

X-ray absorption study at the Fe K-edge of garnets from the Ivrea–Verbano zone

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Abstract

K-edge X-ray absorption spectra of Fe in garnet samples from the Ivrea–Verbano zone were collected using synchrotron radiation. From XANES analysis, the prevalent oxidation state of Fe has been determined as 2+ in all studied samples. Coordination numbers and Fe–O bond lengths derived from the EXAFS analysis are compatible with a dodecahedral environment of Fe atoms and seem to be nearly independent of the variable Fe/Ca ratio of the cations sharing the dodecahedral site in these garnets. This suggests that, since at least up to 0.5 Ca atoms p.f.u. no sensible deformation of the dodecahedron geometry is sensed by the Fe cations, iron might strongly compete with Ca atoms in controlling the entry of rare earth elements in the dodecahedral site of garnets falling within this compositional range. Comparison of the EXAFS results with the data from single crystal X-ray diffraction structure refinements indicates a first shell neighbour distance accuracy of ± 0.02 Å, using theoretical EXAFS phases and amplitudes. The Debye-Waller factors derived from the EXAFS analysis indicate a higher degree of disorder on the four longer Fe–O bond distances, in comparison with the other four shorter distances of the height-coordinated cation; this could be related to the non-rigid polyhedral behaviour of the dodecahedral site.

KEYWORDS: EXAFS and XANES spectroscopy, crystal-chemistry, garnets, Sesia Valley, deep crust.

Introduction

THIS contribution is part of a long-term investigation on the rock-forming minerals of the Ivrea–Verbano area and is particularly concerned with the garnet minerals. Our goal is to determine the local environment (interatomic distances, type and number of first neighbours) of specific chemical species in the garnet structure, in order to point out all geometrical parameters influencing the crystal-chemistry and related diffusion mechanisms of major and trace elements in the structure.

The Ivrea–Verbano area is part of the Hercynian basement of the southern Alps. This region is commonly regarded as an exposed section of the upper mantle and the deep crust, originated by underplating of mantle-derived magma onto the base of continental crust (Voshage *et al.*, 1990). The thick section exposed in the Sesia Valley consists of a layered zone in contact with mantle peridotites and overlain by gabbroic rocks grading upward into diorites. The roof of the

complex is formed by amphibolite-facies meta-sediments (Rivealenti *et al.*, 1984).

Crystal-chemical and structural studies of the rock-forming minerals are of great interest for petrogenetic and petrological purposes, giving insights into the role of potentially useful chemical indicators, such as incompatible trace elements, during the mineral history. In particular, the inter- and intra-crystalline distribution of trace elements (as, for example, the rare earth elements) might be partially or totally controlled by the structural environment of geochemically related major elements. Several studies (see for example McKay, 1989; Apter and Boettcher, 1981; Harrison, 1981; Harrison and Wood, 1980) indicate the preferential entry of the REE in 8-fold coordination. However, no systematic research has related the crystallographic behaviour and the diffusion processes of REE with the structural environments of the major cations (in particular Fe and Ca) placed in the dodecahedral site of garnets.

Experiments using X-ray Absorption Spec-

troscopy (XAS) have been carried out to study garnet minerals from the Ivrea-Verbanò complex, as this technique offers the advantage of being element selective and potentially very sensitive to small concentrations of the trace species. Information on the local environment of a specific element in the presence of other species sharing the same crystallographic site can be obtained by XAS investigations; this information cannot be satisfactorily deduced by diffraction procedures, as these techniques provide inherently space-averaged data. We here present the first data obtained on the Fe absorption *K*-edge, as the first step of the characterisation of the dodecahedral site geometry in garnets having different Ca/Fe ratios. XAS data on the same samples at the Ca and REE absorption edges are in the evaluation process.

XAS (X-ray Absorption Spectroscopy)

Although the technique of X-ray absorption spectroscopy has contributed to the field of solid state physics for a long time, its application to mineralogical and geochemical problems is relatively new (Calas *et al.*, 1984; Brown *et al.*, 1988).

At an absorption edge, one usually considers three distinct regions:

- (a) the absorption edge itself, due to transitions of core level electrons to excited bound states; from the structure of the edge, information on oxidation states, coordination numbers and site distortions can be extracted;
- (b) the region just above the edge, up to ~ 50 eV, related to multiple scattering effects and investigated only in simple compounds to obtain information on site geometry including bond angles; regions (a) and (b) are usually called X-Ray Absorption Near Edge Structures (XANES);
- (c) the oscillations of the absorption coefficient on the high energy side above the edge up to ~ 1000 eV, commonly called Extended X-Ray Absorption Fine Structure (EXAFS); these oscillations result from the interference between the outgoing photoelectron wave and its fraction which is back-scattered by the neighbouring atoms; EXAFS gives structural informations about the coordination shells of the absorbing atoms; the interatomic distances and the nature and number of surrounding atoms can be obtained.

Experimental

The samples examined represent different petrologic and lithologic environments (Mazzu-

chelli *et al.*, 1992; Rivalenti *et al.*, 1984). MP12 and MP18 are large porphyroblastic garnets occurring close to a metasedimentary septum in the UZ unit; the host gabbroic rock contains, other than garnets, plagioclase, biotite, amphibole, clino and orthopyroxene and abundant magnetite. MP17 is a porphyroblastic garnet occurring in a rock with dioritic composition close to the roof of the complex; the other mineralogical phases present in this sample are mainly quartz, plagioclase and minor orthopyroxene and graphite. In all three rocks, garnet is considered to have formed in equilibrium at the liquidus, and to have later re-equilibrated at subsolidus conditions (850°C and 8 kbar for MP12 and MP18; 850°C and 4–6 kbar for MP17) (Mazzucchelli *et al.*, 1992).

As reference compounds with known structure, a natural Fe³⁺ garnet from Bric Canizzi (BRIC) (Basso *et al.*, 1981) and reagent grade hematite (α -Fe₂O₃) (Willis and Rooksby, 1952) were used.

The published chemical analysis of the samples examined by SIMS and EMA methods (Mazzucchelli *et al.*, 1992; Basso *et al.*, 1981) are also reported in Table 1 for major elements.

Homogeneous garnet fragments were extracted from the rock matrix and the absence of alterations and inclusions was checked by an optical microscope at 40 \times . The samples were then finely hand powdered with an agate mortar and deposited on a Millipore membrane: the layer thickness was chosen so to obtain the best absorption contrast at the Fe-*K* edge.

The XAS (XANES + EXAFS) experiments were performed at the Synchrotron Radiation Facility (PULS), Frascati, Italy, using the ADONE storage ring operating at 40 mA and 1.5 GeV. The incident X-ray beam was monochromatized by a channel cut Si(111) crystal. The absorption coefficient in transmission mode at the Fe *K*-edge was determined by using argon-filled ionization chambers. The XANES region was energy scanned with 0.40 eV steps; data acqui-

Table 1

Chemical data (based on 12 oxygens) for the garnets in study (Mazzucchelli *et al.* 1991, Basso *et al.* 1982). The symbols adopted for Ivrea-Verbanò samples are from Parenti (1991).

	MP12	MP17	MP18	BRIC
Si	2.997	2.991	3.012	2.841
Ti	0.004	0.003	0.011	0.210
Al	1.980	1.983	1.962	0.993
Fe	1.558	1.965	1.434	0.935
Mn	0.040	0.045	0.048	0.022
Mg	0.922	0.912	1.059	0.162
Ca	0.513	0.114	0.471	2.671
Cr	0.001	0.003	0.000	0.000

sition in the EXAFS region was achieved with 2 eV steps.

Data analysis

Fe K-edge structure. The XANES raw spectra of the garnet samples and reference compounds were treated prior to examination by subtracting the pre-edge background and normalizing to the absorption coefficient on the high-energy side of the curve. The normalization takes care of the effects resulting from the different sample thicknesses. The XANES spectra are reported in Fig. 1. The edge-feature energies in Table 2 cor-

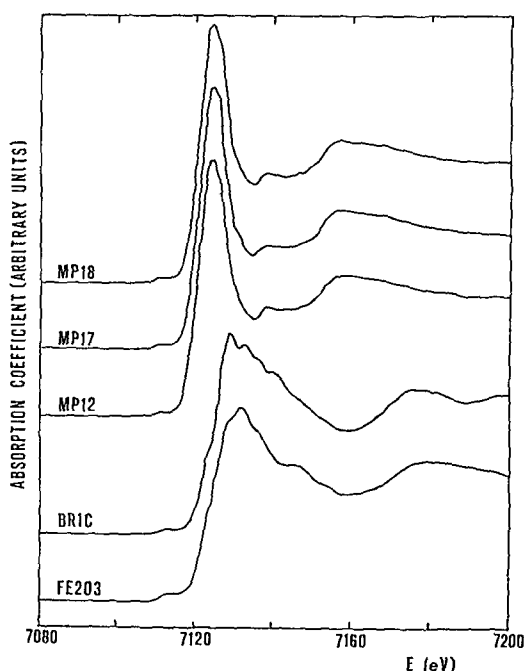


FIG. 1. XANES spectra on Fe K-edge. Individual spectra have been normalized with respect to the high energy side of the curve.

Table 2

Energy (eV) of XANES features and oxidation state of Fe in Ivrea-Verbano samples and reference compounds (Fe203 and BRIC).

	1s→3d (pre-edge)	1s→4s	edge crest	n. ox. Fe
MP12	7110.9	7118.3	7124.3	+2
MP17	7110.9	7119.4	7124.5	+2
MP18	7110.6	7118.3	7124.5	+2
Fe203	7113.3	7122.0	7131.7	+3
BRIC	7113.0	7121.8	7129.0	+3

pond to the zeros of the first derivative of the spectra.

EXAFS spectra. Examples of the sequence in the EXAFS data analysis referring to sample MP18 are reported in Fig. 2a-d.

The analysis of EXAFS data consists of a standard procedure (Teo, 1986) for pre-edge and post-edge background removal and extraction of the EXAFS signal from the raw experimental data (Fig. 2a).

The EXAFS modulation $\chi(k)$ as a function of the photoelectron wave vector (Fig. 2b) may be described, in a one-electron, single scattering approximation, by the sum of damped sinusoids, each one relative to a j atomic shell around the absorbing atom:

$$\chi(k) = \frac{1}{k} \sum_j \frac{N_j}{R_j^2} S_j(k) A_j(k) F_j(k, \pi) \sin(2kR_j + \phi_j(k)) \quad (1)$$

where:

R_j = distance between the absorbing atom and the j th shell atoms;

N_j = coordination number of the j th shell;

$F_j(k, \pi)$ = backscattering amplitude function corresponding to the atomic species in the shell;

$\sin(2kR_j + \phi_j(k))$ = oscillatory term including a phase shift $\phi_j(k)$ due to both the central and backscattering atoms;

$S_j(k)$ = amplitude reduction factor due to many-body relaxation effects of the absorber and to multielectron excitations (Teo, 1986);

$A_j(k)$ = amplitude factor including (i) a damping term similar to a Debye-Waller factor $\exp(-2\sigma_j^2 k^2)$, where $\sigma_j^2(\text{\AA}^2)$ is the mean square relative displacement between the central and the j -th backscattering atom; and (ii) a damping term $\exp(-2R_j \Gamma/k)$, which accounts for inelastic losses, where $\Gamma (\text{\AA}^{-2})$ is a mean free path parameter.

This simple parametrization of the EXAFS function allows a Fourier transformation of $k\chi(k)$ in real space: this produces a sort of radial distribution function whose maxima correspond, apart from the phase shifts, to the distances of the coordination shells of the absorbing atom (Fig. 2c).

An inverse Fourier transformation isolates the EXAFS contribution from a selected shell in real space. The structural parameters are then obtained by fitting the Fourier filtered EXAFS signal with the multi-parameter function given in Eq. (1). Phase and amplitude factors in Eq. (1) can be extracted from a compound with known structure or derived from theoretical calculations. We tested the theoretical Fe-O phase shifts and amplitudes recently calculated by McKale *et al.*

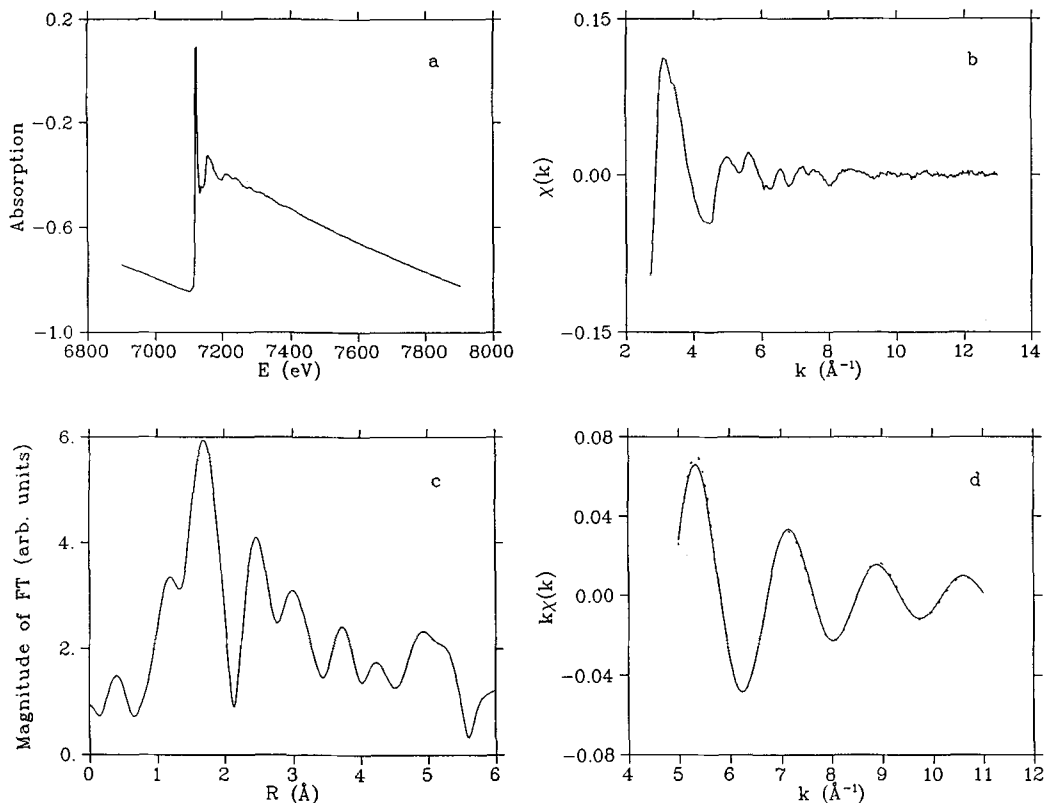


Fig. 2. (a) Raw X-ray absorption spectrum of MP18 (transmission collection); (b) normalized EXAFS modulation function for the same sample; (c) radial distribution function (Fourier transform of 2b); (d) back-transform of the first shell peak from 2c and fit (dashed line).

(1988) on our reference compounds using a two-shell fit for Fe_2O_3 and a one-shell fit for BRIC: the bond length values obtained and coordination numbers (see Table 3) agree well with the results of diffraction experiments (Willis and Rooksby, 1952; Basso *et al.*, 1981). This check enabled us to use theoretical functions in the least-squares fits for the investigated garnets (Fig. 2d).

The EXAFS spectra of the three garnet samples are of comparable quality, with similar signal to noise ratios. The data analysis was performed with the same procedure for all compounds: the Fourier transforms were taken in the interval $2.9\text{--}11.0 \text{ \AA}^{-1}$, the first neighbour peak for the inverse transformer was isolated with a $1.3\text{--}2.1 \text{ \AA}$ window and the Fourier filtered $\chi(k)$ was calculated in the $3.2\text{--}10.7 \text{ \AA}^{-1}$ range. The Γ parameter and the amplitude reduction factor $S_j(k)$ were determined for BRIC and held constant during fitting of all the other spectra.

The parameters R , N and σ^2 resulting from the least-squares fitting are reported in Table 3.

Discussion

In the garnet XANES spectra we observe three main features: a pre-edge peak at $7110.6\text{--}7113.0 \text{ eV}$, a broader maximum or shoulder in the energy range $7118.3\text{--}7122.0 \text{ eV}$ and an edge crest at $7124.3\text{--}7131.7 \text{ eV}$. No other well defined shoulders of maxima are observed, although the shape of the top of the edge varies among the three samples and the reference compounds.

The pre-edge peak is assigned to the $1s \text{ Fe}$ core state to $3d$ crystal field molecular orbital transition and its energy is strongly influenced by the site geometry and the oxidation state of the Fe atom (Tossel *et al.*, 1973, 1974). As can be seen from Table 2, the pre-edge peak has the same energy in all the Ivrea-Verbano samples, which is more than 2 eV lower than the corresponding peak in the two Fe^{3+} reference compounds. A comparable energy shift is shown by the shoulder, which has been assigned to the $1s\text{--}4s$ transition (Waychunas *et al.*, 1983), and by the edge crest.

Table 3

Results of EXAFS analysis of Ivrea-Verbano garnets and reference compounds using theoretical phase parameters from McKale et al. (1988). The corresponding Fe-O bond lengths from single crystal X-ray diffraction structure refinements (Oberti 1991; Willis and Rooksby 1962; Basso et al. 1981) are reported in parentheses.

	R1 (Å)	R2 (Å)	CN1	CN2	σ_1^2 (Å ²)	σ_2^2 (Å ²)
MP12	2.21 (2.231)	2.41 (2.390)	4.8	4.2	0.0050	0.012
MP17	2.21 (2.218)	2.37 (2.369)	5.1	5.8	0.0060	0.018
MP18	2.22 (2.229)	2.38 (2.387)	4.3	4.6	0.0060	0.017
Fe2O3	1.95 (1.96)	2.09 (2.09)	2.6	2.3	0.0040	0.0074
ERIC	2.00 (1.987)		6.0		0.0032	

R1, R2 = Fe-O bond distances in the two coordination shells (± 0.02 Å)
 CN1, CN2 = coordination numbers of the two shells
 σ_1^2, σ_2^2 = EXAFS Debye-Waller factors

This evidence, as reported in other investigations on several Fe²⁺ and Fe³⁺ minerals (Calas *et al.*, 1980; Waychunas *et al.*, 1983, 1986), indicates that the prevalent Fe oxidation state in the garnets here investigated is 2+. Another garnet sample (MP14 in Parenti, 1991), extracted from a depleted granulitic rock of a sedimentary layer at the IZ-UZ transition of the Ivrea-Verbano complex, gave exactly the same XANES results.

Preliminary Mössbauer results (Quartieri *et al.*, 1993) confirm the low Fe³⁺ content in our samples, indicating that no more than 2–5% of iron is in the octahedrally coordinated trivalent state. These percentages are below the limit of the XANES sensitivity, especially when the absorbing element is present in the mineral with more than one oxidation state and coordination number (Brown *et al.*, 1988; Artioli and Geiger, 1991).

During the EXAFS analysis, we attempted for all samples a one-shell fit with a single Fe-O distance, but the results were not acceptable, whereas good fits were obtained by a two-shell fitting procedure. The results in Table 3 show that the Fe-O interatomic distances agree within ± 0.02 Å with the single crystal X-ray diffraction data (Oberti, pers. comm., 1991) and are similar to the Fe-O bond lengths found for the end-member almandine (2.223 and 2.374 Å). Also the coordination numbers for the samples MP12 and MP18 are compatible with a dodecahedral environment of Fe atoms: larger coordination numbers are found for the sample MP17, but in our opinion this is not significant due to the

relatively high uncertainty in the EXAFS determination of this structural parameter. It should be noted that the Fe-O coordination distances are basically the same in the three samples, in spite of the different statistical occupancy of the X site (Fe/Ca ratio ranging from ~ 3.0 in sample MP18 to ~ 18.0 in sample MP17). This suggests that, at least up to 0.5 Ca atoms p.f.u., no deformation of the dodecahedron geometry is sensed by the Fe cations and confirms a similar hypothesis suggested by Amthauer *et al.* (1976). These authors measured the Mössbauer spectra of a number of natural Fe-rich garnets with variable Ca contents and found virtually invariable isomer shift values of the Fe²⁺ dodecahedral doublet. The Mössbauer experiments performed on our garnets (Quartieri *et al.*, 1993) should give more insight on this subject.

The values of the Debye-Waller factors derived from the EXAFS analysis for the two Fe-O bond distances (see the last two columns of Table 3) are particularly interesting: σ_2^2 (relative to the longer Fe-O dodecahedral distance) is much greater than σ_1^2 (relative to the shorter Fe-O distance) for all the garnets examined. This result suggests that the longer Fe-O distances are affected by a greater disorder. Since the EXAFS phenomenon takes place in a time scale much shorter than the time scale of the atomic motion, it is like an instantaneous 'snapshot' of the atomic configuration. However, EXAFS experiments generally require much longer time than molecular vibrations, which means that we perform a time-average over such configurations. Other than this dynamic disorder, the σ^2 factors can also be

affected by static disorder, due for example to the adsorbing species being placed in two different coordination sites, or in slightly different sub-sites of the same polyhedron.

The hypothesis of a static disorder in the X site of garnets, due to an ordering of iron in different dodecahedral sub-sites, was suggested by Kleber *et al.* (1969) for a natural pyrope and by Cressey (1981) for almandine-grossular solid solutions, but was ruled out by Haselton and Westrum (1980) and recently by Armbruster *et al.* (1992). These authors performed a single-crystal X-ray diffraction study on a series of synthetic pyrope-almandine garnets at 100 and 293 K and did not find any evidence of a sub-site ordering of the cations in the X site. The same conclusion was reached by Geiger *et al.* (1992) from a combined temperature-dependent ^{57}Fe Mössbauer and single-crystal X-ray diffraction study of end-member almandine at 100, 293, 420 and 500 K: this study showed no off-centre position for eighth-coordinated Fe^{2+} , but otherwise confirmed the strongly anisotropic thermal motion of this cation, already observed by many other authors (Gibbs and Smith, 1965; Zemann and Zemann, 1961; Novak and Gibbs, 1971; Meagher, 1975; Oberti, pers comm., 1991). In particular, the X-ray results at increasing temperatures showed a larger increase of the longer Fe-O distance ($\Delta d = 0.017 \text{ \AA}$) compared with the shorter Fe-O bond ($\Delta d = 0.006 \text{ \AA}$). Both the magnitude and the anisotropy of the vibrational amplitudes were much greater for Fe^{2+} than for O and this is characteristic of an atom that exhibits anisotropic motion within a more rigid oxygen coordination polyhedron. This behaviour was confirmed by the same authors by the calculation of the difference displacement amplitudes (ΔU 's) along the bonding vectors (Chandrasekhar and Bürgi, 1984; Bürgi, 1989; Armbruster *et al.*, 1990). A strong non-rigid behaviour was noted for the dodecahedron site: ΔU values along the longer Fe-O bond increase with temperature whereas ΔU values along the shorter Fe-O bond remain almost unchanged. This was explained in terms of a higher dynamic disorder of the X cation within the plane defined by the 4 oxygens with the longer bond distances. The largely different Debye-Waller factors obtained in the present study from the EXAFS analysis for the two independent Fe-O distances, can be easily explained on the basis of this strong anisotropic thermal disorder, which seems to be dominant over the structural one (Geiger *et al.*, 1992); moreover they might be considered a confirmation of the non-rigid behaviour of the dodecahedron in comparison with the other coordination polyhedra present in the garnet structure.

Conclusions

This study shows that highly reliable structural information can be extracted from XAS spectra, regarding both accurate first-neighbour distances (with deviations less than 0.02 \AA with respect to X-ray single crystal values) and mean square relative displacement parameters. The largely different values of the Debye-Waller factors derived from the EXAFS analysis for the two independent Fe-O bond distances are in qualitative agreement with the anisotropic thermal motion obtained for the X cation by single-crystal X-ray diffraction studies and might be related to the dynamical nature of the dodecahedral site disorder.

The coordination distances of iron obtained from the EXAFS analysis are very similar for the three samples, indicating an Fe structural environment nearly independent on the variable Fe/Ca ratio of the cations sharing the same crystallographic X site. It should prove very interesting to compare the calcium local 8-fold coordination geometry as derived on the same samples from the absorption spectra obtained at the Ca K-edge, since Fe might strongly compete with Ca atoms in controlling the REE crystallographic behaviour in garnets falling within this compositional range. EXAFS studies on this topic are in progress.

Acknowledgements

Italian CNR and MURST are acknowledged for financial support. Prof. Basso (University of Genova) kindly supplied Bric Canizzi garnet; the authors are greatly indebted to Prof. Rivalenti, Dr. Mazzucchelli, and Dr. Parenti (University of Modena) for providing the Ivrea-Verbanò rock samples, for many useful discussions and their help in improving the manuscript. A particular acknowledgement is due to Dr. Oberti (University of Pavia) for the single crystal X-ray diffraction measurements and for the helpful discussion. Computing time was made available by CICAIA (University of Modena).

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