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# Optical conductivity in substoichiometric titanium carbides

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A theoretical study of the optical absorption of perfectly ordered titanium carbides $TiC_x$ is reported for different carbon concentrations ($x=1$, 0.75, 0.50, and 0.25). The optical conductivity is calculated within the framework of the linear muffin-tin orbital method in the atomic-sphere approximation. The effect of carbon vacancies on the optical conductivity is discussed and the origin of the different absorption peaks is traced back to particular interband transitions. [S0163-1829(98)08731-1]

## I. INTRODUCTION

The binary compounds of a transition metal and one of the nonmetallic elements C, N, or O constitute one of the most relevant systems in material science due to their physical properties. Except for a few exceptions, most of the so-called refractory materials combine the metallic properties like conductivity with typical properties of strong covalent bonding such as extreme hardness and very high melting points.[1] The titanium compounds (and especially TiC) are the most intensively studied both experimentally and theoretically.

The electronic structure of $TiC_x$ ($x \leqslant 1$) has been closely examined in order to understand its physical properties. These compounds have been found with both stoichiometric and substoichiometric compositions. The changes in the relative concentration of Ti and C reflected in the electronic structure should have an influence on physical properties like optical conductivity, which is directly related to the occupied and unoccupied states. In the present work we explore this point.

Ihara *et al.*[2] have performed x-ray photoemission spectroscopy experiments on $TiC_{0.98}$. They found two main structures below the Fermi level ($E_F$). The first one with a binding energy of 10.7 eV corresponds to C 2*s* states, while the second one with two peaks of binding energies 3.4 and 3.7 eV results from the hybridization of C 2*p* and Ti 3*d* states. The density of states at ($E_F$) amounts to 0.22 $eV^{-1}$. These two main structures have been also observed by Johansson *et al.*[3] for $Ti_{0.98}C$ through angle-integrated photoelectron spectroscopy. A broad peak is observed at about 11.0 eV below $E_F$, which originates from C 2*s*. The second large band between 0 and 7 eV below $E_F$ arises from Ti 3*d* and C 2*p* hybridization. This band has an intense peak at 2.9 eV and a shoulder at about 5 eV below $E_F$.

The theoretical studies carried out by different methods[4–10] essentially agree with the experiments, although with some variations in the location of the two main structures. The C 2*s* peak is, generally, reproduced 0.5–1.0 eV closer to $E_F$ as compared to the experimental data. Here, it is worth mentioning that the theoretical studies have been performed for the perfect stoichiometric TiC. Another relevant result is the existence of a pseudogap in the density of states around $E_F$.

Quite recently,[10] nonstoichiometric $TiC_x$ layers have been synthesized through a multiple-energy ion-implantation technique at the surface of pure $\alpha$-Ti. This allows the formation of $TiC_{0.26}$, $TiC_{0.49}$, and $TiC_{0.78}$ besides the perfect stoichiometric TiC. From a theoretical point of view these compounds have been the subject of several band-structure calculations.[4–10] One of the most important conclusions of these studies is that carbon vacancies lead to additional sharp peaks on both sides of $E_F$ in the dip of the density of states (pseudogap) of TiC. The presence of sharp vacancy peaks close to $E_F$ would open transition channels and thus would give rise to optical conductivity peaks as compared to stoichiometric TiC. This particular possibility makes $TiC_x$ an interesting case in the field of band-gap engineering. The aim of the present work is to investigate this point. In the next section a brief account of our theoretical model is given. The results for the optical conductivity of substoichiometric $TiC_x$ are presented and discussed in Sec. III and finally the main conclusions are summarized.

## II. THEORETICAL MODEL

The electronic structures for the optical properties calculation have been self-consistently determined within the linear muffin-tin orbitals with the atomic-sphere approximation (LMTO-ASA) where the combined corrections are included. The ‘‘combined corrections’’ correct the errors introduced due to substitution of touching muffin-tin spheres by overlapping atomic spheres.[11] The exchange and correlation potential has been treated in the local-density approximation.[12] The initial potential is constructed with an isolated atomic charge distribution of neutral atoms by self-consistently solving the scalar relativistic Dirac equation.[13] The core states are kept frozen and the valence electrons considered for initial charge density are $3d^2 4s^2 4p^0$ for titanium and $2s^2 2p^2$ for carbon. The energies and eigenfunctions, during the iterations for self-consistency, are determined by the tetrahedron technique[14,15] with 165 *k* points uniformly distributed over the irreducible Brillouin zone (BZ).

The calculations were performed for a unit cell of the sodium chloride structure composed of two face-centered-

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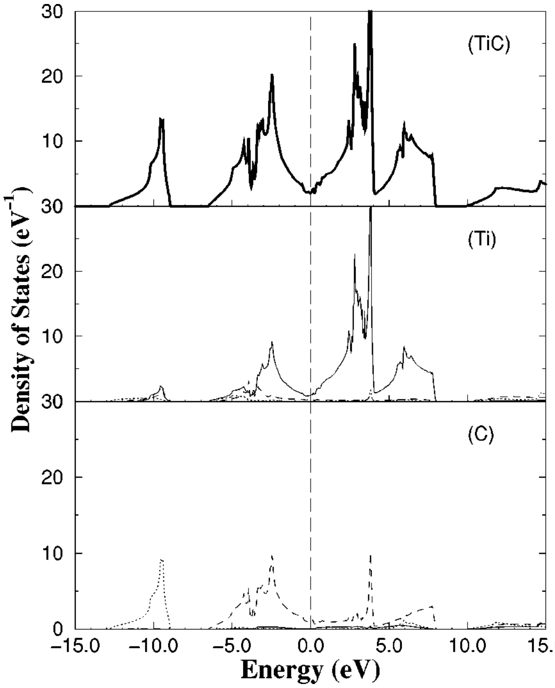

FIG. 1. Total (TiC) and orbital-projected local density of states at each inequivalent atom (Ti and C) of stoichiometric TiC. The dotted line corresponds to the *s* states, the dashed line to the *p* states, and the thin solid line to the *d* states. The vertical dashed line is the position of the Fermi level.

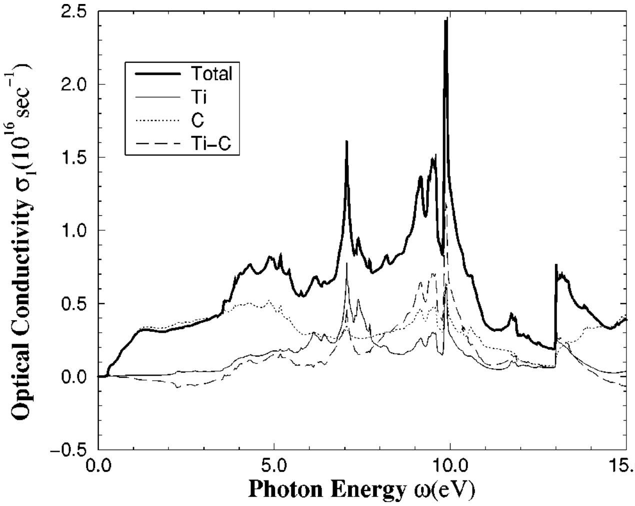

FIG. 2. The different contributions to the optical conductivity $\sigma_1(\omega)$ of TiC: the total contribution (thick solid line), the contribution of the Ti atom (thin solid line), the contribution of the C atom (dotted line), and the cross-term contribution Ti-C (dashed line). The results are reported without the Lorentzian broadening.

cubic (fcc) sublattices, one containing the titanium atoms and the other the carbon atoms. Due to the presence of carbon vacancies, two kinds of Ti atoms are present in the unit cell of the substoichiometric compounds ($x=0.75$, 0.50, and 0.25). Both Ti atomic spheres are assumed to have equal radii and the carbon vacancies are replaced by empty atomic spheres with same radii as that of C atoms.

Once the energies $E_n(\mathbf{k})$ and the functions $|n\mathbf{k}\rangle$ for $n$ bands are self-consistently obtained, one can easily determine the optical absorption of the system. For a given photon energy $\omega$, the optical absorption is directly proportional to the imaginary part of the dielectric function $\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega)$. Neglecting the Drude's term that accounts for intraband transitions and is important only for very low photon energies ($\propto 1/\omega^3$) the $\varepsilon_2(\omega)$ incorporates the allowed interband transitions. The quantity that is often measured by experimentalists is the real part of the optical conductivity $\sigma_1(\omega)=\omega\varepsilon_2(\omega)/4\pi$. In the limit of infinite lifetime of the electronic excitations and at $T=0$ K, it can be obtained through

$$\sigma_1(\omega)=\frac{1}{\pi^2\omega}\sum_{n,n'}\int_{\mathrm{BZ}}\frac{|\mathbf{e}\cdot\mathbf{P}_{nn'}(\mathbf{k})|^2}{|\nabla\omega_{nn'}(\mathbf{k})|}d\mathbf{S}_k, \qquad (1)$$

where $\mathbf{e}$ is the unit vector of light propagation, and $P_{nn'}(\mathbf{k})$ is the dipole matrix element between the initial $|n\mathbf{k}\rangle$ and final $|n'\mathbf{k}\rangle$ states with eigenvalues $E_n(\mathbf{k})$ and $E_{n'}(\mathbf{k})$, respectively. The integration is performed by the tetrahedron technique[14,15] over the Brillouin zone, where the constant surface energy is $S=\{\mathbf{k};E_n'(\mathbf{k})-E_n(\mathbf{k})=\omega_{nn'}(\mathbf{k})=\omega\}$. The above expression (1) is written in atomic units. Not all the peaks we obtain in the absorption spectrum are expected to be observed experimentally and for comparison with available experimental data the $\sigma_1(\omega)$ calculated through Eq. (1) is further broadened by a Lorentzian with a lifetime $\tau$ (i.e., $\tau^{-1}=20$ mRy).

To check the origin of different atomic contributions to the optical conductivity one can decompose $\sigma_1(\omega)$ as follows:

$$\sigma_1(\omega)=\sum_i \sigma_1^{(X_i)}(\omega)+\sigma_1^{(X_1-X_2-X_3-\cdots)}(\omega), \qquad (2)$$

where $\sigma_1^{(X_i)}(\omega)$ is the contribution from the inequivalent atomic spheres $X_i$ and the last term is the interference contribution between them. This cross term contribution can be either positive or negative.[16]

## III. DISCUSSION

The electronic structure of TiC$_x$ was calculated recently within the tight-binding LMTO (TB-LMTO) method[10] and discussed in detail for different concentrations of carbon, i.e., $x=1$, 0.75, 0.50, and 0.25. In Fig. 1 we present the total density of states (DOS) for a stoichiometric TiC as well as the local DOS within Ti and C atomic spheres with partial contributions of $s$, $p$, and $d$ symmetries. Since our DOS and electronic structures are similar to those obtained previously, we focus our attention, mainly, on the behavior of optical conductivity for the substoichiometric compounds.

First we compare our theoretical optical conductivity results for stoichiometric TiC with the experimental ones obtained from the Kramers-Kronig analysis of the reflectivity spectrum by Lye and Logothetis[17] for TiC$_{0.95}$. The theoretical $\sigma_1(\omega)$ spectrum (Fig. 2) exhibits four main peaks ($A$, $B$, $C$, and $D$). Their positions are 5.0, 7.2, 9.4, and 13.2 eV. Experimentally, the corresponding peaks are obtained at 5.6, 7.2, 9.4, and 14.4 eV, as shown in Fig. 3. The origin of the different absorption peaks can be traced back to particular interband transitions from the occupied to the unoccupied parts of the density of states reported in Fig. 1. The contri-

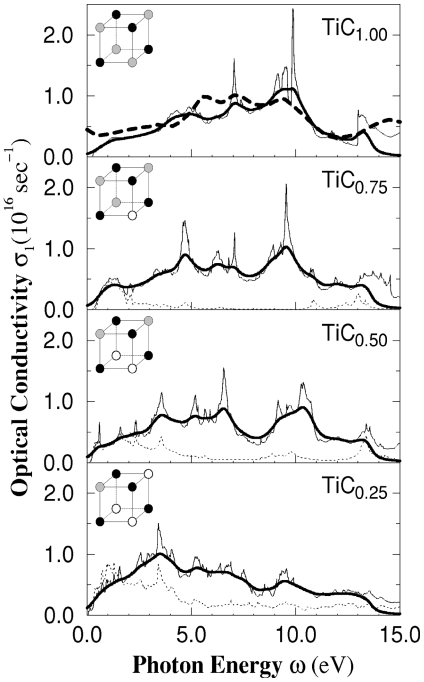

FIG. 3. Optical conductivity for TiC, $\mathrm{TiC}_{0.75}$, $\mathrm{TiC}_{0.50}$, and $\mathrm{TiC}_{0.25}$. Thick continuous line represents the Lorentzian broadening. Thin continuous line represents the total contribution whereas the dotted line is the contribution of the vacancy atomic spheres only. The insets represent $\frac{1}{8}$ of the unit cells of the different $\mathrm{TiC}_x$ compounds. Black circles represent Ti atoms, gray circles C atoms, and empty circles are the carbon vacancies. In the top figure the experimental results of Lye and Logothetis (Ref. 17) are also presented with a thick dashed line.

butions of the different atomic sites to the total conductivity, as expressed by Eq. (2), are reported in Fig. 2. It is clear that these peaks contain contributions from different inequivalent atomic spheres [Eq. (2)], but peaks *A* and *D* are mainly carbon atomic spheres contributions, while *B* and *C* have a major contribution from Ti and the interference term $\sigma_1^{\text{Ti-C}}(\omega)$ in Eq. (2). The discrepancy in the position of peak *D* with respect to the experimental one can be associated with the C 2*s* band that is reproduced closer to the Fermi level in our calculation as compared to the experimental observation.[2] Otherwise, overall agreement between the experimental and theoretical results is fairly good.

When the concentration of C in $\mathrm{TiC}_x$ decreases (from $x=1$ to 0.25), some changes appear in the optical conductivity in the low-energy range ($\omega<12$ eV), whereas high-energy peak *D* remains almost at a fixed position (13.2 eV). The intensity of this *D* structure decreases as the carbon concentration decreases and finally at $x=0.25$ it becomes a shoulderlike structure. The charge transfer in the empty spheres (*E*) increases with the carbon vacancies and additional sharp peaks are present in the density of states near the Fermi level. Due to these energy peaks, the interband transitions in *E* become more probable in the low-energy range.

In the case of $\mathrm{TiC}_{0.75}$, where only one empty sphere is present, we observe one shoulderlike structure at 1.2 eV and then there are two intense peaks at 4.6 and 9.4 eV. In between these two there are two weak structures at 6.2 and 7.0 eV (Fig. 3). The first peak (1.2 eV) is mainly due to the transitions between *s* and *p* bands in the atomic empty sphere *E*. From Fig. 3, one can understand easily the contribution of the carbon vacancy *E* for photon energies $w<2.5$ eV. All the other peaks are mainly due to *p*-*d* electronic transitions in Ti and *p*-*d* transitions in C, as well as the contribution of the interference term [Eq. (2)].

For $\mathrm{TiC}_{0.50}$, the contribution of the empty spheres increases. Now their effect extends up to 4.5 eV whereas in the case of $\mathrm{TiC}_{0.75}$ it was only up to 2.5 eV. There is a peak at 3.5 eV in this energy range. Beyond this there are peaks at 5.2, 6.2, and 10.4 eV of mixed origin as in the previous case.

The effect of the carbon vacancies on the optical conductivity is the most pronounced in the case of $\mathrm{TiC}_{0.25}$ where three empty atomic spheres are present. The optical conductivity exhibits a somewhat smooth spectrum with structures of weak intensities (Fig. 3). It is, nevertheless, possible to distinguish three structures located at 3.5, 5.2, and 9.4 eV, respectively. In this case the contribution of the carbon vacancies *E* to the total optical conductivity is more important than in the other compounds and extends to all the energy range considered in the calculation (Fig. 3). However, the *s*-*p* electronic transitions in *E* are more important for the low photon energies because of the increase of charge transfer to the atomic empty spheres with the decrease of carbon concentration. The *s*-*p* electronic transitions in *E* contribute to all the peaks of the optical spectrum. These peaks have in addition some contribution of *p*-*d* interband transitions in Ti.

Another interesting feature of the optical conductivity of $\mathrm{TiC}_x$ ($x=0.75$, 0.50, and 0.25) is the negative contribution of the cross term [Eq. (2)] in the low-energy range ($w<5$ eV). When the number of empty atomic spheres *E* increases, the contribution of the interband transitions in Ti atomic spheres is canceled by the cross term contribution of Ti with other inequivalent sites. So, in this low-energy region, the optical absorption, mainly, arises from the electronic transitions in *E* atomic spheres.

## IV. SUMMARY

The optical absorption spectrum has been calculated for $\mathrm{TiC}_x$ ($x=1$, 0.75, 0.50, and 0.25) within the framework of the *ab initio* LMTO-ASA method. We have particularly studied the vacancy effects on the optical conductivity. In the case of TiC the origin of the absorption peaks of the optical conductivity is mainly due to *p*-*d* and *s*-*p* interband transitions in Ti and C, respectively, with some significant contribution from the interference term in Eq. (2). With the increase of the carbon vacancies *E*, the charge transfer from Ti to *E* increases and gives rise to *s*-*p* interband transitions in the empty atomic spheres *E*, particularly in the low-energy range ($w<5$ eV). In the case of TiC where no carbon vacancies are present, the spectrum starts with a flat conductivity and the main optical peaks lie in the high-energy region with the last one at 13.2 eV (*D*). This structure persists for different concentrations of C, only that its intensity becomes somewhat weaker when we go from TiC to $\mathrm{TiC}_{0.25}$.

## ACKNOWLEDGMENTS

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