# Dynamic disorder and the $\alpha$ - $\beta$ phase transition in quartz-type FePO<sub>4</sub> at high temperature investigated by total neutron scattering, Raman spectroscopy, and density functional theory

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Quartz-type iron phosphate (FePO<sub>4</sub>) was studied by total neutron scattering and Raman spectroscopy up to 1150 K in order to investigate disorder and the mechanism of the  $\alpha$ - $\beta$  transition. The increasingly large underestimation of P-O and Fe-O distances in Rietveld refinements of the average long-range structure as compared to the bond lengths obtained from the pair distribution function as a function of temperature is a clear indication of the presence of significant dynamic disorder, particularly from 850 K up to and above the  $\alpha$ - $\beta$  transition near 980 K. A significant broadening of the Fe-O distance distribution is also observed. Reverse Monte Carlo modeling confirms the presence of such disorder with broadened angular distributions in this temperature range, in particular for the Fe-O-P and Fe-P-Fe distributions. The Raman spectrum, calculated using density functional theory, is in very good agreement with experiment. These calculations indicate that there is an inversion of two low-energy  $A_1$  vibrational modes with respect to AlPO<sub>4</sub>. The principle mode, which exhibits strong damping in the Raman spectrum above 850 K, is thus not a tetrahedral libration mode, but a mode that principally involves large amplitude translations of the Fe atoms along with a degree of oxygen displacement. The transition mechanism from a dynamic point of view is thus different from the transitions in SiO<sub>2</sub> and AlPO<sub>4</sub>. The strong damping of this mode is also further evidence of a high degree of dynamic disorder, which is different from the disorder observed in  $SiO_2$  and AIPO<sub>4</sub>. This mode does not exhibit any significant softening with temperature near the phase transition, which is further evidence that the  $\alpha$ - $\beta$  transition is not of the simple displacive type. The difference in behavior between FePO<sub>4</sub> and the other quartz homeotypes arises from the weaker bonding between the  $3d^5$  transition metal cation and oxygen.

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# I. INTRODUCTION

Iron phosphate (FePO<sub>4</sub>) belongs to the  $\alpha$ -quartz homeotypic group of materials. As it is a model, simple oxide,  $\alpha$ -quartz is of great interest from a fundamental point of view in Earth science due to its natural abundance and from a technological point of view due to its piezoelectric properties. The piezoelectric properties of  $\alpha$ -quartz are limited due to a relatively low piezoelectric coupling coefficient and low thermal stability due to the  $\alpha$ - $\beta$  phase transition at 846 K and to the strong increase in dynamic disorder well below this temperature.<sup>1</sup> This dynamic disorder is related to thermally excited, rigid unit modes. In  $\alpha$ quartz homeotypes (GeO<sub>2</sub>, BeF<sub>2</sub>, PON,  $ABO_4$ : A = B, Al, Ga, Fe; B = P, As),<sup>2-6</sup> both the piezoelectric coupling coefficient and the thermal stability increase as a function of the structural distortion with respect to the more symmetrical hexagonal  $\beta$ -quartz structure type (P6<sub>4</sub>22 or P6<sub>2</sub>22 space group with Z = 3). The distorted, lower symmetry  $\alpha$ -quartz structure is trigonal  $(P_{3_1}21 \text{ or } P_{3_2}21 \text{ space group with } Z = 3)$ , and the unit cell is doubled along  $\mathbf{c}$  for  $ABO_4$  compounds due to cation ordering. The distortion can be described by two interrelated angles, the intertetrahedral bridging angle  $\theta$  and the tetrahedral tilt angle  $\delta$ , which is the order parameter for the  $\alpha$ - $\beta$  phase transition  $(\delta = 0^{\circ} \text{ for } \beta \text{-quartz}).^{7} \text{ FePO}_{4}$  exhibits atypical behavior as it is relatively highly distorted ( $\delta = 21.5^{\circ}$ )<sup>8,9</sup> with respect to  $\alpha$ -quartz ( $\delta = 16.3^{\circ}$ ); however, its thermal stability is only slightly higher.<sup>10–13</sup> The  $\alpha$ - $\beta$  phase transition occurs in FePO<sub>4</sub> at 980 K. As in quartz, dynamic disorder could be expected to increase prior to the phase transition, thereby limiting the use of this material for piezoelectric applications. A recent hightemperature synchrotron x-ray diffraction study and analysis of the lattice dynamics of FePO<sub>4</sub> confirms the importance of excited rigid-unit modes.<sup>13</sup> In addition, critical fluctuations of the order parameter were not found to be relevant for the  $\alpha$ - $\beta$ transition. The present study of FePO<sub>4</sub> at high temperature by total neutron scattering and Raman spectroscopy aims to provide an insight on the origin of the limited thermal stability of the  $\alpha$  phase and to investigate the dynamic disorder and the phase transition mechanism in this material.

## **II. EXPERIMENTAL**

### A. Sample preparation

FePO<sub>4</sub> powder was prepared by heating the commercial hydrate FePO<sub>4</sub>.xH<sub>2</sub>O up to 1673 K, which is higher that the melting point of anhydrous FePO<sub>4</sub>, followed by annealing in air at 963 K for 1 month. The structure was confirmed to be of the  $\alpha$ -quartz-type using x-ray diffraction data.

#### **B.** Total neutron scattering

FePO<sub>4</sub> was studied as a function of temperature on the General Materials Diffractometer (GEM) time-of-flight (TOF) neutron powder diffractometer<sup>14</sup> at the ISIS spallation source of the Rutherford Appleton Laboratory (RAL). There, 2.7 cm<sup>3</sup> of the  $\alpha$ -quartz-type phase were placed in an 8-mm-diameter cylindrical vanadium sample can in an RAL furnace equipped with a vanadium heating element. Detection was performed

using six banks of ZnS scintillators: bank 1 ( $6^{\circ} < 2\theta < 13^{\circ}$ ), bank 2 ( $14^{\circ} < 2\theta < 21^{\circ}$ ), bank 3 ( $25^{\circ} < 2\theta < 45^{\circ}$ ), bank 4 ( $50^{\circ} < 2\theta < 76^{\circ}$ ), bank 5 ( $79^{\circ} < 2\theta < 104^{\circ}$ ), and bank 6 ( $142^{\circ} < 2\theta < 149^{\circ}$ ). Data were obtained over a TOF range from 0.8 to 20 ms. Calibration runs were performed on a vanadium rod, the empty furnace, the empty can in the furnace, and the empty instrument in order to correctly account for background contributions and to normalize the data on an absolute scale. Total scattering data were acquired for approximately 4 h at each temperature to obtain the needed very good statistics, particularly in the important high-*Q* region, and to cover a wide range of momentum transfers for good real-space resolution. Additionally, the data were normalized with respect to a standard vanadium sample and corrected for absorption for Rietveld structure refinements.

## C. Structure refinements

Rietveld refinements for the  $\alpha$ - and  $\beta$ -quartz-type phases were performed using the program GSAS<sup>15</sup> using the data from detector banks 3 (d = 0.9-6.4 Å), 4 (d = 0.5-4.1 Å), 5 (d =0.5–3 Å), and 6 (d = 0.4-1.8 Å). The cell constants, atomic positions, isotropic (Fe, P) and anisotropic (O1, O2) atomic displacement parameters (U), scale factor and three line shape parameters were varied in the refinements, along with up to 22 background parameters to account for background contributions due to diffuse scattering. No significant improvement to the fit was obtained using anisotropic atomic displacement parameters for the Fe and P atoms.

#### D. Pair distribution functions

The neutron weighted, total pair distribution functions G(r) are the sine Fourier transform of the neutron total scattering structure factors F(Q). In this case, normalized total scattering data from different GEM detector banks are merged together to form one F(Q) for each temperature over as wide a range of Q as possible. The normalization procedure was carried out using the GUDRUN program, which is based on the ATLAS analysis package.<sup>16</sup>

As FePO<sub>4</sub> is paramagnetic above 24 K (Ref. 17), in correcting the data, the magnetic contribution was removed from the data at low-Q. This was calculated from the magnetic form factor and a nominal magnetic moment of 5.0  $\mu_B$  for Fe<sup>3+</sup>. Small inaccuracies in this subtraction appear in the (ideally flat) low-r region of G(r); subtracting the Fourier transform of this region from F(Q) and re-Fourier transforming to G(r)further improved the magnetic subtraction.

The composite F(Q) are then Fourier transformed to G(r) using the following function:<sup>18</sup>

$$G(r) = \frac{1}{(2\pi)^3 \rho_0} \int_0^\infty 4\pi Q^2 F(Q) \frac{\sin(Qr)}{Qr} dQ \qquad (1)$$

where  $\rho_0$  is the number density of the material and G(r) is a neutron weighted summation of the 1/2n(n + 1) partial radial distribution functions,  $g_{ij}(r)$ , given by:

$$G(r) = \sum_{i,j=1}^{n} c_i c_j \bar{b}_i \bar{b}_j [g_{ij}(r) - 1]$$
(2)

where *n* is the number of atom species in the material and  $c_i$  and  $\bar{b}_i$  are the proportion and neutron scattering length of species *i*, respectively. The  $g_{ij}(r)$  functions contain information about the number of atoms of type *i* around an atom of type *j*, averaged over all *j* atoms. They relate to the local structure and as such give complementary structural information to the long-range, average structure determined from Rietveld analysis of Bragg intensities.

### E. Reverse Monte Carlo modeling

Reverse Monte Carlo modeling<sup>19</sup> as incorporated within the program RMCPROFILE<sup>20</sup> was used to obtain bond and bond angle distributions and the overall topology of the instantaneous structure.

The general principles of reverse Monte Carlo (RMC) modeling and how it may be applied to crystalline materials have been reviewed in detail in Refs. 19 and 21, respectively. Briefly, a supercell of the average crystalline unit cell is created and randomly chosen atoms within this supercell are moved one at a time a random amount. Each time a move is attempted, various structural functions are calculated and compared with the equivalent experimental data. If the agreement improves, then the move is accepted, and if the agreement worsens, then the move is accepted with a reduced probability. The process is continued until the agreement function  $\chi^2_{RMC}$  is minimized and further moves cause  $\chi^2_{RMC}$  to fluctuate about this minimum value. Here,  $\chi^2_{RMC}$  is defined as:

$$\chi^2_{\rm RMC} = \chi^2_{\rm Data} + \chi^2_{\rm Restraints} \tag{3}$$

where

$$\chi^{2}_{\text{Data}} = \sum_{n} [F_{\text{Calc}}(Q_{i}) - F_{\text{Exp}}(Q_{i})]^{2} / \sigma_{F(Q)}(Q_{i}) + \sum_{m} [T_{\text{Calc}}(r_{i}) - T_{\text{Exp}}(r_{i})]^{2} / \sigma_{T(r)}(r_{i}) + \sum_{l} [I_{\text{Calc}}(t_{i}) - I_{\text{Exp}}(t_{i})]^{2} / \sigma_{I(i)}(t_{i})$$
(4)

summing over the *n*, *m*, and *l* points of F(Q), T(r), and I(t), respectively. Here, T(r) is related to G(r) defined above (see Ref. 18), and I(t) is the powder profile. Also,  $\chi^2_{\text{Restraints}}$  is defined as:

$$\chi^{2}_{\text{Restraints}} = w_{A-O} \sum_{A-O} (r_{A-O} - R_{A-O})^{2} + w_{O-A-O} \sum_{O-A-O} (\theta_{O-A-O} - \Theta_{O-A-O})^{2}$$
(5)

summing over all the intratetrahedral *A*-O bond lengths and O-*A*-O bond angles within the supercell, respectively. Here,  $R_{P-O}$  and  $R_{Fe-O}$  were determined from the two lowest-*r* peaks in *G*(*r*), respectively, and  $\Theta_{O-P-O}$  and  $\Theta_{O-Fe-O}$  were both set to the ideal tetrahedral angle (109.47°). A low weighting *w* on each restraint was applied to ensure that the low-*r* peaks in *G*(*r*) were not sharper than those observed experimentally and to allow the distributions of distances and angles to reflect the experimental data rather than the restraint. These restraints also ensured that the topology of the network structure was preserved during RMC minimization.

## F. Raman scattering

Raman spectra were obtained on a Jobin-Yvon T64000 spectrometer operating in triple subtractive mode (three 1800 groove/mm gratings) and equipped with a liquid nitrogen cooled CCD detector. The 514.5-nm line of an argon-krypton Coherent Innova 70 Spectrum laser was used for excitation. A BX41 Olympus confocal optical microscope ( $\times$  10 objective) was used to focus the laser into a  $\sim$ 2- $\mu$ m-sized spot on the sample. All experiments were performed in backscattering geometry. High-temperature Raman spectra were obtained using a Linkam TS 1500 heating stage with a Pt thermocouple to measure the temperature.

#### G. Raman calculation and computational details

Dynamic matrix calculation, yielding the phonon frequencies and eigenvectors of FePO<sub>4</sub>, was performed within the framework of spin density functional perturbation theory as implemented in the ABINIT package.<sup>22</sup> The exchangecorrelation energy functional was evaluated within the local density approximation using Perdew-Wang parametrization<sup>23</sup> of Ceperley–Alder homogeneous electron gas data.<sup>24</sup> The all-electron potentials were replaced by norm-conserving pseudopotentials generated according to the Troullier-Martins scheme<sup>25</sup> using a package developed at the Fritz-Haber Institute.<sup>26</sup> Fe  $(3d^6, 4s^2)$ , P  $(3s^2, 3p^3)$ , and O  $(2s^2, 2p^4)$ electrons were considered as valence states in the construction of pseudopotentials. The electronic wave functions were expanded in plane-waves up to a kinetic energy cutoff of 60 Ha. Integrals over the Brillouin zone were approximated by sums over a  $6 \times 6 \times 2$  mesh of special k points according to the Monkhorst–Pack scheme.<sup>27</sup> As the calculations were performed at 0 K, the A-type antiferromagnetic state was considered as experimentally observed by Battle et al.<sup>17</sup> Relaxation of internal atomic positions was performed at experimental lattice parameters by using the Broyden-Fletcher-Goldfarb-Shanno algorithm until the maximum residual forces were less than  $5.10^{-6}$  Ha/Bohr. The magnetic moment on the iron atoms was calculated to be about 4.3  $\mu_B$ . Raman susceptibility tensors were obtained within a nonlinear response formalism taking



FIG. 1. Experimental (dots) and calculated profiles (solid line) from the Rietveld refinement of hexagonal  $\beta$ -quartz-type FePO<sub>4</sub> at 1223 K. Only data from the GEM detector bank 6 (142° < 2 $\theta$  < 149°) are shown here. The difference profile (lower solid line) is on the same scale. Vertical ticks indicate the calculated positions of the reflections.

advantage of the 2n + 1 theorem, and the Raman spectrum was calculated as described in Refs. 28 and 29.

# **III. RESULTS AND DISCUSSION**

#### A. Long-range, average structure: Rietveld refinements

The ambient and high-temperature structure of FePO<sub>4</sub> has been determined in detail by x-ray<sup>8,9,13</sup> and neutron<sup>12</sup> diffraction methods. Based on these results, FePO<sub>4</sub> exhibits an unusual behavior in the  $\alpha$ -quartz family in that the temperature stability does not depend on the initial structural distortion. In this study, the improved data quality, Fig. 1, has enabled us to obtain more precise structural parameters for the  $\alpha$ - and  $\beta$ -quartz-type phases, Tables I and II. The point at 983 K, which is very close to the reported phase transition temperature of 980 K (Ref. 10), was still found to be in the  $\alpha$  phase. The subsequent point at 1003 K corresponded to the  $\beta$ -quartz-type structure.

TABLE I. Unit cell parameters, volume, and agreement factors for trigonal  $\alpha$ -quartz-type and hexagonal  $\beta$ -quartz-type (italics) FePO<sub>4</sub> as a function of temperature.

Т (К)	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å <sup>3</sup> )	Rwp	Rp	$\chi^2$
293	5.03362(4)	11.2325(1)	246.472(4)	0.037	0.037	2.6
373	5.04064(4)	11.2403(1)	247.331(4)	0.036	0.036	2.4
473	5.04973(4)	11.2506(1)	248.453(4)	0.033	0.033	2.3
573	5.05980(4)	11.2622(1)	249.700(4)	0.031	0.032	2.1
673	5.07117(4)	11.2752(1)	251.114(5)	0.030	0.031	2.1
773	5.08451(4)	11.2903(1)	252.775(5)	0.029	0.029	1.9
873	5.10167(5)	11.3101(2)	254.930(5)	0.028	0.028	1.9
943	5.11955(5)	11.3294(2)	257.158(6)	0.029	0.028	1.9
963	5.12744(7)	11.3373(2)	258.132(8)	0.040	0.041	1.3
983	5.14639(8)	11.3557(3)	260.466(9)	0.042	0.044	1.3
1003	5.1607(1)	11.3689(4)	262.22(1)	0.042	0.043	1.3
1023	5.1624(1)	11.3682(3)	262.38(1)	0.031	0.031	2.0
1073	5.1634(1)	11.3679(3)	262.47(1)	0.041	0.042	1.3
1123	5.1634(1)	11.3670(3)	262.45(1)	0.037	0.035	2.4

TABLE II. Fractional atomic coordinates and equivalent isotropic atomic displacement parameters (Å<sup>2</sup>) for  $\alpha$ - and  $\beta$ -quartz-type (italics) FePO<sub>4</sub>. *P*3<sub>1</sub>21-Fe on 3*a* (*x*, 0, 1/3), P on 3*b* (*x*, 0, 5/6), O1, O2 on 6*c* (*x*, *y*, *z*), and *P*6<sub>4</sub>22-Fe on 3*d* (1/2, 0, 1/2), P on 3*c* (1/2, 0, 0), O1 on 12*k* (*x*, *y*, *z*). Note that the origin is shifted by 1/6 along *c* between  $\alpha$ - and  $\beta$ -quartz.

T (K)	X <sub>(Fe)</sub>	$100^*U_{\rm iso}$	X <sub>P</sub>	$100^*_{iso}$	x <sub>O1</sub>	<i>y</i> 01	Z01	$100^* U_{\rm eq}$	x <sub>O2</sub>	<i>y</i> 02	ZO2	$100^*U_{eq}$
293	0.4582(2)	0.85(2)	0.4580(3)	0.54(2)	0.4157(2)	0.3151(2)	0.3963(1)	1.2(1)	0.4113(3)	0.2619(2)	0.8748(1)	1.4(2)
373	0.4593(2)	1.10(2)	0.4590(3)	0.77(3)	0.4149(3)	0.3129(2)	0.3968(1)	1.7(2)	0.4127(3)	0.2608(2)	0.8754(1)	1.9(2)
473	0.4603(2)	1.43(2)	0.4606(3)	0.93(3)	0.4156(3)	0.3114(2)	0.3975(1)	2.2(2)	0.4142(3)	0.2590(2)	0.8761(1)	2.4(2)
573	0.4618(2)	1.69(2)	0.4614(3)	1.30(4)	0.4150(3)	0.3083(2)	0.3982(1)	2.9(2)	0.4155(3)	0.2572(2)	0.8773(1)	3.1(2)
673	0.4635(2)	1.99(3)	0.4624(4)	1.64(4)	0.4151(3)	0.3054(3)	0.3992(1)	3.6(2)	0.4177(4)	0.2552(3)	0.8787(1)	3.8(2)
773	0.4654(2)	2.24(3)	0.4635(4)	2.18(5)	0.4153(4)	0.3023(3)	0.4002(1)	4.4(3)	0.4197(4)	0.2527(3)	0.8808(1)	4.6(3)
873	0.4685(3)	2.64(3)	0.4651(5)	2.56(6)	0.4152(5)	0.2972(4)	0.4021(1)	5.6(3)	0.4224(5)	0.2488(3)	0.8832(1)	5.6(4)
943	0.4729(3)	2.96(4)	0.4681(6)	3.21(7)	0.4154(6)	0.2910(5)	0.4045(1)	6.9(4)	0.4245(7)	0.2439(4)	0.8862(1)	6.7(5)
963	0.4748(6)	3.14(5)	0.470(1)	3.73(10)	0.416(1)	0.2854(8)	0.4057(2)	7.6(7)	0.424(1)	0.2402(7)	0.8878(2)	7.4(7)
983	0.4840(6)	3.69(3)	0.483(1)	4.74(6)	0.4227(5)	0.2676(5)	0.4100(2)	10.6(5)	0.4182(5)	0.2177(5)	0.8944(2)	9.6(5)
1003	0.5	4.54(7)	0.5	4.23(10)	0.4194(3)	0.2348(5)	0.5926(2)	11.5(5)				
1023	0.5	4.65(5)	0.5	4.46(7)	0.4199(2)	0.2357(3)	0.5921(1)	11.8(5)				
1073	0.5	4.84(7)	0.5	4.40(9)	0.4198(3)	0.2358(4)	0.5924(2)	11.9(5)				
1123	0.5	4.99(7)	0.5	4.33(9)	0.4204(3)	0.2373(4)	0.5920(2)	12.0(5)				

As previously found,<sup>12</sup> strong thermal expansion is observed for the  $\alpha$  phase; whereas for the  $\beta$  form, the volume is almost constant (Table I). This can be linked to the loss of the tetrahedral tilting mechanism in the higher-symmetry  $\beta$  form, Fig. 2. The bond lengths, calculated from the time-averaged structure, apparently decrease with increasing temperature in the  $\alpha$  phase (Fig. 3). This behavior is typical for the  $\alpha$ -quartz homeotypes due to the increase in dynamic disorder.<sup>30,31</sup> The room temperature tilt angles of 18.9° and 23.6° for FeO<sub>4</sub> and PO<sub>4</sub> tetrahedra, respectively, are in close agreement with the 19.2° and 23.7° previously obtained.<sup>12</sup> The tilt angles decrease slowly up to about 873 K and then very rapidly to zero just above 983 K. This behavior is similar to AlPO<sub>4</sub> (Ref. 32).

The observed changes in the average structure can be associated with a high degree of disorder in the atomic positions of oxygen. In addition, it can be observed from





FIG. 2. Crystal structure of  $\beta$ -quartz-type FePO<sub>4</sub> at 1123 K. Fe atoms are dark gray, P are white, and O atoms are medium gray. Ellipsoids are plotted at 99% probability.



FIG. 3. Fe-O (squares) and P-O (circles) bond lengths as a function of temperature obtained by Rietveld refinement (open symbols) and by total neutron scattering (filled symbols). The  $\alpha$ - $\beta$  phase transition is represented by the vertical dashed line.

	$100^{*}U_{11}$	$100^*U_{12}$	$100^*U_{13}$	$100^*U_{22}$	$100^*U_{23}$	$100^*U_{33}$
293 K-O1	1.94(6)	1.16(5)	-0.50(4)	1.41(4)	- 0.55(3)	0.68(4)
293 K-O2	2.66(7)	1.58(5)	-0.49(5)	1.42(5)	-0.65(4)	0.96(4)
373 K-O1	2.66(7)	1.68(6)	-0.63(5)	1.93(5)	-0.77(4)	1.08(4)
373 K-O2	3.56(8)	2.11(6)	-0.68(5)	1.91(5)	-0.92(4)	1.34(4)
473 K-O1	3.55(8)	2.14(6)	-0.78(6)	2.42(6)	-0.90(5)	1.52(4)
473 K-O2	4.32(9)	2.61(7)	-0.80(7)	2.35(6)	-1.14(5)	1.87(5)
573 K-O1	4.33(9)	2.77(7)	-0.82(7)	3.24(6)	-1.19(6)	2.25(5)
573 K-O2	5.34(10)	3.14(7)	-1.10(8)	2.93(7)	-1.46(5)	2.40(5)
673 K-O1	5.30(10)	3.39(8)	-0.74(8)	4.08(7)	-1.25(7)	2.91(6)
673 K-O2	6.21(11)	3.67(8)	-1.38(9)	3.55(8)	-1.92(6)	3.25(6)
773 K-O1	5.89(11)	3.78(9)	-0.33(10)	4.79(9)	-1.39(8)	4.09(7)
773 K-O2	7.61(13)	4.68(9)	-2.13(11)	4.60(9)	-2.71(7)	3.86(7)
873 K-O1	6.88(14)	4.60(12)	-0.18(12)	6.15(11)	-1.88(10)	5.46(9)
873 K-O2	8.88(16)	5.44(11)	-2.56(13)	5.38(11)	-3.41(9)	5.08(9)
943 K-O1	8.11(17)	5.23(15)	0.30(14)	7.39(14)	-2.27(12)	6.96(12)
943 K-O2	9.72(19)	6.08(15)	-3.28(15)	6.55(15)	-4.53(10)	6.49(12)
963 K-O1	9.2(3)	5.9(2)	0.4(2)	8.3(2)	-2.6(2)	7.5(2)
963 K-O2	9.9(3)	6.0(2)	-3.4(2)	7.4(2)	-5.2(2)	7.1(2)
983 K-O1	12.8(2)	8.2(1)	1.7(2)	11.2(1)	-3.9(1)	10.8(2)
983 K-O2	12.0(2)	9.2(1)	-2.5(1)	15.2(1)	-7.3(1)	4.9(1)
1003 K-O1	11.8(1)	5.4(2)	2.4(2)	11.5(2)	-5.9(1)	10.7(1)
1023 K-O1	12.4(1)	5.6(1)	1.9(1)	11.3(1)	-6.4(1)	11.4(1)
1073 K-O1	12.1(2)	5.1(2)	2.0(2)	10.9(1)	-6.1(1)	12.0(1)
1123 K-01	12.5(2)	5.5(2)	2.0(2)	10.8(2)	-6.2(1)	12.1(1)

TABLE III. Oxygen anisotropic atomic displacement parameters (Å<sup>2</sup>) for  $\alpha$ - and  $\beta$ -quartz-type (italics) FePO<sub>4</sub>.

of the U values in the present neutron diffraction study being slightly lower. Direct information of this dynamic disorder can be obtained by studying the local structure of this material at high temperature.

### B. Local structure: Total neutron scattering

The room temperature pair distribution function values of the P-O and Fe-O bond lengths (1.533 and 1.853 Å) obtained from Fourier transformation of the total scattering data (Figs. 5–6) are comparable to those obtained on Rietveld

refinement of the neutron scattering data (1.526 and 1.862 Å). These distances are plotted as a function of temperature in Fig. 3. A continuous increase is observed in the distances in the local structure as a function of temperature, and no discontinuity is observed at the phase transition. This is expected due to the normal thermal expansion of the tetrahedra and shows that the phase transition does not involve any substantial change in intratetrahedral geometry. This is in contrast to the average structure, in which both the Fe-O and P-O distances decrease with increasing temperature in the  $\alpha$ -quartz phase and a sharp decrease is observed at the vicinity of phase transition. The increasing difference between the average and local structure indicates the presence of



temperature.

200400600800100012005Temperature (K)FIG. 4. Isotropic or equivalent isotropic atomic displacementparameters from Rietveld refinements of FePO4 as a function of



FIG. 5. Experimental and calculated neutron total scattering structure factors from the reverse Monte Carlo refinement of the neutron data for  $\beta$ -quartz-type FePO<sub>4</sub> at 1123 K.



FIG. 6. Neutron pair distribution functions for  $FePO_4$  as a function of temperature.

thermally induced dynamic disorder as was observed for silica polymorphs previously.<sup>30,33–35</sup> Notably, this difference is of comparable magnitude to SiO<sub>2</sub> (Ref. 30), even though the structure of FePO<sub>4</sub> is more highly distorted. In addition, the width of the Fe-O distance distribution increases by more than 30% from room temperature up to the phase transition temperature, Figs. 6–7, whereas the corresponding increase for the P-O distribution is only 10%. This is consistent with the weaker bonding between the 3*d*<sup>5</sup> transition metal cation and oxygen as compared to the much more covalent P-O bond. The thermally induced disorder can be linked to the excitation of large amplitude, low-energy vibrations (see Sec. III D). These low-frequency modes result in a reduced correlation in atomic pair orientation. This effect is more pronounced on more distant atomic pairs and is evident from broadening of



FIG. 7. Width of the Fe-O and P-O distance distribution from total neutron scattering as a function of temperature. The width corresponds to the full width at half maximum (FWHM) of the Gaussian distribution.



FIG. 8. (Color online) Instantaneous structure of  $\alpha$ -quartz type FePO<sub>4</sub> at 293, 873, and 943 K and the  $\beta$ -quartz phase at 1123 K modeled by RMC and viewed along crystallographic 001 direction. Fe atoms are dark gray, P are green (light gray), and O atoms are red (medium gray).

the pair distribution function beyond the intratetrahedral O-O distances (>3 Å), Fig. 6.

#### C. Instantaneous structure: RMC modeling

Reverse Monte Carlo refinements enable configurations corresponding to the instantaneous structure (Fig. 8) to be obtained as a function of temperature. In the case of the two highest temperatures, 1023 and 1123 K, starting



Fe-P-Fe/P-Fe-P angle (deg)

FIG. 9. Sum of the Fe-P-Fe and P-Fe-P angle distribution as determined from RMC calculations for  $FePO_4$  as a function of temperature.



FIG. 10. (above) Distribution functions of the intertetrahedral Fe-O-P bridging angle in FePO<sub>4</sub> from RMC calculations as a function of temperature. (below) Center and width of the Fe-O-P bridging angle distribution from RMC calculations (solid symbols) along with the average value of the Fe-O-P bridging angle (open symbols) from Rietveld Refinements as a function of temperature.

from an  $\alpha$ -quartz-type configuration, the refinement process spontaneously converged to the  $\beta$ -quartz structure type. A very important change is observed in the cation sublattice at the transition to the higher symmetry  $\beta$ -structure as can be seen from the Fe-P-Fe and the P-Fe-P distributions (Fig. 9). Broadening is observed in these distributions prior to the  $\alpha$ - $\beta$ transition due to dynamic disorder.

The intertetrahedral bridging angles (Fig. 10) also show a discontinuous change upon transition to the  $\beta$ -quartz phase. The value of the bridging angle determined from RMC refinements increases rapidly from 850 K up to the phase transition and then becomes almost constant once the phase transition is complete. A comparison of the room temperature values of  $\theta_{\text{average}}$  (137.7°) and  $\theta_{\text{instantaneous}}$  (137.5°) shows good agreement (Fig. 10), but increasing disagreement is observed as the temperature increases. This large disagreement is a clear indication of the presence of dynamic disorder in the





FIG. 11. Center and width  $\delta$ (FeO<sub>4</sub>; circles) and  $\delta$ (PO<sub>4</sub>; squares) in FePO<sub>4</sub> from RMC calculations (solid symbols) along with the average  $\delta$  values from Rietveld refinements (open symbols) as a function of temperature.

structure, which increases with increasing temperature. The bridging angle increases from the  $\alpha$ -phase value 137.5° at room temperature to 139.3° at 773 K. The value increases rapidly to 141.5° at 943 K before the phase transition and then finally to 145.2° at 1023 K in the  $\beta$  phase. In the higher-temperature range, this increase is much greater than for GaPO<sub>4</sub> with angles of 134.3° and 138.1° at room temperature and at 1223 K, respectively.<sup>30</sup> Dynamic disorder is much less important in the case of GaPO<sub>4</sub> above 850 K. The increasing dynamic disorder can also be seen from the width [full width at half maxima (FWHM)] of the  $\theta_{instantaneous}$  distribution (Fig. 10), which increases relatively slowly from 13° at room temperature to 21° at 773 K. This distribution broadens significantly to  $26^{\circ}$  at 943 K ( $\alpha$ -quartz phase), then increases to  $33^{\circ}$  at 1023 K ( $\beta$ -quartz phase) and widens slightly with increasing temperature in the  $\beta$  phase.

The tilt angles  $(\delta)$ , which have been defined as an order parameter for the  $\alpha$ - $\beta$  phase transition, follow the previously described decrease with increasing temperature<sup>12</sup> and drop to zero at the transition (Fig. 11). The RMC values are typically lower than the average values from the Rietveld refinements



FIG. 12. Distribution functions of the intertetrahedral O-O-O angle from RMC calculations for  $FePO_4$  as a function of temperature.

and also drop to zero at the transition. Dynamic disorder is also obvious from the broadening of the FWHM of the distribution, which increases dramatically in the highly disordered  $\beta$  phase.

Increased dynamic disorder can be clearly observed upon comparing the snapshots from RMC refinement (Fig. 8) at room temperature and close to the phase transition temperature in the  $\alpha$  phase and at 1123 K in the  $\beta$  phase. The RUMs responsible for the dynamic disorder in the oxygen sublattice can be observed by changes in the O-O-O angle distribution for O-O distances of less than 3.59 Å (Fig. 12) due to the fact that the concerned eigenvector corresponds to the rocking motion of tetrahedra with the oxygen atoms at the vertex and cations at the centers.<sup>36,37</sup> The sharp peak at  $60^{\circ}$ , which shows hardly any change with temperature, represents the intratetrahedral O-O-O angle. Other peaks represent several intertetrahedral O-O-O angles, which broaden as a result of increased dynamic disorder in lattice with increasing temperature. This is consistent with the observed increase in oxygen atomic displacement parameters obtained from Rietveld refinements (Fig. 4) and broadened pair distribution function for distances (3-9 Å) greater than O-O intratetrahedral distances. The most spectacular change occurs at the phase transition temperature, above which the intertetrahedral O-O-O angle is represented by a single broad distribution and the corresponding instantaneous structure of  $\beta$  phase is highly disordered (Fig. 12). This is in contrast to the results on  $\alpha$ -quartz<sup>1</sup> for which strong broadening occurs above 473 K, which is well below the phase transition temperature of 846 K.

These observations based on the various distance and angular distributions in the instantaneous structure indicate that the dynamic disorder increases significantly in  $FePO_4$ 



FIG. 13. Experimental (300 K) and calculated (0 K) Raman spectra of  $FePO_4$ . A Lorentzian with a constant line width fixed at 2 cm<sup>-1</sup> has been used in the calculation.

from temperatures above 850 K. It has been shown in previous work that dynamic disorder is closely linked to the degradation of the quality factor Q, whereas the electromechanical

TABLE IV. Wave number (cm<sup>-1</sup>) of the Raman lines in  $\alpha$ -quartz type FePO<sub>4</sub>. Calculated LO wave numbers are in brackets. Calculated IR active A<sub>2</sub> modes: 36 (37), 104 (104), 174 (187), 362 (368), 403 (434), 582 (604), 627 (632), 999 (1000), and 1012 (1156) cm<sup>-1</sup>.

Calcul	ation	Experiment			
Assignment	0 K	300 K	1150 K		
E(TO + LO)	71 (75)	83	80		
E(TO + LO)	97 (97)	98			
$A_1$	108	121	109		
Е	116 (118)				
E(TO + LO)	152 (153)	161	139		
A <sub>1</sub>	193	196	180		
E(TO + LO)	232 (239)	253			
$A_1$	279	276	275		
E(TO + LO)	294 (295)	296			
Е	355 (369) <sup>a</sup>				
E (TO)	380 (394)	389	358		
$A_1$	399	414	407		
E (TO)	418 (437)	428			
A <sub>1</sub>	428	436	446		
E(TO + LO)	460 (461)	450			
E(TO + LO)	580 (583)	588	562		
Е	630 (640) <sup>a</sup>				
$A_1$	637	645	639		
Е	651 (652)	658			
Е	1004 (1012)				
E (TO)	1013 (1028)	1008			
$A_1$	1013	1008	994		
$A_1$	1026	1015			
E (LO)	1031 (1147)	1058	1063		
E(TO + LO)	1150 (1153)	1170	1163		

<sup>a</sup>Very weak intensity predicted by the calculation.

coupling coefficient *k* relates more closely to the average value of structural distortion.<sup>1,31,38</sup> This indicates that FePO<sub>4</sub> may be suitable as a piezoelectric material over a much larger temperature range than quartz. The level of disorder above 850 K is, however, greater than in the case of GaPO<sub>4</sub>. The width of the O-O-O distributions at 943 K is similar to the corresponding distributions in GaPO<sub>4</sub> near 1223 K.

# D. Dynamic disorder and phase transition mechanism: Raman spectroscopy

Group theory predicts that  $\alpha$ -quartz-type FePO<sub>4</sub> (trigonal  $P3_121 D_3^4$ , Z = 3) will exhibit 54 modes of vibration:

$$\Gamma = 8A_1 + 10A_2 + 18E.$$

One  $A_2$  mode and one E mode are acoustic, and the remaining optical modes are:

$$\Gamma = 8A_1 + 9A_2 + 17E.$$

There are 25 modes that are predicted to be Raman active (eight nondegenerate  $A_1 + 17$  doubly degenerate E). The complete Raman spectrum, including both the frequency position and the intensity of the lines, was calculated using DFT (Fig. 13 and Table IV). Very good agreement is obtained with respect to the 20 modes observed in the Raman spectrum of FePO<sub>4</sub>.

Increasing temperature results in a progressive change in wave number and line width [full width at half maxima (FWHM)] of Raman modes, Fig. 14. Figure 15 shows that the wave number of most of the Raman modes decreases with increasing temperature due to reduced oscillator strength caused by thermal expansion. Temperature also results in the broadening of the vibrational modes. The group of peaks in the 300-250-cm<sup>-1</sup> region is replaced by a broad symmetrical band at the phase transition. Group theory predicts 20 Raman active modes for the  $\beta$  phase ( $\Gamma = 3A_1 + 5A_2 + 5B_1 + 5B_2 +$  $10E_1 + 8E_2$ ,  $\Gamma_{Raman} = 3A_1 + 9E_1 + 8E_2$ ) for a hypothetical ordered structure. As shown by the total neutron scattering data, the structure is clearly not ordered. This is confirmed by the persistence of almost all the A<sub>1</sub> modes observed in the low-temperature  $\alpha$  phase up to 1150 K, which is well above the  $\alpha$ - $\beta$  phase transition temperature (Fig. 15). This is in sharp contrast with the prediction of only 3 A1 modes for the ordered hexagonal structure. Instead, at high temperature, the local symmetry must be lower in the disordered structure. Both this distortion and the high degree of disorder is clearly shown from the Fe-O-P angles in the  $\beta$  phase, for which the broad distribution is centered about 145° instead of 154° for a hypothetical, ordered  $\beta$ -quartz-type structure, Fig. 10.

In  $\alpha$ -quartz and the closely related material AlPO<sub>4</sub>, the  $\alpha$ - $\beta$  phase transition is strongly linked to disorder arising from the RUM corresponding to the libration of the constituent essentially rigid tetrahedra.<sup>1,30,39</sup> Upon increasing temperature, this mode undergoes some softening and is subject to strong damping<sup>39–43</sup> due to the high degree of dynamic disorder. In other  $\alpha$ -quartz-type materials, such as GaPO<sub>4</sub> and GaAsO<sub>4</sub>, with structures that are much more distorted with respect to the  $\beta$ -quartz-type, the low-frequency A<sub>1</sub> modes are much more stable.<sup>29,44</sup> In the case of highly distorted GaAsO<sub>4</sub>, it was shown from DFT calculations that the low-energy A<sub>1</sub> mode involving oxygen displacements is not a libration mode,



FIG. 14. Raman spectra of FePO<sub>4</sub> as a function of temperature.



FIG. 15. Wave number of the Raman modes of  $FePO_4$  as a function of temperature.



FIG. 16. (Color online) Calculated  $A_1$  vibrational modes of AlPO<sub>4</sub>, FePO<sub>4</sub>, and GaPO<sub>4</sub> at 0 K. Large purple, medium yellow, and small red spheres represent *A* (Al,Fe,Ga), P. and O atoms, respectively

but has more of a bending character.<sup>29</sup> The low-energy  $A_1$ mode involving oxygen displacements in FePO<sub>4</sub> is found experimentally at 276 cm<sup>-1</sup>, which is intermediate between the corresponding values of GaPO<sub>4</sub> (296 cm<sup>-1</sup>) and GaAsO<sub>4</sub>  $(261 \text{ cm}^{-1}; \text{Refs. } 29 \text{ and } 44)$ . The present DFT calculations show that this oxygen displacement mode is not a libration, but is also a more complex vibration involving bending of the various inter- and intratetrahedral angles in the structure, Fig. 16. This mode in FePO<sub>4</sub> is therefore similar to the corresponding modes in GaPO<sub>4</sub> and GaAsO<sub>4</sub> (Refs. 29 and 44). In contrast, DFT calculations show that the oxygen displacement mode in AlPO<sub>4</sub> at 230 cm<sup>-1</sup> corresponds to libration of the constituent tetrahedra. In addition, with respect to AlPO<sub>4</sub>, the frequencies of the second and third low-frequency  $A_1$  modes of the more distorted materials are inverted, with a mode linked to the translation of the A cation (A = Fe, Ga) appearing at lower frequency than the oxygen displacement mode. In all three phosphates, the lowest frequency  $A_1$  corresponds to a translation of the PO<sub>4</sub> tetrahedra.

In FePO<sub>4</sub>, in spite of the presence of an  $\alpha$ - $\beta$  phase transition, the oxygen displacement mode occurs at relatively high frequency and is not a librational mode as is also the case for GaPO<sub>4</sub> and GaAsO<sub>4</sub> (Refs. 29 and 44). This mode does soften initially, but no strong damping is observed just before or near the phase transition, Fig. 17. This mode stops softening well below the transition. In contrast to this mode, major changes are observed for the A<sub>1</sub> mode initially at 196 cm<sup>-1</sup> corresponding principally to a Fe translation along with some oxygen displacement, Fig 16. This can be linked to the shift in



FIG. 17. Wave number (above) and damping (below) of the low-frequency  $A_1$  Raman modes of FePO<sub>4</sub> involving oxygen and iron displacements as a function of temperature. (The mode damping is compared to that of the mode initially at 121 cm<sup>-1</sup>.)

the fractional atomic coordinate of Fe prior to and at the  $\alpha$ - to  $\beta$ -quartz phase transition, Table II. Both the decrease in wave number and the strong increase in damping, Fig. 17, are similar to that observed for the libration mode in  $AIPO_4$  (Ref. 38), even though the mode is different. This indicates, however, that in each case the mode, which exhibits this behavior, plays a major role in the dynamics of the phase transition mechanism. The wave number of this mode does not exhibit any strong character of mode softening with temperature at the phase transition. This is further evidence that the  $\alpha$ - $\beta$ transition is not of the simple displacive type, but is also linked to a strong increase in dynamic disorder as confirmed by the damping of this mode and the observation of more than three  $A_1$  modes at high temperature. This is also supported by the results of total neutron scattering, in particular for temperatures above 850 K, the strong differences between the average and local structures, the strong increase in the atomic displacement parameters, and the broadening of the Fe-P-Fe, P-Fe-P, Fe-O-P, and O-O-O angular distributions. The  $\beta$  phase is characterized by a distribution of the Fe and P x coordinates about 1/2and the tetrahedral tilt angle around zero as imposed by the higher-symmetry hexagonal structure.

The bonding is very different in  $FePO_4$  due to the *d* orbitals on the Fe<sup>3+</sup> cation. This results in relatively weaker bonding to oxygen than for  $Al^{3+}$  and  $Ga^{3+}$ . In the latter two systems with stronger bonding, the amplitudes of cation displacements are smaller, Fig. 16. The average fractional x coordinate of Fe increases much more rapidly with temperature than the P coordinate, Table II. In AlPO<sub>4</sub> and GaPO<sub>4</sub>, the fractional x coordinates of both the A cation and P increase at a similar rate.<sup>31,32</sup> This weaker Fe-O bonding in FePO<sub>4</sub> is also evident from the preferential increase in the width of the Fe-O distribution with respect to the P-O distribution, Fig. 7. Another signature of this is the fact that the high-frequency modes above 1000 cm<sup>-1</sup> (dominated by symmetric internal vibrations of phosphate groups) remain practically unchanged (Fig. 15) upon undergoing the phase transition. In the hightemperature range, FePO<sub>4</sub> can be considered chemically as a phosphate, with iron ions connecting phosphate tetrahedra. These results clearly indicate that the phase transition mechanism from a dynamic point of view is different for FePO<sub>4</sub> and that this mechanism is primarily linked to Fe translations due to the nature of the comparatively weak Fe-O bond. This result is in very good agreement with the recent high-temperature synchrotron x-ray diffraction study of  $FePO_4$  (Ref. 13) in which it was shown that the anisotropy of the atomic displacement parameters of Fe and P in the  $\beta$ phase at high temperature is consistent with contributions from two RUM's with a RUM involving Fe translations along with tetrahedral rotation predominating.

## **IV. CONCLUSIONS**

Total neutron scattering coupled with RMC refinements and Raman spectroscopic studies have been performed on FePO<sub>4</sub> as a function of temperature up to 1150 K. The average structure obtained from Rietveld refinement and the local structure obtained from total neutron scattering give very different values of bond distances Fe-O and P-O, indicating the presence of a high degree of dynamic disorder from 850 K up to the phase transition temperature. Density functional theory indicates that the low-frequency  $A_1$  mode involving oxygen displacements at 279 cm<sup>-1</sup> is not a librational mode and that the  $A_1$  mode at 193 cm<sup>-1</sup> involves large amplitude translations of Fe. Increasing damping of this  $A_1$  mode involving Fe translations indicates that the phase transition mechanism in FePO<sub>4</sub> is different from those in quartz and AlPO<sub>4</sub> due to the relatively weak Fe-O bond in the constituent tetrahedra, and thus Fe translation predominates with respect to tetrahedral libration. The damping of this mode gradually increases up to 850 K, then exhibits very large increases up to the phase transition temperature due to the strong increase in dynamic disorder.

Upon comparison between representative phosphate piezoelectric materials in terms of tetrahedral bridging angle, dynamic disorder in FePO<sub>4</sub> is found to behave initially in a similar way to GaPO<sub>4</sub> as it is nearer to GaPO<sub>4</sub> in terms of initial structural distortion. At high temperature, the FePO<sub>4</sub> becomes unstable and undergoes an  $\alpha$ - $\beta$  phase transition, as in the case of the less distorted materials quartz and AlPO<sub>4</sub>, although the phonon which is principally responsible for this instability is different. Thus, as also shown by the total neutron scattering results and Raman scattering, FePO<sub>4</sub> exhibits a large temperature range over which the degree of dynamic disorder increases, but remains relatively limited, followed by a strong increase in the temperature range just below the phase transition. Similar thermal instability may be expected in the piezoelectric properties such as the quality factor Q. This strong increase in dynamic disorder, however, occurs in the temperature range between about 850 K and the  $\alpha$ - $\beta$  phase transition temperature. These results suggest that  $\alpha$ -FePO<sub>4</sub> may be a useful piezoelectric material at temperatures below 850 K.

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