Temperature Dependence of Disorder and Correlation Effects in the Almandine X-Site

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Abstract XAFS measurements in the temperature range 20-473 K at the Fe K-edge of synthetic almandine ($\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) allow us to determine the T-dependence of the XAFS Debye-Waller (DW) factors for each of the two crystallographically independent Fe-O bond distances (Fe(1)-O and Fe(2)-O). The XAFS DW factor of the longer Fe(2)-O bond is larger and has a greater T-dependence than the shorter Fe(1)-O bond, which remains constant over the measured T range. The XAFS DW factors are compared with the uncorrelated part of the DW factors derived from a single-crystal X-ray diffraction (XRD) study on almandine and are interpreted on the basis of the Einstein model. A comparison with diffraction data shows that the shorter Fe(1)-O bond is significantly affected by correlation in the atomic displacements.

1. INTRODUCTION

The structure of garnet (general formula $\text{X}_3\text{Y}_2\text{Z}_3\text{O}_{12}$) can be described as a three dimensional framework consisting of corner-sharing SiO_4 tetrahedra and YO_6 octahedra. The structure also contains triangular dodecahedra, XO_8 , consisting of eight oxygens coordinating divalent cations. In almandine, $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, the dodecahedral X-site is occupied by Fe^{2+} and is characterized by two crystallographically independent X-O bonds (labelled X(1)-O and X(2)-O, where the former is shorter than the latter). Geiger et al [1] undertook a single-crystal XRD investigation on synthetic almandine in the temperature range 100-500K. Based on a difference mean-square displacement parameter analysis [2], they computed the $\Delta U = U_{\text{Fe}} - U_{\text{O}}$ values (each U being the component of the XRD atomic displacement parameter in the bonding direction) along the two crystallographically independent Fe-O bonding vectors and concluded that the motion of Fe in the dodecahedral cavity is strongly anisotropic. The ΔU values along the longer Fe(2)-O vector are larger and more strongly T-dependent than those along the shorter Fe(1)-O bond. No T-dependent investigation of garnet has been performed by means of XAFS measurements. This technique, when combined with XRD, can provide complementary information on local atomic displacements. This study is the first example of such a combined approach applied to crystalline solids of geological interest.

1.1 The Debye-Waller factor in XAFS and XRD

In crystalline solids, the XAFS DW is fundamentally different from that in XRD. The former is particularly sensitive to short-range correlations of atomic motions whereas, in the diffraction experiment, the influence of local inter-atomic correlation effects on the DW factor is lost through long-range averaging. The XAFS DW factor is a Mean Square *Relative* Displacement (MSRD) between absorbing and backscattering atoms, whereas from the XRD experiment one may obtain the Mean Square *absolute* Displacements (MSD) of atoms along the bond direction. The difference MSRD-MSD, called the Displacement Correlation Function (DCF), is a measure of the degree of in-phase vibrational motion of the atoms along the bond direction. This term vanishes if the absorbing atom and the backscattering atom vibrate independently. If, on the contrary, the two atoms move as a rigid unit, the last term will reduce strongly the amplitude of the DW factor. Hence, the combination of XRD and XAFS data permits an estimate of the extent of the correlation in motion along interatomic vectors.

2. EXPERIMENTAL DETAILS AND DATA ANALYSIS

The Fe K-edge XAFS spectra were collected in transmission mode at seven different temperatures ranging from 20 to 473 K at GILDA-CRG (ESRF, Grenoble, France), operated at 6 GeV. A double crystal Si(311) monochromator was used to produce an unfocused monochromated beam; a detuning of 80% was applied to eliminate higher harmonics. The experimental data have been analyzed using standard background subtraction and Fourier Filtering, whereas the determination of the structural parameters has been accomplished through FEFFIT (UWXAFS package) [3], which uses theoretical phase functions and amplitudes from FEFF6 software [4,5] to simulate all possible single and multiple scattering paths of the photoelectron. The magnitudes of selected Fourier Transforms (FT) at different temperatures are shown in Fig. 1.

3. TEMPERATURE DEPENDENCE OF THE XAFS SPECTRA

As shown in Fig. 1, the structural features of the almandine spectra, in terms of the peak positions and shapes of the FT, remain essentially unchanged over the measured temperature range, implying that no phase transformation occurred. The effect of temperature is largely on the height of the FT peaks, which decrease measurably for all the coordination shells with increasing temperature. We analyse the first two coordination shells, both consisting of 4 oxygen atoms, which are strongly overlapping in the first peak of the FT. The results of the XAFS analysis relative to the first peak shown in Fig. 1 are reported in Table 1. The two calculated bond distances Fe(1)-O and Fe(2)-O are in good agreement with those determined from

XRD. At each temperature the XAFS DW factor relative to the longer Fe(2)-O bond distance (σ^2_2) is larger than the one relative to the shorter Fe(1)-O bond (σ^2_1). Moreover, σ^2_2 has a larger T-dependence than σ^2_1 , which remains, in comparison, almost constant over the measured temperature range. These results confirm that the dynamic disorder in the X-site of almandine is strongly anisotropic.

Table 1 Results of the XAFS analysis at the different temperatures. The coordination numbers of the two oxygen shells were kept fixed to the crystallographic value (4).

T(K)	$\sigma^2_{\text{Fe(1)-O}}$ ($\text{\AA}^2$)	$\sigma^2_{\text{Fe(2)-O}}$ ($\text{\AA}^2$)	$R_{\text{Fe(1)-O}}$ ($\text{\AA}$)	$R_{\text{Fe(2)-O}}$ ($\text{\AA}$)	R_{fit}
20	0.008(1)	0.011(2)	2.211(7)	2.340(12)	0.03
77	0.008(1)	0.011(2)	2.213(7)	2.347(10)	0.02
100	0.008(1)	0.011(2)	2.210(8)	2.350(12)	0.02
200	0.008(1)	0.015(2)	2.216(7)	2.354(13)	0.02
300	0.008(1)	0.017(3)	2.216(7)	2.352(15)	0.04
373	0.009(1)	0.023(4)	2.219(8)	2.348(21)	0.04
473	0.011(2)	0.026(4)	2.216(8)	2.366(26)	0.04

Fig.1 FT magnitude of $k^2\chi(k)$ at selected temperatures.

4. COMPARISON WITH THE DW FACTORS FROM XRD AND VIBRATIONAL ANALYSIS

A comparison of absolute DW factors between XAFS and XRD is difficult, as, in both techniques, they are known to be affected by correlations between fit parameters and by subtle assumptions made during the data analysis. To avoid these problems, we used relative values normalized to the σ^2 value obtained for the lowest temperature, T_0 , for each technique (20K and 100K for XAFS and XRD experiments, respectively).

The temperature dependence of the DW factor is determined by the local vibrational dynamics related to the relative motion between the absorbing and the backscattering atoms. A fit using a single vibrational frequency characteristic of the bond calculated using the Einstein model is the simplest approach. The fitting parameter ν_E (Einstein frequency) may then be related to an effective bond strength, even if the relationship to the true vibrational frequencies is not that strictly present in complex systems. The differences $\Delta\sigma^2(T)$ between the MSRD at a given temperature and that at $T_0 = 20\text{K}$ have been fitted for both shells by: $\Delta\sigma^2(T) = h/2\mu\nu_E [\coth(h\nu_E/2k_B T) - \coth(h\nu_E/2k_B T_0)]$, where μ is the reduced mass of the Fe-O atomic pair.

The Einstein frequencies $\nu_E = 6.1\text{ THz}$ and 13.1 THz or, in wavenumbers, 207 cm^{-1} and 437 cm^{-1} are obtained for the longer and the shorter bonds, respectively. These results reflect the different effective bond-stretching force constants of the two crystallographically independent X-O bonds in the dodecahedral site of garnet. The Einstein based curves are shown in Fig.2 a,b together with the $\Delta\text{MSD} = \text{MSD}_T - \text{MSD}_{100\text{K}}$ results as obtained from XRD. One observes a good agreement between the T-dependence of ΔMSRD and ΔMSD for the longer Fe(2)-O bond, with a negligible contribution of the correlated motion (Fig. 2b). On the other hand, the ΔMSRD for the shorter bond is significantly lower than the ΔMSD from diffraction, indicating large in-phase Fe-O motion along this direction (Fig. 2a).

Fig.2 Temperature-dependence of ΔMSRD (open squares) (fitted with the Einstein model) and ΔMSD (black solid squares) relative to the shorter Fe(1)-O bond and the longer Fe(2)-O bond.

In summary, this study confirms the potential of combined XAFS and XRD investigations in clarifying the interatomic correlation part of the atomic displacement parameters: the comparison between the thermal disorder parameters probed by the two techniques on almandine reveals a good agreement between the T-dependence of the MSRD and the MSD of the longer Fe(2)-O bond, with a negligible contribution of correlated motion. Conversely, a large in-phase motion characterizes the shorter Fe(1)-O bond.

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