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## Analysis of Si-K edge EXAFS in the low $k$ domain

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**Résumé.** — Nous avons étudié le seuil  $K$  du silicium dans SiC et Si cristallins. Nous montrons que dans ces systèmes, l'EXAFS jusqu'aux très faibles énergies du photoélectron peut être interprété par un formalisme de diffusion simple. Les résultats obtenus nous conduisent à avancer l'hypothèse d'une invariance des déphasages en fonction de  $k$  pour  $k < 4 \text{ \AA}^{-1}$ .

**Abstract.** — Studies of the silicon absorption spectrum above the  $K$ -edge in crystalline silicon carbide SiC and in pure crystalline silicon are reported. We show that for these systems, no high order scattering is needed to interpret the experimental results down to few eV above the edge. This behaviour can be explained assuming, below typically  $4 \text{ \AA}^{-1}$ , a flattening of the phase factors *versus*  $k$ : all the data are understood in terms of single backscattering of the photoelectron by the neighbours and then can be analysed with a simple Fourier transform.

Recently there has been a large effort put into the understanding of the low-energy range just above the threshold of the X-ray absorption spectra. Since the first theories of the EXAFS, it has been pointed out that a single scattering, plane wave approximation should not be able to explain the experimental features below — say — 50 eV [1-4]. In order to overcome this difficulty, various multiple scattering theories have been developed, which take into account the increase, at low values of the photoelectron wavevector, of the so-called « mean free path » of this photoelectron. In some cases, these calculations are in good agreement with experiments, and, in particular, are able to reproduce the main differences between different symmetries of the ligands (tetrahedral *versus* octahedral) around the central atom [5-6].

The experimental results described in this paper look peculiar in that sense that no high order scattering is needed to explain the experimental spectra down to few eV above the edge, except for the well-known focusing effect due to colinear atoms. Therefore, with the hypothesis that phase factors become  $k$ -independent at low  $k$  values (below typically  $4 \text{ \AA}^{-1}$ ) all the data are understood in terms of single backscattering of the photoelectron by the neighbours and then can be analysed with a simple Fourier transform.

### 1. Experimental results.

In this paper the silicon absorption spectrum above the  $K$ -edge in crystalline silicon carbide SiC and also

in pure crystalline silicon has been studied over the same energy range.

Absorption experiments have been carried out on the two-crystal monochromator at ACO, using InSb crystals as a monochromator, and an ion chamber filled with a low pressure of air as a detector. Samples are powders of pure SiC finely ground and deposited onto a Millipore polycarbonate membrane — 5  $\mu$  thick. The result is a very homogeneous film of SiC on this transparent support. Figure 1 shows an electron

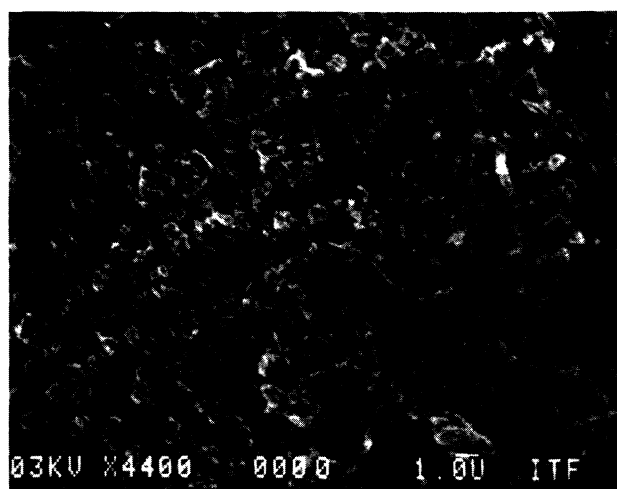


Fig. 1. — Electron microscopy result of the powdered SiC samples deposited on a millipore sheet.

microscopy picture of this type of sample. Crystalline silicon has been obtained from an evaporation of  $2.5 \mu$  of Si on a  $10 \mu$  beryllium foil which has been annealed above the transition temperature, and slowly cooled down.

The SiC experimental absorption spectrum is shown in figure 2. Glitches on the InSb monochromator appear at about 2 100 eV, and, on the SiC sample, a spurious absorption spectrum appears around 2 140 eV. We have determined that this effect is due to a small amount of phosphorus in the millipore sheet, since the same feature is present on the absorption spectrum of the support alone. Therefore, most of the analysis will be limited to a high energy value of 2 100 eV.

## 2. Analysis and results.

The absorption spectra of SiC have been processed with the classical EXAFS analysis, the background « atomic » absorption being modelled with a 3-region cubic spline spanning over the whole post-edge region. The EXAFS spectrum, which extends from 0 to 300 eV, is then Fourier transformed after various  $k$  weightings and figure 3 shows the extracted EXAFS data for SiC within the energy domain we are going to use later.

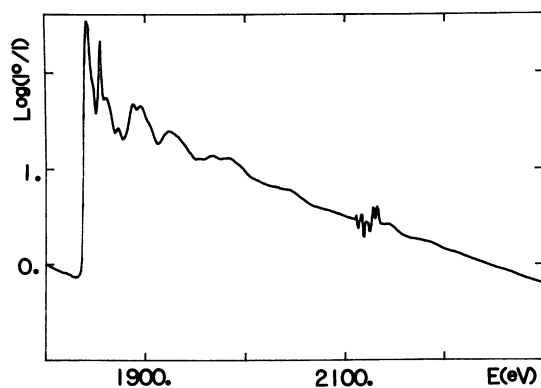


Fig. 2. — The absorption spectrum of SiC above the Si edge at 1836 eV. The spurious absorption around 2140 eV is due to phosphorus in the support.

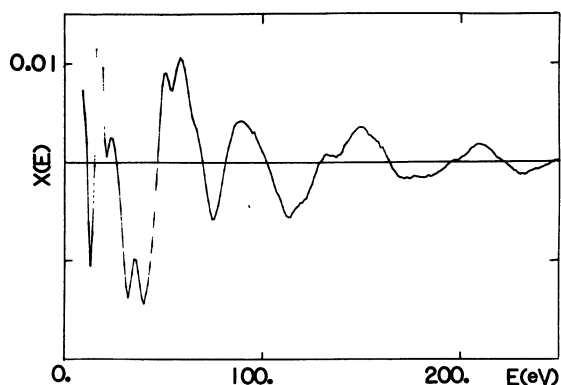


Fig. 3. — Raw EXAFS data of SiC.

Figure 4 shows the magnitude and the imaginary part of the  $k^2$  weighted Fourier transform (F.T.), using a Hanning window which cuts off the signal before 11 eV : therefore all the EXAFS data beyond the base of the main peak at the edge are taken into account. The positions of the different peaks in the magnitude of the F.T. are listed in table I, as well as the interatomic distances of crystalline SiC which is known to have the zinc-blende structure. In figure 4, we also show the F.T. of the same data but limited to the range 50-250 eV instead of the 11-250 eV of the previous analysis. The differences between these two analysis will be explained below while discussing all the results.

The striking features are the following : the first two peaks can be attributed to the nearest (carbons) and next nearest (silicons) neighbours of one silicon, at the real distances of 1.89 and 3.08 Å. The shift between the

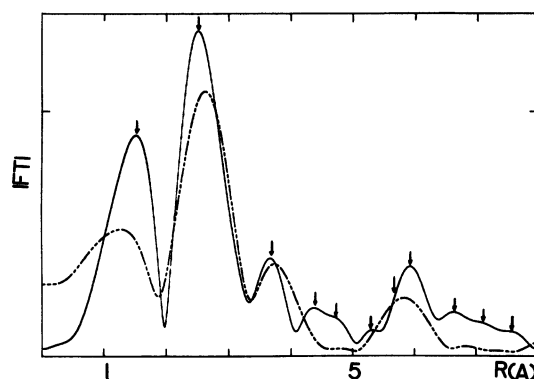


Fig. 4. — Solid line : Fourier transform of SiC EXAFS spectrum,  $k^2$  weighted, taken from 11 eV to 260 eV ( $1.7$  to  $8.2 \text{ \AA}^{-1}$ ). The origin of energies is 1835.3 eV. Arrows indicates the peaks positions on the F.T., listed in table I. Dash-dotted line : Fourier transform of the same data within the range 50-260 eV ( $3.6$  to  $8.2 \text{ \AA}^{-1}$ ).

Table I. — Comparison between the crystallographic distances and the peaks' position of the Fourier transform of the EXAFS data for crystalline silicon carbide.

Crystalline SiC	
Crystallographic values (Å)	Measured values (arrows)
—	—
1.88	1.51
3.07	2.50
3.60	3.64
4.34	4.35
4.73	4.72
5.32	5.32
5.64	5.64
6.14	5.94
6.43	6.65
6.87	
7.12	7.12
7.53	7.55

measured and the exact values is the well-known phase shift effect in the EXAFS analysis. However, beyond this second shell, all the measured distances match the crystallographic distances, up to the tenth shell, except for the main peak at 6 Å. Figure 5 shows the same type of analysis for crystalline silicon (the window now extends from 5 to 250 eV). Again the first three peaks are shifted from their normal values, but above 4.5 Å, the agreement between the measured and the crystallographic distances is striking. The comparison between these numbers for c-Si is given in table II.

Finally, since it is well known that the choice of the origin of the photoelectron energies can affect the Fourier transform, specially at low  $k$  values, we have done the same analysis after the origin of energies has been shifted by 4 eV. Comparing to the result of figure 4, we immediately have seen that this new choice of  $E^0$  does not obey the criterion of Lee and Beni [7] about the coincidence of the modulus and the maximum of the imaginary part. Therefore, in terms of EXAFS analysis, the choice of  $E^0$  in figure 4 seems to be the better one. An hypothesis could be, at first, a fortuitous coincidence between peaks coming from noise in the experimental spectrum and real peaks on the radial distribution function. As it can be seen in figure 2, the noise level is very low; moreover a spectrum of amorphous silicon, prepared and collected in the same conditions as the crystal, exhibits, on the F.T., spurious ripples beyond 4 Å with an amplitude less than 10 % of the amplitude on crystalline silicon we are considering here. We can therefore exclude any contribution from a bad signal-to-noise ratio in the original data.

These « experimental » results give rise to several questions, keeping in mind the general theory of EXAFS: why is there such a coincidence between the F.T. and the crystallographic values beyond the first shells and why is there no evidence for multiple scattering involving non-colinear atoms ?

### 3. Discussion.

From a mathematical point of view, we ask the Fourier transform of  $\sin(2k \cdot R^0 + \Phi(k))$  to be a Dirac peak at  $R = R^0$  (the width of the actual F.T. of the experimental data coming from the amplitude, Debye-Waller and mean free path terms on the EXAFS formula). Two solutions are then possible: either  $\Phi(k) = -4kR^0 + b$ , a linear decreasing, shell-dependent phase shift, or  $\Phi(k) = \text{Cte}$ . For obvious reasons the first solution is physically unreasonable.

Then let us assume that the overall phase-shift  $\Phi(k)$ , which enters the sine term in the EXAFS formula, becomes  $k$ -independent in the range  $0-4 \text{ \AA}^{-1}$  ( $0-50 \text{ eV}$ ), whereas it is known to be almost a linear function of  $k$  at large  $k$  values. In the same energy domain, two multiplicative factors have also a strong  $k$ -dependence: the mean free path term increases dramatically when  $k$  decreases and the Debye-Waller term has its usual exponential dependence.

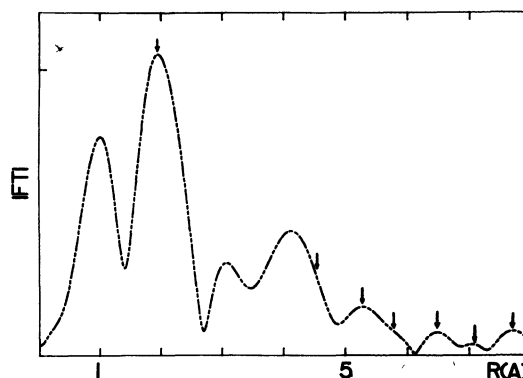


Fig. 5. — Fourier transform of crystalline silicon over the range 5-260 eV. As in figure 4, arrows indicate the peaks' position (cf. Tab. II).

Table II. — Comparison between the crystallographic distances and the peaks' position of the F.T. of the EXAFS data of c-Si.

Crystalline Silicon	
Crystallographic values (Å)	Measured values (arrows)
—	—
2.35	1.96
3.84	3.07
4.50	4.15
5.43	5.30
5.91	5.87
6.65	6.52
7.05	7.06
7.68	7.70

Therefore, in the low- $k$  region ( $0-4 \text{ \AA}^{-1}$ ) the relative weight, in the EXAFS data, of the high order shells becomes very important. At large  $k$ , the mean free path parameter and the Debye-Waller term will kill the contributions of these shells beyond the first three (typically). This general feature is especially reinforced for light elements, for which the backscattering amplitude is a monotonously decreasing function of  $k$ . Therefore, if, in the same energy range ( $0-50 \text{ eV}$ ), the overall phase-shift term is  $k$ -independent, a Fourier transform of the data will peak at the exact  $R$  values for these high order shells.

A simple way to check this hypothesis, is to compare the F.T. of the same data using two different windows, one limited to the low-energy domain, the other one spanning up to 300 eV ( $9 \text{ \AA}^{-1}$ ) as in figures 4 and 5. We have done this on crystalline silicon, as well as on SiC, obviously using in both analyses the same origin of photoelectron energies. Figure 6b shows this analysis for crystalline silicon: the result is identical to that published by F. Comin *et al.* [8] where the data has been taken using LVV Auger electrons and therefore limited to the energy of

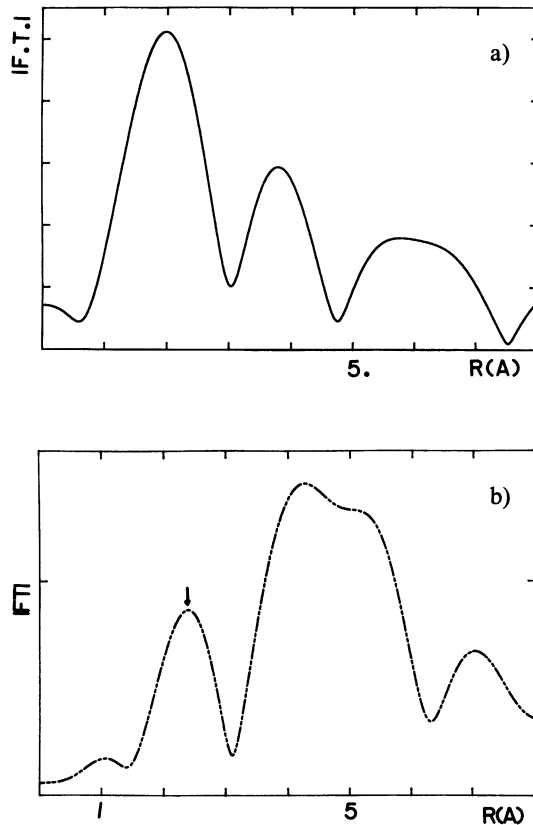


Fig. 6. — a) SiC data analysed in the range 11-60 eV : the first peak appears at the correct value of 1.9 Å. b) Crystalline silicon data analysed in the range 5-60 eV : the first peak appears at 2.35 Å.

these electrons (about 85 eV). We now see that the first shell peaks at the correct value of 2.35 Å. Figure 6a gives the corresponding analysis for c-SiC. The same behaviour appears for the first shell (4 carbons) which is shifted back to its exact value (1.9 Å) when the data is analysed in the low  $k$  domain. The behaviour of the higher (2nd and 3rd) shells is due to the backscattering amplitudes of C and Si below  $4 \text{ \AA}^{-1}$  : the calculations of Teo and Lee [9] show a ratio of 3, at  $4 \text{ \AA}^{-1}$ , between  $f(\pi) \text{ C}$  and  $f(\pi) \text{ Si}$ , but this ratio can increase at low  $k$  values.

Within this  $k$ -independent hypothesis of the phase shifts all these results appear to be consistent. The differences between the solid and the dotted line in figure 4, where the F.T. analysis starts at 11 eV or 50 eV, is just a consequence of the behaviour of the scattering amplitude of carbon and silicon *versus*  $k$  : removing the low energy part of the spectrum damps at the same time the carbon contribution of the first shell (due to amplitude effects) and the contributions from high order shells (due to mean free path effects) except for the large peak at 6 Å which is the 4<sup>th</sup> shell contribution of an fcc structure in the silicon sublattice : this is the well known shadowing effect. Because of the very limited  $k$  range used in both figures 6a and b, we expect the contributions from

other shells beyond the first one to be strongly damped just for mathematical reasons.

Finally, in order to check the consistency between the two results, we have tried to analyse the Si-Si shell of SiC at 3.07 Å using empirical phase shifts and amplitude extracted from c-Si on the same  $k$ -domain. This leads to a very good agreement, as shown in figure 7, provided a  $\Delta E^0 = -6 \text{ eV}$  is used which does not appear unreasonable considering the very different (semiconductor *versus* insulator) properties of the two materials.

**3.1 MULTIPLE SCATTERING.** — We have shown that, in some special cases like silicon, an EXAFS-like analysis is still possible at very low  $k$ . It seems to lead to the conclusion that the overall phase-shift of the EXAFS formula becomes  $k$ -independent at low  $k$ -values. Many reasons can be invoked for this : either the breakdown of the plane wave approximation used in most of the calculations or the breakdown of the description of the mean free path of the photoelectron as a single, real term. Classically speaking the single scattering plane wave model of EXAFS is non-valid in the low energy range at least if we keep the phase-shift formalism of one electron scattered by the atomic potentials :

a) the elastic mean free path increases strongly, so that a non-colinear path involving more than one scatterer should become more probable.

b) the use of the plane wave approximation of one photoelectron outgoing wave breaks down, and the well known « curved wave » model should be used [10]. A simple geometrical argument shows that the main effect of cancelling the plane wave approximation appears in the phase shift [11] : it increases by  $k |f(\pi)|^2/R$ , a positive quantity which decays with  $k$  because of the  $1/k$  behaviour of  $f(\pi)$ .

Diamond lattice is an open structure where the multiple scattering paths are expected to be not very important. Actually on the F.T. of both pure silicon and silicon carbide, no evidence for scatterings other

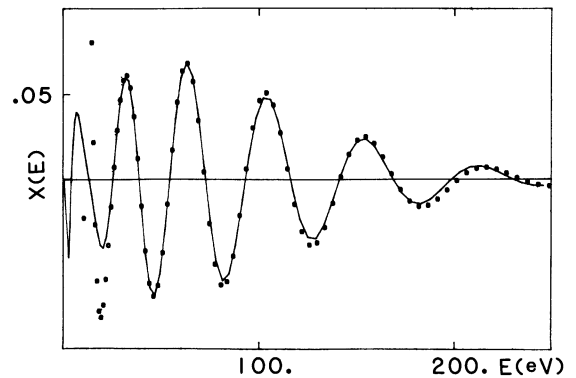


Fig. 7. — Fit of the SiC silicon first shell at 3.07 Å using empirical phase shift and amplitude extracted from crystalline silicon and the crystallographic parameters, provided an origin of energies shift of  $-6 \text{ eV}$ .

than the single ones can be detected (except of course for the 4th shell one). This is in line with the angle dependence of the scattering functions which are strongly peaked for forward and backward scatterings while on the contrary, this  $f(0)$  function becomes more spherically symmetric at low energies of the incident electron. The problem of the single *versus* multiple scattering in X-ray absorption spectra of crystalline materials has been addressed many times in the last three years. As pointed out by Müller and Schaich [12], Schaich [13, 14] and more recently by Rehr *et al.* [15], most of the absorption features down to the edge energy can be explained only (except for the shadowing effect) by a simple scattering approach provided that the spherical wave corrections are correctly taken into account at low  $k$ .

Moreover, while the third (X3) and fourth (X4) multiple scattering orders do exist in the tetrahedral structure, it has been shown [5] that the X3 and X4 terms cancel in the octahedral geometry, for symmetry reasons, when a  $\pi$  phase difference occurs because of  $f(0)$ . In the diamond structure, we can expect X3 from the first shell to appear mainly at the  $R$  value of the second shell in the X2 term (EXAFS term) : actually,  $1.8 * 1.9 \text{ \AA}$  is close to  $3.07 \text{ \AA}$  in SiC while  $1.8 * 2.35 \text{ \AA}$  is not far from  $3.85 \text{ \AA}$  in pure silicon (having in mind that 1.8 is the ratio between a three-atom path and a two-atom path in the tetrahedral structure and that the scatterings implied in these triple paths induce a larger phase shift than a single scattering). Therefore, the triple first shell scattering is buried into the main EXAFS contributions of the second or third shell and, because of the high symmetry of the second shell in the diamond structure, we can expect the multiple scattering from this shell to be low, as also found in copper [15] and platinum [16]. Experimentally, with an analysis close to ours, Bunker *et al.* [17] in the case of  $\text{KMnO}_4$  at the manganese edge found that the amplitude of this triple scattering is very low beyond 13 eV, and should be even smaller for first interatomic distances larger than  $2 \text{ \AA}$ .

**3.2  $k$  DEPENDENCE OF THE PHASE FACTORS.** — Recently, G. E. Laramore [18] has made calculations of these phase factors to be used in EXAFS and EAPFS in the low  $k$  range ( $2$  to  $4 \text{ \AA}^{-1}$ ) for light elements such as oxygen, silicon or aluminium, within a cluster model where the potentials are structure dependent and within the plane wave approximation, even for these low electron energies. His results show that any extrapolation of the calculations of Teo and Lee to low momentum is not correct. However, they appear to be model-dependent with, in some cases, an oscillatory behaviour around a constant value below  $4 \text{ \AA}^{-1}$ . A more complete calculation of Rehr *et al.* [15], who compare at the same time plane wave and curved wave approaches on copper, shows a flattening of the backscattering phase between  $4$  and  $7 \text{ \AA}^{-1}$ , with a dip at  $2 \text{ \AA}^{-1}$  : it can be reasonably assumed that these features will appear at much lower values of  $k$  in

silicon and carbon, if we keep in mind the behaviour of these peaks and valleys *versus* atomic number in the calculations of Teo and Lee. As already pointed out, the correction from plane to curved wave calculation is a positive one, which decreases as  $k$  increases and which is shell dependent. Calculations of the overall phase factor for silicon, using a structure dependent potential and a spherical wave approximation [19] do not seem to show such a flattening *versus*  $k$ , as well as recent calculation on oxygen by A. G. McKale *et al.* [20] : the backscattering of oxygen behaves as a monotonic decreasing  $k$  function between  $1.86$  and  $15 \text{ \AA}^{-1}$ .

The small  $k$  domain analysis could be biased by the width of the resulting Fourier transform in  $R$ -space due to the limited  $k$  domain ( $\Delta R \sim 2 \pi / \Delta k \sim 1.5 \text{ \AA}$ ) and it could be argued that this first peak is just an average of the first and second distances : in that case, this « small  $k$ -domain » peak would depend on the relative amount of first *versus* higher shell contributions. This is definitely not the case as seen on the comparison between amorphous and crystalline silicon [8].

Finally, we have analysed both the SiC and Si systems using the large  $k$ -domains by setting the  $E^0$  value *plus* or *minus* 6 eV from our original choice, i.e., the inflexion point. As expected from simple arguments, all peaks shift toward lower or higher  $R$  values depending on the  $\Delta E^0$  sign. Nevertheless this shift is an increasing function of the shell distance up to  $4 \text{ \AA}$  : beyond this value, the  $\Delta R$  shift remains constant : in agreement with curved wave calculations the overall phase shift is  $R$  dependent but its dependence dies off with the distance.

Therefore, the connection between these « experimental » results and the more sophisticated calculations of the phase factors is still an open question : on the one hand theoretical calculations, on the other hand EXAFS analysis with a Fourier transform close to the edge are, very sensitive to the value of the origin energy of the photoelectrons. Any comparison between these two analyses must take this point into account, while a  $\pm 5$  eV shift of  $E^0$  in a conventional EXAFS study has only little effect.

Finally, we must point out that an experimental result similar to ours has been reported by G. Margaritondo *et al.* [21] although the elements involved are quite different : from an angle integrated photoemission experiment, they calculate the overall backscattering phase-shifts in the range  $0$  to  $5 \text{ \AA}^{-1}$ . Within the experimental error bars, these phase functions appear to be also  $k$ -independent in this energy domain.

#### 4. Conclusions.

We have shown that, at least in the special case of silicon and silicon carbide, a Fourier analysis of the EXAFS data starting very close from the edge represents, in the high  $R$  domain (say, above  $4.5 \text{ \AA}$ ), the exact radial distribution function as far as the peak

positions are considered. This behaviour can be explained assuming, below typically  $4 \text{ \AA}^{-1}$ , a flattening of the phase factors *versus*  $k$  and consequently a cancellation of the shift, in the F.T., between the real peaks positions and the measured ones. Moreover, most of the absorption spectrum in these materials seems to arise from the single scattering processes.

The low multiple scattering contribution in a diamond type structure is quite easy to understand here : we are in low  $Z$  element systems, and may be the multiple scattering features in higher  $Z$  elements (like germanium) are smeared out by resolution effects.

The behaviour of high order peaks in the Fourier transform is less obvious and we cannot claim about

the generality of these results which are may-be strongly related to a special  $E^0$  choice, and to low  $Z$  elements without peaks and valleys in their phase factors. Nevertheless, it would be very interesting to compare these results with calculations using the same starting parameters.

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#### References

- [1] BIANCONI, A., *Appl. Surf. Science* **6** (1980) 392.
- [2] PENDRY, J. B., EXAFS and Near Edge Structure, *Chemical Physics* **27** ;  
BIANCONI, A., INCOCIA, L., STIPCICH, S., ed. (Springer) 1983, p. 4.
- [3] DURHAM, P. J., *id.* p. 37.
- [4] NATOLI, C. R., *id.* p. 43.
- [5] BENFATTO, M., NATOLI, C. R., BIANCONI, A., GARCIA, J., MARCELLI, A. and DAVOLI, I., *Phys. Rev. B* (to be published).
- [6] BIANCONI, A., GARCIA, J., MARCELLI, A., BENFATTO, M., NATOLI, C. R. and DAVOLI, I. (preprint).
- [7] LEE, P. A. and BENI, G., *Phys. Rev. B* **15** (1977) 2862.
- [8] COMIN, F., INCOCIA, L., LAGARDE, P., ROSSI, G. and CITRIN, P. H., *Phys. Rev. Lett.* **54** (1985) 122.
- [9] TEO, B. K. and LEE, P. A., *J. Am. Chem. Soc.* **101** (1979) 2815.
- [10] GURMAN, S. J., BINSTED, N. and ROSS, I., *J. Phys. C* **17** (1984) 143.
- [11] LEE, P. A. and PENDRY, J. B., *Phys. Rev. B* **11** (1975) 2795.
- [12] MÜLLER, J. E. and SCHAICH, W. L., *Phys. Rev. B* **27** (1983) 6489.
- [13] SCHAICH, W. L., *Phys. Rev. B* **29** (1984) 6513.
- [14] SCHAICH, W. L., *EXAFS and Near Edge Structure III*, K. O. Hodgson, B. Hedman and J. E. Penner-Hahn eds. (Springer-Verlag) 1984, p. 2.
- [15] REHR, J. J., ALBERS, R. C., NATOLI, C. R. and STERN, E. A. (preprint).
- [16] BIEBESHEIMER, V. A., MARQUES, E. C., SANDSTROM, D. R., LYTLE, F. W. and GREGOR, R. B., *J. Chem. Phys.* **81** (1984) 2599.
- [17] BUNKER, G. and STERN, E. A., *Phys. Rev. Lett.* **52** (1984) 1990.
- [18] LARAMORE, G. E., *Phys. Rev. B* **28** (1983) 4778.
- [19] NATOLI, C. R. (private communication).
- [20] MCKALE, A. G., KNAPP, G. S. and CHAN, S. K., *Phys. Rev. B* **33** (1986).
- [21] MARGARITONDO, G. and STOFFEL, N. G., *Phys. Rev. Lett.* **42** (1969) 1567.