High-Temperature Lithium Mobility in α-$LiZr_2(PO_4)_3$ NASICON by Neutron Diffraction

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Powder neutron diffraction data at high resolution (HRPD instrument, ISIS Facility, U.K.) were collected on the lithium ion conductor α-$LiZr_2(PO_4)_3$ at 673 K ($a = 8.84448(3)$ Å, $c = 22.2875(1)$ Å), and 873 K ($a = 8.83667(4)$ Å, $c = 22.4177(2)$ Å). Previous data measured at 423 K were included in the analysis. By Fourier maps and Rietveld refinement of the rhombohedral $R\bar{3}c$ crystal structure, it was shown that most lithium occupies the 6-fold disordered primary Li1 site, located off the symmetry center, at all temperatures. However, a 3-fold disordered secondary Li2 site was discovered, between two adjacent ZrO_6 octahedra along the z axis, where a minor part of lithium is located. The fraction of lithium on Li2 increases with temperature from 10% (423 K) to 22% (873 K), and this may affect the mechanism of Li^+ ion mobility. Li2 was not taken into account in the previous analysis of the 423 K data. Small but significant configurational changes of the Li1 and Li2 coordination environments occur between 423 and 873 K, which can account for the second-order phase transformation suggested in the literature to occur in the range 553 to 623 K on the basis of NMR and electrical conductivity data.

I. Introduction

Alkali-ion conductors with the NASICON structure (rhombohedral $R\bar{3}c$, hereafter α phase) have been raising the interest of materials chemists for many years. This is partly due to the complex and subtle interactions between NASICON framework and mobile ions, which play a key role in accounting for the high ionic conductivity of several of these phases.[1−7] Also H-substituted NASICON phases, of interest for protonic conductivity, have been recently investigated.[8]

Despite many efforts and significant advances in the field, some crucial aspects of the interactions involving active ions and framework, and of the underlying structural features, have not yet been fully clarified. This holds more for Li and H compounds than for the sodium ones, as it is difficult to locate lithium and hydrogen accurately by X-ray diffraction methods, owing to their small atomic numbers. Further, lithium exhibits a very flexible crystal-chemical behavior, with coordination number ranging from four to six, and it can be accommodated in a great variety of structural environments because of its small size.

We are concerned here with the first-studied and simplest Li−NASICON phase: α-$LiZr_2(PO_4)_3$, which is stable above about 320 K and transforms into a triclinic α′ modification below that temperature.[5] The ionic conductivities of the α and α′ phases are reported to be $\sigma = 10^{-5}$ and 5×10^{-8} Ω^{1-} cm^{-1}, respectively, in the neighborhood of room temperature.[9,10] Both phases are often referred to as HT (high-temperature) forms of $LiZr_2(PO_4)_3$, as their synthesis is performed by solid-state reaction at 1473 K. On the other hand, by operating below 1173 K the LT (low-temperature) forms β (orthorhombic $Pbna$, stable above 573 K) and β' (monoclinic $P2_1/n$, stable below 573 K) are obtained, with lower conductivities than the α modification. Their crystal structures[11] are related to that of $Sc_2(WO_4)_3$ (β)[12] and of monoclinic $Fe_2(SO_4)_3$ (β').

An early X-ray diffraction study[13] of α-$LiZr_2(PO_4)_3$ claimed that lithium would be located on Wyckoff position 6b ($x = 0$, $y = 0$, $z = 0$, site symmetry $\bar{3}$, hereafter site M′, corresponding to M1 in other authors' notation[7,14]) of space group $R\bar{3}c$, in octahedral coordination with six O neighbors at 2.50 Å distance, i.e., in a configuration quite similar to that found for sodium in $NaZr_2(PO_4)_3$.[1] This result was at variance with the usual

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crystal chemical behavior of lithium, which shows the much smaller average Li−O bond length of 2.12 Å for octahedral coordination, on the basis of the sum of the corresponding ionic radii.[15] On the other hand, the very anisotropic thermal displacement of Li given in the quoted study,[13] with an unusually large component in the (001) plane ($U_{11} = 0.095$ Å^2), suggested strongly that lithium should be actually located off the 3-fold axis in disordered position. With the aim of solving this problem, we had performed a structural investigation at 423 K on α-$LiZr_2(PO_4)_3$ by high-resolution powder neutron diffraction, which definitely proved Li to be displaced from the M′ site, and to attain a tetrahedral coordination with average Li−O bond length of 2.27 Å.[16] The disorder and 4-fold coordination of lithium in the rhombohedral α phase was also recently confirmed by NMR−MAS measurements.[17]

An important point, relevant for the ion mobility mechanisms, was however left open: the structural behavior of lithium in α-$LiZr_2(PO_4)_3$ on raising temperature. In particular, in the study by Petit et al.[13] a broad phase transition was found to occur in the range 553 to 623 K, on the basis of NMR data of transverse relaxation times versus temperature. No thermal effects could be detected by differential scanning calorimetry (DSC) measurements, suggesting a second-order character of the transition. Such a structural transformation would account for a change of activation energy (from 0.76 to 0.44 eV) observed in the Arrhenius plot of Log(σT) vs $1/T$, according to the cited authors, in the same thermal range as that of the phase transition.

Further, the lithium mobility in α-$LiZr_2(PO_4)_3$ was recently simulated in the 400−940 K range by classical molecular dynamics (MD).[18] In that work, it was claimed that below 550 K lithium would be located on the M′ site only, whereas above that temperature both the M′ and M″ (corresponding to M1 and M2 in a different notation[7,14]) sites would be occupied, according to the structural model proposed in the early X-ray study.[13]

We therefore decided that, to clarify all these points, an accurate experimental study by high-resolution neutron diffraction had to be performed on α-$LiZr_2(PO_4)_3$ at higher temperature (up to 873 K) than previously done.[16]

II. Experimental Section

The triclinic α′ phase of $LiZr_2(PO_4)_3$, stable at room temperature, was synthesized by solid-state reaction at 1473 K from reagent-grade Li_2CO_3, ZrO_2, and $NH_4H_2PO_4$ in stoichiometric ratios.[5,13] Differential scanning calorimetry under N_2 atmosphere (Mettler Toledo Star) showed an endothermic peak at 329 K (onset temperature 326 K), corresponding to the reversible first-order α′ to α phase transition; virtually no hysteresis was observed, and the transition enthalpy was 16 Jg^{-1}.

Neutron diffraction data were collected at 673 and 873 K on the time-of-flight high-resolution powder diffractometer (HRPD) at the ISIS spallation pulsed source, Rutherford Appleton Laboratory (Chilton, U.K.). Measurement conditions used were similar to those used for the previous experiment carried out at 423 K on the same sample.[16] A powder specimen of about 2 cm^3, put in a vanadium can under vacuum, and surrounded by a resistance furnace, was employed. By use of the backscattering counter bank at $2\theta = 168.3°$, full intensity profiles were recorded in the d_{hkl} range 0.7 to 2.5 Å with maximum resolution of $\Delta d/d \approx 4 \times 10^{-4}$. Preliminary data reductions were performed, including merging of outputs from single counters in the bank and correction for detector efficiency as a function of neutron wavelength.

The Rietveld refinements of the crystal structure of α-$LiZr_2(PO_4)_3$ at each temperature were performed by the GSAS computer package.[19] A Chebyshev polynomial of first kind with 12 coefficients was used to model the intensity background, and the peak shape was represented by a convolution of a pseudo-Voigt function (linear combination of Gaussian and Lorentzian components, with σ and γ half-widths, respectively: sample contribution) with two back-to-back exponentials (instrumental and moderator contributions).[20] Linear dependences of the σ and γ parameters on d_{hkl} were assumed: $\sigma = \sigma_1 d_{hkl}$, $\gamma = \gamma_1 d_{hkl}$. The mixing coefficient and the full width of the pseudo-Voigt function depend on σ and γ according to equations given in the literature.[21]

III. Results

The crystal structure of α-$LiZr_2(PO_4)_3$ at 423 K,[16] without lithium atoms, was taken as starting point for the refinement of data collected at 673 and 873 K. In each case, after refining the atomic parameters of the incomplete structure the lithium positions were searched for on Fourier difference maps. At both temperatures, Li was located in a disordered (fractional occupancy $^1/_6$) position intermediate between the M′ and M″ sites, corresponding very roughly to the ≪mid-Li≫ analogue of the mid-Na site of sodium NASICON.[4] However, a significant shift along the z axis was observed, with respect to the position found at 423 K.[16] This was confirmed after including the Li atomic parameters in the least-squares refinement; thermal factors were anisotropic for all atoms but lithium.

As the occupancy of Li was significantly smaller than 0.167, corresponding to 6 lithium atoms per unit-cell and to one atom per formula unit, subsequent Fourier difference maps were computed and explored with great care, searching for residual negative peaks (the neutron scattering length of Li is negative). No scattering density could be detected on the M′ site (6b Wyckoff position) at 0, 0, 0, confirming the results of the previous study at 423 K. Only one peak was found with acceptable distances to neighboring oxygen atoms, in special position 18e, corresponding to a possible secondary disordered site for lithium (fractional occupancy $^1/_3$). Although the Wyckoff position is the same as that of site M″ (x, 0, $^1/_4$), the observed x coordinate (0.90) is far from the 0.67 value of M″. The coordinates of this Li2 atom could be refined successfully, attaining a quite reasonable oxygen coordination environment. Then both the Li1 and Li2 atomic parameters were included in the Rietveld refinement, with the constraint $(\text{o.f.})_1 + (\text{o.f.})_2/2 = {}^1/_6$ on their occupation factors in order to achieve a full lithium atom per formula unit, and $U(\text{Li1}) = U(\text{Li2})$ on their thermal factors to avoid correlation with the occupancy ratio.

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Table 1. Unit-Cell and Other Rietveld Refinement Results for α-$LiZr_2(PO_4)_3$ (Space Group $R\bar{3}c$, $Z = 6$) at 423, 673, and 873 K

T (K)	423[a]	673	873
a (Å)	8.85490(3)	8.84448(3)	8.83667(4)
c (Å)	22.1442(1)	22.2875(1)	22.4177(2)
V (Å^3)	1503.69(1)	1509.864(8)	1516.00(1)
data	4084	4199	4047
variables	49	49	49
Rp	0.0310	0.0257	0.0347
wRp	0.0383	0.0310	0.0409
R(F^2)	0.0702	0.0925	0.1127

[a] Cf. also ref 16.

Convergence was attained in the final cycle with the agreement factors reported in Table 1, where the refined lattice constants are also given. The final atomic coordinates, occupancies, and isotropic displacement factors are reported in Table 2. At this stage, the data collected at 423 K in the previous experiment[16] were reconsidered, and by a careful examination of their difference Fourier maps a negative peak similar to that labeled Li2 in the higher temperature data was detected. The structure refinement was thus performed again by including Li2 in the same way as explained above, and these results are also given in Tables 1 and 2.

The experimental, calculated, and difference profiles corresponding to $T = 673$ and 873 K are shown in Figures 1 and 2, respectively. Relevant interatomic distances of the crystal structure of α-$LiZr_2(PO_4)_3$ at the three temperatures of 423, 673, and 873 K are given in Table 3.

IV. Discussion

From the temperature-dependence of lattice constants (Table 1), the well-known negative thermal expansion of NASICON structures within the (001) plane[22-25] is confirmed. In particular, by interpolating parabolically the unit-cell parameters vs temperature, the following thermal expansion coefficients of α-$LiZr_2(PO_4)_3$ are obtained at $T = 423$ K (673 K): $\alpha_a = -4.86\ (-4.54) \times 10^{-6}\ K^{-1}$; $\alpha_c = 23.9\ (27.7) \times 10^{-6}\ K^{-1}$; $\alpha_V = 14.2\ (18.6) \times 10^{-6}\ K^{-1}$. Such values are in the range of previous measurements by X-ray diffraction,[23,24] but they indicate a decrease of $|\alpha_a|$ with increasing temperature, at variance with one of the quoted studies.[23] Models have been proposed to relate the peculiar thermal expansion behavior of NASICON phases to cooperative rotations of the coordination polyhedra[2] and/or to transverse thermal motion of the oxygen atoms at their corners.[12,26]

A continuous evolution with rising temperature can be observed for the geometry of the ZrO_6 and PO_4 coordination polyhedra (Table 3). The Zr octahedron becomes more regular, keeping the average Zr−O bond length substantially unchanged, whereas the P tetrahedron shrinks slightly on heating without altering its distortion. Such a small contraction of PO_4 groups could be apparent and due actually to transverse thermal motion of the oxygen atoms.

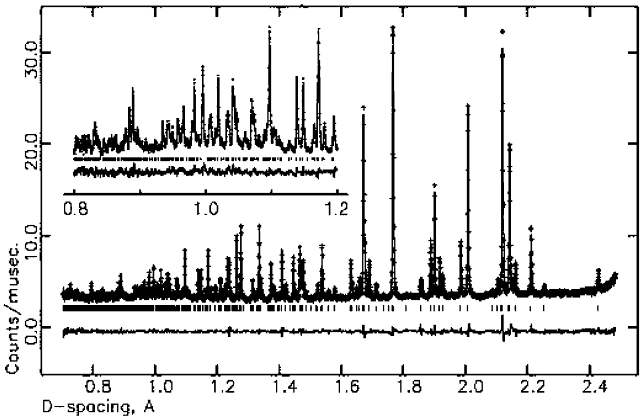

Figure 1. Experimental (crosses), calculated and difference profiles of the powder neutron diffraction pattern of α-$LiZr_2(PO_4)_3$ at $T = 673$.

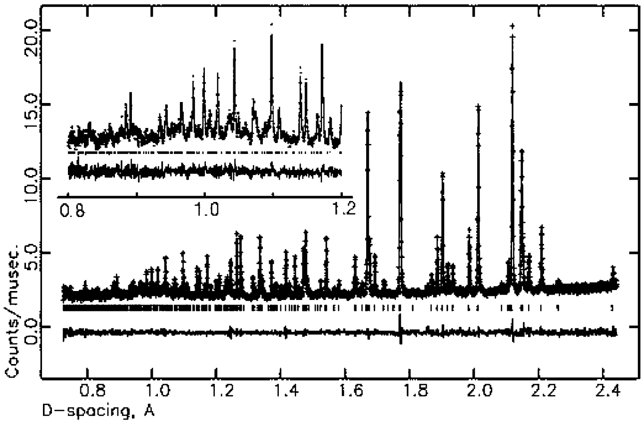

Figure 2. Experimental (crosses), calculated and difference profiles of the powder neutron diffraction pattern of α-$LiZr_2(PO_4)_3$ at $T = 873$ K.

The most important outcome of the structural study of Li−NASICON at variable temperature is discovery of a secondary Li2 site for lithium, which explains where the missing lithium from incomplete occupation of the Li1 site goes to. From the occupancies reported in Table 2, the Li distribution over the two sites is observed to vary from 90% (423 and 673 K) to 78% in Li1 (873 K), with the Li2 fraction rising correspondingly from 10 to 22% on heating. A small discontinuity in the relative population of the lithium sites would thus seem to occur above 673 K. It should be remarked that neither the M′ nor the M″ sites are occupied by lithium in the wide thermal range explored, in contrast with what was suggested by the molecular dynamics study previously quoted.[18]

As for the Li1 coordination environment, Table 2 shows that the z(Li1) coordinate increases appreciably below 673 K ($\Delta z = 0.010$, corresponding to an absolute shift of 0.22 Å along the c axis), whereas the shift within the (001) plane is smaller. By the shift between configuration I ($T = 423$ K, Figure 3) and II ($T = 673$ and 873 K, Figure 4), Li1 approaches both the M′ and M″ neighboring sites, so as to come nearer to the straight line connecting them and thus to be in a more favorable position for hopping along the mobility pathway. By examining the thermal evolution of the chemical bonding geometry of Li1, the distorted tetrahedral coordination appears to be preserved, with a slight increase of

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Table 2. Atomic Occupation Factors, Fractional Coordinates, and Isotropic (Li) or Equivalent Isotropic (Zr, P, O) Thermal Factors of α-$LiZr_2(PO_4)_3$ at 423, 673, and 873 K[a]

	site	T (K)	o.f.	x	y	z	U or U_{eq} (10^{-2} Å^2)
Li1	36f	423	0.15(1)	0.028(5)	0.174(5)	0.006(1)	7(1)
		673	0.15(1)	0.038(7)	0.167(7)	0.016(2)	11(1)
		873	0.13(1)	0.056(9)	0.184(9)	0.014(3)	9(2)
Li2	18e	423	0.04(1)	0.90(2)	0	0.25	7(1)
		673	0.04(1)	0.88(3)	0	0.25	11(1)
		873	0.07(1)	0.93(1)	0	0.25	9(2)
Zr	12c	423	1	0	0	0.14244(6)	1.16(4)
		673	1	0	0	0.14277(7)	1.11(5)
		873	1	0	0	0.1430(1)	1.47(7)
P	18e	423	1	0.2882(1)	0	0.25	0.88(6)
		673	1	0.2885(2)	0	0.25	0.77(6)
		873	1	0.2877(2)	0	0.25	0.97(9)
O1	36f	423	1	0.1853(1)	−0.0116(1)	0.19365(5)	2.20(7)
		673	1	0.1835(2)	−0.0154(2)	0.19442(6)	3.25(8)
		873	1	0.1817(2)	−0.0190(3)	0.19497(8)	3.9(1)
O2	36f	423	1	0.1968(1)	0.1718(1)	0.08484(5)	1.41(6)
		673	1	0.1974(1)	0.1720(1)	0.08624(5)	1.81(8)
		873	1	0.1980(2)	0.1724(2)	0.08763(8)	2.6(1)

[a] The estimated standard deviations are reported in parentheses.

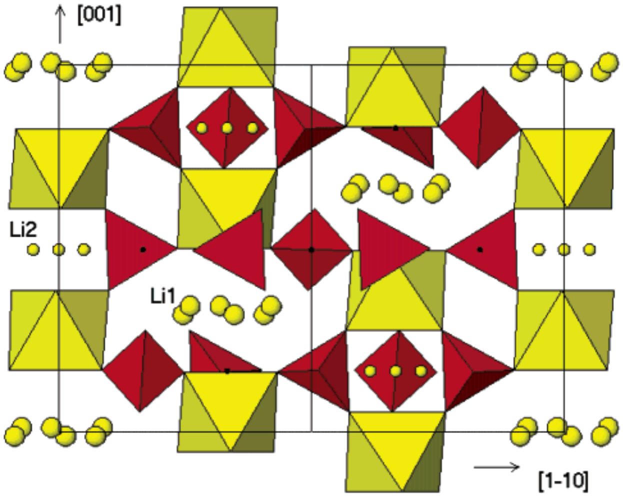

Figure 3. Half unit-cell of α-$LiZr_2(PO_4)_3$ projected onto the (110) plane (T = 423 K). The PO_4 and ZrO_6 coordination polyhedra and the Li1 and Li2 atoms (large and small spheres, respectively) are emphasized. Full dots denote the M″ sites of the NASICON structure.

the average Li1−O bond distance (Table 3). In the passage from configuration I to II, Li1 gets closer to O2 and farther from the O2″ oxygen atom, consistent with the shift toward the M′−M″ line (Figures 3 and 4).

A closer inspection of the crystal chemical features of the Li2 site is necessary. This is located on a 2-fold symmetry axis, at the same z level as P atoms and M″ sites, halfway the vertical pair of ZrO_6 octahedra sharing corners with three PO_4 tetrahedra between (Oc_2T_3 unit), as shown in Figures 3 and 4. The 3-fold disorder, to be compared to the 6-fold disorder of Li1, is displayed on the (001) view in Figure 5. It should also be observed that, on heating from 423 to 873 K, Li2 approaches the special position 6c with symmetry 32 at 0, 0, $^1/_4$. Chemical bonding of Li2 is provided by a distorted tetrahedral coordination with four surrounding oxygen atoms, with surprisingly short bond distances if compared to the Li1 case: we have 1.93 against 2.31 Å for the average Li−O bond length, indicating that Li2 is bonded to neighboring oxygens more strongly than Li1. The coordination environment of Li2 resembles a flattened tetrahedron, with O−Li2−O angles in the range from 80 to 175°, and two farther O atoms at 2.65 Å.

Table 3. Interatomic Distances (Å) in α-$LiZr_2(PO_4)_3$ at 423, 673, and 873 K[a]

T (K)	423	673	873
Li1−O1	2.40(4)	2.52(6)	2.39(7)
O2	2.30(3)	2.10(5)	2.11(6)
O2′	2.36(3)	2.27(5)	2.44(6)
O2″	2.03(3)	2.30(4)	2.30(6)
<Li1−O>	2.27	2.30	2.31
Li2−O1	1.892(4) × 2	1.88(1) × 2	1.89(2) × 2
O1′	1.961(9) × 2	1.99(4) × 2	1.97(1) × 2
<Li2−O>	1.93	1.94	1.93
P−O1	1.518(1) × 2	1.513(1) × 2	1.507(2) × 2
O2	1.527(1) × 2	1.522(2) × 2	1.522(2) × 2
<P−O>	1.523	1.518	1.515
Zr−O1	2.039(1) × 3	2.049(2) × 3	2.058(2) × 3
O2	2.080(1) × 3	2.072(2) × 3	2.063(2) × 3
<Zr−O>	2.060	2.061	2.061

[a] The estimated standard deviations are reported in parentheses.

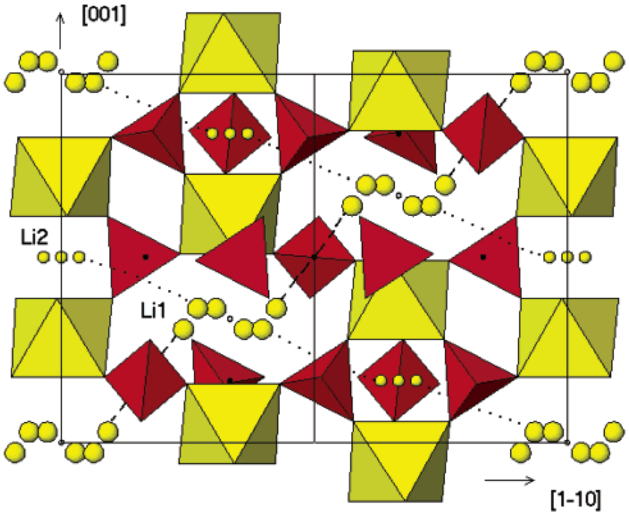

Figure 4. Half unit-cell of α-$LiZr_2(PO_4)_3$ projected onto the (110) plane (T = 873 K). Open dots denote the M′ sites of the NASICON structure. Dashed and dotted lines represent Li1−Li1′ and Li1−Li2 mobility paths of lithium, respectively.

Both pathways connecting the Li1−Li1′ and Li1−Li2 site pairs pass in the neighborhood of the M″ site (Figure 5). In particular, lithium seems to get trapped in the Li2 position by a lateral deviation from its main

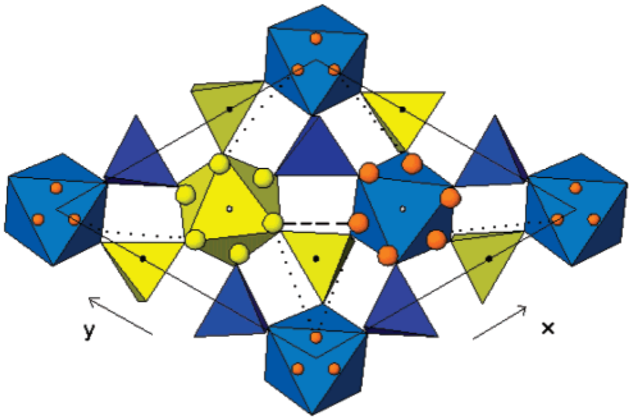

Figure 5. Projection of part of the unit-cell of α-$LiZr_2(PO_4)_3$ onto the (001) plane (T = 873 K). Symbols same as those in Figures 3 and 4.

Table 4. Lithium−Lithium Interatomic Distances (Å) along the Suggested Mobility Pathways[a]

T (K)	423	673	873
Li1−Li1′	4.20(6)	3.93(9)	3.86(11)
Li1−Li2	3.7(1)	3.6(2)	3.9(1)
	3.7(1)	3.8(1)	3.9(1)

[a] The estimated standard deviations are reported in parentheses.

mobility path along the Li1−Li1′−Li1″.... network within the NASICON structure. The Li−Li′ distances along the two paths are reported in Table 4. A clear decrease of the Li1−Li1′ spacing with rising temperature appears, indicating that a transport mechanism based on direct hopping between primary lithium sites is favored by heating. This is consistent with the jump of z coordinate observed from configuration I to II, as discussed above. The comparably short Li1−Li2 distances would suggest that an indirect mechanism involving Li2 as intermediate site could also be feasible, particularly at lower temperature where Li1−Li2 is even shorter than Li1−Li1′. However, Li2 seems to be more strongly bonded than Li1, because the Li2−O bond lengths are shorter than the Li1−O ones, so that the role played by Li2 in the mobility process is probably minor. This is confirmed by a bond valence calculation, according to a widely used exponential relationship to bond distances,[27] which gives bond valence sums of 0.49 *e* for Li1 and 1.16 *e* for Li2 at 423 K. The underbonding of Li1 is outstanding, and it is clearly consistent with the high mobility of lithium on this site.

The second-order phase transition suggested by electrical conductivity and NMR results[13] to occur between 553 and 623 K is supported by our neutron diffraction results, insofar as small but significant discontinuous structural changes affect the two Li1 and Li2 lithium sites and their environments in a similar thermal range.

V. Conclusions

It has been confirmed, by a careful high-resolution powder neutron diffraction study in the 423−873 K range, that neither the M′ nor the M″ site of the NASICON structure of α-$LiZr_2(PO_4)_3$ are suitable for hosting a lithium atom, unlike that which happens for the corresponding sodium compound, and at variance with models recently proposed on the basis of molecular dynamics simulations.[18] This is essentially due to the smaller size of Li compared to that of Na. It should be noticed, however, that in the more compact structure of $LiTi_2(PO_4)_3$ (a = 8.511, c = 20.843 Å) lithium was recently found to be located on the M′ site with six Li−O bonds of 2.266 Å.[14]

Lithium occupies a primary Li1 and a secondary Li2 disordered site, which are displaced from M′ and M″, respectively, and are each coordinated to four neighboring O atoms. Li2 is bonded to oxygens more strongly than Li1, and is probably a trapping site for lithium during its main mobility path along the ...Li1−Li1′... network. No structural phase transitions occur in the thermal range explored, but a small configurational discontinuity of both lithium sites is observed in the middle of such range, which may account for the second-order NMR and electrical conductivity anomalies at about 550 K reported in the literature.

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