize, general rules for Shockley states allow the detection of strong covalency and thus permit an analysis of bonding in a crystal[4,5]. A HG is then indicative of covalent bond in the system. The surface plane can be thought of as an imaginary plane in the bulk which cuts all interactions. Those which are of strong covalent character can be detected by the direct use of general rules.

RESULTS AND DISCUSSION

Since niobium carbide crystalizes in the rock-salt structure which arises by superposition of two FCC lattices, the surface Brillouin zone of the (111) face is a regular hexagon[8]. The center of this zone is denoted by $\bar{\Gamma}$, the corners by $\bar{K}$, and the center of the hexagon side by $\bar{M}$. The bands at $\bar{\Gamma}$ in Fig. 1 are projections of volume states along Λ of the (3-dimensional) Brillouin zone. Volume states along Δ and Σ project on $\bar{\Sigma} = \overline{\Gamma M}$ and those along a certain part of Σ project on $\bar{T} = \overline{K\Gamma}$.

Fig. 1 shows that there are a number of gaps in the projected surface energy band structure of the (111) surface of NbC. They all are NHG with the exception of two.

TABLE I

Illustrative Example to the Definition of a Hybridizational Gap

Irreducible representations (IR), energy (E) and the percentage of the p or d character of wave functions in the muffin-tin spheres of Nb or C atoms for the two strongly hybridized energy curves Λ_3. Data taken from ref.[11]. The "missing" charge falls essentially outside the muffin-tin spheres.

Point	Γ	Λ (middle)	L	
IR	25′	3	3′	
E(Ry)[a]	0·7345	0·5656	0·4718	lower Λ_3 curve
p(C) %	—	38·33	38·96	
d(Nb) %	68·92[b]	37·75	38·33	
IR	15	3	3′	
E(Ry)	0·8229	0·8471	0·9803	upper Λ_3 curve
p(C) %	74·66	3·14	3·47	
d(Nb) %	—	72·51	83·14	

[a] 1 Ry = $2{\cdot}178 \,.\, 10^{-18}$ J; [b] pure t_{2g} symmetry.

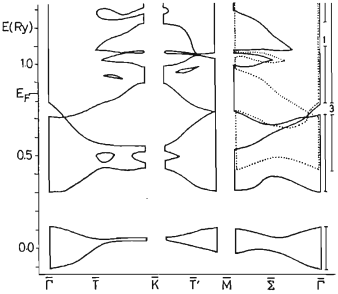

FIG. 1

Projected Surface Energy Bands of (111) Face of Niobium Carbide for High-Symmetry Directions of the Surface Brillouin Zone

Along Σ, the areas within full lines belong to energy bands corresponding to the symmetrical irreducible representation Σ_1 of group C_s, those within dotted lines to the antisymmetrical irreducible representation Σ_2. At Γ, the energy bands are labelled by the respective irreducible representations.

The first HG just below E_F is of (p, t_{2g}) type and extends in the neighborhood of $\bar{\Gamma}$. States which are bonding with respect to this HG are fully occupied whereas the antibonding states are partly empty. At $\bar{\Gamma}$, this gap originates from $\bar{\Gamma}_3(\Lambda_3)$ states which can be shown to hybridize according to the data of ref.[10,11]. To put it more explicitly, this HG lies between two dispersion curves $\Gamma_{25'} - \Lambda_3 - L_{3'}$ (lower branch) and $\Gamma_{15} - \Lambda_3 - L_{3'}$ (upper branch). As seen from Table I, along the lower branch the character of the wave function varies from pure d on the Nb atom at Γ to strong p on the C atom at $L_{3'}^{\text{lower}}$. The situation is reversed along the upper branch. These two branches can be thought of as originating from two non-hybridized Bloch waves of purely d (Nb) and p (C) character, respectively, the dispersion curves $E^0(\boldsymbol{k})$ of which cross each other. The crossing non-interacting curves are $\Gamma_{25'} - \Lambda_3 - L_{3'}^{\text{upper}}$ and $\Gamma_{15} - \Lambda_3 - L_{3'}^{\text{lower}}$, respectively. When hybridization is switched on, the cross-over is removed according to the *non-crossing rule*[26]. For other gaps, the analysis is analogous (see also ref.[28]). Fig. 1 shows that along the $\bar{\Sigma}$ and $\bar{T}$ directions, the (p, t_{2g}) HG closes at a certain distance from $\bar{\Gamma}$ and immediately reopens as a NHG. Hence, it is a double gap[7,8]. Along the $\bar{\Sigma}$ direction there are also two double gaps, namely for $\bar{\Sigma}_1$ and $\bar{\Sigma}_2$ states. The HG part near $\bar{\Gamma}$ is essentially the same for both symmetries. The edges of the $\bar{\Sigma}_1$ HG are formed by the Δ_1 and Δ_5 branches of volume states, whereas the edges of the $\bar{\Sigma}_2$ and $\bar{T}$ HG come from Σ_2 and Σ_4 branches.

It can be shown that the HG of (p, t_{2g}) character exists also on (001) and (011) faces[28,31] of niobium carbide in the same energy region. In both of these cases there is a resonance gap near $\bar{\Gamma}$ which extends along the high symmetry directions of the corresponding surface Brillouin zone. By a resonance gap we mean a gap in the states of one symmetry overlapped by states of different symmetry. Using the arguments of the preceding section regarding the relation between the existence of a HG and the nature of bonding from which this HG originates, it follows that there exists a strong covalency component of (p, t_{2g}) type between the carbon and niobium atoms in NbC. However, if an analysis similar to that of NbC is performed for transition metal nitrides and oxides (using the band structure of ref.[17]) the hybridization of (p, t_{2g}) character which was strong for carbides is weak for nitrides and almost disappears for oxides. For nitrides, it can still bring a non-negligible contribution to the cohesive energy, for example. However, it cannot lead to the appearance of Shockley surface states. The bonding picture which emerges from the present analysis is consistent with the model of ref.[18] proposed in connection with the interpretation of superconductivity of NbC.

Two types of surfaces are possible for an ideal (111) surface of a NbC crystal; the first layer contains either only Nb atoms or C atoms. On each of these surfaces there should be a Shockley surface state (doubly degenerate at least in $\bar{\Gamma}$) in the (p, t_{2g}) HG according to general rules. Wave functions of Shockley states of the Nb surface are of t_{2g} character (xz, yz, with the z-axis perpendicular to the surface) having two lobes with different signs reaching out of the surface. The wave functions corresponding to the C surface are of *p*-type with one of the *p*-lobes outside the surface. Owing to special symmetry properties and two-fold degeneracy of t_{2g} type Shockley states, the Nb surface could exhibit interesting properties in chemisorption and catalysis[29-31] *via* Woodward–Hoffmann rules[32].

The second HG on the (111) face is at about 1·05 Ry (Fig. 1), *i.e.* above E_F and is of (e_g, t_{2g}) character. It is centred around $\overline{M}$, extending in the $\overline{T}'$ and $\overline{\Sigma}$ directions where it belongs to $\overline{\Sigma}_2$ states. Along $\overline{T}'$, it is a part of a double gap. Due to its *d*-character, this gap can give rise to Shockley surface states on the Nb surface only.

There are arguments[19,20] in favour of strong hybridization between occupied *s*, *p* states on carbon and unoccupied *s*, *p* states on niobium. This hybridization could not be detected in the present analysis since the corresponding data are not available.

Shockley surface states of (p, t_{2g}) and (e_g, t_{2g}) character on the (111) face of NbC have not yet been found experimentally. It would be interesting to confirm their existence. This should be possible, for example, by angle-resolved uv photoemission[33] for the first of the Shockley states and by electron energy-loss spectroscopy[34] for the second.

Note: The present qualitative analysis has recently been confirmed by quantitative calculations[35] performed for the point $\overline{\Gamma}$ of both the (111) and (001) faces of NbC and NbN. In agreement with qualitative predictions, Shockley surface states have been found for NbC but not for NbN.

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