

EXAFS and Raman spectroscopy study of binary indium fluoride glasses

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Extended X-ray absorption fine spectroscopy (EXAFS) and Raman scattering studies of $\text{InF}_3\text{--BaF}_2$ and $\text{InF}_3\text{--SrF}_2$ binary glasses are reported. For all compositions, the local structure of the glasses is built with InF_6 units. For all glasses studied, the indium neighbour's number and the In–F mean bond length are equal to the values of the InF_3 crystalline phase (6 and 0.205 nm, respectively).

1. Introduction

The study of heavy metal fluoride glasses has received great attention in the last decade and several technological applications can be foreseen in areas such as telecommunications and infrared devices. The glasses most studied so far have been those based on ZrF_4 [1,2]. However, these glasses have a low chemical durability, a great tendency to crystallize and their optical transparency is limited to about 4 μm .

The recent discovery of new glasses based on InF_3 , which present a higher optical transmission range in the infrared (up to 8 μm) and better chemical durability [3], has revived technological interest. Related to the structural aspect of these glasses, a preliminary work was published [4], where the molecular structure of binary indium–barium and indium–strontium glasses was analysed by Raman spectroscopy. Almeida *et al.* [4] could not explicate any specific contribution from the modifier ions (Ba^{2+} and Sr^{2+}) in the Raman spectra.

In this paper the authors present results of Raman vibrational spectroscopy and extended X-ray absorption fine structure spectroscopy (EXAFS) to obtain the order at short distance (a few nanometres) in $(\text{InF}_3)_x(\text{BaF}_2)_{1-x}$ and $(\text{InF}_3)_x(\text{SrF}_2)_{1-x}$ glasses ($0.5 < x < 0.67$). Vibrational spectroscopy allows one to obtain the vibrational modes of the basic structure of the glass, while EXAFS allows one to obtain the mean bond distance between the neighbouring ions with a precision of ± 0.001 nm and a mean co-ordination number (± 0.5 atom) associated with each atomic species of the system.

2. Experimental procedure

The fluoride glass compositions studied are presented in Table I. The raw materials were In_2O_3 (Meta-

leurop), BaF_2 and SrF_2 (BDH Fluortran). In_2O_3 was first fluorinated with $\text{NH}_4\text{F--HF}$ and the glass batches were then melted in a dry box under Ar atmosphere (< 5 p.p.m. H_2O).

The EXAFS spectra were obtained at the K edge of the indium atom (27940 eV) using the EXAFS transmission mode. The experiments were realized at room and low (80 K) temperatures at the French synchrotron radiation ring (DCI–LURE, Orsay). The spectra were obtained at the EXAFS I station with a channel-cut Si-331 as monochromator and ionization chambers as detectors; the energy steps of the monochromator were 3 eV at the indium–K edge. During measurement, the synchrotron ring operated typically at 1.85 GeV with a current of 250 mA. The samples were in powder form and deposited on a Millipore membrane.

In the approximation of simple scattering and plane waves, the EXAFS results can be interpreted with the following equation

$$\chi(k) = \sum_j \frac{N_j}{kR_j^2} F_j(k, \pi) \exp(-2\sigma_j^2 k^2) \times \exp(-2R_j/\lambda \sin[2kR_j + \phi_j(k)])$$

where k is the wavevector of the photoelectrons, $F_j(k, \pi)$ is the amplitude of the backscattering of each of the N_j neighbouring equivalent atoms localized at a mean bond distance, R_j , of the absorber atom; σ_j is the Debye–Waller factor; $\lambda(k)$ is the mean free path of the photoelectrons and $\phi_j(k)$ is the phase shift including the absorber atom (in this case In) and the backscattering atoms (in this case F).

The EXAFS oscillations have been analysed by conventional methods including normalization,

TABLE I Room temperature EXAFS simulation at K edge of In for the indium–barium and indium–strontium glasses: $N_{\text{In F}}$, first neighbour's number; $R_{\text{In F}}$, In–F mean bond length; and $\Delta\sigma_{\text{In F}}^2$, Debye–Waller factor

Samples		$N_{\text{In F}} (\pm 0.3)$	$R_{\text{In F}} (\text{nm} \pm 0.001)$	$\Delta\sigma_{\text{In F}}^2 (\text{nm}^2 \pm 0.0003)$	λ^a
InF_3	Crystal ^b	6.0	0.205	–	1
0.67 InF_3 –0.33 BaF_2	Glass 1	6.2	0.206	0.0048	1
0.60 InF_3 –0.40 BaF_2	Glass 2	6.3	0.205	0.0045	1
0.58 InF_3 –0.42 BaF_2	Glass 3	5.8	0.206	0.0047	1
0.55 InF_3 –0.45 BaF_2	Glass 4	6.2	0.205	0.0046	1
0.59 InF_3 –0.41 SrF_2	Glass 5	6.0	0.206	0.0045	1
0.54 InF_3 –0.46 SrF_2	Glass 6	6.3	0.207	0.0050	1
0.50 InF_3 –0.50 SrF_2	Glass 7	6.2	0.206	0.0048	1

^a Fixed during the simulation.

^b Data from [5].

background removal and Fourier transform of the EXAFS spectra. To determine the structural parameters R , N and σ_j , the Fourier transform method was used [6]. The data were analysed using the available simulation programs on Macintosh computers [7]. To obtain the Fourier transform, for all samples, the EXAFS spectra were multiplied by the factor k^3 , and a Kaiser cutting window was used between 0.35 and 1.2 nm^{-1} , with $\tau = 3.5$. A polycrystalline InF_3 powder was used as reference during simulation of the spectra for the first co-ordination sphere around the indium atom (six fluor atoms situated at a mean distance of 0.205 nm [5]).

Polarized Raman scattering spectra were obtained with bulk samples using the 514.5 nm line ($\approx 200 \text{ mW}$) of an argon ion Spectra–Physics laser as excitation source. The detection set-up consisted of a Jobin Yvon triple monochromator and a Hamamatsu photo multiplier. The 90° geometry was utilized and the resolution routinely set at $\approx 5 \text{ cm}^{-1}$. In the following, spectra are denoted VV (polarized) and VH (depolarized).

3. Results

3.1. EXAFS at 293 K

Fig. 1 shows a comparison of the Fourier transform of the crystalline InF_3 reference with two glass samples for both systems (see Table I for glass identification). Note that the distances are not corrected due to the phase shift that exists in the EXAFS equation. For a crystalline InF_3 , one observes the presence of two peaks; the first is due to the interaction of In–F and the second to In–In. In glasses one does not observe this second peak. Qualitatively, one can state that the In–F interaction distances in glasses are identical to those of the crystalline phase.

Fig. 2 shows a comparison of the Fourier transform of crystalline InF_3 with barium and strontium glasses with approximately the same compositions. As one can see, the amplitudes of the Fourier transforms of the glasses are equal, showing no influence of the modifier atom (Ba^{2+} and Sr^{2+} in this case).

3.2. EXAFS at 80 K

In order to obtain more structural information concerning medium range order in these glasses, com-

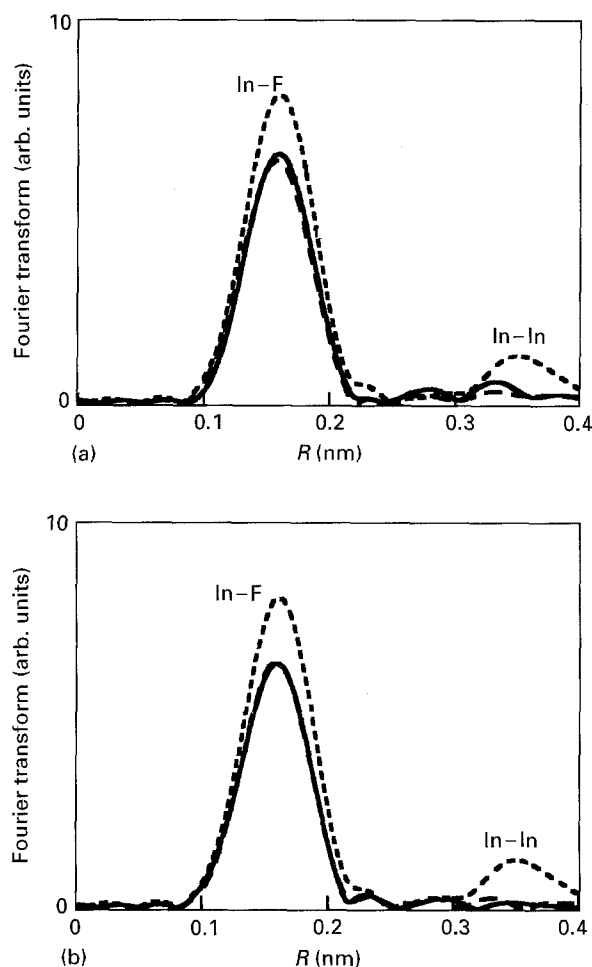


Figure 1 Room temperature Fourier transforms at In–K edge of: (a) InF_3 crystalline phase (---) and indium–barium glasses (glass 1 & 2) (—, ---), and (b) InF_3 crystalline phase (---) and indium–strontium glasses (glass 5 & 7) (—, ---).

plementary experiments at low temperature at the indium–K edge were made for both glass compositions and for the InF_3 reference compound. Fig. 3 presents the Fourier transform for barium and strontium glass systems compared to the reference compound. As was observed at room temperature, in both systems, the amplitudes of the Fourier transforms for the glassy compositions are equal, and even at low temperature one did not observe the second shell characteristic of the InF_3 crystalline compound. One should note that, at low temperature, the difference in

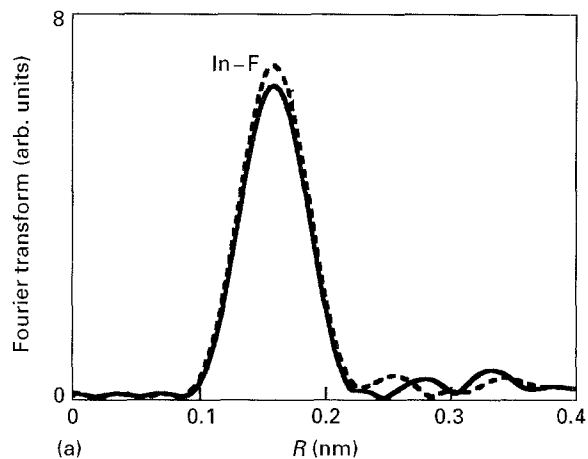
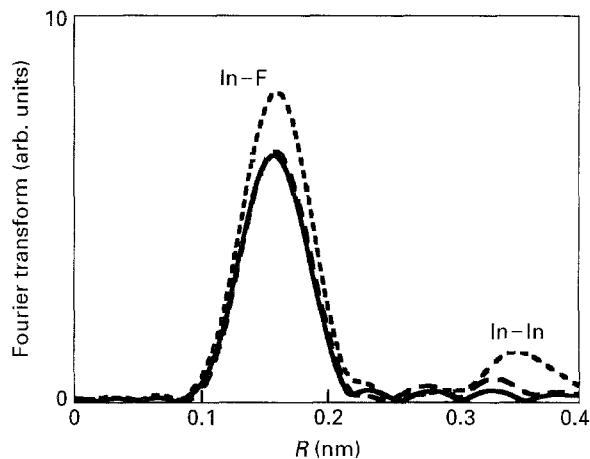


Figure 2 Room temperature comparison of the Fourier transforms at In-K edge of the InF_3 crystalline phase (---) and indium-barium (---) and indium-strontium (—) glasses (glasses 2 and 5 respectively) with practically the same composition.

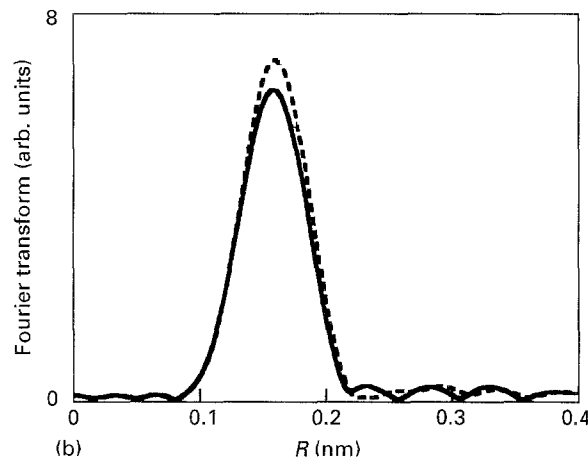
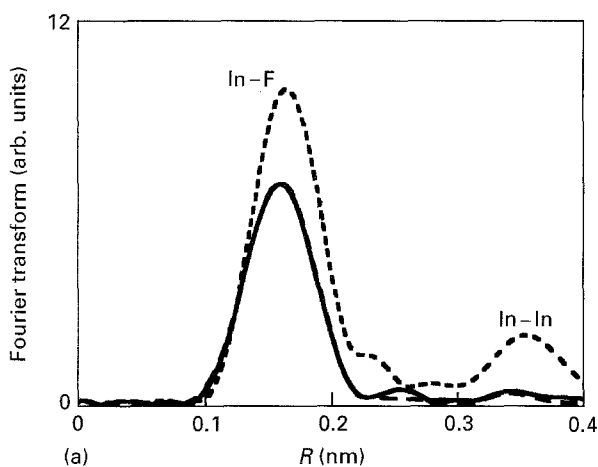


Figure 4 Comparison of the Fourier transforms obtained at room (—) and low (---) temperatures at In-K edge: (a) indium-barium glasses (glass 2), and (b) indium-strontium glasses (glass 5).

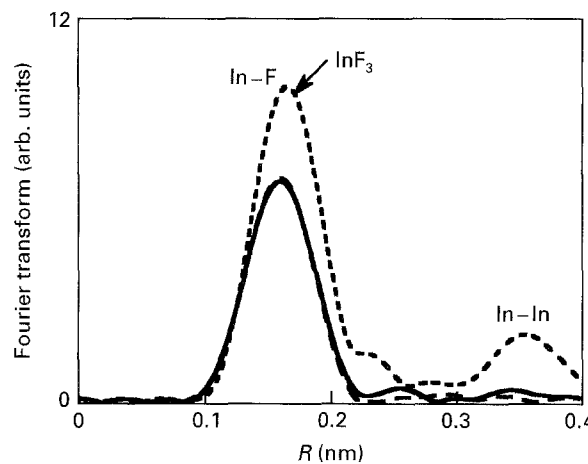
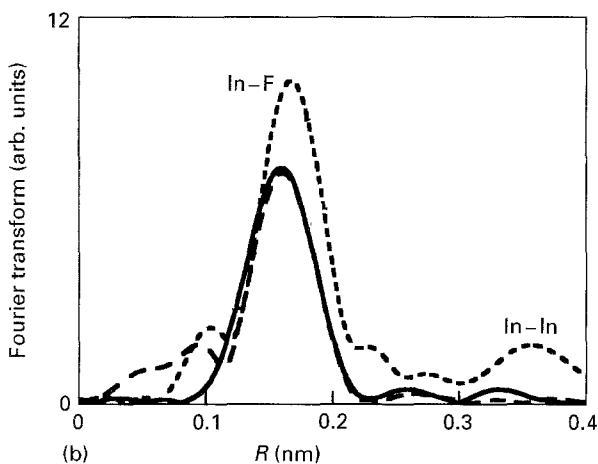


Figure 3 Low temperature (80 K) Fourier transforms at In-K edge of: (a) InF_3 crystalline phase (---) and indium-barium glasses (glass 1 and 2) (---), and (b) InF_3 crystalline phase (---) and indium-strontium glasses (glass 5 and 7) (---).

Figure 5 Comparison of the Fourier transforms obtained at In-K edge at low temperature (80 K): InF_3 crystalline phase (---), indium-barium (glass 2) (---), and indium-strontium (glass 5) (—) glasses with practically the same composition.

the amplitude of the Fourier transform first peak between the InF_3 compound and the glasses is a little higher when compared to the room temperature results (Fig. 1).

Fig. 4 shows a comparison of the Fourier transform obtained at room and low temperature for glass 2 (barium system) and glass 5 (strontium system). One

can observe only an increase of the amplitude in the first peak of Fourier transform for glasses measured at low temperature. Fig. 5 shows a comparison of the Fourier transform for barium and strontium glasses with approximately the same compositions. Confirming the room temperature results, in low temperature experiments, no differences were observed between the two glasses.

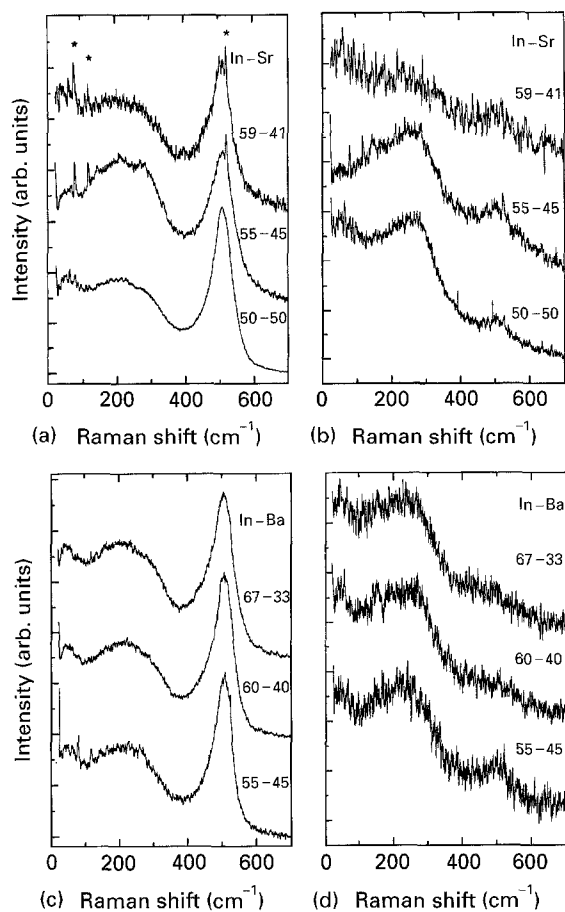


Figure 6 VV (a,c) and VH (b,d) spectra for three glasses in the $\text{InF}_3\text{-SrF}_2$ (a,b) and $\text{InF}_3\text{-BaF}_2$ (c,d) binary systems, respectively, (* are the laser parasites' peaks).

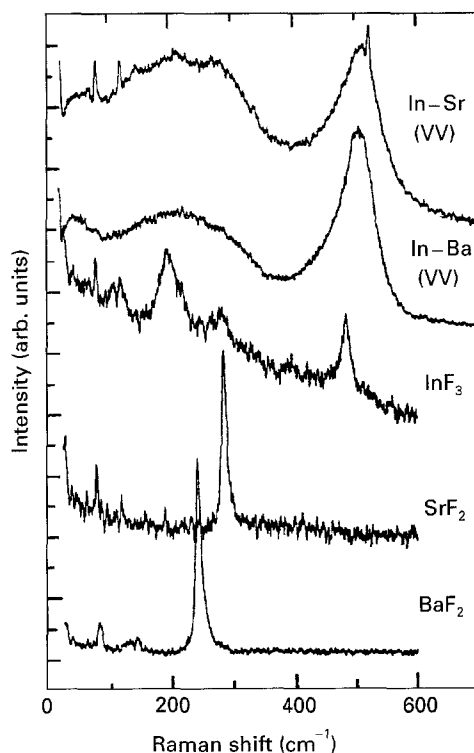


Figure 7 VV spectra obtained for glasses in both binary systems and powder spectra obtained for the crystalline starting materials.

3.3. Raman spectroscopy

Fig. 6 shows VV and VH spectra for three glasses in the $\text{InF}_3\text{-BaF}_2$ and $\text{InF}_3\text{-SrF}_2$ binary systems, respectively.

One observes a strongly polarized band at $\cong 507\text{ cm}^{-1}$, a broad depolarized band at $100\text{--}300\text{ cm}^{-1}$, and another depolarized band which peaks at $\cong 50\text{ cm}^{-1}$ for $\text{InF}_3\text{-BaF}_2$ glasses and at $\cong 60\text{ cm}^{-1}$ for $\text{InF}_3\text{-SrF}_2$ glasses. These last low frequency bands are known as Boson peaks, and are characteristic of the glassy state [8].

Fig. 7 shows VV spectra obtained for glasses in both binary systems and powder spectra obtained for the crystalline starting materials. One observes for the InF_3 crystalline compound three main bands at 483 , 282 and 196 cm^{-1} ; for the SrF_2 crystalline compound one main band at $\cong 290\text{ cm}^{-1}$; and for the BaF_2 crystalline compound one main band at $\cong 240\text{ cm}^{-1}$.

4. Discussion

To obtain quantitative results and to interpret the amplitude variation observed in the first peak of the Fourier transform, a simulation of the EXAFS spectra was realized. The results are presented in Tables I (room temperature experiments) and Table II (low temperature experiments). Fig. 8 shows a comparison of the experimental EXAFS curve to that calculated for one glass (at room and low temperature). The quality of the simulation results for the other glass is similar.

From analysis of these results one can state that:

1. $N_{\text{In-F}}$ and $R_{\text{In-F}}$ do not depend on the composition or modifier atom (Ba or Sr) and are equal to the value of the crystalline compound (6 and 0.205 nm , respectively).

2. The variation of amplitude between the crystalline and amorphous phases observed at room and low temperature (Figs 1 and 3) is due to the existence of a higher degree of disorder in the glasses, which gives a high value of the Debye-Waller factor ($\Delta\sigma \cong 0.0005\text{ nm}^2$).

3. Variation of amplitude between the amorphous phases obtained at low and room temperature (Fig. 4) is due to the existence of a low degree of thermal disorder in the low temperature glass.

4. For both glass systems, and even in low temperature experiments, a second shell feature corresponding to the In-In neighbours (as is observed in the InF_3 crystalline compound) was not observed.

Concerning the difference observed in the amplitude of the Fourier transform first peak between the InF_3 compound and the glasses when one compares room and low temperature results (Figs 1 and 3), the fitting results show that this difference is only related to the variation in the Debye-Waller factor. In fact, the Debye-Waller factor of each shell is written as the sum of two contributions: $\sigma^2 = \sigma_{\text{static}}^2 + \sigma_{\text{vibrational}}^2$. The first term is temperature independent and corresponds to the dispersion of bond lengths without vibration; the latter is due to thermal vibration. Thus, for low temperature EXAFS spectra a decrease in the σ^2 Debye-Waller factor value is expected. Moreover, in the fitting procedure, the Debye-Waller factor is taken relative to the reference compound ($\Delta\sigma^2 = \sigma_{\text{sample}}^2 - \sigma_{\text{reference}}^2$). As shown in Table II, the values for the Debye-Waller factor are a little higher when

TABLE II 80 K EXAFS simulation at K edge of In for the indium–barium and indium–strontium glasses: $N_{\text{In F}}$, first neighbour's number; $R_{\text{In F}}$, In–F mean bond length; and $\Delta\sigma_{\text{In F}}$, Debye–Waller factor

Samples		$N_{\text{In F}} (\pm 0.3)$	$R_{\text{In F}} (\text{nm} \pm 0.001)$	$\Delta\sigma_{\text{In F}}^2 (\text{nm}^2 \pm 0.0003)$	λ^a
InF ₃	Crystal ^b	6.0	0.205	–	1
0.67 InF ₃ –0.33 BaF ₂	Glass 1	6.2	0.207	0.0054	1
0.60 InF ₃ –0.40 BaF ₂	Glass 2	6.0	0.207	0.0057	1
0.58 InF ₃ –0.42 BaF ₂	Glass 3	6.0	0.206	0.0058	1
0.55 InF ₃ –0.45 BaF ₂	Glass 4	6.1	0.207	0.0056	1
0.59 InF ₃ –0.41 SrF ₂	Glass 5	5.9	0.207	0.0054	1
0.54 InF ₃ –0.46 SrF ₂	Glass 6	6.0	0.207	0.0055	1
0.50 InF ₃ –0.50 SrF ₂	Glass 7	6.2	0.206	0.0057	1

^a Fixed during the simulation.

^b Data from [5].

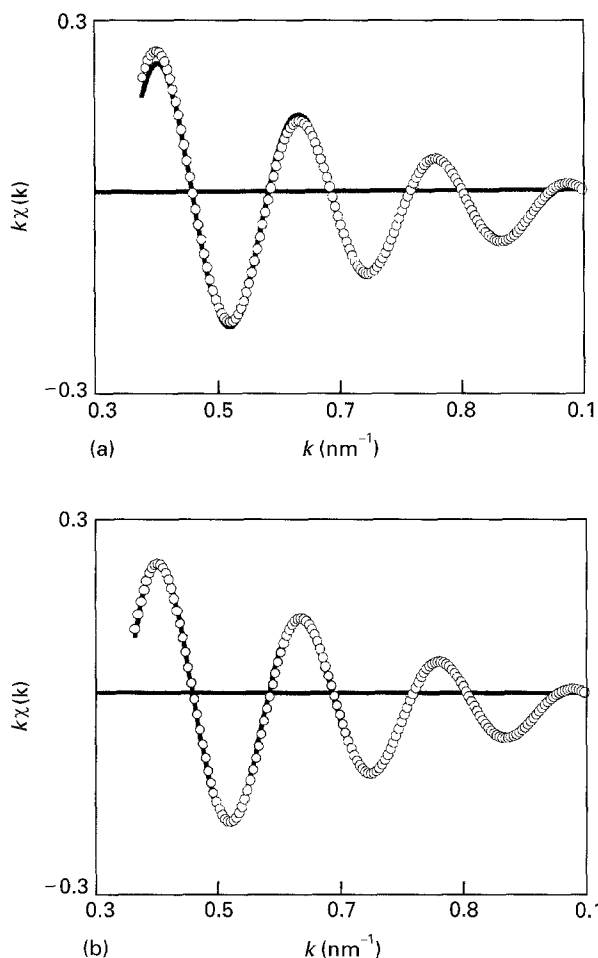


Figure 8 Comparison between the experimental (—) and theoretical (○) EXAFS curves for glass 1: (a) room temperature, and (b) low temperature (80 K).

compared to the room temperature values (Table I). Thus, this result can only be explained if one considers that at low temperature the decrease in the Debye–Waller factor was more important for the InF₃ sample (when compared to the low temperature glass values).

Concerning the Raman results shown in Fig. 6, the bands at $E > 100 \text{ cm}^{-1}$ have been analysed by Almeida *et al.* [4] taking into account the vibrational modes of an $[\text{InF}_6]^{3-}$ octahedral complex ion. Following this interpretation, the Raman modes at $\cong 203$ and $\cong 507 \text{ cm}^{-1}$ have been assigned to vibrational modes related to bending and symmetric stretching of non-bending fluorine atoms, respectively.

Toth *et al.* [9] give the following interpretation for an octahedral molecular complex, as observed in the Raman spectra of the InF₃ crystalline compound shown in Fig. 7: the high frequency band at 483 cm^{-1} could be assigned to the $\nu_1 (A_{1g})$ octahedral vibrational mode and the two bands observed at 196.6 and 282.2 cm^{-1} could be assigned to the $\nu_5 (T_{2g})$ mode. Thus, these vibrational modes are present in glasses as confirmed by the close resemblance between the crystal and glass spectra.

Almeida *et al.* [4] observed no contribution from modifier ions (Ba^{2+} and Sr^{2+} in this case) to the Raman spectra. In fact one could observe the contributions of the main peaks of SrF₂ and BaF₂ crystalline phases to the scattered glass intensities in the 300 cm^{-1} region. A preliminary shape analysis in terms of Gaussian decomposition indicates that a broad medium frequency band can be fitted to a single Gaussian component centred at $\cong 210 \text{ cm}^{-1}$ for InF₃–BaF₂ glasses. For InF₃–SrF₂ and specially for the $(\text{InF}_3)_{0.55}(\text{SrF}_2)_{0.45}$ composition, the same quality fit can only be attained if one related vibrational mode could indeed contribute to the scattered intensity in this spectral region. However, for the $(\text{InF}_3)_{0.59}(\text{SrF}_2)_{0.41}$ and $(\text{InF}_3)_{0.50}(\text{SrF}_2)_{0.50}$ compositions, these vibrational modes are not well identified. Thus, this observation must be confirmed by further measurements with samples presenting improved optical quality, since optical misalignment could produce the same effects in the measured spectra.

5. Conclusions

The local structure of glasses belonging to the indium fluoride system have been studied using EXAFS and Raman techniques. Both results show no influence of composition and modifier atom in the local structure around indium atoms. Observation of only the first shell in low temperature EXAFS experiments indicates clearly a high degree of topological disorder in these glasses.

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