Ab Initio Self-Consistent Calculations of the Polarizability and Related Functions of Cubic SiC

David Ayma, Albert Lichanot, and Michel Rérat*

Laboratoire de Chimie Structurale, UMR 5624, Université de Pau et des Pays de l'Adour, IFR, Rue Jules Ferry, 64000 Pau, France

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Crystalline orbitals obtained by the linear combination of atomic orbitals−self consistent field (LCAO−SCF) method at the Hartree−Fock (HF) and Kohn−Sham (KS) levels, are used to calculate the polarizability and related functions such as dielectric constant, reflectance, and energy-loss function (ELF). Comparison of our calculations with experiment leads to a satisfactory agreement. The ELF spectra show clearly the energy ranges corresponding to the electronic excitations of the different orbitals. The carbon K-edge range is accurately analyzed in connection with the density of states.

1. Introduction

The cubic zinc-blende polytype silicon carbide (3C SiC) is a very interesting material because it presents a lot of attractive properties such as high thermal, mechanical, and chemical stability and large thermal conductivity. These characteristics allow it to be a high-frequency, high-temperature, and high-power semiconductor device[1] and then is used in blue-light emitting diodes in optoelectronic applications. In addition, its optical properties have been studied by a lot of authors in connection with its growing industrial interest. Experimental studies of optical properties are available as reflectivity,[2−4] dielectric constant,[5−7] refractive index,[8] and EXELF for the K-edges[9] or for plasmon energy[10] of ELF spectra. Calculations of the static dielectric constant and refractive index of 3C SiC have been reported both by Rohlfing et al.[11] and by Balzaretti et al.[8] using the local density approximation (LDA) and the linear muffin tin orbital method (LMTO), respectively. Recently, different ab initio methods have been used to calculate the dynamic optical properties of 3C SiC within the LDA method. For example, the dielectric function is calculated by Lee et al.[12] using a pseudopotential method while the LMTO approach has been adopted by Lambrecht et al.[3] to obtain the reflectivity.

In this work, the polarizability and its related functions (dielectric constant, reflectance, energy-loss function (ELF)) are calculated using a dynamic uncoupled Hartree−Fock (UCHF) or Kohn−Sham (UCKS) method. This method has been recently presented[13] and performs from the wave function calculated at the HF or KS level by the CRYSTAL 95 code.[14] The crystalline wave functions or crystalline orbitals (OC) are obtained by the linear combination of atomic orbitals − self consistent field (LCAO−SCF) method from atomic orbitals centered on the atoms (Gaussian−type orbitals), i.e., from localized functions (and not "muffin tin" with plane wave functions) generally used in quantum chemistry for describing ground and first excited states of molecules. Then, this ab initio LCAO−SCF has been adapted for periodic systems and implemented in the CRYSTAL 95 program (see ref 15). Generally speaking, the properties describing the ground state of the solid are accurately reproduced by this method as the charge density and Compton profiles of 3C SiC show.[16] We are interested here in the calculation of the polarizability and of its related functions which depend also on the description of the excited states. That can be considered as a challenge since it is well known that the HF and DFT approaches overestimate and underestimate the gap, respectively, i.e., the location of the excited levels with respect to the occupied ones. However, the use of AO basis sets of quality describing Si and C and of the best computational conditions has allowed us to test validly the accuracy of our approach with respect to the experimental data which are of good quality.

This paper is organized as follows. The computational procedure and theoretical background used in this work are summarized in section 2. The results are compared with the experimental data and discussed in section 3. Conclusions are drawn in section 4.

2. Computational Details and Theoretical Background

2-1. Computational Details. The computational procedure of the crystalline wave function and the description of the atomic orbitals (AO) basis sets of silicon and carbon are summarized as follows. Regarding the computational conditions embodied in the CRYSTAL 95 code, the numerical values of the tolerance parameters involved in the evaluation of the infinite bielectronic Coulomb and exchanges series are the standard ones[14] and chosen to ensure high numerical accuracy. The shrinking factor ($S = 8$) defining the reciprocal space net produces 29 reciprocal $\vec{k}$ points in which the Fock matrix is diagonalized. The CRYSTAL 95 code contains a DFT option where the Kohn−Sham one-electron equations are solved self-consistently. The exchange correlation (XC) potential introduced in the KS operator is represented as a linear combination of Gaussian-type functions (GTFs). Several models of XC potential are available in the CRSYTAL 95 code according to whether the electronic density is corrected either by a local (local density approximation (LDA)) or non local (generalized gradient approximation (GGA)) approach. In the local correction of the electronic density, the LDA[17] and the Perdew−Zunger[18] parameterizations of the exchange and correlation have been adopted, respectively. In the gradient corrected DFT, the exchange and correlation potentials correspond to the Becke[19] and Perdew−Wang[20] models, respectively.

Regarding the basis sets, all-electron atomic orbital basis sets are adopted to describe the Si and C atoms within the cell. The

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TABLE 1: Direct and Indirect Gap (in eV) of the Band Structure, Oscillator Strengths, $\sum_n f_n$ per Unit Cell and Dielectric Constant ϵ Calculated at the HF, LDA, and GGA Levels for Diamond, Silicon, and 3C SiC

	diamond				silicon				3C SiC			
	HF	LDA	GGA	experimental	HF	LDA	GGA	experimental	HF	LDA	GGA	experimental
direct gap	14.29	5.51	5.63	6.0^a $7.3^{b,c}$	8.64	2.48	2.59	3.4^b	14.97	6.29	6.20	6.0^h 7.4^i 7.75^c
indirect gap	12.84	4.49	4.58	5.4^d $5.5^{a,c}$	6.24	0.49	0.73	1.11^d	8.76	1.57	1.64	2.390^c $2.417^{h,i,j}$
$\sum_n f_n$	12.96	8.98	9.1	12	15.65	9.91	9.70	28 11.4^f	14.01	9.28	9.18	20 6.22^k
ϵ	2.46	4.65	4.60	$5.7^{d,e}$	3.0	11.18	11.03	11.8^d $12.0^{e,g}$	2.53	6.46	6.16	6.52^l 6.7^m

^{a} Ref 45. ^{b} Ref 46. ^{c} Ref 47. ^{d} Ref 48. ^{e} Ref 49. ^{f} Ref 29. ^{g} Ref 50. ^{h} Ref 51. ^{i} Ref 3. ^{j} Ref 52 at 5 K. ^{k} Ref 5. ^{l} Ref 6. ^{m} Ref 7.

basis set is of the 8-841G* type for silicon (the first shell is of s-type and is a contraction of 8 GTFs, then there are three sp and one d shells) and has been already defined in the study of silicon.[21] The carbon basis set is of the 7-31G* type.[22] The exponents ξ of the most diffuse sp and d shells of each atom have been optimized by searching for the minimum HF crystalline total energy at the experimental geometry. The following values have been obtained (Si: $\xi(sp) = 0.1141$, $\xi(d) = 0.4781$; C: $\xi(sp) = 0.2788$, $\xi(d) = 0.4781$).

2-2. Method of Calculation of Polarizability and Related Functions. In the dielectric dipole Hamiltonian gauge, the dynamic expression of the mean polarizability which represents the linear response of the electric dipole of an electronic system in an electric field is given according to[23]

$$\alpha(\omega) = \sum_n f_n \left[\frac{\Delta E_n^2 - \omega^2 + i\Gamma_n\omega}{(\Delta E_n^2 - \omega^2)^2 + \omega^2\Gamma_n^2} \right] \quad (1)$$

where f_n, ΔE_n, and ω are the oscillator strength, transition energy corresponding to the n state, and the electric field pulsation, respectively. Γ_n is the probability of de-excitation of excited states due for example to impurities or just to the natural radiative relaxation of the levels.[24,25] Following the results obtained by Eremets et al.[26] about the cubic boron nitride which has the same zinc-blende structure as 3C SiC, we have adopted for each Γ_n a unique value ($\Gamma_1 = 0.005$ au). This Γ_1 value comes from a satisfactory fit between experimental and calculated dielectric constants[26] and corresponds to an instrumental resolution value generally obtained in electron energy loss spectroscopy. In our uncoupled HF or KS method already described in refs 13 and 27, ΔE_n and f_n are given by

$$\Delta E_n = \epsilon_j^{\vec{k}} - \epsilon_i^{\vec{k}} \quad (2)$$

and

$$f_n = \frac{2}{3}(\epsilon_j^{\vec{k}} - \epsilon_i^{\vec{k}})\langle\varphi_i^{\vec{k}}|\vec{r}|\varphi_j^{\vec{k}}\rangle\langle\varphi_j^{\vec{k}}|\vec{r}|\varphi_i^{\vec{k}}\rangle \quad (3)$$

where $\varphi_i^{\vec{k}}$ and $\epsilon_i^{\vec{k}}$ are the eigenvectors and the eigenvalues of the unperturbed Hamiltonian for each $\vec{k}$ point of the first Brillouin zone. The sum over all of the states n in eq 1 is then replaced by sums over occupied i and virtual j orbitals and $\vec{k}$ points.

To calculate validly the macroscopic dielectric constant ϵ of a crystal from its polarizability α, local field effects have to be taken into account. In this work, the Lorentz−Lorenz formula, which represents in itself a form of local field correction,[28] has been used

$$\epsilon - 1 = \frac{4\pi N(\alpha - C)}{1 - \frac{4\pi N}{3}(\alpha - C)} \quad (4)$$

N is the number of cells per unit volume, α is the polarizability of the compound per unit cell, and C is a reduction term due to polarization of the charges in the cell by their own field. As Adler[28] shows, the C term of eq 4 can be calculated from the dielectric tensor over the reciprocal lattice vectors. In the LCAO method used here, this calculation is not possible at the moment (work is in progress in this sense). In these conditions, C has been omitted leading therefore to overestimated ϵ values.

The dynamic reflectance $R(\omega)$, which corresponds to the ratio of the intensities of the reflected and incident electric field, is given by[29,30]

$$R(\omega) = \frac{[1 - \text{Re}(\sqrt{\epsilon(\omega)})]^2 + [\text{Im}(\sqrt{\epsilon(\omega)})]^2}{[1 + \text{Re}(\sqrt{\epsilon(\omega)})]^2 + [\text{Im}(\sqrt{\epsilon(\omega)})]^2} \quad (5)$$

and the energy-loss function (ELF) is deduced from the dielectric constant by

$$\text{ELF} = -\text{Im}\left[\frac{1}{\epsilon(\omega)}\right] \quad (6)$$

This function is important because it allows us to compare the theoretical results with experimental data of sophisticated (EELS, EXELF) spectroscopy which provide information about the electronic system interacting with an incident electron beam.[31,32]

3. Results and Discussion

Static Polarizability and Dielectric Constant. The static ($\omega = 0$) polarizability and dielectric constant of 3C SiC calculated at the HF, local (LDA), and gradient (GGA) corrected DFT levels are reported in Table 1 with the corresponding values for silicon and diamond. Experimental data are given for comparison. The direct gaps corresponding to the smallest $\epsilon_j^{\vec{k}} - \epsilon_i^{\vec{k}}$ differences at the Γ point are overestimated as expected[33] by about a factor of 2 at the HF level with respect to experiment and underestimated in the LDA and GGA methods as generally expected for semiconductors.[34]

The sum of the oscillator strengths,

$$\sum_n f_n = \frac{2}{3}\sum_{\vec{k}}\Omega(\vec{k})\sum_{i,j}\langle i|\vec{r}|j\rangle_{\vec{k}}\langle j|\vec{r}|i\rangle_{\vec{k}}(\epsilon_j^{\vec{k}} - \epsilon_i^{\vec{k}})$$

which should be equal to the number of electrons per unit cell, is much better evaluated by the HF approach than by the LDA

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or GGA methods. In the HF method of calculation, the values of the transition moments are underestimated since the transition energies are too large and the oscillator strengths are well reproduced. This conclusion is confirmed at the LDA and GGA corrected DFT levels because the products of the transition moments by the transition energies become too small despite better reproduced transition energies (gap slightly too small). This conclusion shows a limit of the LCAO method to accurately describe the excited states since the transition moments depend both on them and on the ground state which is well described in this approach. Nevertheless, the LDA and GGA values of the static dielectric constant, which are very close, are in satisfactory agreement with experiment (Table 1) except for diamond, which is probably due to a basis set effect. This seems to indicate that the α values are well calculated in LDA and GGA corrected DFT schemes. It is noted that the values of the numerator and denominator of the α expression are both underestimated at the LDA and GGA levels. Errors compensate one another, and the comparison with the HF results shows that the effect of the gap is larger than that of the oscillator strengths.

Moreover, the experimental ϵ values which are relatively well reproduced by our uncoupled Kohn-Sham method seem to indicate also that the approximation used in this work ($C = 0$ in eq 4) for the local field effect is valid for diamond, silicon, and silicon carbide.

Comparison of our LDA values (Table 1) with other first principles LDA−LAPW calculations using a coupled method leads to negative deviations of 15% for silicon[35] and 7% for 3C SiC.[36] This result is attributable in a great part to the wave function relaxations not considered in our uncoupled model, as Champagne et al.[37] have shown in polyacetylene chains, and also to the different basis sets used in the methods.

Table 1 shows also that the 3C SiC dielectric constant is found between the two values of silicon and diamond. Given that the polarizability represents the capacity of the electron cloud for getting out of shape, this property has to be connected with the shape of the valence charge density such as it is reported in the deformation charge density maps. These maps are available for silicon, diamond, and 3C SiC in the study on semiconductors made by Orlando et al.[33] They show that, among the three compounds, silicon has the most diffuse valence electron cloud. This cloud is centered at the midpoint of the Si−Si bond and its large diffuse character explains, for example, the antibonding interactions between the second nearest neighbors as shown in the Compton profile anisotropy study.[16,38] In diamond, the valence electron cloud is much less diffuse than in silicon. It is elongated along the C−C bond because of the lack of core p electrons which allows it to get nearer the C nuclei. Finally, in 3C SiC, the buildup of electronic charge along the Si−C bond is slightly shifted towards the C atom following the charge transfer from silicon towards carbon, and a part of the valence electrons remains localized near the C nucleus. These results explain rather well the sequence of the values of the polarizability or dielectric constant ϵ(Si) > ϵ(3C SiC) > ϵ(C).

Reflectance. The use of an uncoupled approach allows us to calculate easily the dynamic properties as the reflectance and energy loss function for solids.

The shape of the reflectance spectra calculated at the HF, LDA, and GGA levels is identical but the relative position in the energy scale is different following the gap value associated with each formalism. For clarity, Figure 1 reports only the GGA $R(\omega)$ curve (dotted line) compared to the experimental results of Weeler.[2] Following the scissor operator method used by
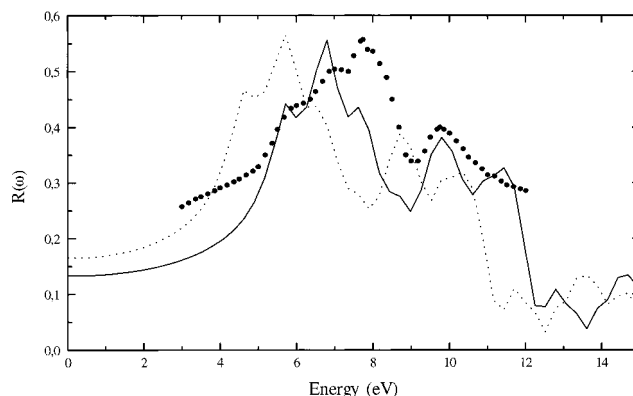

Figure 1. Reflectance spectra of 3C SiC calculated from the dielectric function at the GGA level without (dotted line) and with (solid line) the scissor operator method. The experimental data taken from ref 2 are given as full circles.
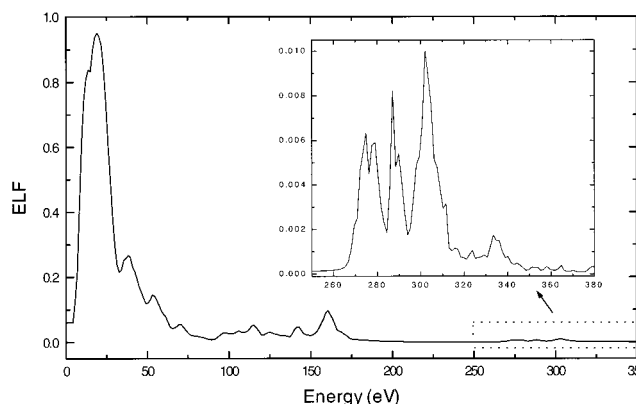

Figure 2. Energy-loss function at the GGA level for 3C SiC. The window gives the carbon K-edge spectrum.

Ching et al.,[39] the dotted line is shifted toward the experimental data and changed to the full line. This method shifts all of the transition energies $\epsilon_j^{\vec{k}} - \epsilon_i^{\vec{k}}$ by a δ parameter corresponding to the difference between the experimental and calculated direct gaps. Comparison of our calculated spectra with the experimental data of Weeler leads to a satisfactory agreement. As a matter of fact, in the two cases, a first broad band appears which includes three peaks located at 5.7, 6.7, and 7.5 eV to be compared to the 5.9, 7.1, and 7.7 eV values reported by Weeler; the fourth peak located to 10 eV is common to the two studies. However, a slight discrepancy can be pointed about the experimental and theoretical intensity of the third peak of the spectrum. Given that the experimental and theoretical shapes of the reflectance curves are very similar, the Γ_1 value chosen in eq 1 is quite justified.

Energy Loss Function. At the small scattering angles, the ELF has been deduced from the dynamic dielectric constant using eq 6. This function depends on the real and imaginary parts of $\epsilon(\omega)$ which have been calculated here only at the GGA corrected DFT scheme. For this function, we shall restrict ourselves to underline the very satisfactory agreement between the shapes of the imaginary part $\epsilon_2(\omega)$ (not reported here for reasons of clarity) and that of Lee et al.[12] obtained from first principles pseudopotential calculations within the LDA corrected DFT. Figure 2 reports the ELF curve. In the low energy range, the band which includes two peaks represents the interaction between the electron beam and the valence electrons of 3C SiC. As expected, the energy of the highest peak ($\hbar\omega_p = 19eV$) corresponds to the plasmon energy. This value is smaller than the experimental value[10] (22.1 eV) and the theoretical values

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of Backes et al.[40] (22.4 eV) deduced from the plasmonpole mode of Engel and Farid[41] using an LDA calculation. The displacement of our spectra toward the low energies corresponds to the underestimation of the gap by about 1 eV (Table 1). Considering the classical relationship between the plasmon energy and the number N of "free" electrons per unit volume which take place in the plasma oscillations

$$\hbar\omega_p = \left(\frac{Ne^2}{\epsilon_o m}\right)^{1/2}$$

(e, m, and ϵ_o are the electronic charge, the mass of the electron, and the permittivity of the free space), the N value obtained is 2.7, to be compared with the experimental value (3.7).

When the energy increases, the ELF spectra show ranges corresponding to the Si L-edge (90−170 eV), C K-edge (270−350 eV) and Si K-edge (1770−1880 eV) excitations, respectively. This sequence corresponds well to the energy position of the different atomic orbitals in the band structure. The 1s orbitals of silicon and carbon occupy pure levels located at 1780.1 and 267.5 eV, respectively, whereas the levels associated with the 2s and 2p orbitals of silicon are also pure and located at 135.9 and 92.9 eV, respectively. Particular attention is devoted to the two regions of the ELF spectra corresponding to the excitations of the 1s core electrons (270−350 eV for C, 1770−1880 eV for Si) where the experimental spectra of Sarikaya et al.[9] are available. In the C K-edge region, our calculations show three peaks at 275, 287, and 302 eV with a very small one at 333 eV, to be compared to a unique large peak at 290 eV including two shoulders at about 300 and 340 eV observed in the spectra of Sarikaya. This slight discrepancy between the calculated and the experimental peaks can have its origins in the two following features. First of all, it is possible that a better instrumental resolution reduces the difference between the calculated and observed spectra around 300 eV. Then, the lower energy location of the calculated peaks with respect to experiment is probably attributable to the uncoupled Kohn−Sham method which neglects the relaxation of orbitals after the excitation. It has to be underlined that the energy difference of about 12 eV between the two first peaks of the spectrum is characteristic of the zinc-blende type structure of the compound as mentioned by McKenzie.[42] In his study, McKenzie obtains also the same value (12 eV) which is slightly larger than the experimental one (10 eV) of Sarikaya et al.[9] This result is confirmed by the observation of the two first peaks of the Si K-edge spectrum in 3C SiC which lie at 1786 and 1800 eV. For other compounds which have the same zinc-blende type structure as diamond and cubic boron nitride (cBN), Egerton gives 12 eV,[43] whereas Gonnet[31] measures an energy separation of 18 eV between the two first peaks of the ELF spectrum. In the range of high energies (Si K-edge range), the three peaks calculated at 1786, 1800, and 1810 eV are located at energies significantly smaller than the experimental ones (1840, 1855, and 1900 eV). It can be thought that the electric dipole Hamiltonian approximation is no longer strictly valid for our calculations because the electric field cannot be considered as uniform in the cell. For example, an electric field with $\lambda \approx 7$ Å in the free space, which represents a value close to the lattice parameter, corresponds to an energy of 1800 eV. To examine the effect of this approximation, the transition moments have been also calculated with the $e^{i\vec{q}.\vec{r}}$ operator using $\|\vec{q}\| \approx 0.8$ au along the [111] direction. Little changes in the shape of the ELF curves have been observed, and the peak positions are practically not perturbed. That is also observed by Forsyth et
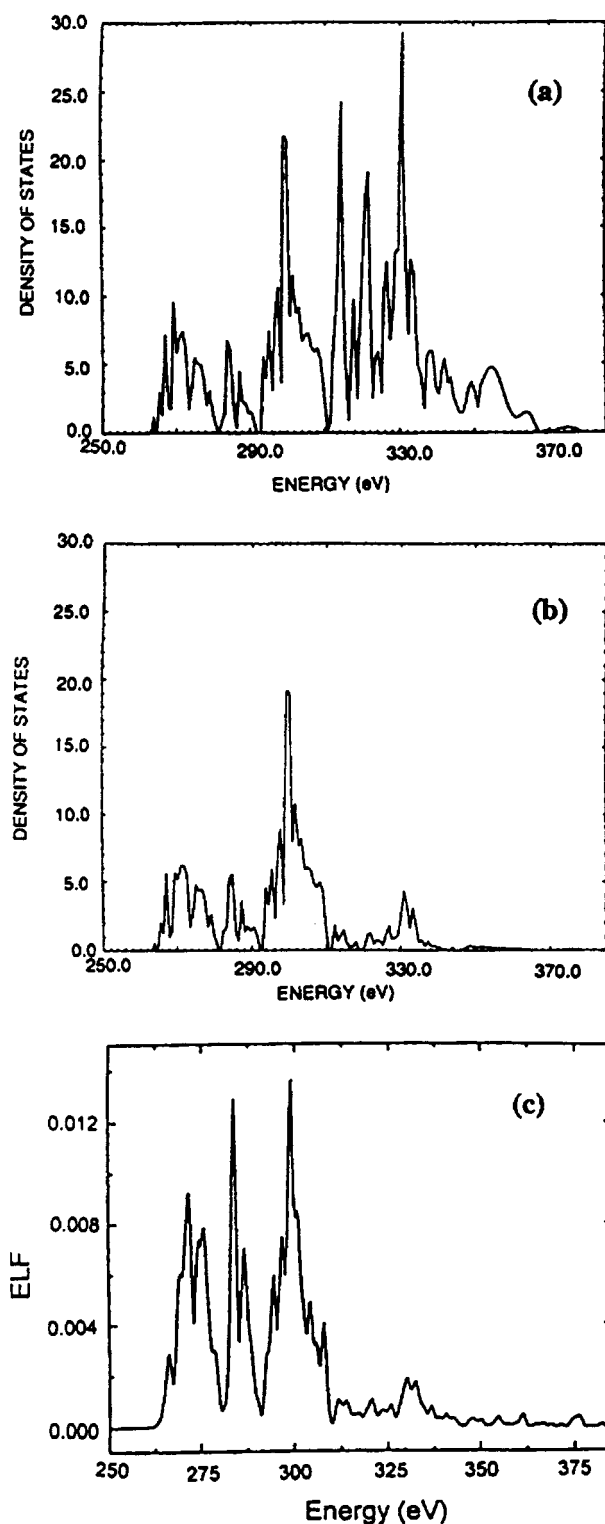

Figure 3. Comparison between the total DOS of carbon in the conduction band (a), the density of p states of carbon in the conduction band (b), and the calculated carbon K-edge ELF (c) at the GGA level. The energy origin is fixed at the 1s orbital of C for the DOS.

al.[44] in the plasmon energy range occurring at small scattering angles ($\|\vec{q}\| <$ 1au).

Finally, in order to understand the shape of the C K-edge peaks, for example, the density of states (DOSs) of the carbon p-orbitals have been projected onto the conduction band (Figure 3a and b energy origin fixed at the 1s C eigenvalue). It appears that the shape of the ELF curve (Figure 3c) is similar to that of the density of p-states in the conduction band. This result is

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attributable to the p symmetry of the dipole $\vec{r}$ operator in the R^3 group. All of the integrals of the transition moments from the 1s state toward excited states are zero except those corresponding to p states. The energy position of ELF peaks is the same as that of p DOS orbitals in the conduction band, but the relative intensities in the ELF spectrum are modified according to the corresponding oscillator strength values.

4. Conclusion

A simple method of ab initio calculations of polarizability, dielectric constant, reflectance, and ELF spectra has been applied to the cubic silicon carbide and its two components silicon and diamond. This method proceeds from an uncoupled method neglecting the relaxation of orbitals after the excitation but allowing the easy introduction of electric field frequency. It uses the crystalline wave functions calculated with the CRYSTAL 95 code which implements the LCAO method constructed from functions (atomic orbitals) localized on atoms. Generally speaking, the ground state properties are well reproduced by this method specially when the atoms are described by extended all-electron basis sets, but the description of the excited states is not as good as indicated, for example, by the gap values obtained at the HF level.

However, the result of the calculations is significantly improved when a part of the electronic correlation is taken into account with the LDA or the GGA corrected scheme. As a consequence, the reflectance and ELF calculated spectra agree rather well with the experimental ones despite a shifted energy attributable to the different energetic location, and the relative positions of the peaks are well represented and reproduce satisfactorily the main experimental features such as the plasmon energy characteristic of the zinc-blende structure. Finally, the analysis of the carbon K-edge peaks corresponding to the excitation of core electrons in connection with the density of states curves allows us to attribute unambiguously the nature of the transitions toward the p excited states of the conduction band. The relative good agreement between our calculations and experiment for these properties which depend on both ground and excited states indicates that the conduction band obtained at the DFT level by CRYSTAL 95 leads to qualitatively good information.

Work is in progress to improve and extend this method to the study of electronic spectra of non cubic systems beyond the dipolar approximation.

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