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Structural study of polymorphism and thermal behavior of $CaZr(PO_4)_2$

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Abstract

The crystal structure of $CaZr(PO_4)_2$ has been revised by *ab initio* Rietveld analysis of X-ray powder diffraction data. At room temperature, $CaZr(PO_4)_2$ crystallizes in the orthorhombic space group $Pna2_1$ (Z = 4). Differential thermal analysis suggests a reversible second order transition at 1000°C confirmed by high temperature XRD analysis that brings out the existence of a high temperature form, very similar to the room temperature one, but more symmetrical (*Pnma*, Z = 4). Analysis of the crystal parameters evolution during heating reveals that $CaZr(PO_4)_2$ exhibits a quite low thermal expansion coefficient of 6.11 $10^{-6}K^{-1}$. This value stems from a combination of several mechanisms, including Coulombic repulsion and bridging oxygen rocking motion.

Keywords: Crystal structure; thermal expansion; calcium zirconium phosphate

Highlights:

Room temperature structure $CaZr(PO_4)_2$ was revised

A high temperature form of $CaZr(PO_4)_2$ was described for the first time

Thermal expansion of $CaZr(PO_4)_2$ was studied on the basis of the evolution of the crystal parameters evolution during heating

1. Introduction

$M^{II}M'^{IV}(PO_4)_2$ compounds (M^{II}= Cd, Ca, Sr, Pb, Ba; M'^{IV}= Ge, Ti, Mo, Sn, Hf, Zr, Pu, Np, U, Th) are subject of intensive research since they are proved to be interesting as ionic conductors, dielectrics, catalysts, ion exchangers, luminescent materials and UV-emitting X-ray phosphors [1-7]. They also find applications in the nuclear cycle, either as host matrices for actinide radwastes or, more recently, as products of the reaction of the spent nuclear fuel with tributyl phosphate during the reprocessing [8-22].

$M^{II}M'^{IV}(PO_4)_2$ can be classified according to their crystal structure. One can distinguish two main groups, depending on the cations size:

- The cheralite-type compounds, analogues of monazite $CePO_4$, where trivalent Ce is replaced randomly by *M* and *M'*. The archetype, $CaTh(PO_4)_2$, also named brabantite, was described by Rose *et al.* in 1980 [23]. Cheralite compounds crystallize in the monoclinic $P2_1/n$ space group (Z = 4) [24]. This structure consists of chains made up by alternating edges-linked irregular ninefold-coordinated *M*/*M'* cations and distorted tetrahedral phosphate groups. This structural form can be found for high radius *M'* cations (*i.e.* actinides).
- For smaller M'^{IV} cations, like those of the *p*- and *d*-blocks, most of the $M^{II}M'^{IV}(PO_4)_2$ compounds crystallize in the yavapaiite-type structure (isotype of $KFe(SO_4)_2$), which consists of layers running parallel to the (001) plane built up of corner-connected MO_6 octahedra and PO_4 tetrahedra. The M^{II} cation takes place into the interlayer, in a ten-fold oxygen environment [25]. Several derivatives of this archetype, or "distorted yavapaiites" have been observed, according the M^{II} and M'^{IV} cation size [26-28].

Nevertheless, some compositions exhibit a clearly different crystal structure, like $CaZr(PO_4)_2$, $PbSn(PO_4)_2$ and $SrNp(PO_4)_2$ [1,29,30]. The structure of $CaZr(PO_4)_2$ was determined for the first time by Fukuda *et al.* from powder diffraction data [31]. The structure was found to be orthorhombic (space group $P2_12_12_1$, Z = 4). Ca and Zr cations are both sevenfold coordinated

but are located in different sites, unlike in the cheralite structure. On the other hand, the structure is not a layered one, as observed for yavapaiite compounds. Within the $M^{II}M'^{IV}(PO_4)_2$ family, $CaZr(PO_4)_2$ is the compound in which the best optical properties were observed [32]. For such applications, a perfect description of the crystal structure, including a very accurate knowledge of cations environment and atomic distances is required, especially for crystal field calculations. As described in the following sections, our XRD observations suggest that the crystal structure proposed by Fukuda *et al.* is not the most relevant one. In this paper, we propose a revision of the crystal structure of $CaZr(PO_4)_2$. A low and a high temperature forms are proposed. The mechanisms of the phase transition and the thermal expansion of the low temperature form are also described from the lattice thermal evolution during heating.

2. Experimental

2.1. Synthesis and characterization

$CaZr(PO_4)_2$ compounds were obtained from a conventional solid state route. Based on the previous work of Popa *et al.*, a mixture of $CaCO_3$ (Prolabo, 99.5%), ZrO_2 (Aldrich, 99.9%) and 15 wt.% excess of $NH_4H_2PO_4$ (Aldrich, 99.99%) were ground and fired slowly in air up to 1200°C for 10h in a platinum crucible [33]. The thermal cycle was performed twice in order to avoid the presence of unreacted phases. Powder purity was checked by X-Ray powder diffraction. Thermal stability and possible phase transition were studied under air using a Setaram DTA-TG instrument. XRPD was performed on a Panalytical X'Pert Pro diffractometer with an incident-beam Ge monochromator, at U = 45 kV and I = 40 mA. The apparatus was equipped with an Anton Paar HTK 1200 N furnace for high temperature diffraction. The patterns for structural analysis were recorded over 8h in the $8 \leq 2\theta \leq 140°$ range (130° at high temperature), step 0.013°. For the measurement of the thermal expansion,

the patterns were recorded at high temperature in the same range but over 1h. The Rietveld analyses were carried out with the Fullprof suite [34]. Structures were drawn using the VESTA software [35].

2.2. Structure resolution

Except for minor reflections ascribed to spurious NZP-like $Ca_{0.5}Zr_2(PO_4)_3$ (< 5 %), the powder XRD pattern of the sample appears very similar to that reported by the ICDD file 73-2816 calculated from Fukuda's structural data. Nevertheless, while the $P2_12_12_1$ space group proposed by these authors supposes that systematic extinction only affects the *h*00, 0*k*0 and 00*l* reflections with odd Miller indexes, clear hints of the presence of two glide mirrors are observed: a *c* one perpendicular to Fukuda's cell edge *a* and a *n* one perpendicular to the *c* edge. For instance, the relevant reflections (0*kl*, $k = 2n+1$ and *hk*0, $h+k = 2n+1$, barring overlapped ones) are extremely weak, respectively less than 0.1 and 0.6 % in intensity in the ICDD file. From our own XRD pattern, those peaks (25 in the $0 < 2\theta < 80°$ range) were all found to be non-observable. Likewise, the Rietveld analysis performed in Le Bail's (profile matching) mode with the symmorphic *Pmmm* space group resulted in a mean intensity of less than 0.1 % for all of them. In Fukuda's axes setting, these conditions account either for acentric space group $Pc2_1n$ ($Pna2_1$ in standard setting) or for centric *Pcmn* (*Pnma*). A test of second harmonic generation with an incident YAG:Nd laser beam at 1060 nm was negative, thus no conclusion could be achieved on this basis.

The three most probable space groups ($Pna2_1$, *Pnma*, $P2_12_12_1$) were considered for the refinement of the crystal structure at room temperature, termed α-$CaZr(PO_4)_2$. Anisotropic thermal displacements were refined for the heavy Ca and Zr atoms, but all the oxygen atoms of a same PO_4 tetrahedron were given the same isotropic factor. The anisotropic Lorentzian peaks broadening due to crystallites size effects was modeled using the spherical harmonic

profile function. Spurious $Ca_{0.5}Zr_2(PO_4)_3$ was treated as a secondary phase in the Rietveld analysis. For all the models, the refinements performed with "free" oxygen coordinates resulted in poorly realistic P-O distances (1.46-1.61 Å), like in Fukuda's reported data (1.46-1.59 Å). Considering the covalency of the P-O bond that makes its length highly predictable in a monophosphate (1.54 Å), soft constraints were applied on these distances.

3. Results and discussion

3.1 *Crystal structure of the room-temperature form α-CaZr(PO$_4$)$_2$*

The following discussion deals mainly with the determination of the space group of the room-temperature form. This point is pretty delicate, on the one hand because the two hemihedral groups (*Pna*2_1 and *P*$2_12_12_1$) are subgroups of the holohedral one (*Pnma*), on the other hand, because the three structural models only show minor differences after refinement. As shown by Fukuda, the edge-connected CaO_7 and ZrO_7 polyhedra form linear chains. The $P1O_4$ tetrahedron shares two opposite edges with CaO_7 polyhedra and the $P2O_4$ tetrahedra shares an edge with a ZrO_7. Setting the floating z_{Zr} coordinate in the polar *Pna*2_1 space group at the same value as in the *P*$2_12_12_1$ model, the atomic positions appear only faintly distant between the two hemihedral models (Zr: 0.02 Å; Ca: 0.03 Å; P1: 0.07 Å; P2: 0.01 Å; distances between oxygen positions are not significant because of the lower weight of these atoms and the application of soft constraints). The reliability factors are not significantly different (R_{Bragg} = 0.0308 for *Pna*2_1, 0.0324 for *P*$2_12_12_1$), but the systematic absences (see *Experimental*) account for the *Pna*2_1 solution rather than for the *P*$2_12_12_1$ one, defended by Fukuda *et al*.

The choice between the *Pna*2_1 and *Pnma* space groups (with *b*-*c* axes permutation) can hardly be made on the sole basis of the reliability factors (R_{Bragg} = 0.0308 and 0.0387 respectively) because of the lesser number of intensity-dependent parameters in the latter form (52 and 35 respectively). Indeed, the decision hangs on the existence of the *m* mirror. In the holohedral

form, all the cations and half of the oxygen anions are supposed to occupy this special (1/4 or 3/4) position. Once again, the variations of the cations positions are faint (Zr: 0.00 Å; Ca: 0.01 Å; P1: 0.06 Å; P2: 0.04 Å), but in this case the shifts of the oxygen anions involved in edge-sharing between Ca and P1 on the one hand (0.21 and 0.15 Å) and Zr and P2 on the other hand (0.27 and 0.25 Å) are significant enough to be taken into account. Actually, these shared edges, ideally parallel to the *b*-axis in the *Pnma* cell, exhibit a clear zig-zag geometry in the *Pna*2_1 one as a result of the distortion of the PO_4 tetrahedra (Fig. 1. lower view). The same distortion is observed in Fukuda's structure. Besides, the O23-P2-O24 (96.5(8)°) angle corresponding to the shared edge between Zr and P2 is low, because of the Coulombic inter-cations repulsion. As will be shown in the following, these structural features play a role in the peculiar thermal expansion of the compound. Main acquisition and refinement parameters are reported in Table 1, atomic coordinates in Table 2 and bond lengths in Table 3. The crystal structure of α-$CaZr(PO_4)_2$ is drawn in Fig. 1. The resulting final Rietveld plots are shown in Fig. 2.

3.2. Phase transition and high-temperature form β-$CaZr(PO_4)_2$

$CaZr(PO_4)_2$ appears to be stable up to 1200 °C and melts between 1300°C and 1400°C. No peak can be observed by conventional differential thermal analysis between 1000°C and 1200°C, suggesting that the α to β transition could be a reversible second order phase transition. Because no significant variation was observed in the diffraction pattern above this temperature, we refined the structure again in the *Pna*2_1 space group (Tables 1-2). This time, the cations positions turned out to be so faintly shifted (< 0.004 Å, lower than the estimated standard deviations) that they could be considered as located right on the *m*-mirror of the *Pnma* setting. This high-temperature form will be termed β-$CaZr(PO_4)_2$ in the following. As shown by Table 3, its crystal structure is very similar to that of α-$CaZr(PO_4)_2$. Therefore, the

α-β transition appears as a typical second-order phenomenon in agreement with its thermal signature.

3.3 Thermal expansion

The relative variation with temperature of the cell parameters and Ca-P and Zr-P distances of α-$CaZr(PO_4)_2$ is plotted on Fig. 3.

Thermal expansion was calculated according to the following linear equation:

$$\alpha_x = \frac{dx}{x_0}\frac{1}{dT} \qquad \text{(i)}$$

Values are reported on Table 4. The mean relative linear thermal expansion (l) was determined by dividing the volume expansion by 3.

The resulting relative linear thermal expansion appears to be quite low compared to that of the most common oxides (6.11 *vs.* 7-8, 8-12, 9-12 $10^{-6}.K^{-1}$ for alumina, zirconia, magnesia, respectively). Results also show that thermal expansion is rather anisotropic ($\Delta\alpha = 6.7\ 10^{-6}.K^{-1}$). α-$CaZr(PO_4)_2$ mostly expands along the *a*-axis. *b*- and *c*- axes exhibit similar thermal expansion coefficients. Comparison of thermal behavior of $CaZr(PO_4)_2$ with that of some other phosphates (Table 5) reveals that this compound exhibits a interesting combination between low value and moderate anisotropy of thermal expansion. Associated with a good thermal stability (up to 1200 °C), $CaZr(PO_4)_2$ appears to be an interesting material for applications that require a good dimensional stability with temperature.

The thermal expansion behavior of $CaZr(PO_4)_2$ can be explained regarding the polyhedral connections (see Fig. 1). In this structure, different thermal expansion mechanisms can be observed, all described by Sleight on other materials [42]. Along the *a* axis, strong Coulombic repulsion occurs between edge-sharing Zr^{4+} and P^{5+} cations since the Zr-P2(a) distance are short and oxygen atoms screening effect is low, resulting in a strong thermal expansion of the

Zr-P2(a) distance (Figs. 1 and 3, Table 4). On the opposite, when polyhedra are corner-connected, the oxygen shared by the ZrO_7 and $P2(b)O_4$ polyhedra oscillates within an ellipsoid oriented roughly perpendicular to the Zr–O–P axis. Since the Zr-O and P-O bonds are strong enough to present negligible thermal expansion, the transverse motion of oxygen pulls the cations closer together. This so-called "rocking effect" can explain the quite negligible thermal expansion of the Zr-P2(b) distance. CaO_7 polyhedra are only linked by edge to the two PO_4 tetrahedra. The Coulombic repulsion is weaker than in the case of Zr^{4+} because of the lower valency and higher ionic radius of Ca^{2+} leading to a lower thermal expansion. Note that the shortest Ca-P distance (*i.e.* Ca-P1(a)) shows the highest thermal expansion coefficient. The combination of these phenomena leads to a moderate thermal expansion along the *a* axis. The Coulombic repulsion between cations along the *a* axis has a consequence on the thermal expansion along *c*. The oxygen atoms involved in the edges perpendicular to the *M*-P bonds are getting closer, leading to a low thermal expansion along *c* (Fig. 4). Along *b*, the structure presents several connections by corners, especially between CaO_7 and PO_4. This results in a very low thermal expansion along this direction by oxygen rocking effect.

4. Conclusion

A revised structure of $CaZr(PO_4)_2$ has been proposed. For the first time, the existence of a high temperature form of this compound has been highlighted. These structures are strongly different to that of most of the other compounds of the $M^{II}M'^{IV}(PO_4)_2$ family (yavapaiite and cheralite). Analysis of the crystal parameters evolution during heating reveals that $CaZr(PO_4)_2$ exhibits a quite low thermal expansion coefficient of 6.11 $10^{-6}K^{-1}$, suggesting that this compounds could find applications when dimensional stability is required.

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Appendix A. Supplementary data

Supplementary data related to this article:

- CIF and CheckCIF files of α-$CaZr(PO_4)_2$
- CIF and CheckCIF files of β-$CaZr(PO_4)_2$
- CSD number of α-$CaZr(PO_4)_2$: 428800
- CSD number of β-$CaZr(PO_4)_2$: 428801
- Peak list file of α-$CaZr(PO_4)_2$

References

[1] E. Morin, G. Wallez, S. Jaulmes, J.C. Couturier, M. Quarton, J. Solid State Chem.137 (1998) 283.

[2] F. Tudorache, K. Popa, L. Mitoseriu, N. Lupu, D. Bregiroux, G. Wallez, J. Alloys Compd 509 (2011) 9127

[3] K. Fukuda, A. Moriyama, T. Iwata, J. Solid State Chem.178 (2005) 2144.

[4] G. Blasse, G.J. Dirksen, Chem. Phys. Lett. 62 (1979) 19.

[5] C.R. Miao, C.C. Torardi, J. Solid State Chem.155 (2000) 229.

[6] Z.J. Zhang, J.L. Yuan, X.J. Wang, D.B. Xiong, H.H. Chen, J.T. Zhao, Y.B. Fu, Z.M. Qi, G.B. Zhang, C.S. Shi, J. Phys. D: Appl. Phys. 40 (2007) 1910.

[7] W.-L. Zhang, C.-S. Lin, Z.-Z. He, H. Zhang, Z.-Z. Luo, W.-D. Cheng, CrystEngComm 15 (2013) 7089.

[8] I.W. Donald, Waste immobilization in glass and ceramic based hosts. Radioactive, toxic and hasardous wastes, Wiley, Chichester, UK, 2010.

[9] W.C. Overstreet, U.S. Geological Survey Professional Paper 530 (1967) 1.

[10] C.M. Gramaccioli, T.V. Segalstad, Am. Mineral. 63 (1978) 757.

[11] B.C. Sales, C.W. White, L.A. Boatner, Nucl.Chem. Waste Managem.4 (1983) 266.

[12] L.A. Boatner, G.W. Beall, M.M. Abraham, C.B. Finch, P.G. Hurray, M. Rappaz, p. 289 in Scientific Basis for Nuclear Waste Management, Vol. 2, Edited by C.J.M. Northrup Jr. Material Research Society, Warrendale, PA, USA, New York, 1980.

[13] L.A. Boatner, B.C. Sales, in Radioactive waste forms for the future, Edited by W. Lutze, R.C. Ewing, North Holland, Amsterdam (1988) 495.

[14] A. Meldrum, L.A. Boatner, W.J. Weber, R.C. Ewing, Geochim. Cosmochim. Acta 62 (1998) 2509.

[15] O. Terra, N. Clavier, N. Dacheux, R. Podor, New J. Chem. 27 (2003) 957.

[16] R.C. Ewing, Progr. Nucl. Energy 49 (2007) 635.

[17] D. Olander, J. Nucl. Mater. 389 (2009) 1.

[18] H. Schlenz, J. Heuser, A. Neumann, Z. Kristallogr 228 (2013) 113.

[19] N. Dacheux, N. Clavier, R. Podor, Am. Mineral. 98 (2013) 833.

[20] R.L. Murray, K.E. Holbert, chap. 23: Radioactive Waste Disposal, in « Nuclear Energy » (7th edition), Elsevier, 2014, 395-426.

[21] O. Terra, N. Dacheux, F. Audubert, R. Podor, J. Nucl. Mater. 352 (2006) 224.

[22] E. Veilly, E. du Fou de Kerdaniel, J. Roques, N. Dacheux, N. Clavier, Inorg. Chem. 47 (2008) 10971.

[23] D. Rose, Neues Jahr. Mineral. Monat.6 (1980) 247.

[24] G.W. Beall, L.A. Boatner, D.F. Mullica, W.O. Milligan, J. Inorg. Nucl. Chem. 43 (1981) 101.

[25] E.J. Graeber, A. Rosenzweig, Amer. Min. 56 (1971) 1917.

[26] D. Bregiroux, K. Popa, R. Jardin, P.E. Raison, G. Wallez, M. Quarton, M. Brunelli, C. Ferrero, R. Caciuffo, J. Solid State Chem. 182 (2009) 1115.

[27] K. Popa, G. Wallez, D. Bregiroux, P. Loiseau, J. Solid State Chem. 184 (2011) 2629.

[28] G. Wallez, D. Bregiroux, K. Popa, P.E. Raison, C. Apostolidis, P. Lindqvist-Reis, R.J.M. Konings, A.F. Popa, Eur. J. Inorg. Chem. (2011) 110.

[29] K. Fukuda, K. Fukutani, Powder Diffr. 18 (2003) 296.

[30] K. Popa, G. Wallez, P.E. Raison, D. Bregiroux, C. Apostolidis, P. Lindqvist-Reis, R.J.M. Konings, Inorg. Chem. 49 (2010) 6904.

[31] K. Fukuda, K. Fukutani, Powder Diffr. 18(4) (2003) 296.

[32] J.-C. Zhang, Y.-Z. Long, H.-D. Zhang, B. Sun, W.-P. Han, X.-Y. Sun, J. Mater. Chem. C, 2 (2014) 312.

[33] K. Popa, R.J.M. Konings, P. Boulet, D. Bouëxière, A.F. Popa, Thermochim. Acta 436 (2005) 51.

[34] J. Rodriguez-Carvajal, FULLPROF.2k : Rietveld, profile matching and integrated intensity refinement of X-ray and neutron data, V 1.9c, Laboratoire Léon Brillouin, CEA, Saclay, France, 2001.

[35] K. Momma, F. Izumi, J. Appl. Crystallogr., 44 (2011) 1272.

[36] N.E. Breese, M. O'Keeffe, Acta Cryst. B47 (1991) 192.

[37] A.I. Orlova, D.V. Kemenov, S.G. Samoilov, G.N. Kazantsev, V.I. Pet'kov, Inorg. Mater., 36 (2000) 830.

[38] D. Bregiroux, F. Audubert, E. Champion, D. Bernache-Assollant, Mater. Lett. 57 (2003) 3526.

[39] T. Tonegawa, T. Ikoma, Y. Suetsugu, N. Igawa, Y. Matsushita, T. Yoshioka, N. Hanagata, J. Tanaka, Mater. Sci. Eng. B, 173 (2010) 171.

[40] L. Perrière, D. Bregiroux, B. Naitali, F. Audubert, E. Champion, D.S. Smith, D. Bernache-Assollant, J.Eur. Ceram. Soc. 27 (2007) 3207.

[41] G. Wallez, D. Bregiroux, M. Quarton, J. Solid State Chem. 181 (2008) 1413.

[42] A.W. Sleight, Inorg. Chem. 37 (1998) 2854.

Tables caption

Table 1

Main acquisition, refinement and lattice data for α- and β-$CaZr(PO_4)_2$.

Table 2

Atomic positions and thermal factors for α- and β-$CaZr(PO_4)_2$.

Table 3

Bond lengths in α- and β-$CaZr(PO_4)_2$ (in Å).

Table 4

Thermal expansion in α-$CaZr(PO_4)_2$.

Table 5

Comparison of thermal expansion of $CaZr(PO_4)_2$ with some other phosphates

Figures caption

Fig. 1. Views of the structure of α-$CaZr(PO_4)_2$

Fig. 2. Rietveld plots for α-$CaZr(PO_4)_2$ and β-$CaZr(PO_4)_2$: y_{obs} (dots), y_{calc} (solid, upper), y_{obs}-y_{calc} (solid, lower), Bragg positions (bars)

Fig. 3. Thermal evolution of the cell parameters (a) and Ca-P and Zr-P distances (b, see Fig. 1. for atoms nomenclature)

Fig. 4. Coulombic repulsions between cations lead to high thermal expansion along *a* and low thermal expansion along *c*

Table 1

Main acquisition, refinement and lattice data for α- and β-$CaZr(PO_4)_2$.

Apparatus	Panalytical X'Pert Pro	
Anode, monochromator	CuKα1 (40 kV, 45 mA), Ge (111)	
Form	α-$CaZr(PO_4)_2$	β-$CaZr(PO_4)_2$
Temperature	20 °C	1200 °C
Scan range, step, time	$8.00 \leq 2\theta \leq 140.00°$, 0.013°, 8 h	$8.00 \leq 2\theta \leq 130.00°$, 0.013°, 8 h
Measured reflections	626	576
Intensity / profile parameters	52 / 14	35 / 14
Reliability factors	R_P = 0.012 R_{WP} = 0.018 R_{Bragg} = 0.035 χ^2 = 8.2	R_P = 0.15 R_{WP} = 0.20 R_{Bragg} = 0.073 χ^2 = 6.4
System, space group	orthorhombic, *Pna*2_1 (33)	orthorhombic, *Pnma* (62)
Cell parameters, volume	a = 6.2330(2) Å b = 14.4852(5) Å c = 6.7213(3) Å V = 606.84(7) Å^3	a = 6.3125(2) Å (= a_α) b = 6.7512(2) Å (= c_α) c = 14.5537(4) Å (= b_α) V = 620.23(6) Å^3
Formula per cell / calc. density	4 / 3.52	4 / 3.44

Table 2

Atomic positions and thermal factors for α- and β-$CaZr(PO_4)_2$.

	α-$CaZr(PO_4)_2$				β-$CaZr(PO_4)_2$			
Atom	*x*	*y*	*z*	*B** (Å^2)	*x*	*y*	*z*	*B** (Å^2)
Ca	0.5492(2)	0.3518(1)	0.256(2)	1.74(4)	0.5466(5)	1/4	0.3534(3)	3.82(9)
Zr	0.8239(1)	0.3907(1)	0.75	1.61(1)	0.8340(2)	3/4	0.3896(1)	2.07(3)
P1	0.5459(2)	0.1151(1)	0.2435(4)	2.05(6)	0.5385(5)	1/4	0.1146(3)	2.26(8)
O11	0.6996(6)	0.0306(2)	0.244(4)	1.24(6)	0.687(1)	1/4	0.0292(5)	3.4(1)
O12	0.6784(7)	0.2051(2)	0.238(3)	"	0.681(1)	1/4	0.2001(5)	"
O13**	0.396(2)	0.1194(7)	0.425(2)	"	0.3901(8)	0.4308(7)	0.1119(5)	"
O14**	0.389(2)	0.1043(6)	0.067(2)	"				
P2	0.1313(2)	0.8533(1)	0.2480(4)	2.16(6)	0.1281(5)	1/4	0.8520(2)	2.5(1)
O21	0.1728(7)	0.7493(2)	0.268(2)	1.43(7)	0.169(1)	1/4	0.7482(4)	3.5(1)
O22	0.3425(5)	0.9078(3)	0.259(3)	"	0.339(1)	1/4	0.9037(6)	"
O23**	-0.014(2)	0.8730(6)	0.428(1)	"	-0.146(8)	0.4196(8)	0.8815(5)	"
O24**	-0.016(2)	0.8970(5)	0.091(1)	"				

* given values are B_{iso} for oxygen and phosphorus; B_{eq} for calcium and zirconium. For B_{aniso}, see supplementary material

** atoms O13 and O14 of α-$CaZr(PO_4)_2$ merge into a single atom in the β-form, idem for O23 and O24

Table 3

Bond lengths in α- and β-$CaZr(PO_4)_2$ (in Å).

Bond	α-$CaZr(PO_4)_2$	β-$CaZr(PO_4)_2$	Bond	α-$CaZr(PO_4)_2$	β-$CaZr(PO_4)_2$
Ca-O11	2.766(4)	2.842(9)	Zr-O22	2.095(3)	2.073(7)
Ca-O12	2.275(4)	2.387(9)	Zr-O23	2.287(9)	2.322(6)
Ca-O12	2.457(5)	2.435(9)	Zr-O24	2.20(1)	“
Ca-O13	2.48(1)	2.539(6)	P1-O11	1.553(4)	1.556(9)
Ca-O14	2.55(1)	“	P1-O12	1.545(4)	1.536(9)
Ca-O23	2.23(1)	2.276(6)	P1-O13	1.54(1)	1.539(5)
Ca-O24	2.35(1)	“	P1-O14	1.54(1)	“
Zr-O11	2.033(3)	2.035(7)	P2-O21	1.533(3)	1.532(7)
Zr-O13	2.23(1)	2.184(5)	P2-O22	1.536(4)	1.530(8)
Zr-O14	2.17(1)	“	P2-O23	1.537(9)	1.519(6)
Zr-O21	2.032(3)	2.006(6)	P2-O24	1.538(9)	“

Bond valence sums (v.u.) from [36]: Ca : 2.12 (α), 1.99 (β); Zr: 4.06 (α), 4.06 (β); for O-P-O angles, see supplementary material

Table 4

Thermal expansion in α-$CaZr(PO_4)_2$.

Parameter	α ($10^{-6}.K^{-1}$)	Distance	α ($10^{-6}.K^{-1}$)
a	10.3	Zr-P2(a)	16.4
b	4.1	Zr-P2(b)	0.6
c	3.8	Ca-P1(a)	13.9
l	6.1	Ca-P1(b)	5.9

Note that P1(a)/P1(b) and P2(a)/P2(b) refer to the same atom P1 and P2, respectively.

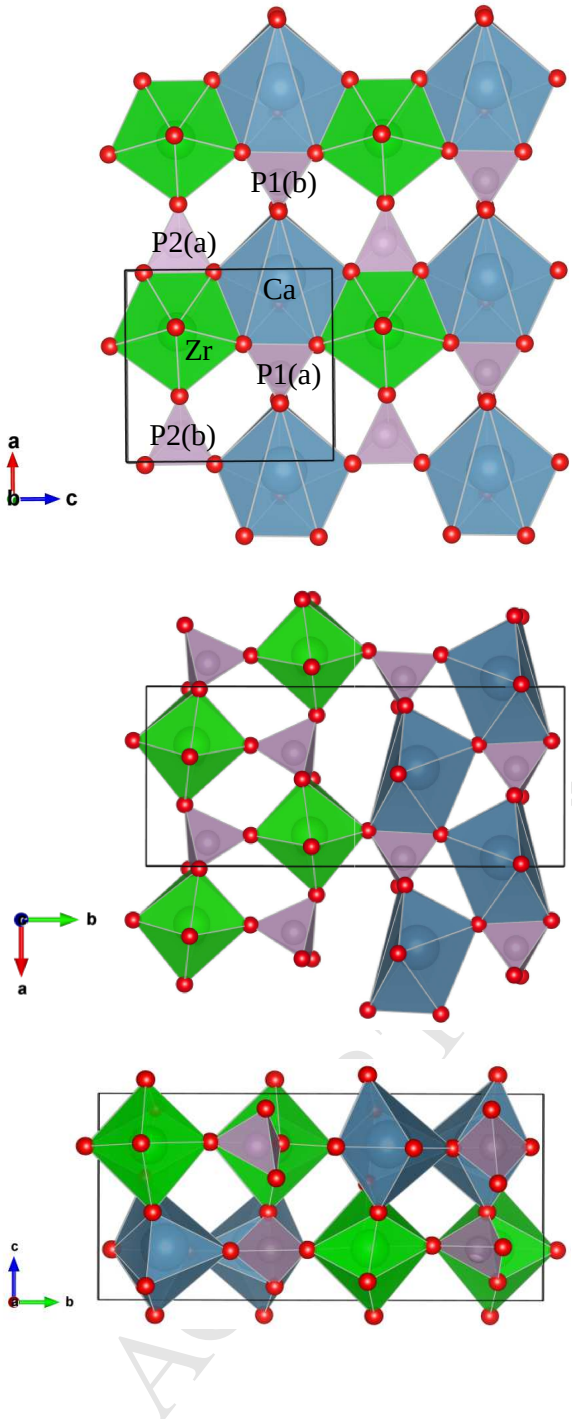

Fig. 1. Views of the structure of α-$CaZr(PO_4)_2$

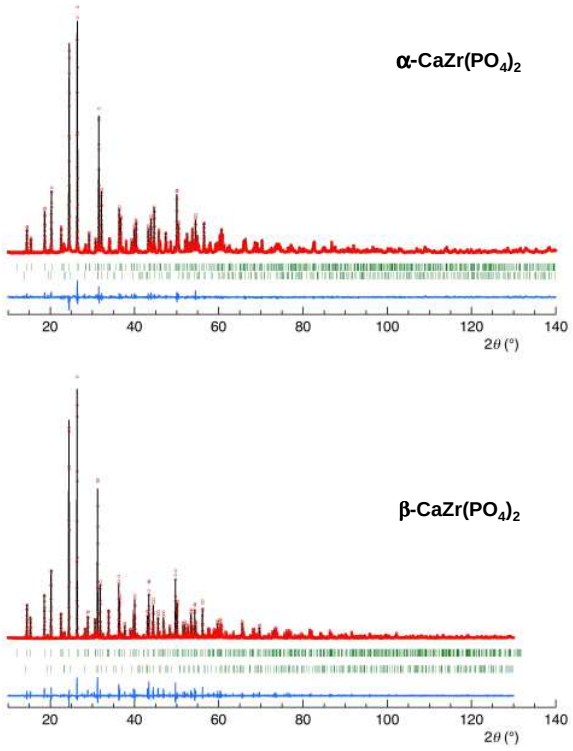

Fig. 2. Rietveld plots for α-$CaZr(PO_4)_2$ and β-$CaZr(PO_4)_2$: y_{obs} (dots), y_{calc} (solid, upper), y_{obs}-y_{calc} (solid, lower), Bragg positions (bars)

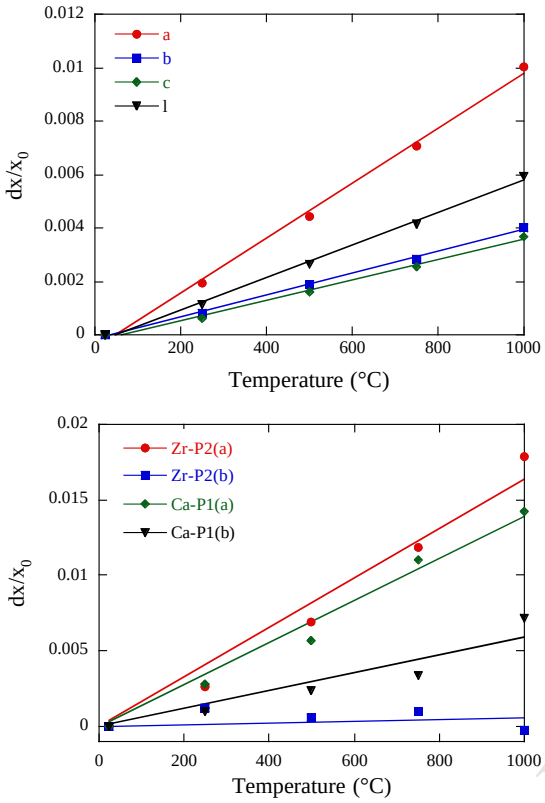

Fig. 3. Thermal evolution of the cell parameters (a) and Ca-P and Zr-P distances (b, see Fig. 1. for atoms nomenclature)

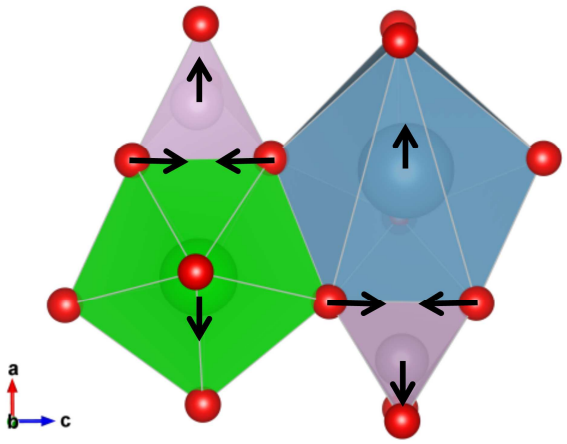

Fig. 4. Coulombic repulsions between cations lead to high thermal expansion along *a* and low thermal expansion along *c*

Highlights:

Room temperature structure $CaZr(PO_4)_2$ was revised

A high temperature form of $CaZr(PO_4)_2$ was described for the first time

Thermal expansion of $CaZr(PO_4)_2$ was studied on the basis of the evolution of the crystal parameters evolution during heating

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: I

Bond precision: P- O = 0.0074 A Wavelength=1.54180

Cell: a=6.2330(1) b=14.4852(4) c=6.72130(1)
alpha=90 beta=90 gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	606.841(19)	606.841(19)
Space group	P n a 21	P n a 21
Hall group	P 2c -2n	P 2c -2n
Moiety formula	O8 P2 Zr, Ca	O8 P2 Zr, Ca
Sum formula	Ca O8 P2 Zr	Ca1 O8 P2 Zr
Mr	321.24	321.24
Dx,g cm-3	3.516	3.516
Z	4	4
Mu (mm-1)	27.547	27.547
F000	616.0	616.0
F000'	620.78	
h,k,lmax	7,17,8	7,17,8
Nref	1147[626]	626
Tmin,Tmax		
Tmin'		

Correction method= Not given

Data completeness= 1.00/0.55 Theta(max)= 69.998

R(reflections)= wR2(reflections)=

S = Npar=

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT111_ALERT_2_B ADDSYM Detects (Pseudo) Centre of Symmetry ..... 100 %Fit

---

Alert level C

PLAT163_ALERT_4_C Missing or Zero su (esd) on z-coordinate for ... ZR
PLAT213_ALERT_2_C Atom Ca has ADP max/min Ratio ..... 3.9 prolat

---

Alert level G

PLAT004_ALERT_5_G Polymeric Structure Found with Dimension ..... 3 Info
PLAT112_ALERT_2_G ADDSYM Detects Additional (Pseudo) Symm. Elem... m Check
PLAT113_ALERT_2_G ADDSYM Suggests Possible Pseudo/New Space group. Pnma Check
PLAT143_ALERT_4_G su on c - Axis Small or Missing ..... 0.00001 Ang.
PLAT794_ALERT_5_G Tentative Bond Valency for Zr (IV) ..... 4.33 Note
PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 8 Note
PLAT982_ALERT_1_G The Ca-f'= 0.341 Deviates from the IT-value 0.364 Check
PLAT982_ALERT_1_G The O-f'= 0.047 Deviates from the IT-value 0.049 Check
PLAT982_ALERT_1_G The P-f'= 0.283 Deviates from the IT-value 0.296 Check
PLAT982_ALERT_1_G The Zr-f'= -0.314 Deviates from the IT-value -0.186 Check

---

0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
2 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
10 **ALERT level G** = General information/check it is not something unexpected

4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
4 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

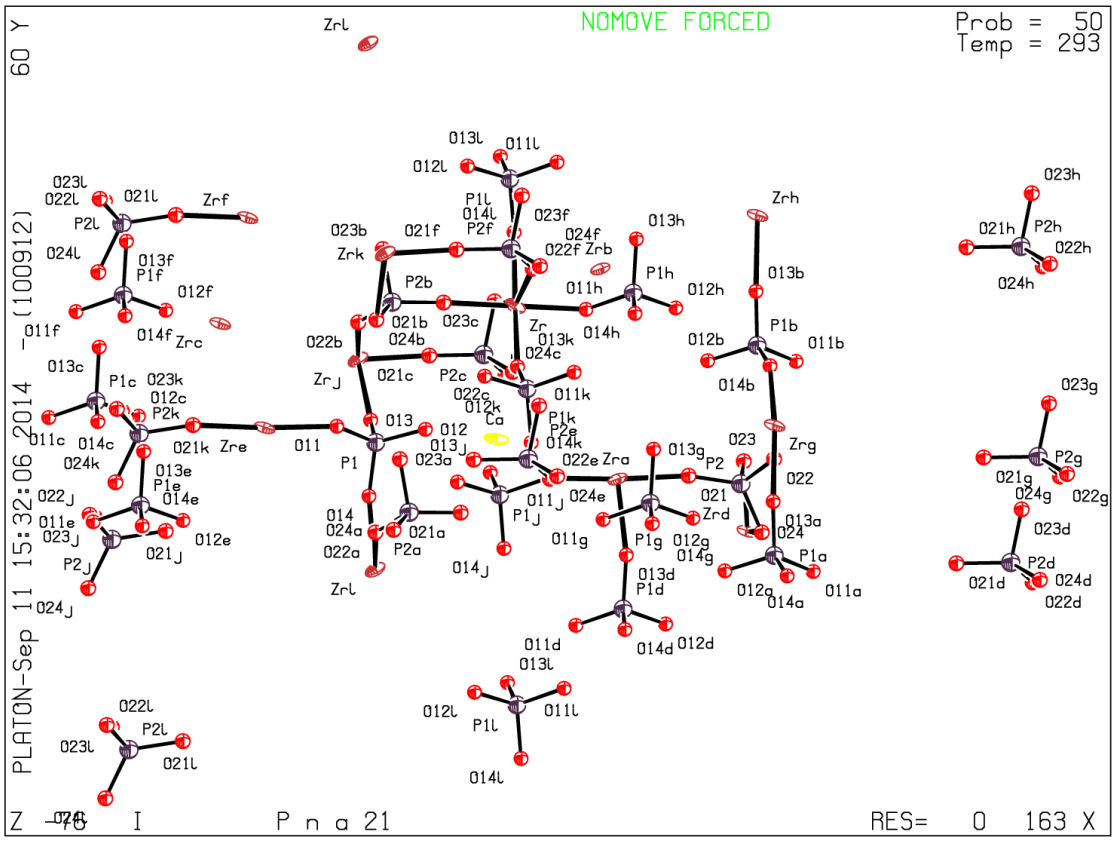
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 20/08/2014; check.def file version of 18/08/2014

Datablock I - ellipsoid plot



checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: I

Bond precision: P- O = 0.0070 A Wavelength=1.54180

Cell: a=6.3125(2) b=6.7512(2) c=14.5537(4)
alpha=90 beta=90 gamma=90
Temperature: ?

	Calculated	Reported
Volume	620.23(3)	620.23(3)
Space group	P n m a	P n m a
Hall group	-P 2ac 2n	-P 2ac 2n
Moiety formula	O8 P2 Zr, Ca	O8 P2 Zr, Ca
Sum formula	Ca O8 P2 Zr	Ca1 O8 P2 Zr
Mr	321.24	321.24
Dx,g cm-3	3.440	3.440
Z	4	4
Mu (mm-1)	26.953	26.953
F000	616.0	616.0
F000’	620.78	
h,k,lmax	7,7,17	7,7,17
Nref	576	576
Tmin,Tmax		
Tmin’		

Correction method= Not given

Data completeness= 1.000 Theta(max)= 64.996

R(reflections)= wR2(reflections)=

S = Npar=

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level G

```
PLAT004_ALERT_5_G Polymeric Structure Found with Dimension .......          3 Info
PLAT794_ALERT_5_G Tentative Bond Valency for Zr      (IV)    .....       4.22 Note
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............          6 Note
PLAT982_ALERT_1_G The Ca-f'=     0.341 Deviates from the  IT-value      0.364 Check
PLAT982_ALERT_1_G The  O-f'=     0.047 Deviates from the  IT-value      0.049 Check
PLAT982_ALERT_1_G The  P-f'=     0.283 Deviates from the  IT-value      0.296 Check
PLAT982_ALERT_1_G The Zr-f'=    -0.314 Deviates from the  IT-value     -0.186 Check
```

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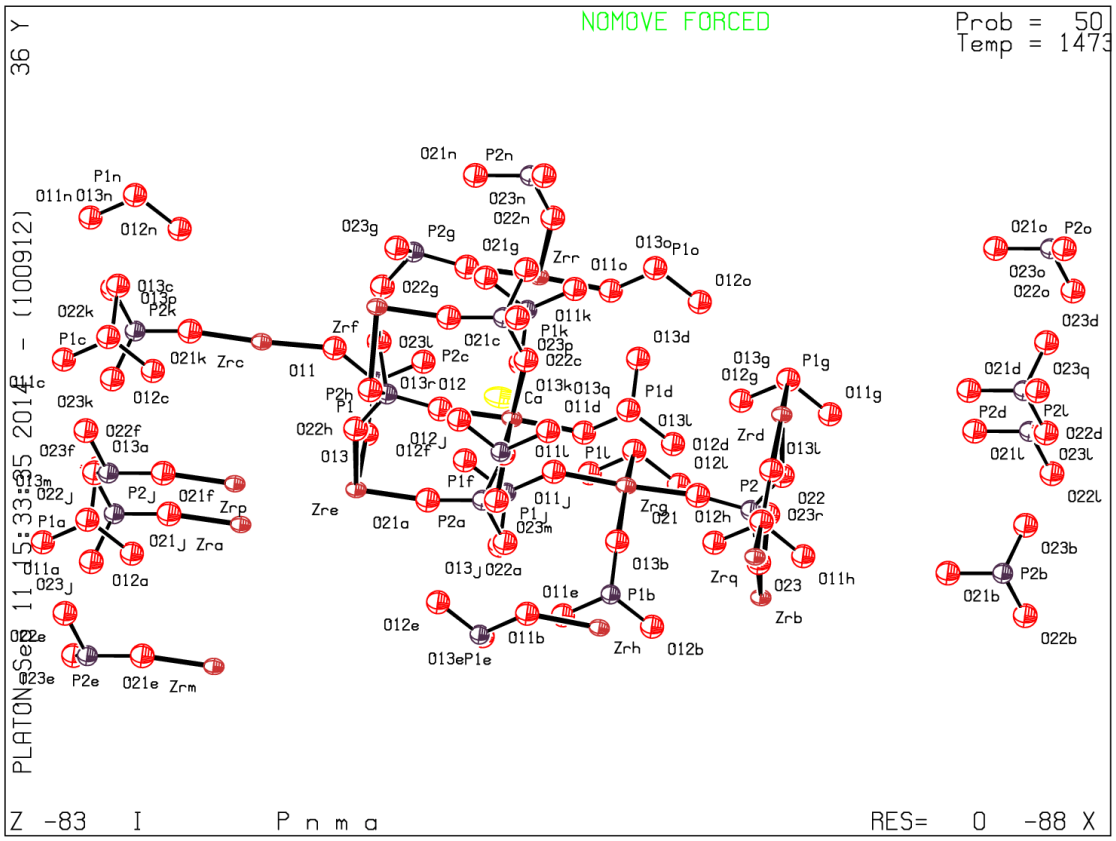
PLATON version of 20/08/2014; check.def file version of 18/08/2014

Datablock I - ellipsoid plot



The following list summarizes all the diffraction peaks of $CaZr(PO_4)_2$ up to 80 °, measured by Fullprof assuming Fukuda's $P2_12_12_1$ space group. Maximum intensity is 26204 counts (002). Reflections in red, all below detection threshold, account for 0*kl*, *k*+*l*=2*n*+1 or *h*0*l*, *h*=2*n*+1 extinctions. Strongly overlapped peaks, yellow highlighted, should not be taken into account.

h	k	l	Mult	Freal	Fimag	2T	Intensity	Code
0	2	0	2	0.0000	0.0000	12.2092	0.0000	0
0	1	1	4	0.0000	0.0000	14.5146	2997.7495	0
1	1	0	4	0.0000	0.0000	15.4620	1794.1384	0
0	2	1	4	0.0000	0.0000	17.9882	0.0000	0
1	2	0	4	0.0000	0.0000	18.7653	5256.6631	0
1	0	1	4	0.0000	0.0000	19.4039	0.0771	0
1	1	1	8	0.0000	0.0000	20.3566	7532.6211	0
0	3	1	4	0.0000	0.0000	22.6540	3273.5964	0
1	2	1	8	0.0000	0.0000	22.9886	33.3553	0
1	3	0	4	0.0000	0.0000	23.2818	665.7825	0
0	4	0	2	0.0000	0.0000	24.5598	24134.3359	0
0	**0**	**2**	**2**	**0.0000**	**0.0000**	**26.4976**	**26204.9336**	**0**
1	3	1	8	0.0000	0.0000	26.8350	0.9629	0
0	1	2	4	0.0000	0.0000	27.2148	31.4433	0
0	4	1	4	0.0000	0.0000	27.9611	0.5058	0
1	4	0	4	0.0000	0.0000	28.4792	1015.1817	0
2	0	0	2	0.0000	0.0000	28.6161	0.3218	0
0	2	2	4	0.0000	0.0000	29.2689	693.7385	0
2	1	0	4	0.0000	0.0000	29.2854	1676.3821	0
1	0	2	4	0.0000	0.0000	30.1840	0.0000	0
1	1	2	8	0.0000	0.0000	30.8223	1527.0349	0
2	2	0	4	0.0000	0.0000	31.2148	112.6263	0
1	4	1	8	0.0000	0.0000	31.4903	140.5853	0

2	0	1	4	0.0000	0.0000	31.6153	16395.0742	0
2	1	1	8	0.0000	0.0000	32.2281	7420.8955	0
0	3	2	4	0.0000	0.0000	32.4284	25.3111	0
1	2	2	8	0.0000	0.0000	32.6696	497.6013	0
0	5	1	4	0.0000	0.0000	33.6564	0.0000	0
2	2	1	8	0.0000	0.0000	34.0071	608.8705	0
1	5	0	4	0.0000	0.0000	34.0960	1613.0172	0
2	3	0	4	0.0000	0.0000	34.2125	1666.0769	0
1	3	2	8	0.0000	0.0000	35.5583	311.9702	0
0	4	2	4	0.0000	0.0000	36.4398	6432.3965	0
1	5	1	8	0.0000	0.0000	36.6940	1251.1421	0
2	3	1	8	0.0000	0.0000	36.8034	4458.2886	0
0	6	0	2	0.0000	0.0000	37.2087	630.6879	0
2	4	0	4	0.0000	0.0000	38.0590	1598.5714	0
1	4	2	8	0.0000	0.0000	39.2907	425.3597	0
2	0	2	4	0.0000	0.0000	39.3939	1463.3533	0
0	6	1	4	0.0000	0.0000	39.6303	2.4266	0
2	1	2	8	0.0000	0.0000	39.9016	287.0677	0
1	6	0	4	0.0000	0.0000	40.0129	3504.2375	0
2	4	1	8	0.0000	0.0000	40.4374	4483.2822	0
0	1	3	4	0.0000	0.0000	40.7127	343.4568	0
0	5	2	4	0.0000	0.0000	41.0976	0.0063	0
2	2	2	8	0.0000	0.0000	41.3937	178.6885	0
0	2	3	4	0.0000	0.0000	42.1811	0.0000	0
1	6	1	8	0.0000	0.0000	42.2994	65.0679	0
2	5	0	4	0.0000	0.0000	42.5671	182.8900	0
1	0	3	4	0.0000	0.0000	42.8526	0.0865	0

1	1	3	8	0.0000	0.0000	43.3268	3044.1064	0
1	5	2	8	0.0000	0.0000	43.6929	1936.4833	0
2	3	2	8	0.0000	0.0000	43.7875	161.4776	0
3	1	0	4	0.0000	0.0000	43.9864	4267.2622	0
0	3	3	4	0.0000	0.0000	44.5406	988.0898	0
1	2	3	8	0.0000	0.0000	44.7254	4386.1328	0
2	5	1	8	0.0000	0.0000	44.7468	1966.4749	0
3	2	0	4	0.0000	0.0000	45.3688	41.4814	0
3	0	1	4	0.0000	0.0000	45.6614	0.0442	0
0	7	1	4	0.0000	0.0000	45.8397	3269.4043	0
3	1	1	8	0.0000	0.0000	46.1127	1037.3604	0
1	7	0	4	0.0000	0.0000	46.1803	859.2186	0
0	6	2	4	0.0000	0.0000	46.2597	75.4083	0
2	4	2	8	0.0000	0.0000	46.9741	25.9204	0
1	3	3	8	0.0000	0.0000	46.9830	116.1449	0
3	2	1	8	0.0000	0.0000	47.4464	2516.9441	0
2	6	0	4	0.0000	0.0000	47.6012	646.9089	0
3	3	0	4	0.0000	0.0000	47.6026	650.9114	0
0	4	3	4	0.0000	0.0000	47.6877	5.3313	0
1	7	1	8	0.0000	0.0000	48.2309	374.4616	0
1	6	2	8	0.0000	0.0000	48.6350	1783.9128	0
2	6	1	8	0.0000	0.0000	49.6072	336.2360	0
3	3	1	8	0.0000	0.0000	49.6085	342.2342	0
1	4	3	8	0.0000	0.0000	50.0115	97.7406	0
2	0	3	4	0.0000	0.0000	50.0968	7612.5518	0
0	8	0	2	0.0000	0.0000	50.3488	2862.1204	0
2	1	3	8	0.0000	0.0000	50.5179	3663.6912	0

3	4	0	4	0.0000	0.0000	50.6032	82.4974	0
2	5	2	8	0.0000	0.0000	50.8436	37.3449	0
0	5	3	4	0.0000	0.0000	51.5171	61.5790	0
3	0	2	4	0.0000	0.0000	51.6757	1.3276	0
2	2	3	8	0.0000	0.0000	51.7660	87.8422	0
0	7	2	4	0.0000	0.0000	51.8383	16.0640	0
3	1	2	8	0.0000	0.0000	52.0875	1467.9346	0
0	8	1	4	0.0000	0.0000	52.2766	16.3894	0
3	4	1	8	0.0000	0.0000	52.5243	2072.3459	0
1	8	0	4	0.0000	0.0000	52.5857	818.1835	0
2	7	0	4	0.0000	0.0000	53.0744	1383.9629	0
3	2	2	8	0.0000	0.0000	53.3094	386.5337	0
1	5	3	8	0.0000	0.0000	53.7192	1152.9529	0
2	3	3	8	0.0000	0.0000	53.8003	2949.6833	0
1	7	2	8	0.0000	0.0000	54.0312	463.6395	0
3	5	0	4	0.0000	0.0000	54.2820	1270.4956	0
1	8	1	8	0.0000	0.0000	54.4571	0.0563	0
0	0	4	2	0.0000	0.0000	54.5627	4191.3540	0
2	7	1	8	0.0000	0.0000	54.9342	1801.9020	0
0	1	4	4	0.0000	0.0000	54.9594	395.2951	0
2	6	2	8	0.0000	0.0000	55.3028	414.8722	0
3	3	2	8	0.0000	0.0000	55.3041	421.5350	0
0	6	3	4	0.0000	0.0000	55.9385	0.0000	0
3	5	1	8	0.0000	0.0000	56.1145	7.5141	0
0	2	4	4	0.0000	0.0000	56.1381	2.8176	0
2	4	3	8	0.0000	0.0000	56.5630	4396.1016	0
1	0	4	4	0.0000	0.0000	56.6828	173.4236	0

1	1	4	8	0.0000	0.0000	57.0697	253.7804	0
0	8	2	4	0.0000	0.0000	57.7872	1060.2554	0
3	4	2	8	0.0000	0.0000	58.0189	755.2390	0
1	6	3	8	0.0000	0.0000	58.0253	546.9765	0
0	3	4	4	0.0000	0.0000	58.0674	99.0517	0
1	2	4	8	0.0000	0.0000	58.2202	346.3297	0
3	6	0	4	0.0000	0.0000	58.5606	0.0000	0
2	8	0	4	0.0000	0.0000	58.9383	28.3580	0
0	9	1	4	0.0000	0.0000	58.9541	39.6393	0
1	9	0	4	0.0000	0.0000	59.2397	475.3760	0
4	0	0	2	0.0000	0.0000	59.2433	548.9984	0
4	1	0	4	0.0000	0.0000	59.6196	1106.3279	0
1	8	2	8	0.0000	0.0000	59.8327	554.9004	0
2	5	3	8	0.0000	0.0000	59.9914	1265.1919	0
1	3	4	8	0.0000	0.0000	60.1069	106.1573	0
2	7	2	8	0.0000	0.0000	60.2820	1011.7947	0
3	6	1	8	0.0000	0.0000	60.3081	1732.4614	0
2	8	1	8	0.0000	0.0000	60.6792	1939.9963	0
0	4	4	4	0.0000	0.0000	60.7028	1070.0323	0
3	0	3	4	0.0000	0.0000	60.7381	227.4752	0
4	2	0	4	0.0000	0.0000	60.7399	231.7396	0
0	7	3	4	0.0000	0.0000	60.8844	1333.6071	0
1	9	1	8	0.0000	0.0000	60.9753	1024.7820	0
4	0	1	4	0.0000	0.0000	60.9789	991.2356	0
3	1	3	8	0.0000	0.0000	61.1088	186.9957	0
4	1	1	8	0.0000	0.0000	61.3487	657.1586	0
3	5	2	8	0.0000	0.0000	61.3963	339.9083	0

3	2	3	8	0.0000	0.0000	62.2131	498.6354	0
4	2	1	8	0.0000	0.0000	62.4506	22.3768	0
4	3	0	4	0.0000	0.0000	62.5804	853.1497	0
1	4	4	8	0.0000	0.0000	62.6902	121.0082	0
2	0	4	4	0.0000	0.0000	62.7638	199.6674	0
1	7	3	8	0.0000	0.0000	62.8684	68.6504	0
2	1	4	8	0.0000	0.0000	63.1276	199.2425	0
3	7	0	4	0.0000	0.0000	63.3789	0.0000	0
0	5	4	4	0.0000	0.0000	63.9950	63.7381	0
2	6	3	8	0.0000	0.0000	64.0281	66.8532	0
3	3	3	8	0.0000	0.0000	64.0293	53.3899	0
0	9	2	4	0.0000	0.0000	64.0913	26.7765	0
2	2	4	8	0.0000	0.0000	64.2121	44.4616	0
0	10	0	2	0.0000	0.0000	64.2433	189.9777	0
4	3	1	8	0.0000	0.0000	64.2630	325.2186	0
3	7	1	8	0.0000	0.0000	65.0500	276.8649	0
4	4	0	4	0.0000	0.0000	65.1072	57.4412	0
2	9	0	4	0.0000	0.0000	65.1759	39.5526	0
3	6	2	8	0.0000	0.0000	65.3830	467.1862	0
2	8	2	8	0.0000	0.0000	65.7378	63.7310	0
0	10	1	4	0.0000	0.0000	65.9026	284.3600	0
1	5	4	8	0.0000	0.0000	65.9263	366.6651	0
2	3	4	8	0.0000	0.0000	65.9980	415.4911	0
1	9	2	8	0.0000	0.0000	66.0211	732.0118	0
4	0	2	4	0.0000	0.0000	66.0245	581.8456	0
1	10	0	4	0.0000	0.0000	66.1707	304.7988	0
0	8	3	4	0.0000	0.0000	66.3120	60.9734	0

4	1	2	8	0.0000	0.0000	66.3786	1677.4912	0
3	4	3	8	0.0000	0.0000	66.5261	897.4345	0
4	4	1	8	0.0000	0.0000	66.7552	27.3313	0
2	9	1	8	0.0000	0.0000	66.8230	73.7172	0
4	2	2	8	0.0000	0.0000	67.4352	39.1420	0
1	10	1	8	0.0000	0.0000	67.8056	54.7734	0
0	6	4	4	0.0000	0.0000	67.8984	33.7244	0
1	8	3	8	0.0000	0.0000	68.2092	128.9127	0
4	5	0	4	0.0000	0.0000	68.2825	474.0534	0
2	4	4	8	0.0000	0.0000	68.4577	63.3874	0
2	7	3	8	0.0000	0.0000	68.6280	1628.9163	0
3	8	0	4	0.0000	0.0000	68.6988	213.5349	0
4	3	2	8	0.0000	0.0000	69.1786	1449.4451	0
3	5	3	8	0.0000	0.0000	69.6692	80.0715	0
1	6	4	8	0.0000	0.0000	69.7748	570.3260	0
4	5	1	8	0.0000	0.0000	69.8933	203.7105	0
3	7	2	8	0.0000	0.0000	69.9377	156.1405	0
0	1	5	4	0.0000	0.0000	70.2571	107.3998	0
3	8	1	8	0.0000	0.0000	70.3052	2200.3604	0
0	10	2	4	0.0000	0.0000	70.7614	11.0434	0
0	2	5	4	0.0000	0.0000	71.2864	7.5031	0
2	5	4	8	0.0000	0.0000	71.5609	60.2032	0
4	4	2	8	0.0000	0.0000	71.5864	63.8000	0
2	9	2	8	0.0000	0.0000	71.6520	0.0016	0
1	0	5	4	0.0000	0.0000	71.7649	5.2505	0
2	10	0	4	0.0000	0.0000	71.7961	51.9457	0
4	6	0	4	0.0000	0.0000	72.0714	0.0003	0

1	1	5	8	0.0000	0.0000	72.1057	173.8652	0
0	9	3	4	0.0000	0.0000	72.2039	0.0000	0
3	0	4	4	0.0000	0.0000	72.2436	0.0000	0
0	7	4	4	0.0000	0.0000	72.3777	0.0000	0
3	1	4	8	0.0000	0.0000	72.5835	281.5065	0
1	10	2	8	0.0000	0.0000	72.6045	0.0015	0
0	3	5	4	0.0000	0.0000	72.9884	0.0000	0
1	2	5	8	0.0000	0.0000	73.1241	0.0000	0
0	11	1	4	0.0000	0.0000	73.1693	0.0000	0
2	10	1	8	0.0000	0.0000	73.3732	0.0000	0
1	11	0	4	0.0000	0.0000	73.4251	212.2202	0
3	6	3	8	0.0000	0.0000	73.4268	169.8904	0
3	2	4	8	0.0000	0.0000	73.5994	37.1505	0
4	6	1	8	0.0000	0.0000	73.6461	325.2185	0
2	8	3	8	0.0000	0.0000	73.7634	1026.1586	0
1	9	3	8	0.0000	0.0000	74.0325	351.4339	0
4	0	3	4	0.0000	0.0000	74.0358	617.0917	0
1	7	4	8	0.0000	0.0000	74.2046	116.0688	0
4	1	3	8	0.0000	0.0000	74.3725	875.0704	0
3	9	0	4	0.0000	0.0000	74.5056	469.5375	0
4	5	2	8	0.0000	0.0000	74.6340	528.3604	0
1	3	5	8	0.0000	0.0000	74.8097	0.0000	0
1	11	1	8	0.0000	0.0000	74.9889	24.4383	0
3	8	2	8	0.0000	0.0000	75.0353	84.9668	0
2	6	4	8	0.0000	0.0000	75.2799	82.8550	0
3	3	4	8	0.0000	0.0000	75.2809	150.2051	0
0	4	5	4	0.0000	0.0000	75.3459	0.5766	0

4	2	3	8	0.0000	0.0000	75.3793	0.0020	0
3	9	1	8	0.0000	0.0000	76.0613	161.4098	0
4	7	0	4	0.0000	0.0000	76.4483	930.6663	0
5	1	0	4	0.0000	0.0000	76.6501	243.6470	0
4	3	3	8	0.0000	0.0000	77.0473	888.1843	0
1	4	5	8	0.0000	0.0000	77.1473	99.7833	0
2	0	5	4	0.0000	0.0000	77.2144	1014.6197	0
0	8	4	4	0.0000	0.0000	77.4129	635.8745	0
2	1	5	8	0.0000	0.0000	77.5464	585.2836	0
3	4	4	8	0.0000	0.0000	77.6139	77.4292	0
5	2	0	4	0.0000	0.0000	77.6470	24.0890	0
3	7	3	8	0.0000	0.0000	77.7761	139.5154	0
0	11	2	4	0.0000	0.0000	77.8332	25.3627	0
5	0	1	4	0.0000	0.0000	77.8606	13.4447	0
4	7	1	8	0.0000	0.0000	77.9912	78.7823	0
2	10	2	8	0.0000	0.0000	78.0328	336.6565	0
5	1	1	8	0.0000	0.0000	78.1918	76.2758	0
4	6	2	8	0.0000	0.0000	78.3002	0.5663	0
0	5	5	4	0.0000	0.0000	78.3406	0.0471	0
2	2	5	8	0.0000	0.0000	78.5399	0.0001	0
0	10	3	4	0.0000	0.0000	78.5686	0.0208	0
2	11	0	4	0.0000	0.0000	78.8339	26.1129	0
5	2	1	8	0.0000	0.0000	79.1830	380.6018	0
1	8	4	8	0.0000	0.0000	79.1997	377.9432	0
0	12	0	2	0.0000	0.0000	79.2950	78.8172	0
5	3	0	4	0.0000	0.0000	79.3003	70.4852	0
4	4	3	8	0.0000	0.0000	79.3642	54.1716	0

2	9	3	8	0.0000	0.0000	79.4276	128.1648	0
2	7	4	8	0.0000	0.0000	79.5959	281.9768	0
1	11	2	8	0.0000	0.0000	79.6174	330.2433	0