

EXAFS: Determination of cation distribution in spinels

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Abstract. In oxidic spinels containing transition metal ions, the tetrahedral and octahedral bond distances differ by less than 0.25 Å. Therefore, in the case of a cation occupying both the sites, the normalized EXAFS for first coordination shell gives the average bond distance and average coordination number respectively over all the bonds and the positions of the cation under investigation. EXAFS analysis of fourteen mixed lithium ferrite spinels was carried out to show how the average bond distance can fruitfully be used to obtain the exact cation distribution, in conformity with X-ray diffraction data.

Keywords. EXAFS technique; cation distribution; spinels; X-ray diffraction data; spectrometer; average bond length; average coordination number.

1. Introduction

The properties of oxide spinels are known to depend on the charge and site distribution of the cations. The distribution of cations in the tetrahedral and octahedral sites can be estimated from knowledge of the size and site preference of a cation and the nature of the chemical bond. X-ray diffraction data together with information on the above parameters help us to predict the cation distribution with a fair degree of accuracy.

The transition metal ions owing to their several possible oxidation states, pose serious problems in deciding site distribution in spinel structure. It is further complicated by the fact that two or more metal ions in a compound may have isoelectronic structure. In such a situation X-ray diffraction data alone do not give unambiguous cation distribution (Kulkarni 1970). Also, when the cation under investigation has a small, either tetrahedral (site-A) or octahedral (site-B) site preference energy, then, in the presence of other cation, it is very difficult to estimate the fraction of a given cation present at A-site and B-site. In such cases, Mössbauer spectroscopy (De Grave *et al* 1976) or neutron diffraction is known to give the cation distribution. The X-ray absorption process is very specific about the state of the absorbing atom, i.e. electronic structure, nature of bond, bond distance, type of environment, coordinating atoms, etc. However, so far, X-ray spectroscopic technique has not been used to estimate the distribution of cation in the compound. We attempt in this paper to show how easily and quickly the EXAFS technique gives the cation distribution in the lattice.

2. Preparation of materials

Fourteen different mixed lithium ferrite spinels with general chemical formula $\text{Li}_x\text{M}_x\text{N}_{1-2x}\text{Fe}_2\text{O}_4$ (where M stands for either chromium, manganese, iron or cobalt; N for either zinc or magnesium; and subscript x takes one of the values 0.0, 0.25,

0.50) were prepared by sintering the mixture at 1000°C for 120 h (Economos 1955). The formation of the compounds was confirmed by X-ray diffraction studies. All the observed reflections were indexed and their intensities compared with data in the earlier work of Bisht (1986). All the compounds were found to crystallize in a cubic symmetry without any trace of impurity and superlattice lines.

3. Experimental technique

An automated linear spectrometer of the Johansson type, developed by Deshpande *et al* (1991), was used to record the X-ray absorption spectrum. High X-ray flux was obtained from a rotating anode X-ray tube (Rigaku RV200) with focus size of 0.5 mm × 10 mm. The linear motion of the crystal and the receiving slit including the detector assembly was achieved by DC motors controlled by a computer. Position sensing was achieved by optical encoders. The X-ray incident intensity I_0 and transmitted intensity I were measured using a (Na: I) scintillation detector by keeping the sample alternately in and out of the path of the X-ray beam. The spectrometer

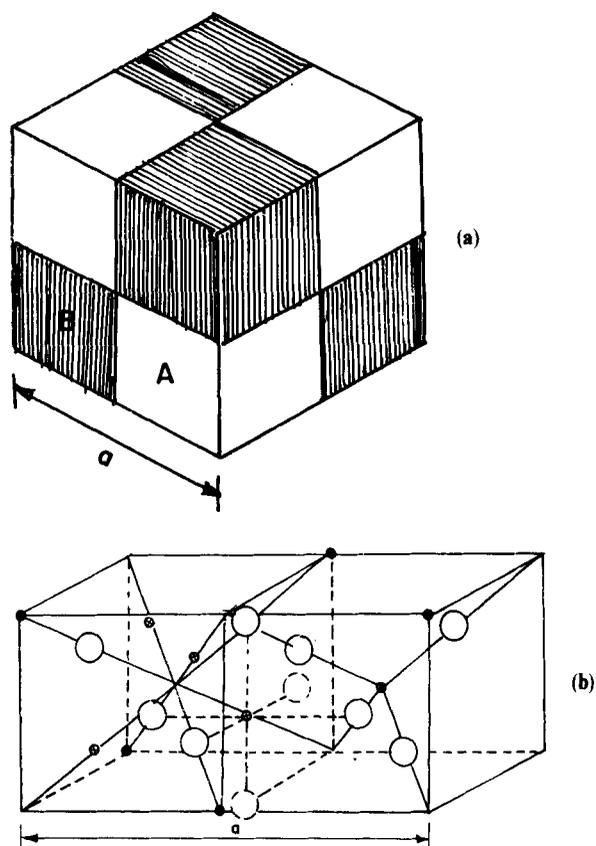


Figure 1. a. The eight octants in the unit cell. The shaded and non-shaded octants are occupied by octahedral and tetrahedral metal ions respectively, and b. Two adjacent octants of the spinel structure. \circ , O^{2-} ions, \otimes , octahedral ions; \bullet , tetrahedral ions and \circ , O^{2-} ions outside the octant.

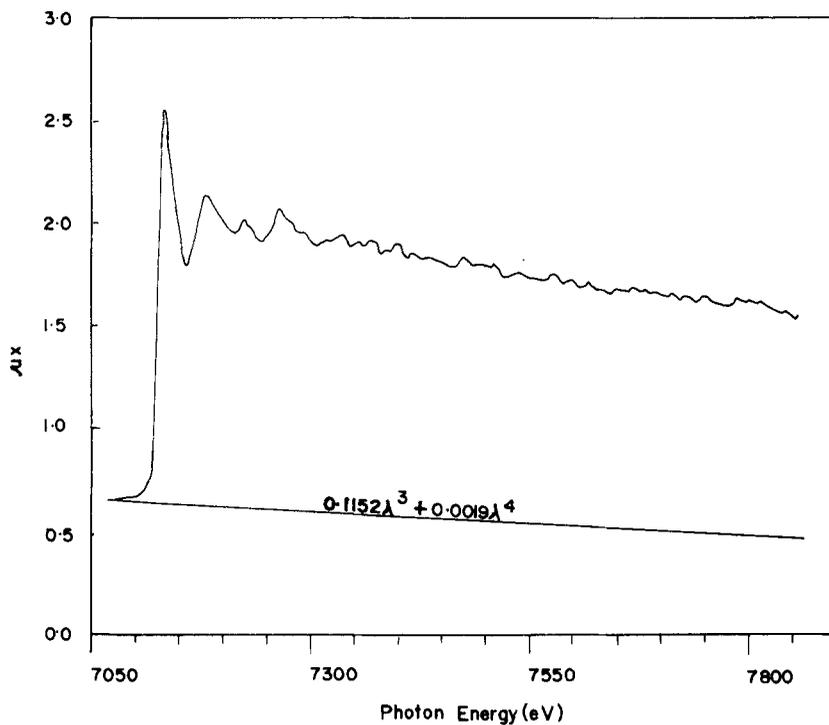


Figure 2a. For caption, see p. 247.

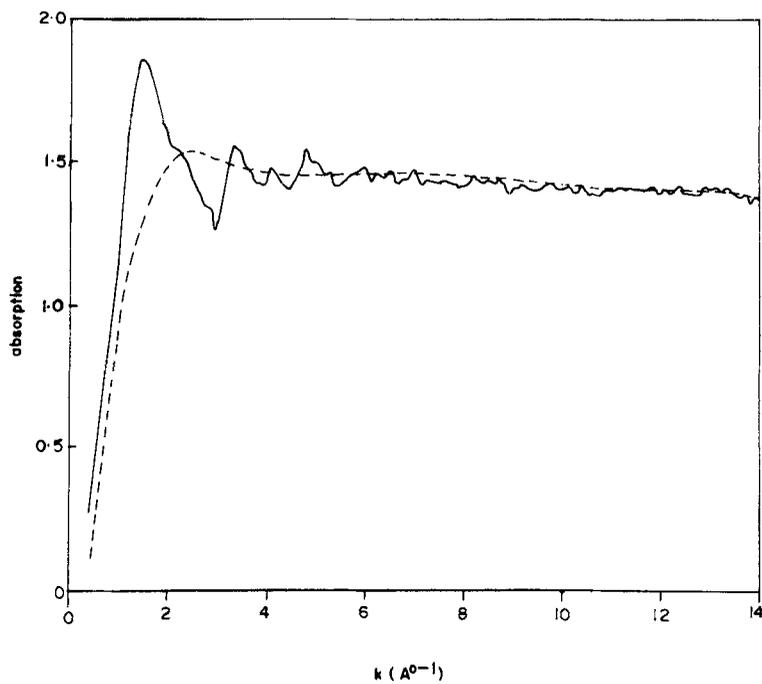


Figure 2b. For caption, see p. 247.

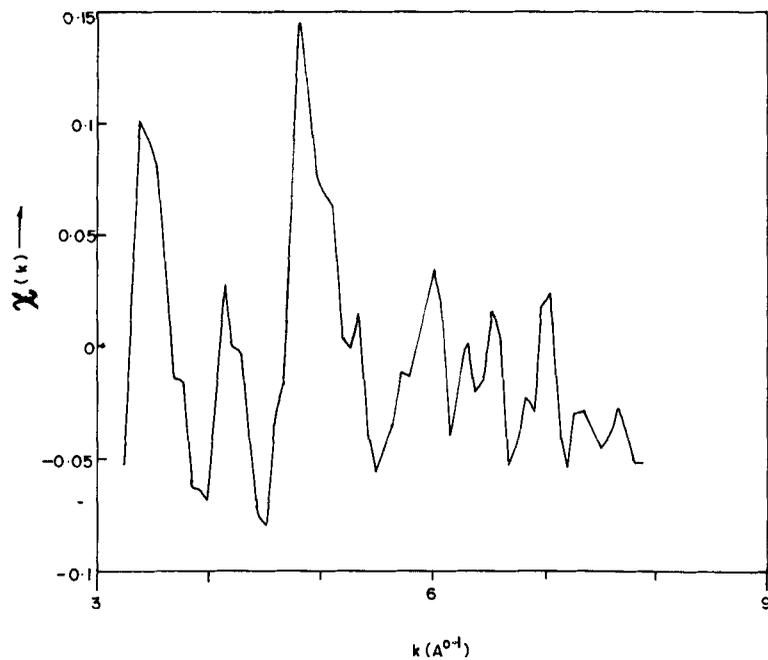


Figure 2c. For caption, see p. 247.

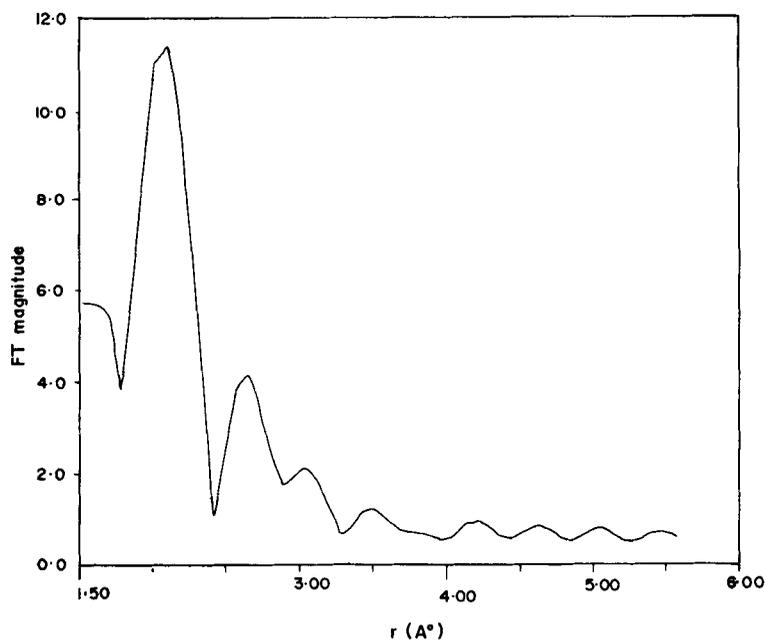


Figure 2d. For caption, see p. 247.

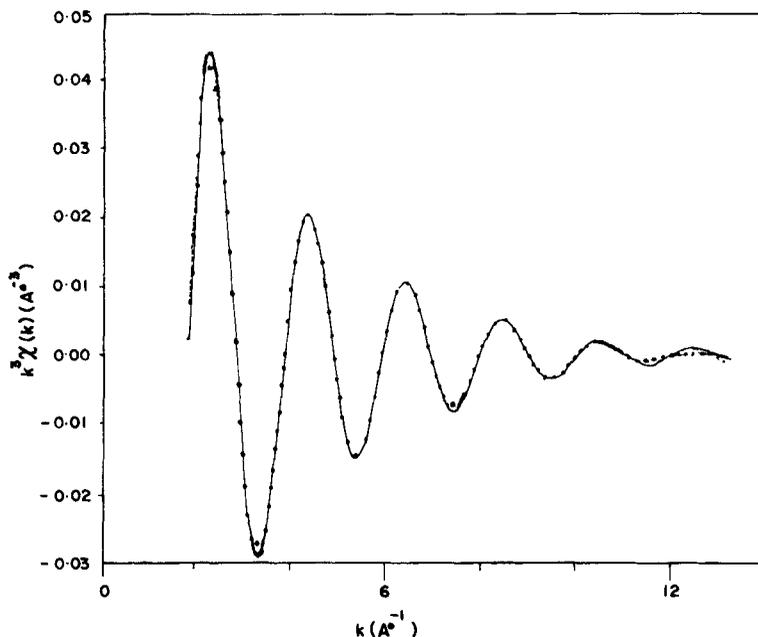


Figure 2. a. X-ray absorption spectrum of K-Fe edge in ZnFe_2O_4 with background fitting by a Victoreen function (bottom line), b. fitting of smooth function (dashed line) over the EXAFS, c. EXAFS function obtained from the spectrum of figure 2b, d. radial distribution function and e. comparison between experimental EXAFS spectrum of Fe in ZnFe_2O_4 (dotted) and theoretical (continuous).

was equipped with a silicon crystal ($\text{Si}(111)$, $d = 3.135 \text{ \AA}$) as a monochromator, of size $10 \text{ mm} \times 50 \text{ mm}$. The Rowland circle radius was 400 mm .

EXAFS spectra of iron in all the compounds were recorded in fixed time mode ($t = 8 \text{ sec}$). The increment θ , before the preabsorption edge, in the XANES region, and in EXAFS was, respectively, 0.025° , 0.0025° and 0.01° . The complete spectrum (about 700 eV above the inflection point) was recorded in 75 min . The width of the receiving slit was $50 \mu\text{m}$. The spectra were recorded using an X-ray tube operating at 15 kV and 60 mA .

4. EXAFS analysis

EXAFS function $\chi(k)$ (Sayers *et al* 1971) is defined in terms of atomic absorption coefficient as

$$\chi(k) = \frac{\mu(k) - \mu_0(k)}{\mu_0(k)},$$

where $\mu(k)$ is the absorption by an atom surrounded by ligand and $\mu_0(k)$ the absorption by an atom in the free state.

The EXAFS function $\chi(k)$, based on single scattering approximation of the ejected photoelectron by the atoms in the immediate vicinity of the absorbing atom, is given

by Sayers *et al* (1971) as

$$\chi(k) = \sum_j A_j(k) \sin\{2kR_j + \delta_j(k)\}, \quad (1)$$

where the summation is over all the shells and for all kinds of atoms, R_j is the average near-neighbour distance of the j th coordination shell from the absorbing atom, $\delta_j(k)$ the composite phase shift, and k the photoelectron wavenumber given by

$$k = \left[\frac{2m}{\hbar^2} (E - E_0) \right]^{1/2}.$$

Furthermore, E is the energy of the ejected photoelectron, E_0 the threshold energy, m the mass of the electron, and $A_j(k)$ the amplitude function given by

$$A_j(k) = - \sum_j \frac{N_j}{kR_j^2} F_j(k, \pi) \exp(-2R_j/\lambda_j) \cdot \exp(-2k^2\sigma_j^2).$$

In the above expression N_j is the number of atoms in the j th shell, σ_j the r.m.s. deviation about R_j , $F_j(k, \pi)$ the back scattering amplitude of the scatterer atom of the j th coordination shell, and λ_j the mean free path for the inelastic scattering.

The analysis of EXAFS data for obtaining structural information (N_j , R_j , α_j , λ_j) generally proceeds by the use of Fourier transform and nonlinear least square technique. $|\phi(r_j)|$, the radial structure function for the j th coordination shell, can be obtained from normalized $\chi(k)$ as

$$\phi(r) = (1/2\pi)^{1/2} \int_{k_{\min}}^{k_{\max}} k^n \chi(k) \exp(-2ikr) WF(k) dk, \quad (2)$$

where $WF(k)$ is the window function and the integral is extended over the available k -range.

The EXAFS function $\chi(k)$ for j th coordination shell is obtained by taking the inverse Fourier transform of the radial structure function as

$$\chi_j(k) = (2/\pi)^{1/2} (1/k^n) WF(k) \int_{R_{1j}}^{R_{2j}} \phi(r) \exp(-2ikr) dr. \quad (3)$$

The amplitude envelope function $A_j(k)$ of (1) is modulated by the empirical relation

$$A_j(k) = C_0 \exp(-C_1 k^2/k^{C_2}) \quad (4)$$

and the phase shift function $\delta_j(k)$ is expressed by the relation

$$\delta_j(k) = A_0 + A_1 k + A_2 k^2. \quad (5)$$

Thus the empirical relation for EXAFS function for j th coordination shell is written as

$$\chi_j(k) = C_0 \exp(-C_1 k^2/k^{C_2}) \sin(2kR_j + A_0 + A_1 k + A_2 k^2). \quad (6)$$

The structural parameters for any coordination shell are determined by fitting the empirical relation given by (6) with $\chi_j(k)$ derived from (1).

Knowledge of composite phase shift $\delta_j(k)$ (phase shift due to central absorbing atom and the scatterer from the j th coordination shell) is essential for evaluation of bond length from the EXAFS function. Normally $\sigma_j(k)$ is obtained from EXAFS measurements of a model compound of known structure or from the theoretical

calculation developed by Lee *et al* (1977a, b) and Teo *et al* (1979). The former method depends on the phase transferability, the validity of which has been questioned by Cargill (1984) and Paul (1985) independently. The latter involves complicated calculations and Bunker *et al* (1983) have shown them to be less reliable than those derived from model compounds. They give only qualitative success according to Paul (1985). Because of limitations, we have attempted to determine the composite phase shift from experimental EXAFS peaks for various values of k .

Various workers (Lytle *et al* 1975; Lee *et al* 1977a, b; Eccles 1978; Teo *et al* 1979; Halaka *et al* 1984a) have given different empirical relations for the phase shift. In all these relations phase shift is divergent as k tends to ∞ . According to Levinson's (1964) theorem, Halaka *et al* (1984b) concluded that the true phase shift should be bounded, defined at $k=0$ and $k=\infty$ simultaneously, and to satisfy the above requirement have suggested the exponential form of phase shift as

$$\delta_j(k) = B_0 + B_1 \exp(-B_2 k). \quad (7)$$

The total phase shift is therefore given by

$$\phi_j(k) = 2R_j k + B_0 + B_1 \exp(-B_2 k) \quad (8)$$

and can be obtained experimentally for various values of k corresponding to different EXAFS peaks and is given by the expression

$$2R_j k + B_0 + B_1 \exp(-B_2 k) = [n + (1/2)]\Pi, \quad (9)$$

where $n=0, 2, 4, \dots$ for maxima and $n=1, 3, 5, \dots$ for minima in the EXAFS of the j th coordination shell.

The constants R , B_0 , B_1 , B_2 can be determined by the least square fit technique (Bhongale 1992). Mahato *et al* (1987) have shown that accurate determination of bond distance, R , by the above method is possible. Knowing B_0 , B_1 , B_2 from (9) and using them in (7), $\delta_j(k)$, the composite phase shift, can be determined for various values of k . Using these $\delta_j(k)$ for various values of k in (5) and taking the least square fit (Bhongale 1992), A_0 , A_1 , A_2 are determined. Further, by using the values of A_0 , A_1 , A_2 in ABRF program (Indrea and Aldea 1980), near-neighbour distance and number of coordinating atoms are obtained. Among the various methods of phase shift determination, the present method is simple and reliable.

The analysis was carried out by using a self-contained Fortran program (ABRF) which utilizes the empirical relation of $\chi(k)$ given by (6). The raw data was first smoothed out, a suitable background correction applied, and then EXAFS function for first coordination shell isolated by using Fourier transform technique. A weighting function k^n ($n=3$), as suggested by Mahato *et al* (1987), was used.

The present system of 14 compounds is structurally and chemically similar, with threshold energy, E_0 , in the range 7119 eV to 7123 eV.

It is interesting to note that k^3 multiplication to $\chi(k)$ has the effect of weighting EXAFS more uniformly over the range $k=3 \text{ \AA}^{-1}$ to 14 \AA^{-1} . In other words, multiplication by k^3 to $\chi(k)$ and then taking the Fourier transform has the effect of making the Fourier transform less sensitive to threshold energy, E_0 , or reduces the error due to wrong selection of E_0 to a minimum at large value of k . This permits the variation in E_0 in its neighbourhood without affecting $\chi(k)$ significantly. This step in the analysis is important as it prevents the larger amplitude oscillations from dominating the smaller ones in determination of the interatomic distances, which

depend only on the frequency of EXAFS oscillations and not on the amplitude of the sinusoidal function given by (1). Also, the k^3 weighting assures that the chemical effects on EXAFS, which are more significant at small values of k , are effectively reduced to sufficiently low levels. Thus the incorporation of k^3 with $\chi(k)$ can generate much cleaner EXAFS data.

It is well known that spinels are an ordered mixture of zinc blend and rock salt structure (Ballal *et al* 1977). A unit cell of spinel contains eight formula units of AB_2O_4 (figure 1a). The A-site cation is surrounded by four anions and hence in a unit cell there are $8 \times 4 = 32$ A-X type bonds per A-type cation. Similarly, there are $2 \times 8 \times 6 = 96$ B-X type bonds. The B-site cation is surrounded by six anions and each formula unit contains two B-type cations. Therefore one can assume that there are 48 B-X type bonds per B-type cation in a unit cell (figure 1b).

If in a compound the same type of cation is present at both the sites, then the cation at A site will have R_A as the radius of the first coordination shell and another similar cation at B site will have R_B as the radius of the first coordination shell. Generally, in the spinel structure these two radii are known to differ by less than 0.25 Å. Therefore EXAFS will reveal average bond distance given by

$$R_{\text{EXAFS}} = \frac{32xR_A + 48yR_B}{32x + 48y}, \quad (10)$$

where x and y are the fractions of cation present at A and B sites respectively.

Rearranging the terms, we get the expression for the cation distribution as

$$x = \frac{3(x+y)(R_B - R_{\text{EXAFS}})}{3R_B - 2R_A - R_{\text{EXAFS}}}, \quad (11)$$

where $(x+y)$ is the total number of atoms (of interest) per formula present in the compound. In this expression R_A and R_B can be known from crystallographic data and R_{EXAFS} is determined by using EXAFS data.

It can also be shown very easily that, in the spinel, the average coordination number of one type of cation occupying both the sites can be expressed as

$$N_{\text{avg}} = \frac{32x + 48y}{8(x+y)}. \quad (12)$$

5. Results and discussion

Figure 2a shows the typical EXAFS spectrum of k -absorption edge of Fe in the compound $ZnFe_2O_4$ along with the fitting of the background by Victoreen function of the form $A\lambda^3 + B\lambda^4$ to the pre-edge data and extrapolating this into the EXAFS region. Figure 2b shows the EXAFS spectrum after background removal and fitting with a smooth function as an approximation for μ_0 . The fine structure containing information from various coordination shells obtained from figure 2b is shown in figure 2c. The Fourier transform of this EXAFS function in the photoelectron wave vector, k , over the range from 3 \AA^{-1} to 14 \AA^{-1} (computed using Filon's quadrature formula of Abramowitz *et al* 1965) is shown in figure 2d. The normalized EXAFS function, $\chi(k)$ (figure 2e), for the first coordination shell is obtained by taking the inverse Fourier transform of the first shell peak in the range 1.775 \AA to 2.428 \AA . Figure 2e

also shows the fitting of experimental $\chi(k)$ with the theoretically calculated $\chi(k)$. The slight mismatch between them at large k values is probably due to truncation ripple in the windowing process in the Fourier transform.

The distribution of Fe^{3+} ions calculated by using (11) is in fair agreement with those reported by Bisht (1986) using X-ray and neutron diffraction techniques (table 1). In an ideal case, the numbers of coordinating atoms at A and B sites are 4 and 6. In reality some ions occupy both the sites (in the present case Fe^{3+} ions) and therefore the concept of average coordination which in fact, weighted average of occupied sites at possible voids given by (12) and the figure therefore may be fraction. The mere average cannot show a specific site and hence both A and B sites are involved. For example, ZnFe_2O_4 , which is a normal spinel, has Fe^{3+} ions at B site alone. Therefore the N_{avg} would be closer to 6 (in the present case, it is 5.96) and a slight deviation may be assigned to a small fraction $x = 0.04$ going to A site. The basis of fraction x lies in the average bond length R_{EXAFS} , which is not the same as the length intercepted between the anion and the cation at a given site, but is a proper mixture of bonds of both the sites and thus provides information on the degree of inversion. Equations (10) and (11) show that the accuracy in determination of mean bond length, R_{EXAFS} , is the same as the accuracy of the degree of inversion x . The bond lengths determined from EXAFS data are accurate (within $\pm 0.01 \text{ \AA}$) and hence the degree of inversion can be estimated with high accuracy.

It is worth while to mention here that such a correlation between the cation distribution and mean bond lengths has not been given by any of the earlier workers. It is not mere surmise that changes in the site distribution show changes in the mean bond distance. In the case where the ion finds a unique place at a given site, the mean value of bond distance, R_{EXAFS} , is very close to the crystallographic interatomic

Table 1. Fraction of Fe present at A-site.

| Compound | R_A (\AA) | R_B (\AA) | R_{EXAFS} (\AA) | x | | |
|---|---------------------------|---------------------------|--|----------------------|--------|-------------------|
| | | | | X-ray diffraction | | EXAFS analysis |
| $\text{Li}_{.5}\text{Cr}_{.5}\text{Fe}_2\text{O}_4$ | 1.869 | 2.034 | 1.968 | 1.00 | 1.00* | 1.00 |
| $\text{Li}_{.5}\text{Mn}_{.5}\text{Fe}_2\text{O}_4$ | 1.951 | 2.006 | 1.987 | 0.90 | | 0.88 |
| $\text{Li}_{.5}\text{Fe}_{2.5}\text{O}_4$ | 1.919 | 2.028 | 1.995 | 1.00 | | 0.98 |
| $\text{Li}_{.5}\text{Co}_{.5}\text{Fe}_2\text{O}_4$ | 1.824 | 2.082 | 1.996 | 0.85 | | 0.86 |
| $\text{Li}_{.25}\text{Mg}_{.5}\text{Fe}_{2.25}\text{O}_4$ | 1.869 | 2.034 | 1.968 | 0.95 | 0.96** | 0.81 |
| $\text{Li}_{.25}\text{Zn}_{.5}\text{Fe}_{2.25}\text{O}_4$ | 1.933 | 2.038 | 2.032 | 0.50 | 0.50* | 0.47 |
| $\text{Li}_{.25}\text{Cr}_{.25}\text{Mg}_{.5}\text{Fe}_2\text{O}_4$ | 1.948 | 2.003 | 1.983 | 0.88 | 0.88* | 0.91 |
| $\text{Li}_{.25}\text{Mn}_{.25}\text{Mg}_{.5}\text{Fe}_2\text{O}_4$ | 1.912 | 2.010 | 1.976 | 0.90 | | 0.89 |
| $\text{Li}_{.25}\text{Co}_{.25}\text{Mg}_{.5}\text{Fe}_2\text{O}_4$ | 1.839 | 2.073 | 1.987 | 0.85 | 0.87** | 0.93 |
| $\text{Li}_{.25}\text{Cr}_{.25}\text{Zn}_{.5}\text{Fe}_2\text{O}_4$ | 1.912 | 2.034 | 2.010 | 0.50 | 0.50* | 0.53 |
| $\text{Li}_{.25}\text{Mn}_{.25}\text{Mg}_{.5}\text{Fe}_2\text{O}_4$ | 1.991 | 1.975 | 1.978 | 0.50 | | 0.54 |
| $\text{Li}_{.25}\text{Co}_{.25}\text{Zn}_{.5}\text{Fe}_2\text{O}_4$ | 1.936 | 2.036 | 2.018 | 0.45 | | 0.49 |
| MgFe_2O_4 | 1.928 | 2.027 | 1.990 | 0.90 | 0.95** | 0.94 |
| ZnFe_2O_4 | 1.917 | 2.061 | 2.058 | 0.00 | | 0.04 |

*Neutron diffraction; **Mössbauer spectroscopy;
 R_A and R_B are the crystallographic bond distance.

Table 2. Average near-neighbours for Fe³⁺.

| Compound | x (From EXAFS) | N _{EXAFS} (Observed) | N _{avg} (Calculated) |
|--|-------------------|----------------------------------|----------------------------------|
| Li _{0.5} Cr _{0.5} Fe ₂ O ₄ | 1.00 | 5.13 | 5.00 |
| Li _{0.5} Mn _{0.5} Fe ₂ O ₄ | 0.88 | 5.10 | 5.12 |
| Li _{0.5} Fe _{2.5} O ₄ | 0.98 | 5.31 | 5.32 |
| Li _{0.5} Co _{0.5} Fe ₂ O ₄ | 0.86 | 5.15 | 5.14 |
| Li _{0.25} Mg _{0.5} Fe _{2.25} O ₄ | 0.81 | 5.18 | 5.19 |
| Li _{0.25} Zn _{0.5} Fe _{2.25} O ₄ | 0.47 | 5.61 | 5.58 |
| Li _{0.25} Cr _{0.25} Mg _{0.5} Fe ₂ O ₄ | 0.91 | 5.13 | 5.09 |
| Li _{0.25} Mn _{0.25} Mg _{0.5} Fe ₂ O ₄ | 0.89 | 5.00 | 5.11 |
| Li _{0.25} Co _{0.25} Mg _{0.5} Fe ₂ O ₄ | 0.93 | 5.41 | 5.07 |
| Li _{0.25} Cr _{0.25} Zn _{0.5} Fe ₂ O ₄ | 0.53 | 5.56 | 5.47 |
| Li _{0.25} Mn _{0.25} Mg _{0.5} Fe ₂ O ₄ | 0.54 | 5.63 | 5.46 |
| Li _{0.25} Co _{0.25} Zn _{0.5} Fe ₂ O ₄ | 0.49 | 5.54 | 5.51 |
| MgFe ₂ O ₄ | 0.94 | 4.99 | 5.06 |
| ZnFe ₂ O ₄ | 0.04 | 6.00 | 5.96 |

distance. For example, in the case of ZnFe₂O₄, XRD gives Fe–O distance as 2.06 Å and EXAFS bond distance has been determined as 2.058 Å.

Table 1 also includes results of Mössbauer spectroscopy (Bhongale 1992). They are in good agreement with the EXAFS results.

Table 2 gives the values of average coordination number calculated using the distribution parameter, *x*, in (12), obtained from EXAFS. The values of *N*_{avg} (calculated) and *N*_{EXAFS} (observed) also show a good agreement. It is also observed from table 2 that the changes in the site distribution, *x*, alter the average coordination of Fe³⁺ ions. This is because the proportion of Fe³⁺ ions at A and B sites depends on the concentration of Fe³⁺ ions in the compound along with the other cations and relative site preferences of Fe³⁺ ions *vis-a-vis* other cations in the lattice.

6. Conclusion

EXAFS analysis appears to be a useful tool for predicting the cation distribution in various compounds wherein the crystal structure, different coordinations and their bond lengths are known.

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