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A MULTIPLE SCATTERING SCHEME WITH COMPLEX POTENTIAL FOR STRUCTURAL ANALYSIS OF X-RAY ABSORPTION SPECTRA IN CONDENSED MATTER

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ABSTRACT

In this paper we present a general multiple scattering scheme using complex potential for the calculation and the interpretation of inner-shell X-ray absorption spectra in condensed matter. The application of the theory to SF₆, GeCl₄ and Br₂ molecules shows that one can obtain amplitude agreement without introducing any adjustable parameters and/or intrinsic loss reduction factors. The consequences in the structural analysis are also discussed.

INTRODUCTION

Since the work of Lee and Pendry⁽¹⁾ multiple-scattering (MS) theory has been widely and successfully used to interpret the modulation of X-Ray Absorption Spectra (XAS) in a great variety of material like molecules, periodic and disordered extended systems. Used as a guide for analyzing data it becomes a powerful technique for structural analysis in many different systems⁽²⁾. It is therefore of utmost of importance to develop the theory further in order to eliminate the remaining discrepancies with experiments. The most important "dark" aspect to be investigate is the invariable discrepancy between measured and calculated amplitude of the modulation of the normalized absorption spectrum⁽³⁾. This fact has forced and still forces investigator to simultaneously fit electronic scattering amplitudes, Debye-Waller factors and coordination numbers to the experimental data. It is clear that this procedure presents the risk of obtaining unreliable results due to the presence of "false minima" in the minimization routine because of the high statistical correlation among these parameters. The reason for this discrepancy is the use of real potential to calculate atomic scattering amplitudes and the consequent neglect of inelastic excitations of different type. A many-body approach is therefore needed in understanding the kind of effective one-electron theory^(4,5) one has to use since a complete solution of the many-body problems is out of question.

In this paper we present a MS approach to the XAS problem using complex potential built as a sum of the Hedin-Lundquist (HL) energy-dependent exchange-correlation potential⁽⁶⁾ and the energy-independent coulomb potential. We demonstrate that this formulation is able for a "first principle" calculation of single and multiple-scattering signals as shown in the case of SF₆, GeCl₄ and Br₂ molecules.

THEORY

Introducing the many-body N-particle functions Ψ_G^N and Ψ_f^N (with energies E_G^N and E_f^N) for the ground state and the final state of the system under study, the total absorption cross section at a given energy ω and for light polarized in the \hat{e} direction can be written as:

$$\sigma(\omega) = 4\pi^2 \omega \alpha \left| \langle \Psi_f^N | \hat{e} \cdot \sum_i \vec{r}_i | \Psi_G^N \rangle \right|^2 \delta(\omega + E_G^N - E_f^N)$$

where α is the fine structure constant ($\alpha=1/137$). Following the arguments in Ref. 5 the deep core initial state can be written as a product of the core wave function $\phi_{L_i}^c(\vec{r})$ and a term Ψ_G^{N-1} formed by a linear combination of Slater's determinants describing the various configurations present in the ground state. At the same time the final state is given by a similar linear combination of terms formed by the product of a wave function supposed to describe the excited photoelectron and a wave function Ψ_{nf}^{N-1} describing the rest of the system in the presence of the core-hole. In this way it is possible to define a one-particle Green function $G(\vec{r}, \vec{r}'; \omega)$, that gives the propagation of the excited photoelectron from \vec{r} to \vec{r}' in the presence of core-hole, and to write the total cross section as:

$$\sigma(\omega) = -4\alpha\pi\omega \sum_{m_i\sigma_i} \int d^3r \int d^3r' \phi_{L_i}^c(\vec{r}) (\hat{e} \cdot \vec{r}) \text{Im} G(\vec{r}, \vec{r}'; \omega + E_0^N) (\hat{e} \cdot \vec{r}') \phi_{L_i}^c$$

where $L_i \equiv (l_i, m_i)$ is the angular momentum of the initial core state and σ_i belongs to the spin space. The propagation of the photoelectron takes place in the state Ψ_G^{N-1} that is itself excited with respect to the relaxed configurations Ψ_{nf}^{N-1} . In this way the photoelectron, besides losing energy in exciting plasmons on its way out of the system (extrinsic losses), can also pick-up (or lose) energy from the relaxation processes occurring inside and in the neighbors of the absorbing atom. These processes are termed intrinsic losses. It is possible to separate the two processes expanding Ψ_G^{N-1} in term of the Ψ_{nf}^{N-1} 's and defining an overlapping factor S_n as:

$$\Psi_G^{N-1} = \sum_n \Psi_{nf}^{N-1} (\Psi_{nf}^{N-1} | \Psi_G^{N-1}) = \sum_n \Psi_{nf}^{N-1} S_n$$

We do not repeat the derivation for the total cross section referring to our paper (see Ref.4) for a complete discussion. We want only to note that S_n in the sudden approximation is just the amplitude probability that the excited state created in the photoabsorbing processes relaxes into the state Ψ_{nf}^{N-1} . In Ref.4 we have shown rigorously that the high energy limit of the total cross section is given by the sudden approximation. In the following we assume the sudden limit that seems to be a good approximation valid in the whole energy range of the spectrum except the first tens of eV. Of course there are some more complex case as the rare earth where different electronic configurations are explicitly present. In the sudden limit the total cross section becomes:

$$\sigma(\omega) = 4\alpha\pi\omega \sum_n |S_n|^2 \sum_{m_i \sigma_i} \int d^3r \int d^3r' \phi_{L_i}^c(\vec{r}) (\hat{e} \cdot \vec{r}) \text{Im} G_{n,n}(\vec{r}, \vec{r}'; \omega + E_0^N) (\hat{e} \cdot \vec{r}') \phi_L^c$$

The propagation described by $G_n \equiv G_{nn}$ refers now to the relaxed state Ψ_{nf}^{N-1} and takes place with wave vector

$$k_n^2 = \omega + E_0^N - E_n^{N-1} = \omega - I_0 - \Delta E_n$$

where $I_0 = E_0^{N-1} - E_0^N$ is the core ionization limit (lowest binding energy in a photoemission experiment) and $\Delta E_n = E_n^{N-1} - E_0^{N-1}$ is the excitation energy released to the system due to the relaxation around the core hole (shake-up and shake-off). The intrinsic losses are incorporated in the Green function $G_n(\vec{r}, \vec{r}'; \omega)$ which also contain all the MS structures due to the geometrical environment of the photoabsorber. Since, at least $|S_0|^2 \approx 0.7 - 0.80$ or more, most of the intensity goes into the elastic or completely relaxed channel. Therefore the rest of the sum over n appears as a modest modification of the amplitude and phase of the structural signal in the $n=0$ channel. This modification is easily performed as a phasor summation. In this paper we concentrate our attention only in studying the propagation of the photoelectron in the system described by $G(\vec{r}, \vec{r}'; \omega)$, dropping the index n . As it is well known, the single particle Green's function obeys to a Dyson's equation of the type:

$$(\nabla^2 + E - V_C(\vec{r})) G(\vec{r}, \vec{r}'; \omega) - \int d^3r'' \Sigma(\vec{r}, \vec{r}''; \omega) G(\vec{r}'', \vec{r}'; \omega) = \delta(\vec{r} - \vec{r}')$$

where $\Sigma(\vec{r}, \vec{r}'; \omega)$ is an energy dependent, complex and in general non-local, effective exchange and correlation potential that plays the role of an optical potential, whereas $V_c(\vec{r})$ is the usual Coulomb or Hartree potential. Much work has gone into approximating the self-energy by a functional form suitable for numerical applications. We use the Hedin and Lundqvist (HL) approximation⁽⁶⁾ derived in the framework of the Sham-Kohn density functional formalism using a single plasmon pole approximation for the electronic gas dielectric function. We assume, according Lee and Beni⁽⁷⁾, that this scheme is valid also for excited states and in the core region. In this way the self-energy becomes a local function and it is essentially the self-energy of an electron in an interacting homogeneous electron gas depending on the local electron density of the physical system.

The Dyson's equation can be solved and we write the solution⁽⁸⁾ for a collection of muffin-tin type of potential. The solution (referred to the the right wave boundary condition for photoabsorbing processes) is:

$$G(\vec{r}, \vec{r}', \omega) = - \sum_{L, L'} f_L^{i_0}(\vec{r}) \tau_{L, L'}^{i_0 i_0} f_{L'}^{i_0}(\vec{r}') - \sum_L f_L^{i_0}(\vec{r}) S_L^{i_0}(\vec{r}')$$

where \vec{r} and \vec{r}' are inside the central MT sphere (Ω_{i_0}), that represents the photoabsorber.

It is important to note the presence of the irregular term. $S_L^{i_0}(\vec{r}) = S_{-L}^{i_0}(r) Y_L(\hat{r})$. For a complex potential this term gives a contribute that can be included into the atomic cross section. Following the derivation of Ref. 5 we can write down the total cross section (after summation over polarization of the light, spin and magnetic quantum numbers) as:

$$\sigma(\omega) = -\frac{8}{3} \pi^2 \alpha \omega \sum_n |S_n|^2 [(1_{i+1}) \text{Im} \left\{ \frac{1}{(2i+1)} \sum_m R_{1_i, 1}^2 [\tau(k_n)]_{1m, 1m}^{i_0 i_0} \right. \\ \left. + R_{1_i, 1} S_{1_i, 1} \right\}_{1=1_i+1} + 1_i \text{Im} \{ \dots \}_{1=1_i-1}]$$

The $R_{1_i, 1}$ and $S_{1_i, 1}$ are the radial integrals between the core wave function of the initial state and the regular and irregular solution respectively. All the other quantities have the same definition as in the real case⁽⁹⁾ but the photoelectron wave vector has now an imaginary component. As in the real potential the scattering-path operator τ can be developed in series obtaining the individual atomic and MS contributions but, contrary to the real case, the atomic absorption is no longer separable from the structural factor, so that we have to redefine the MS contributions. For brevity we do not write down explicitly the atomic $\sigma^0(\omega)$ and the oscillatory MS signal $\sigma^n(\omega)$ of order n (in a given final channel l) but, in view of experimental analysis, we give the definition of the total fine structure signal in a channel l as:

$$\chi_1^1(\omega) = \frac{\sigma_1(\omega)}{\sigma_1(\omega)} - 1$$

and the various individual MS signals of order n as:

$$\chi_1^n(\omega) = \frac{\sigma_1^n(\omega)}{\sigma_1(\omega)}$$

In these expression both intrinsic and extrinsic inelastic contribution are included. Before to close this section we want to clarify the effect of using complex potential. The MS series is formed by two building blocks: the propagator $G_{LL}^{m,n}$ between site m and n and the l-wave atomic t-matrix (given in term of the phase shifts δ_l^m) $t_l^m = e^{i\delta_l^m} \sin \delta_l^m$ of the atom at site m. Both enter in the definition of the scattering path operator. The general term of the series is built by several repetition of the product $t_l^m G_{LL}^{m,n}$ which brings out a factor: $e^{-2\delta_2^1} e^{-k_2 R_{mn}}$ when complex potential is used. Here δ_2^1 and k_2 are the complex part of the atomic phase shift and wave vector respectively. In this way the effect of complex potential results in a damping factor that reduces the amplitude of the elastic signals. It is possible to define an associated mean free path that can be shown to be path dependent.

EXPERIMENTAL AND DISCUSSION

In this section we apply our approach to the analysis of single a multiple scattering signals of SF₆, GeCl₄ and Br₂ molecules. The sulphur K-edge absorption measurement of SF₆ was performed at the Stanford Synchrotron Radiation Laboratory in fluorescence signal mode. The experimental resolution was about 0.5 eV. The other two spectra were taken from the literature. Data analysis followed the standard procedure of normalization of the post edge region to unity after the subtraction of the pre-edge region. A self-consistent potential was used to obtain the atomic phase shifts of the various species. A detailed analysis of the total energy of the different configurations used for the ground and excited states allowed us to determine the ionization threshold. In this way we was able to fix the k-scale in the SF₆ and Br₂ cases. All the single scattering (SS) signal are calculated according the theory presented in the previous section and multiplied by a Debye-Waller function $\exp(-2k^2 \sigma^2)$, with σ^2 given by the "experimental" value taken from literature or calculated using vibrational data. Moreover the S_0^2 was fixed to one in all our calculations.

In Fig. 1 we show the comparison between the experimental signal $\chi_{\text{exp}}(k)$ and the calculated SS signal for SF₆ molecule. More precisely the actual comparison in Fig.1 is between $k \chi_{\text{exp}}(k)$ and $k \chi_2(k)$

There is no adjustment of the photoelectron reference level, which has been taken to be the physical ionization threshold in both spectra. Note that it is the natural one since in our theoretical calculation the reference level is different in different regions of space and depends on the energy via the exchange part of the potential. The SS signal models rather accurately the experimental data for $k > 6 \text{ \AA}^{-1}$ which is the energy region where the MS contributions are negligible.

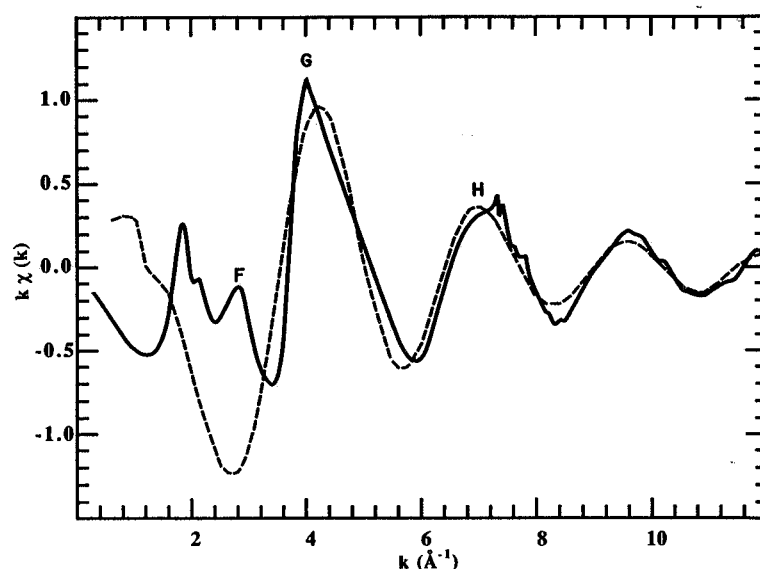


FIG. 1 - Comparison between calculated SS signals and experimental normalized data for SF₆ molecule.

In Fig. 2 we show the difference between measured spectrum and the calculated SS signal (solid line) plotted against a calculated MS signal which includes contributions from all double, triple and quadruple scattering paths (dotted line). The inset displays the separate MS contributions. Among these MS contributions the signals corresponding to collinear paths are the dominant one due to the focussing effect. The dashed line in Fig.2 represents the contributions of the triple scattering paths of the type S-F1-S-F1-S, S-F1-S-F1'-S and S-F1-S-F2-S where F1 and F1' are trans and F2 are cis. There is a reasonable amplitude agreement with the experimental residual signal at least for the first three oscillations but other signals coming from other MS paths of higher order should be included in the calculation to obtain better agreement. This is due to the high value of the spectral radius (roughly 0.80) of the MS series in this energy range.

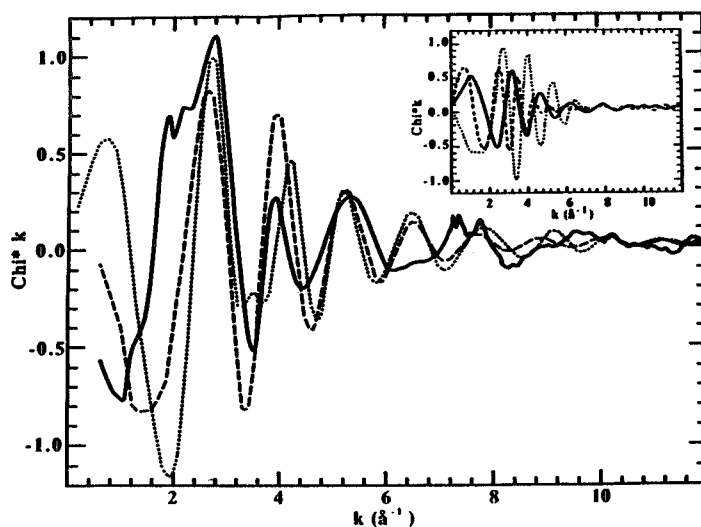


FIG. 2 - Comparison between residual experimental and theoretical MS signal coming from various paths as indicated in the main text. In the inset the solid line is the individual double scattering, the dotted line is the triple scattering and the long-dashed line represents the quadruple scattering.

It is important to outline that we obtain a "first principle" agreement between experimental data and theoretical calculation without having to set free parameters in the theory except the size of the atomic radii used in the muffin-tin approximation. We have verified that other choices (within a 10% of variation) do not change our results.

In Fig. 3 we report the same comparison for the GeCl_4 molecule. The experiment was carried out by Bouldin and Banker⁽¹⁰⁾ in transmission mode using ion chamber detectors and Si(111) monochromator. As in the previous case we obtain a good agreement between experimental and theoretical amplitude although there is a slight mismatch in the total phase.

Contrary to the SF_6 case we note the absence of large MS signals in the experimental data. This is due to a strong cancellation among the individual MS signals resulting from the particular geometry and atomic phase shifts involved. This is shown in Fig. 4 where the total fine structure signal (solid line), the SS signal (dotted line) and the sum of the first three MS signals (dashed line, $n=3, 4$ and 5) are depicted.

It is clear that above 50 eV the SS is indistinguishable from the total fine structure signal. Of course this massive cancellation can be no more effective in a different geometrical arrangement and/or with different type of ligands. This fact reconciles the apparently contradicting findings in GeCl_4 and MnO_4^- concerning the amount of the total MS signals⁽⁹⁾ present in the respective absorption spectra.

As final application we compare our computation of SS spectra of Br_2 molecule with experimental data, made by Stern et al.⁽¹¹⁾, in Fig. 5.

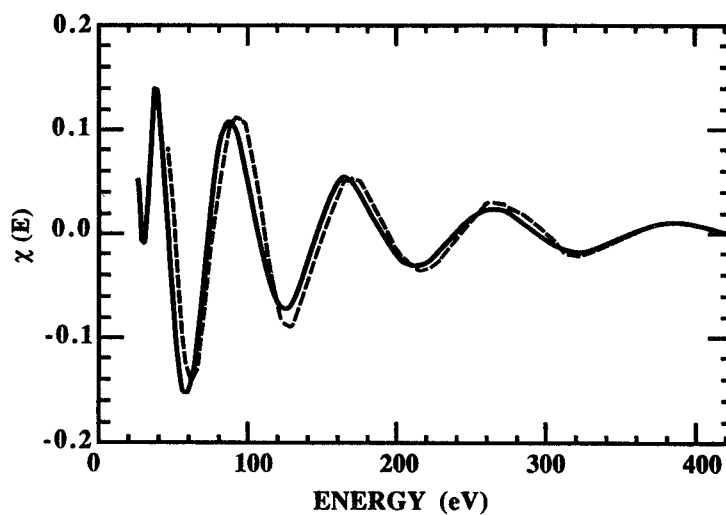


FIG. 3 - Comparison between calculated SS signals and experimental normalized data for GeCl_4 molecule.

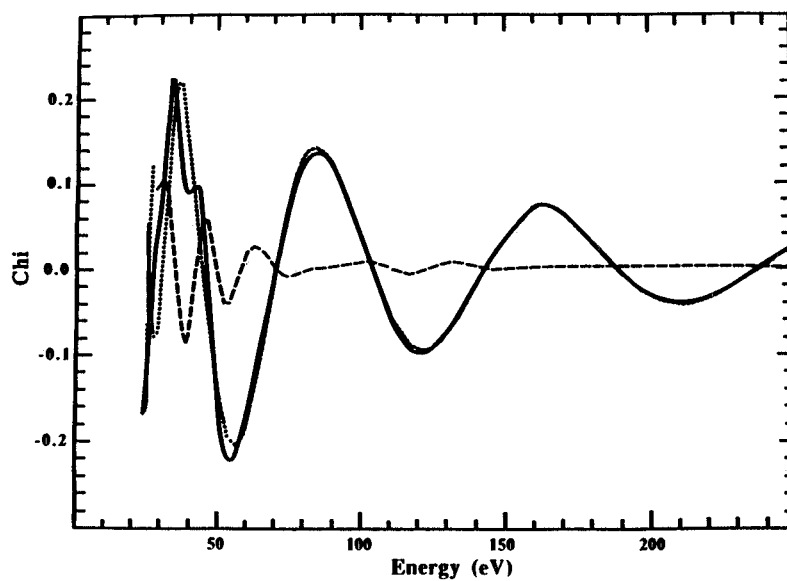


FIG. 4 - Comparison among the total fine structure signal (solid line), SS signal (dotted line) and the sum of the first three MS signals (dashed line) for GeCl_4 molecule.

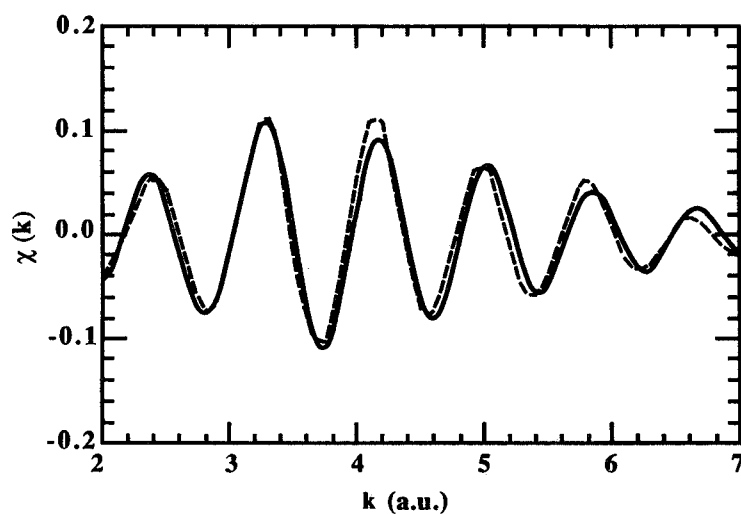


FIG. 5 - Comparison between calculated SS signals and experimental normalized data for Br₂ molecule.

As in the other gases there is no problem with amplitude agreement indicating that the inclusion of intrinsic losses is not necessary in the calculation. In this last case the MS signal of triple scattering type is practically negligible as shown in Fig. 6 where the total fine structure signal (solid line), the single scattering signal (dotted line) and the total triple scattering signal (dashed line) are reported.

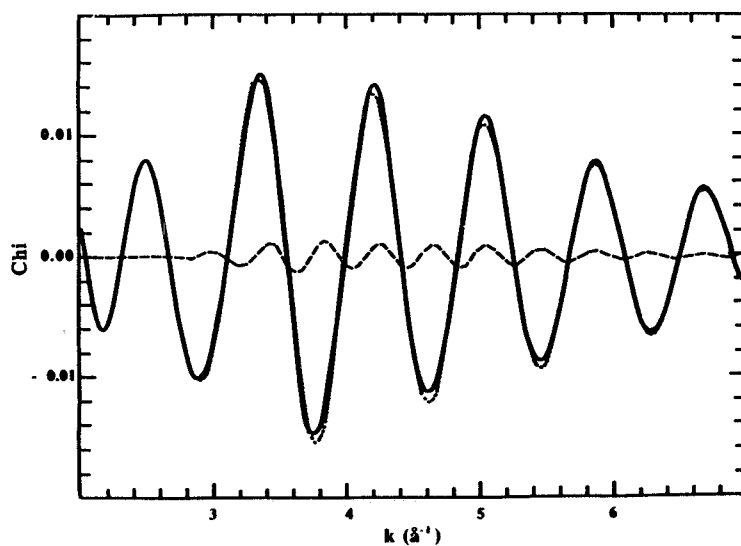


FIG. 6 - Comparison among the total fine structure signal (solid line), SS signal (dotted line) and the sum of the first three MS signals (dashed line) for Br₂ molecule.

CONCLUSIONS

In this paper we have presented a generalized MS approach with complex potential of HL type in order to account extrinsic losses of the photoelectron in the final state. We have given a precise prescription for the derivation of the various MS signals and for their comparison with experimental data.

In the three cases studied we find amplitude agreement between calculated and experimental fine structure signal without having to introduce any "free" parameters and putting always S_0^2 equal to one. This fact indicates that the corrections due to the intrinsic losses processes are negligible although further applications are necessary to substantiate this and to clarify the presence of the slight mismatch between calculated and experimental total phase found in two molecules. In any cases our scheme seems to produce "good" amplitude of the calculated fine structure signal. This possibility has big implication in the structural analysis of absorption spectra. In fact we can avoid to fit simultaneously electronic scattering amplitude and structural parameters (Debye-Waller factors and coordination numbers) to the experimental data diminishing the risk of unreliable results in the minimization procedure ("false minima" problem) due to the high statistical correlation among these parameters. In an other paper we present an application of this procedure to the analysis of a-Si in terms of the three-body correlation function⁽¹²⁾.

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