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An EXAFS investigation of the local structure of $R_8Mg_{42}Zn_{50}$ icosahedral quasicrystals (R=Y, Dy)

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Abstract

EXAFS experiments have been performed on the icosahedral quasicrystals $R_8Mg_{42}Zn_{50}$ (R=Y, Dy) at the Y K, Dy L_{III} and Zn K edges. Isomorphism of Y- and Dy-based quasicrystals is clearly evidenced. The rare earth is found to be essentially surrounded by Zn atoms with a small amount of Mg atoms. The surrounding of Zn appears less spherical than that of the rare earth and includes the three elements in almost stoichiometric proportion. The relation between structure and magnetic properties is discussed.

Keywords: EXAFS spectroscopy; Quasicrystals; Rare earth compounds

1. Introduction

The series of icosahedral quasicrystals (QC) $R_8Mg_{42}Zn_{50}$ (R=Rare Earth) was recently shown to exhibit very original magnetic behaviour [1]: both short range and long range magnetic correlations coexist at low temperature in some of these compounds (R=Tb and Ho) while only short range ordering is present with R=Dy and Er. In these materials the only magnetic atoms are the rare earths, for which the magnetism is *localized* as the 4f magnetic shell is an inner shell. This magnetism strongly depends on the atomic structure, in particular on the local environment surrounding the rare earth atoms. These crystal field effects have deciding consequences on the magnetic anisotropy for example. In rare earth-based quasicrystals it is therefore of great interest to investigate the local atomic environment surrounding the rare earth, in order to properly understand their astonishing magnetic properties. Until now the atomic structure has not been yet fully resolved, however the atomic arrangements have been shown to be new and completely different from known quasicrystal structures [2,3]. EXAFS (Extended X-Ray Absorption Fine Structure) measurements appear as a very suited tool for such an investigation, allowing us to provide local information around selected types of atom in the structure. Such an experiment has then been performed in Y- and Dy-based quasicrystals. After a description of the experimental details and of the procedure used to reduce the data (Section 2), the local environment around the rare earth (Section 3) and zinc (Section 4) will be presented. Section 5 will be devoted to the discussion.

2. Experimental details

The experiments were performed on the CRG/IF line BM32 at the ESRF facilities in Grenoble. The instrument was equipped with a Si(111) double crystal monochromator. Spectra were collected in transmission geometry. The flux on the sample was about 10^{11} photons $s^{-1}m^{-2}$. The expected energy resolution ranges from $5\cdot10^{-5}$ to $2\cdot10^{-4}$. The experiments were performed at the edge of two different rare earths, namely the Y K and the Dy L_{III} edges, as well as at the Zn K edge. All the measurements were performed at room temperature. The preparation of the quasicrystalline samples is described elsewhere [4]. Three crystalline samples were also studied to be used as reference compounds in order to calibrate some electronic parameters: YZn, YMg and DyMg. All of them crystallize within the cubic CsCl-type structure.

The experimental data were analyzed by standard procedure of normalization and background correction. They

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were converted to k space by using the relation $E-E_o=\hbar k^2/(2m)$, E_o being the threshold energy origin. For sake of calibration of the experimental setup, a small additional correction ΔE_o has been introduced. The EXAFS signal $\chi(k)$ could then be analyzed by using the following expression in the harmonic approximation (gaussian distribution) [5]:

$$\chi(k) = -\sum_j \frac{N_j}{kR_j^2}.B_j(k).\exp\left(-2\sigma_j^2 k^2 - \frac{2R_j}{\lambda}\right) .\sin[2kR_j + 2\delta + \phi_j(k)] \quad (1)$$

N_j is the number of atoms on the jth shell at the distance R_j from the absorbing atom. $B_j(k)$ and $\phi_j(k)$ are the backscattering amplitude and the phase shift, respectively, experienced by the photoelectron scattered by the corresponding atom. The values tabulated by McKale et al. [6] have been used. δ is the phase shift of the central atom. The remaining two parameters, namely the mean-square displacement σ_j^2 and the electron mean free path $\lambda(k)=k/\Gamma$ have been approximated by those obtained by fitting the EXAFS spectra of the reference compounds RZn and RMg. The closer the structures of both reference and quasicrystalline compounds are, the better this approximation is. Fourier transforms have been also calculated in order to estimate the radial distribution functions *F(r)*. As usually accepted, the function actually fitted is the product $k\cdot\chi(k)$ obtained by inverse Fourier transforming *F(r)* after having selected an appropriate radial window. It is worth noting that, in the analysis program [7], both the statistic noise of the instrument and the correlations between the different parameters are included in the error bars.

3. Local environment around the rare earth

The environment surrounding the magnetic atoms requires to be carefully analyzed because it strongly influences the magnetic properties through the crystal field effects. Comparison of the EXAFS oscillations for Y–QC and Dy–QC and for some crystalline references gives some information about this local environment. Fig. 1 shows the $k\cdot\chi(k)$ signal for Y–QC and YZn on one hand, and Dy–QC and DyMg on the other hand, measured at the K edge of Y ($E_0=16900$ eV) and the L_{III} edge of Dy ($E_0=7790$ eV), respectively. It turns out that Y–QC and Dy–QC signals are out of phase, as δ between both cases differs from $\pi/2$. Apart from this shift, it can be seen that the EXAFS oscillations for both compounds are very similar as far as their period and amplitude are concerned. This supports the idea that both quasicrystals are *isomorphous*, as it is often observed for Y and Dy crystalline intermetallic compounds. Fig. 1 moreover shows that experimental oscillations in Y–QC and YZn are well in phase in the whole k range. The only difference between both spectra is the very first oscillation (at ~3.5 Å^{-1}) which appears more apparent in Y–QC. This is reminiscent of the still more pronounced oscillation observed around

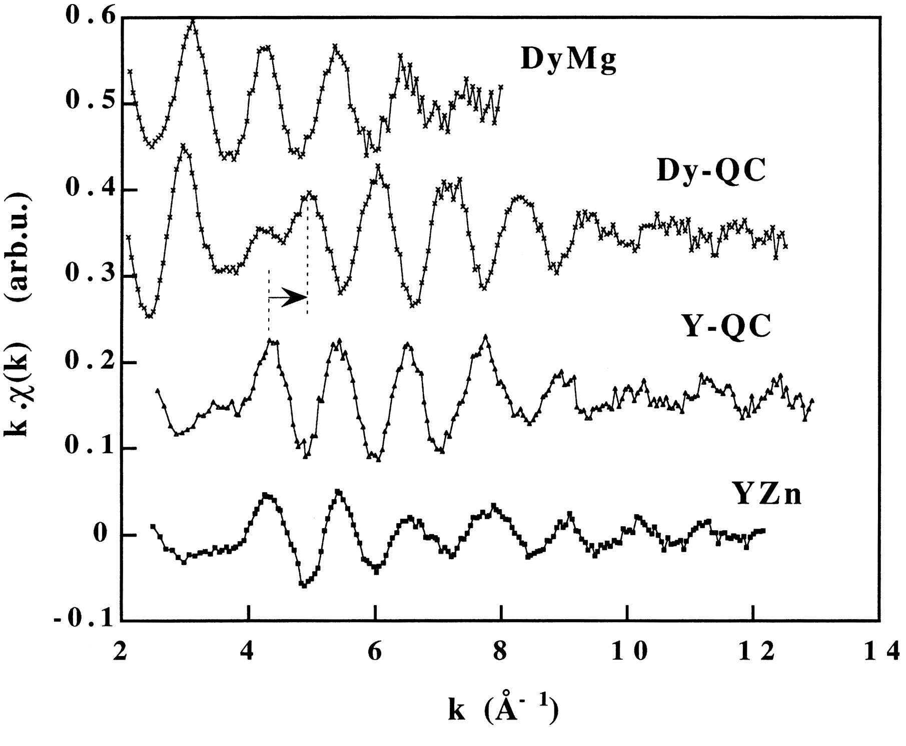

Fig. 1. EXAFS spectra at the Dy L_{III} or Y K edges in Y- and Dy-based quasicrystals as well as in the crystalline reference compounds YZn and DyMg. The arrow shows the phase shift arising from the different edge investigated.

4.5 Å^{-1} in Dy–QC. The comparison with DyMg, in particular the close similarity between DyMg and Dy–QC spectra at low k values (<5 Å^{-1}), strongly suggests that these low k oscillations mainly originate from Mg atoms. This is consistent with the backscattering amplitude of Mg, which is much larger in that k range than the Zn one [6]. More generally, it turns out that, due to the difference of electronic structure and of the number of electrons, the Mg signal is predominant at low k, while the Zn signal becomes significantly larger at high k. This specificity may allow us to make easier the distinction between both contributions in the experimental oscillations. Qualitatively, the rare earth in the quasicrystal is then essentially surrounded by zinc atoms, with possibly some magnesium atoms leading to the beat evidenced at low k.

A more quantitative description can be made now by using the formalism described above. The DyMg cubic compound was first analyzed at the Dy edge, according to the known crystallographic parameters and to the McKale functions, allowing us to deduce ΔE_0, σ and Γ values. All these three parameters were then kept constant for the case of Dy–QC. Fig. 2 shows that the EXAFS signal $k \cdot \chi(k)$ of DyMg is fairly well fitted up to ~8 Å^{-1} by using the known crystallographic parameters of the first two shells (i.e. 8 Mg at 3.25 Å and 6 Dy at 3.76 Å). Fitting at higher k values appears less reliable as the environment of Dy involves many Mg atoms at larger distances, whose signature is rather weak at large k. The different parameters of Eq. (1) for the first two shells around Dy in Dy–QC could then be determined (see Table 1). The corresponding fit of the $k \cdot \chi(k)$ function is shown in Fig. 3. As it can be seen, the agreement is satisfactory. In particular, the oscillations below 5 Å^{-1} are well accounted for by considering a small amount of Mg. However, the neighbourhood of Dy remains predominantly constituted by Zn atoms. Moreover, given the closeness of both Dy–Mg and Dy–Zn distances, it can be considered that one single, highly symmetric and nearly spherical shell consisting of 16 atoms (about three Mg and 13 Zn) constitutes the nearest surrounding of the rare earth.

Table 1
Environment of Dy in Dy–QC from Dy L_{III} edge data: Z is the atomic number, N the number of atoms at distance R and σ the disorder parameter

Shell	Z (atom)	N	R (Å)	$10^2 \cdot \sigma^2$
1	12 (Mg)	3.2±0.5	3.09±0.02	1.06±0.01
2	30 (Zn)	12.7±0.5	3.12±0.02	1.64±0.01

A first comment can be made about these results. The relatively high values of σ_i^2 are mainly due to the fact that the experiments were performed at room temperature (σ_i^2 accounts for structural disorder as well as for thermally induced agitation). Indeed the σ_i^2 values obtained with the reference sample are also rather large, and close to those found for the quasicrystal. As the reference sample is structurally well ordered, it must be concluded that the distances between neighbouring atoms in Dy–QC are *not* too much distributed around Dy.

Looking carefully at the results of the fit indicates that this environment is actually very close from what was

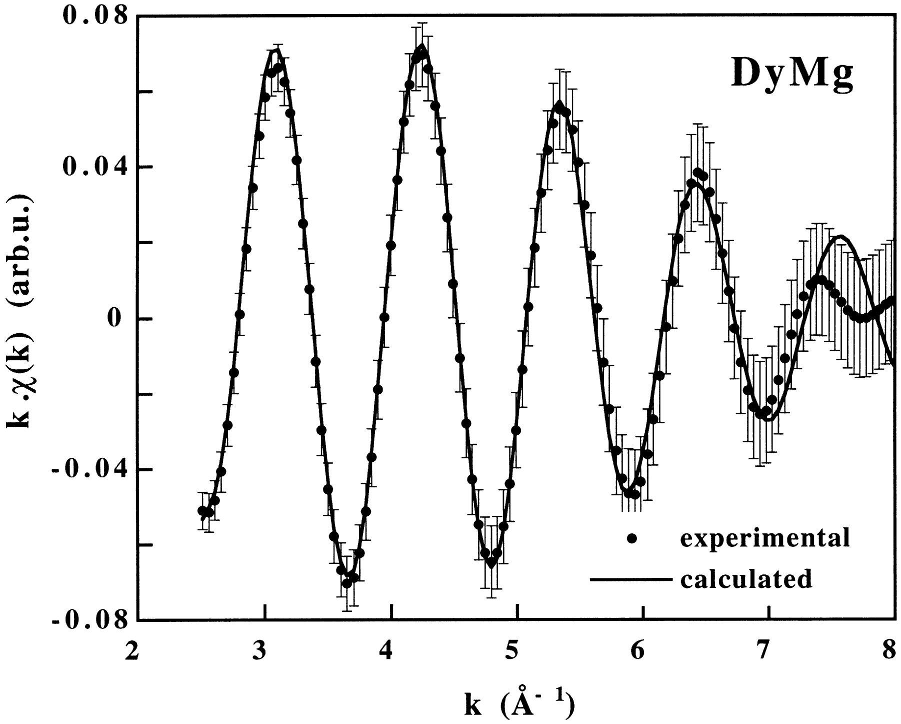

Fig. 2. Experimental and calculated EXAFS spectra in DyMg cubic compound.

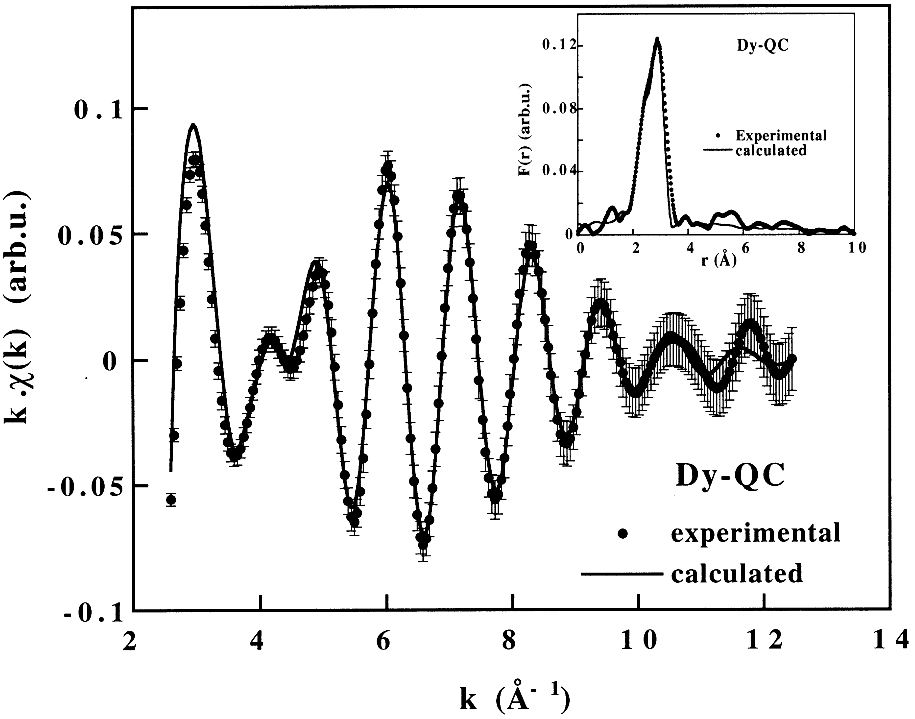

Fig. 3. Experimental and calculated EXAFS spectra in Dy–QC; parameters are given in Table 1; inset: corresponding radial distribution obtained by Fourier transform.

observed in some crystalline compounds. Let us consider the binary hexagonal compound $Gd_{13}Zn_{58}$ where an accurate description of all the sites occupied by either Gd or Zn has been given [8]. Averaging the number of neighbours and their distance to Gd over all the sites of Zn weighted by their multiplicity gives the following result: Gd is surrounded by 16.3 Zn at 3.196 Å and 0.7 Gd at 4.47 Å. If we compare with Dy–QC where 15.9±1 atoms locate at 3.10±0.18 Å from Dy, it can be seen that both results are surprisingly very close to each other. The difference between both systems can be even reduced by considering the lanthanide contraction (from Gd to Dy). It can be therefore concluded that the average local environment around the rare earth in the quasicrystal looks like that in the binary phase $R_{13}Zn_{58}$. This approach may appear as not really surprising taking into account the large cell parameters of $Gd_{13}Zn_{58}$ (142 atoms in the hexagonal unit cell with $a=14.35$ Å and $c=14.21$ Å). Some Gd moreover have a coordination close to the icosahedral one so that the binary compound $Y_{13}Zn_{58}$ has already been evoked as being a possible approximant of the $R_8Mg_{42}Zn_{50}$ quasicrystals [9].

As far as the third and possibly the fourth shells are concerned, they are well identifiable on the Fourier transform of the experimental oscillations (see inset of Fig. 3). However, it appears rather difficult to obtain reliable information on the detailed environment situated as far as 5 or 6 Å: a very rough analysis suggests that both of these shells located in the range 5.3–5.8 Å from the rare earth could be occupied by heavy atoms (Zn or RE). Such information should nevertheless be considered very carefully.

Considering now the Y edge results in Y–QC, the fitting procedure, in particular the determination of the number of Mg, is more delicate than for the above description of Dy–QC, as most of the oscillations attributed to Mg atoms in the neighbourhood of the rare earth occur at much lower *k* values, i.e. below the accessible *k* window. Nevertheless, calculating the $k\cdot\chi(k)$ curve with the same parameters as for Dy–QC (Table 1) leads to a satisfactory agreement.

4. Local environment around Zn atoms

Fig. 4 presents the experimental $k\cdot\chi(k)$ signal measured at the K edge of Zn (9657 eV) in Y–QC, Dy–QC and in the reference compound YZn. The spectra of the former two compounds appear very similar and indicate a close isomorphism between both Y and Dy quasicrystals, as far as the neighbourhood of Zn is concerned. On the other hand, comparison with the reference sample clearly shows that environment around Zn atoms are clearly different in both types of system.

Fitting the EXAFS curves appears more delicate here than in the case of the rare earth edges, due to the absence of reference compounds with similar oscillations. We nevertheless examined first the Zn environment in the $Mg_{51}Zn_{20}$ orthorhombic phase which has been previously measured by EXAFS [10]. Although the spectrum of this crystalline compound is quite different from the present

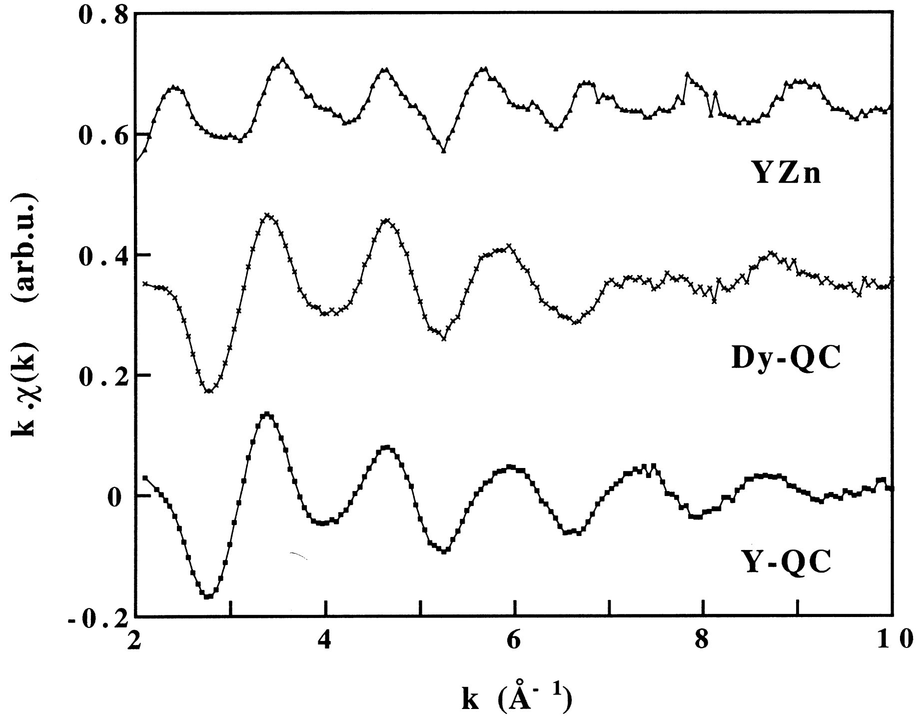

Fig. 4. EXAFS spectra at the Zn K edge in Y- and Dy-based quasicrystals as well as in the crystalline reference compound YZn.

results, its analysis showed that the Zn atoms are surrounded, on average, by 1.95 Zn at 2.75 Å and 9.75 Mg at 3.00 Å. That surprisingly indicates that Zn can be surrounded by other Zn atoms as nearest neighbours, while Mg atoms could have been expected to be the closest ones, being more numerous. We then assumed that the same phenomenon could also occur in our quasicrystalline compounds. Moreover, the presence of rare earth-zinc pairs at 3.12 Å as seen at the rare earth edges (see Sect. 3) imposes to include a shell with a few rare earths at the same distance around Zn. At last, the EXAFS oscillations are still pronounced at large *k* values. It can be concluded that the Zn atoms see other heavy (Zn) atoms at larger distances. Table 2 shows the final parameters leading to the best fit of our experimental results in Y–QC (Fig. 5).

As it can be seen in Table 2, the uncertainty on the number of atoms located in the third and fourth shells is rather large. This comes from the fact that both shells contribute essentially in the region of 7–9 Å^{-1}, where a broadening of the experimental oscillations is clearly noticeable: this beat is attributed to the third and fourth shells, but remains delicate to fit as the signal becomes more noisy for these *k* values.

Table 2
Environment of Zn in Y–QC from Zn K edge data: *Z* is the atomic number, *N* the number of atoms at distance *R* and *σ* the disorder parameter

Shell	*Z* (atom)	*N*	*R* (Å)	$10^2 \cdot \sigma^2$
#1	30 (Zn)	3.1±0.5	2.55±0.02	1.00±0.1
#2	12 (Mg)	8.3±0.5	2.82±0.02	1.35±0.01
#3	39 (Y)	2.6±1.0	3.11±0.02	1.02±0.1
#4	30 (Zn)	6.1±1.0	3.24±0.02	1.00±0.1

5. Discussion

The present EXAFS study provides a first *average* description of the local environments around the rare earth R (Dy or Y) as well as the Zn atoms within the icosahedral $R_8Mg_{42}Zn_{50}$ phase. It appears that the magnetic atoms are essentially surrounded by Zn, with a small amount of Mg. Both shells lie at about the same distance, so that the rare earth mainly sees a first shell with 16 atoms. This nearly spherical environment has been shown to be extremely similar to the average surrounding of R in the crystalline phase $R_{13}Zn_{58}$. Besides, the environment of Zn in the icosahedral structure is less spherical, being composed of at least four shells more spread out than around the rare earth. Moreover, these shells include about 17 atoms of Zn, Mg and rare earth almost in the stoichiometric proportion.

The present results give a new insight into the possible relation between atomic structure and magnetism. The nearly spherical shell seen by the rare earth means in turn that the crystal field produced by these atoms is probably highly symmetrical. This conclusion is consistent with other magnetic measurements, such as specific heat and inelastic neutron scattering data, which lead to a crystal field level scheme not wider than 100 K, i.e. much less than usual rare earth intermetallics [11]. Besides, it would

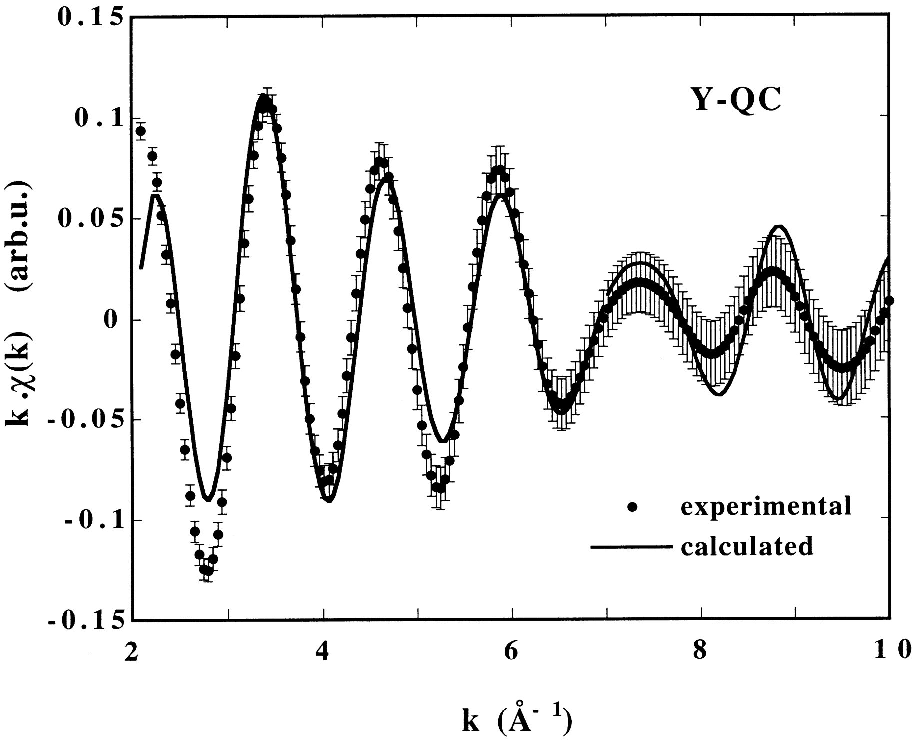

Fig. 5. Experimental and calculated EXAFS spectra in Y–QC; parameters are given in Table 2.

be interesting to correlate the present results with the R–R radial spin correlation functions deduced from neutron diffraction data [1,12]. Unfortunately, it appears that the main R–R distances extracted from the latter data are much larger (5.2 and 8.7 Å) than the present ones, and far above the range of investigation of the EXAFS measurements which remain rather local. Therefore, a direct comparison between both types of experiment is not possible. Finally, detailed structural models are now highly desirable to test the present EXAFS results.

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