

Influence of the focusing effect on XAFS in ReO_3 , WO_{3-x} and FeF_3

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Abstract

The role of the focusing effect in the formation of X-ray absorption fine structure (XAFS) is considered for ReO_3 , non-stoichiometric tungsten oxides WO_{3-x} and FeF_3 having the perovskite-type structure. Two cases are mainly discussed: (1) an admixture of rhenium and tungsten L_2 -edge XAFS in ReO_3 and WO_{3-x} crystals to the one above rhenium and tungsten L_1 -edge and (2) high-order superfocusing effect in $\text{Fe}_0\text{--F}_1\text{--Fe}_2\text{--F}_3\text{--Fe}_4$ atomic chain in iron K-edge XAFS of FeF_3 which is analysed using an ab initio multiple-scattering approach.

A significant role of the multiple-scattering (MS) effects in the formation of X-ray absorption fine structure (XAFS) is now well established [1–3]. Generally, their influence on XAFS depends strongly on the structure of a compound and the scattering properties of atoms involved in the XAFS generation. It is known that usually the MS signals, related to linear or near-linear atomic chains, produce the main contribution to XAFS among all other MS paths due to the so-called ‘focusing’ effect (FE) [1]. This phenomenon consists in a strong increase of the amplitude of the photoelectron wave in the forward-scattering process and is very sensitive to the scattering amplitude function of atoms forming the chain. There are three types of FE [2–4] related to (1) the first coordination shell when the MS signal is generated within $L_1\text{--Me}_0\text{--}L_2$ chains (Me_0 is the absorber and $L_{1,2}$ are two ligand atoms), (2) the second coordination shell when the MS signal is generated within $\text{Me}_0\text{--}L_1\text{--Me}_2$ chains and (3) the long near-linear chains as $\text{Me}_0\text{--}\dots\text{--Me}_n$ when the so-called ‘superfocusing’ effect can be observed.

Further we will discuss the importance and the behaviour of these three types MS signals for transition metal–ligand (oxygen or fluorine) chains in perovskite-type compounds having great applied interest as superconductors, ferroelectrics, electrochromic systems, etc. In particular, the systems as ReO_3 , WO_{3-x} and FeF_3 will be considered. Experimental XAFS signals measured above the Re and W L_3 -edges and Fe K-edge are shown in Fig. 1 together with their Fourier transforms [2, 4, 5]. Three intervals A, B and C, marked in Fig. 1(b), correspond, respectively, to the ranges where the three types of the MS signals, pointed out above contribute.

The first type of the MS signals [2, 3] contributes mainly at low k -values ($0\text{--}7\text{ \AA}^{-1}$) and is responsible for the peaks marked by A in Fig. 1(b) and located in the FT between the first and second shells from ~ 2 to $\sim 3\text{ \AA}$.

The second type of the MS signals [2–6] increases the amplitude of the XAFS signals from the second shell at high k -values ($> 10\text{ \AA}^{-1}$), when heavy elements are present as in ReO_3 [2, 3, 6] and WO_x [5], and at low k -values ($2\text{--}7\text{ \AA}^{-1}$), when there are more light elements as in FeF_3 [4], due to the focusing effect (Fig. 2). The difference in the range of contribution is explained by the

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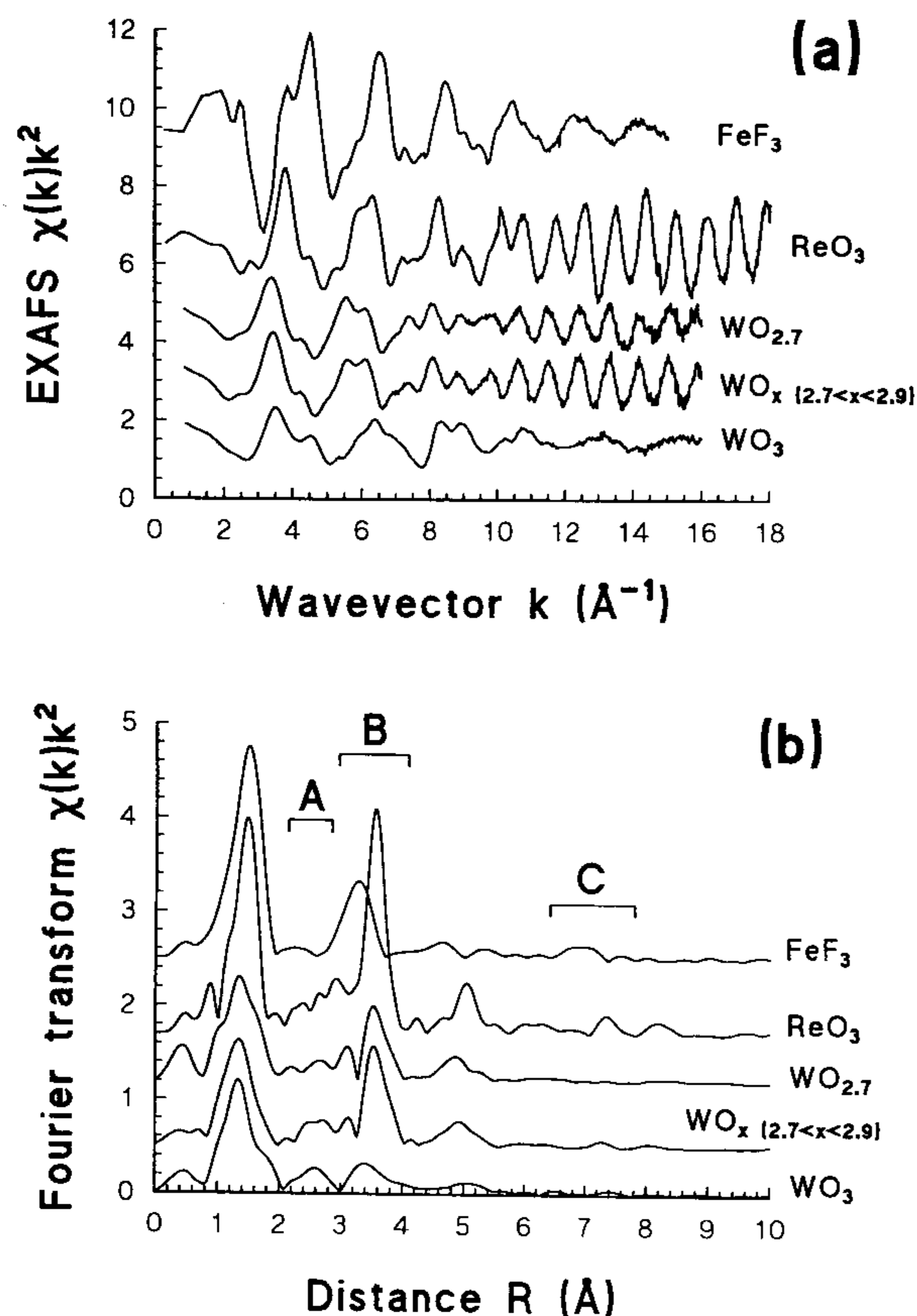


Fig. 1. Experimental XAFS spectra measured at the Re and W L₃-edge and Fe K-edge (a) and their Fourier transforms (b).

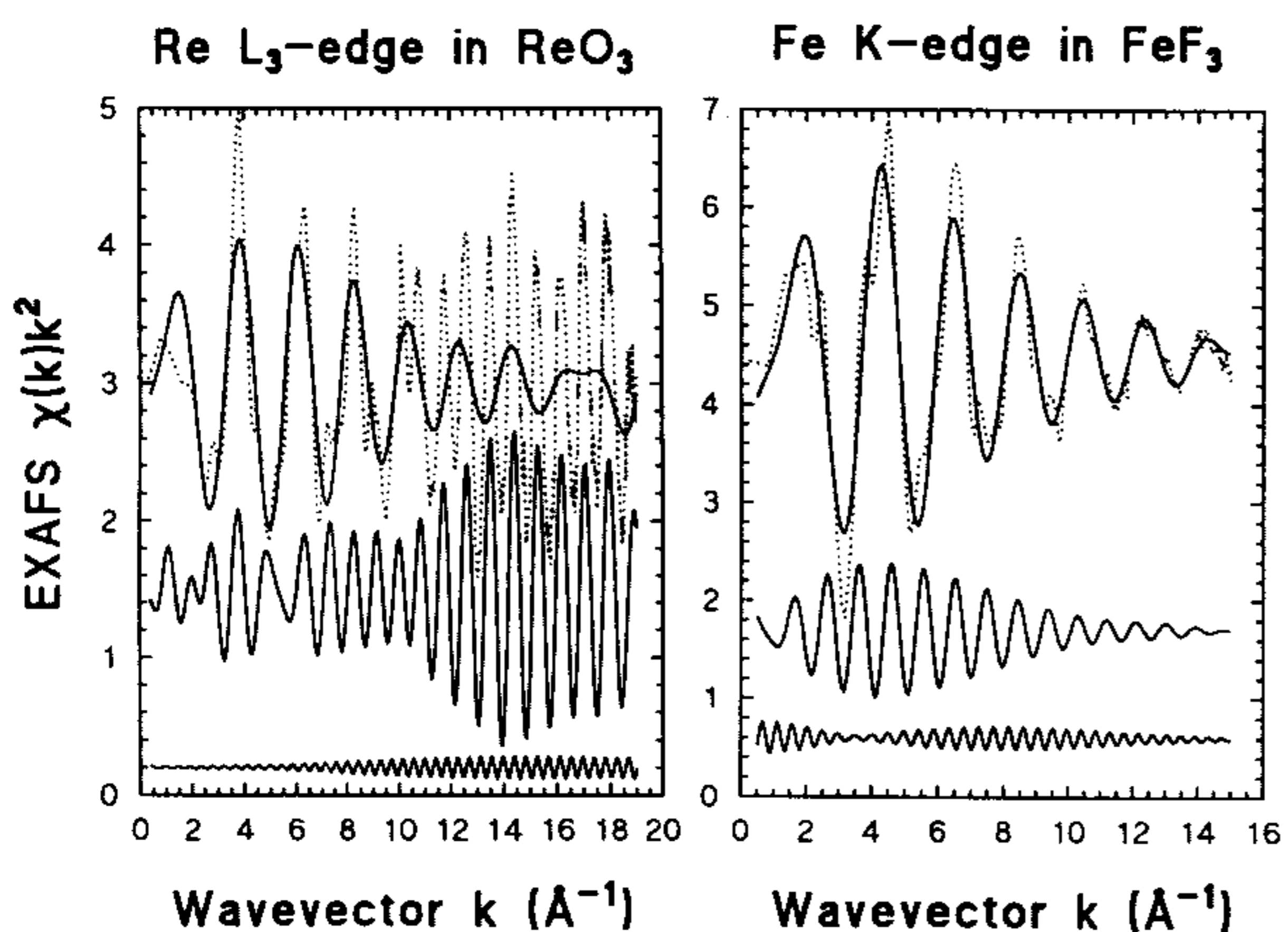


Fig. 2. Separate contributions to the experimental XAFS (dotted line) of the first shell (top solid curve), peak B (middle solid curve) and peak C (bottom solid curve) marked in Fig. 1(b).

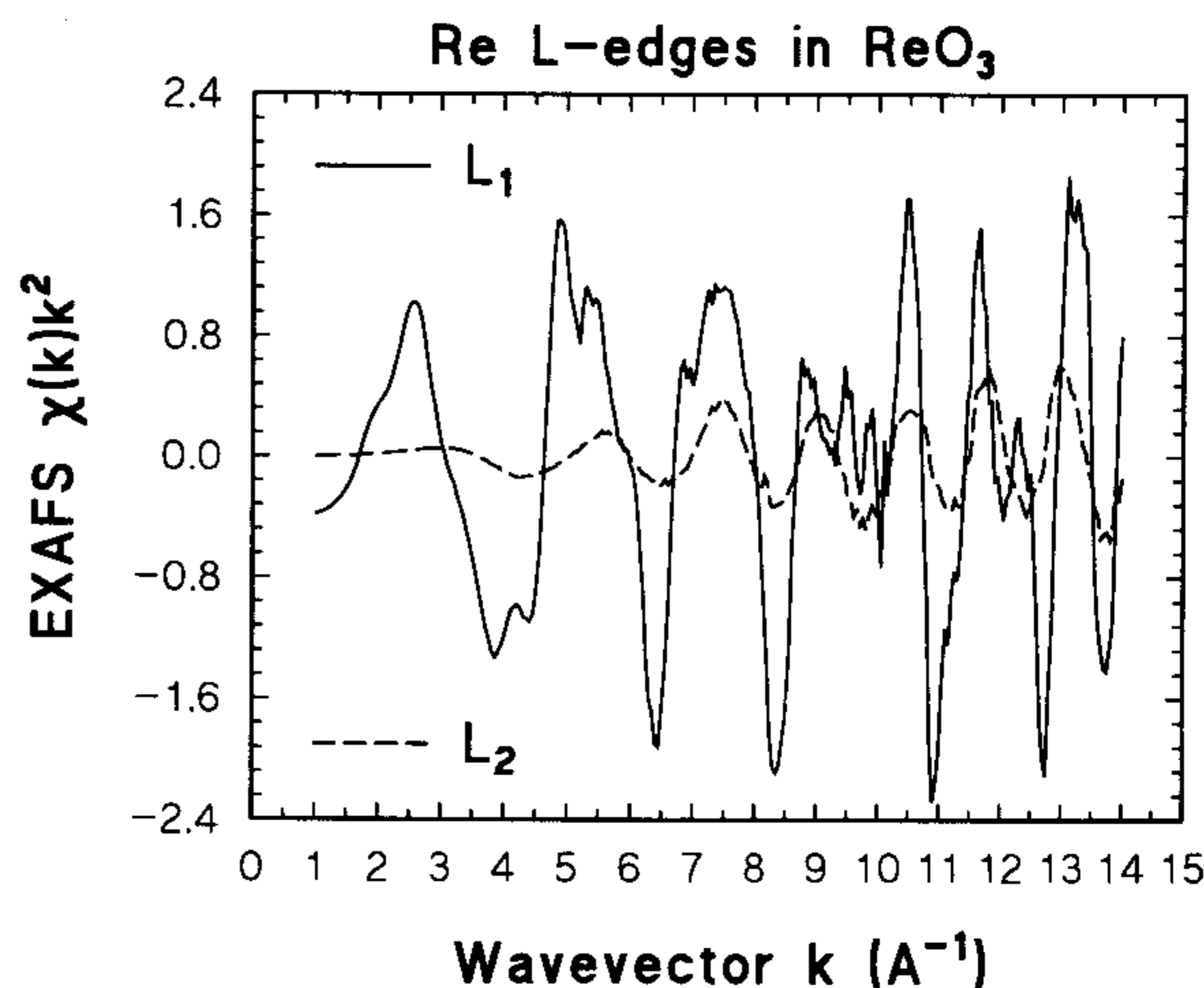


Fig. 3. Effect of mixing between L₁- and L₂-edges XAFS in ReO₃.

peculiarity of the scattering amplitude functions. In WO_{2.7}, this effect is smaller since the $\overline{\text{WOW}}$ angle deviates from 180°, and in WO₃, having $\overline{\text{WOW}} \simeq 159^\circ$, no XAFS amplitude increase is present at high k -values (Fig. 1(a)). These MS signals give an origin for the peak marked by B in Fig. 1(b) and located in the FT from ~ 3 to 4 Å. In the case of ReO₃ and WO_{3-x} compounds, this contribution is also responsible for the mixing [7] of the L₁ and L₂ edges XAFS (Fig. 3) [2, 5].

The third 'superfocusing' effect is due to several successive forward scatterings of the photoelectron. It can be observed only when long near-linear chains are present in the structure of a compound (as in ReO₃, WO_x (2.7 < x < 2.9) and FeF₃ [4]) (see the peak C in Fig. 1(b) and bottom curve in Fig. 2).

As a conclusion, it is necessary to point out that the MS signals can contribute significantly in the high-energy region of XAFS when the focusing effect takes place.

References

- [1] P.A. Lee and J.B. Pendry, Phys. Rev. B 11 (1975) 2795; C.A. Ashley and S. Doniach, Phys. Rev. B 11 (1975) 1279.
- [2] A. Kuzmin, J. Purans, M. Benfatto and C.R. Natoli, Phys. Rev. B 47 (1993) 2480.
- [3] A. Kuzmin and J. Purans, J. Phys.: Condens. Matter 5 (1993) 267.
- [4] A. Kuzmin and Ph. Parent, J. Phys.: Condens. Matter 6 (1994) 4395.
- [5] A. Kuzmin and J. Purans, J. Phys.: Condens. Matter 5 (1993) 9423.
- [6] N. Alberding, E.D. Crozier, R. Ingals and B. Houser, J. Phys. (Paris) 47 (1986) 681.
- [7] P. Rabe, G. Tolkiehr and A. Werner, J. Phys. C 12 (1979) 899.