The Transition Metal-rich Orthophosphate Arrojadite with Special Structural Features

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The crystal structure of the transition metal-rich orthophosphate mineral arrojadite was reexamined, and the disorder phenomena were analyzed applying modern X-ray single-crystal diffraction and refinement methods on samples from Nickel Plate (USA) and Hagendorf (Germany). As a new feature of the arrojadite structure, two different types of channels oriented along [010] are described. The occupancy of the atomic positions inside these channels have been elucidated.

Key words: Arrojadite, Defect Structure, Crystal Structure

Introduction

Since the first report on the mineral arrojadite [1] much work has been carried out on the description of various locations and mineral paragenesis. Investigations of the physical and chemical properties of arrojadite performed during the last half century include chemical analyses, phase analysis by X-ray powder diffraction (XRD) [2], investigations of the thermal behavior [3, 4], preparation of synthetic Fe-arrojadite [5], and Mössbauer-spectroscopic studies [6]. In addition, new deposits and new members of the dickinsonite-arrojadite mineral series (*e. g.*, sigismundite from Italy [7]) were discovered. Until today, the complexity of the crystal structure and chemical composition of arrojadite has prompted further extensive studies. The first single-crystal X-ray diffraction studies were carried out in 1979 [8] on samples from Nickel Plate (USA). In the proposed model, orthophosphate anions form a common framework together with Fe, Mn, Al, Ca, Mg, and Li cations. The refinement of the structure with isotropic displacement parameters for all atoms and the assumption of an ordered structure resulted in a poor $R1$ value of 0.135. A second study [9, 10] was carried out on samples from Branchville, Nancy Mine and Nickel Plate (USA), and a disorder model for one phosphate anion together with complex statistical occupation of several cationic sites was introduced. The refinement, applying anisotropic treatment for the displacement parameters, resulted in $R1$ values ranging from 0.063 to 0.078. This model was, on the whole, corroborated by the work on synthetic Fe-arrojadites [5]. Two studies on the structure [11] and nomenclature [12] of arrojadite-group minerals were published recently. The authors suggested Cc to be the “true” space group for arrojadite minerals. The studies by Lindberg [2] were the first ones based on combined XRD and chemical analysis, subsequently extended with determinations of the Sr and Ba contents [13]. When applying the structural model of Moore [10] *viz.* the x-, y-, z-coordinates of the atoms and their related occupancy factors, to our data, no convergence could be achieved. Therefore, we decided to reexamine the single-crystal structure of different arrojadite samples. The plausibility of applying the centrosymmetric space group $C2/c$ rather than the acentric couterparts Cc or $C2$ is discussed with respect to structural features in the resulting models and the significance of the corresponding R values.

We considered it worthwhile to analyze different arrojadite samples with SEM-EDX[1], ICP-OES[2] and ICP-MS[3] [14], as well as the thermal behavior of arrojadite, applying high-resolution synchrotron pow-

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[1] *S*canning *E*lectron *M*icroscopy with *E*nergy-*D*ispersive *X*-Ray analyzator

[2] *I*nductively *C*oupled *P*lasma with *O*ptical *E*mission *S*pectrometry

[3] *I*nductively *C*oupled *P*lasma with *M*ass *S*pectrometry

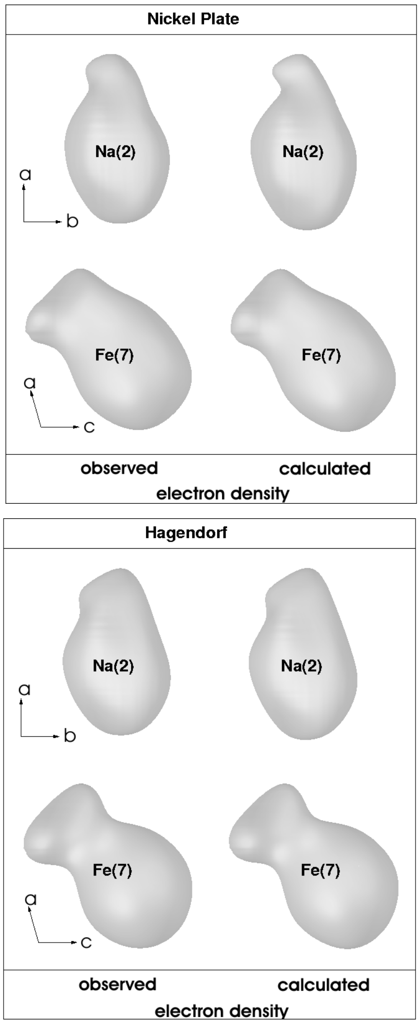

Fig. 1. Observed electron densities and refined 3rd order tensors [20] for the atoms Na(2) and Fe(7) in the structures of the arrojadite samples from Nickel Plate (top) and Hagendorf (bottom).

der diffraction, thermogravimetry (TG), differential scanning calorimetry (DSC), and mass-spectrometry (MS) [15]. Previous work [3, 4] on this subject had been carried out prior to the first crystallographic studies. As an extension of the present X-ray study and in order to improve our model of the arrojadite structure, further single-crystal measurements using neutron radiation were performed [16].

Table 1. Selected crystallographic data and details on data collection and refinement of arrojadite samples from Nickel Plate (USA) and Hagendorf (Germany). Standard deviations of the last digit are given in parentheses.

Empirical formula	$Na_3K_{1.22}AlCr_{0.88}$-$Mn_6Fe_{7.47}(PO_4)_{12}$ $\cdot 2H_2O$	$Na_3SrAlCr$-$Mn_6Fe_{7.13}(PO_4)_{12}$ $\cdot 1H_2O$
Location	Nickel Plate (NP)	Hagendorf (HD)
Molar weight, g mol^{-1}	8423.7	8539.1
Min./max. crystal size, mm	0.12/0.23	0.15/0.32
Crystal color	pale green, transparent	
Crystal shape	xenomorphic fragment	
Diffractometer	IPDS II, Stoe & Cie, Darmstadt (Germany)	
Measurement method	ω-scan	
Wavelength, pm	71,073 (MoK_α)	
Crystal system	monoclinic	
Space group	$C2/c$ (no. 15)	
Lattice constants, pm, deg	a = 1664.4(1) b = 1012.5(1) c = 2486.9(1) β = 105.84(1)	a = 1663.1(1) b = 1007.4(1) c = 2487.7(1) β = 105.13(1)
Cell volume, 10^6 pm^3	4032	4023
Z	4	4
Density (calc.), g cm^{-3}	3.37	3.52
Density (meas.), g cm^{-3}	3.560(4)	not measured
Absorption coeff. μ, mm^{-1}	5.4	6.6
F(000), e	4075	4106
Data collection range, deg ϑ	1.70 – 29.12	1.70 – 29.24
Index range	$-22 \geq h \geq 22$ $-13 \geq k \geq 13$ $-34 \geq l \geq 34$	$-22 \geq h \geq 22$ $-13 \geq k \geq 13$ $-34 \geq l \geq 31$
Measured refl.	16456	19060
Independent refl.	5379	5371
R_{int}	0.0301	0.0220
Corrections	Lorentz, polarization [17], absorption (semiempirical [18])	
Max./min. transmission	0.696/0.234	0.766/0.345
Structure refinement	JANA2000 [20] full-matrix least-squares on F^2	
No. of l. s. variables	417	413
R values [refl. with $I \geq 2\sigma(I)$]	$R1$ = 0.0553 $wR2$ = 0.0871	$R1$ = 0.0378 $wR2$ = 0.0448
R values (all refl.)	$R1$ = 0.0644 $wR2$ = 0.1136	$R1$ = 0.0498 $wR2$ = 0.0872
Residual e$^-$ density, 10^{-6} pm^{-3}	+3.9/−2.9	+5.1/−1.5

Experimental Section

Transparent pale-green single-crystals of arrojadite from two different locations (Nickel Plate, USA (NP) and Hagendorf, Germany (HD), xenomorphic fragments of 0.12 to 0.32 mm in size) were measured at r. t. on a two-circle diffractometer with image plate detector (IPDS II, Stoe & Cie., Darmstadt, Germany) using graphite-monochromatized MoK_α radiation in ω-scan technique ($0 \leq \omega \leq 180°$, $\Delta\omega = 0.6°$). Both data sets could be indexed with monoclinic unit cells in space group $C2/c$ with a = 1664.4(1)/1663.1(1), b = 1012.5(1)/1007.4(1), c = 2486.9(1)/2487.7(1) pm and β = 105.84(1)/105.13(1)° (NP/HD, respectively). The cell parameters were refined using 32104/27679 reflections between 2ϑ = 1.70°/1.70° and 2ϑ = 29.21°/29.24° (NP/HD,

Table 2. Fractional atomic coordinates in standardized setting [23], equivalent isotropic displacement parameters (pm^2) and occupancy parameters for arrojadite samples from Nickel Plate (USA) and Hagendorf (Germany). Atoms refined by applying 3rd order tensors are marked with an asterisk. Standard deviations of the last digit are given in parentheses. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor. The last column indicates the numbering of the atomic positions as they appear in Moore's model [10].

Nickel Plate (NP)						Hagendorf (HD)						Moore
Atom	*x*	*y*	*z*	U_{eq}	Occup.	Atom	*x*	*y*	*z*	U_{eq}	Occup.	Atom
Na(1)	0	0	0	280(9)	1	Na(1)	0	0	0	270(5)	1	*X*(3)
Na(2)*	0.1339(4)	0.4853(5)	0.1194(2)	578(12)	1	Na(2)*	0.1382(2)	0.4826(3)	0.1186(1)	516(6)	1	*X*(2)
K(1)	0	0.4962(2)	1/4	398(7)	1	Sr(1)	0	0.5012(1)	1/4	304(1)	1	*X*(5)
K(2)	0	0.3339(12)	1/4	611(52)	0.212(9)							*X*(4)
Mn(1)	0.20448(4)	0.30069(6)	0.35175(3)	100(2)	1	Mn(1)	0.20589(2)	0.30006(4)	0.35184(2)	101(1)	1	*M*(6)
Mn(2)	0.28068(4)	0.20576(7)	0.15669(3)	127(2)	1	Mn(2)	0.28095(2)	0.20900(4)	0.15755(2)	108(1)	1	*M*(7)
Mn(3)	0.28728(4)	0.49229(7)	0.23232(3)	99(2)	1	Mn(3)	0.28725(2)	0.49137(4)	0.23317(2)	115(1)	1	*M*(2)
Fe(4)	0.10679(4)	0.01421(7)	0.63925(3)	187(2)	1	Fe(4)	0.10404(2)	0.01380(4)	0.64052(2)	107(1)	1	*M*(3)
Fe(5)	0.03349(4)	0.25655(6)	0.40052(3)	84(2)	1	Fe(5)	0.03462(2)	0.25693(4)	0.39971(2)	102(1)	1	*M*(5)
Fe(6)	0.47775(4)	0.25053(6)	0.09636(3)	92(2)	1	Fe(6)	0.47873(2)	0.24893(4)	0.09742(2)	119(1)	1	*M*(4)
Fe(7)*	0.2188(1)	0.0953(3)	0.4716(1)	389(6)	0.764(4)	Fe(7)*	0.2201(1)	0.0973(1)	0.4743(1)	403(4)	0.625(2)	*M*(1)
Al(1)	0	1/2	0	34(4)	1	Al(1)	0	1/2	0	56(3)	1	Al(1)
Cr(1)	0.2686(1)	0.2785(1)	0.01562(7)	243(7)	1/2	Cr(1)	0.26961(5)	0.28348(9)	0.01665(4)	236(3)	1/2	*X*(1)
P(1)	0.12588(6)	0.2515(1)	0.53842(5)	50(3)	1	P(1)	0.12513(4)	0.25097(6)	0.53813(3)	71(2)	1	P(3)
P(2)	0.13043(7)	0.2754(1)	0.21143(5)	72(3)	1	P(2)	0.12604(4)	0.27936(6)	0.21340(3)	75(2)	1	P(5)
P(3)	0.35711(7)	0.2035(1)	0.29534(5)	91(3)	1	P(3)	0.35867(4)	0.19936(6)	0.29485(3)	104(2)	1	P(6)
P(4)	0.10272(7)	0.2328(1)	0.04721(5)	60(3)	1	P(4)	0.10287(4)	0.23396(6)	0.04790(3)	77(2)	1	P(4)
P(5)	0.36993(7)	0.03318(9)	0.07556(5)	66(3)	1	P(5)	0.36905(4)	0.03500(5)	0.07586(3)	79(2)	1	P(2)
P(61)	0.3853(1)	0.4908(2)	0.1322(1)	56(6)	0.642(5)	P(61)	0.38200(5)	0.4893(1)	0.13076(4)	81(3)	0.677(2)	P(1)
P(62)	0.0818(3)	0.0059(4)	0.3372(2)	179(14)	0.358(5)	P(62)	0.0823(1)	0.0059(2)	0.33579(9)	102(7)	0.323(2)	P(1X)
O(11)	0.5947(2)	0.1048(3)	0.0361(1)	75(9)	1	O(11)	0.5935(1)	0.1050(2)	0.03567(8)	97(5)	1	O(10)
O(12)	0.0848(2)	0.1666(3)	0.5746(1)	100(10)	1	O(12)	0.0839(1)	0.1670(2)	0.57500(8)	129(6)	1	O(9)
O(13)	0.2782(2)	0.2480(3)	0.4376(1)	115(9)	1	O(13)	0.27900(9)	0.2485(2)	0.43822(8)	128(5)	1	O(12)
O(14)	0.1070(2)	0.1899(3)	0.4795(1)	131(10)	1	O(14)	0.1066(1)	0.1877(2)	0.47988(8)	138(6)	1	O(11)
O(21)	0.1397(2)	0.1244(3)	0.2083(2)	226(13)	1	O(21)	0.1320(1)	0.1260(2)	0.21166(9)	174(6)	1	O(19)
O(22)	0.1315(2)	0.3204(3)	0.2700(1)	173(11)	1	O(22)	0.1264(1)	0.3321(2)	0.27106(8)	126(6)	1	O(18)
O(23)	0.2043(2)	0.3399(2)	0.1937(1)	150(11)	1	O(23)	0.2016(1)	0.3370(2)	0.19524(9)	132(6)	1	O(20)
O(24)	0.0488(2)	0.3205(3)	0.1705(1)	167(11)	1	O(24)	0.0453(1)	0.3290(2)	0.17268(9)	138(6)	1	O(17)
O(31)	0.2852(2)	0.1462(3)	0.3180(2)	184(11)	1	O(31)	0.2847(1)	0.1483(2)	0.31706(9)	172(6)	1	O(24)
O(32)	0.3501(2)	0.3556(3)	0.2950(2)	144(11)	1	O(32)	0.3546(1)	0.3523(2)	0.29380(9)	138(6)	1	O(23)
O(33)	0.3486(3)	0.1506(3)	0.2367(2)	307(13)	1	O(33)	0.3510(1)	0.1408(2)	0.23677(9)	248(7)	1	O(22)
O(34)	0.4418(2)	0.1610(3)	0.3347(1)	146(11)	1	O(34)	0.4414(1)	0.1508(2)	0.33334(9)	179(6)	1	O(21)
O(41)	0.4035(2)	0.3137(3)	0.0124(1)	121(9)	1	O(41)	0.4032(1)	0.3155(2)	0.01104(8)	139(6)	1	O(15)
O(42)	0.1937(2)	0.2637(3)	0.0769(1)	147(10)	1	O(42)	0.1936(1)	0.2671(2)	0.07717(8)	147(6)	1	O(16)
O(43)	0.0467(2)	0.3575(3)	0.0479(1)	86(9)	1	O(43)	0.0469(1)	0.3581(2)	0.04819(7)	78(5)	1	O(13)
O(44)	0.0663(2)	0.1288(3)	0.0795(1)	110(10)	1	O(44)	0.0654(1)	0.1307(2)	0.08046(8)	119(6)	1	O(14)
O(51)	0.2902(2)	0.0378(3)	0.0268(1)	189(10)	1	O(51)	0.2893(1)	0.0431(2)	0.02857(8)	213(6)	1	O(8)
O(52)	0.3714(2)	0.1551(3)	0.1137(1)	134(11)	1	O(52)	0.3714(1)	0.1553(2)	0.11515(8)	145(6)	1	O(7)
O(53)	0.4497(2)	0.0560(2)	0.0553(1)	70(9)	1	O(53)	0.4483(1)	0.0560(1)	0.05492(8)	86(5)	1	O(5)
O(54)	0.1212(2)	0.4022(3)	0.3926(1)	126(10)	1	O(54)	0.1231(1)	0.4027(2)	0.39283(9)	156(6)	1	O(6)
O(61)	0.3883(2)	0.6404(3)	0.1364(1)	144(11)	1	O(61)	0.4714(1)	0.4381(2)	0.13107(8)	139(6)	1	O(1)
O(62)	0.0246(2)	0.0613(3)	0.3673(1)	112(10)	1	O(62)	0.1141(1)	0.1392(2)	0.36282(8)	129(6)	1	O(2)
O(63)	0.3574(3)	0.4231(3)	0.1782(2)	356(16)	1	O(63)	0.3506(1)	0.4187(2)	0.1748(1)	222(7)	1	O(3)
O(614)	0.3198(3)	0.4539(6)	0.0779(3)	333(18)	0.642(5)	O(614)	0.3175(2)	0.4566(3)	0.0756(1)	216(9)	0.677(2)	O(4)
O(624)	0	0.1527(8)	1/4	333(18)	0.358(5)	O(624)	0.0164(3)	0.0279(5)	0.2659(3)	216(9)	0.323(2)	O(3X)
O(7)	0.2312(2)	0.0013(3)	0.1378(1)	107(8)	1	O(7)	0.23118(8)	0.0003(2)	0.14090(7)	137(5)	1	F(1)

respectively). The intensity data were corrected for Lorentz and polarization effects [17]. Absorption effects were corrected semiempirically utilizing the redundancy of the data sets [18]. Starting parameters for the refinements were taken from the structural model published by Yakubovich [5], and the structure was subsequently refined in full-matrix-least-squares cycles using the programs SHELXL-97 [19] and JANA2000 [20], treating most atoms anisotropically. As a result of the refinement, the atoms Na(2) and Fe(7) showed unusual displacement parameters and could be described satisfyingly with anharmonic 3rd order tensors (Fig. 1).

Relevant information concerning data collection and structure refinement are presented in Table 1. Fractional atomic parameters and equivalent isotropic displacement parameters of the atoms are shown in Table 2.

Further details on the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html), on quoting the depositary numbers CSD-417405 and CSD-417406 for the HD and the NP sample, respectively.

The density of NP samples was determined on 52.8(1) mg of handpicked grains in a gas pycnometer (Micromeritics GmbH, Germany). The amount of pure sample material from HD was not sufficient to obtain reliable results.

Results and Discussion

The refinements of the structures of two arrojadite crystals from Nickel Plate (NP) and from Hagendorf (HD) were performed in space group $C2/c$. A simple significance test as proposed by Hamilton [21] suggested that the decrease in R values by refining in the acentric group Cc [11] is merely due to the increased number of variables. During refinement in Cc we did not observe ordering of atoms suffering from orientational disorder or underoccupation as in the $C2/c$ model. No atom was shifted significantly from its position in the centrosymmetric model, and the correlation matrix for atomic positions, displacement vectors, and occupancy factors of the atoms was in all cases at a level of 0.9 for the pairs of atoms connected by an inversion center in the $C2/c$ model. During refinements in Cc, the Flack x parameter [22] demanded the application of the twin matrix for inversion twins, and the batch scale factors [19] refined to 1/2 within the error margin. For crystallographic reasons it is not necessary and – in the sense of Ockham's rule [24] not recommended – to choose the acentric space group for refinement of the arrojadite structure.

Both NP and HD crystal structure models show similar main features and are basically in agreement with the model proposed by Moore [10]. Differences between NP and HD samples and the models proposed in the literature are due to variations in the chemical composition and to disorder and partial occupation phenomena.

The arrojadite structure shows six crystallographically independent orthophosphate anions per asymmetric unit, five of which exhibit geometrical features well known for orthophosphates ($d_{\text{P–O}}$ ranging from 151.0(3) pm to 156.6(4) pm, angles differing only slightly from 109.5°), the sixth one is disordered. The electron density map shows two clearly separated peaks belonging to the positions of P(61) and P(62) ($d_{\text{P(61)–P(62)}}$ about 80 pm) indicating two possible orientations of the sixth phosphate anion. Three of the oxygen atoms (O(61)-O(63)) are identical for the two orientations, O(614) belongs to orientation 1 and O(624) to orientation 2. Free refinements of the occupation factors of P(61) and O(614) resp. P(62) and O(624) suggested a coupling and thus a restraint for these atoms in order to yield a full occupation for this phosphate anion. The occupation of the two phosphate anion orientations in both NP and HD crystal refinements is about 65 % *vs.* 35 % (Table 2). A projection of the structure along [010] is shown in Fig. 2.

The general formula of arrojadites can be denoted as $A_3BC_2\text{Al}M_{14}(\text{PO}_4)_{12}\cdot nX$ (4 formula units per unit cell, A = Na^+; B = K^+ (NP) or Sr^{2+} (HD); C = Al^{3+}; Fe^{3+}; M = Mn^{2+}; Fe^{2+}; X = H_2O). The B, C, and M positions can be occupied by a large variety of different cations (leading to the expression "wastebasket sites" in Moore's description of the arrojadite structure). However, in our refinements only Fe, Al, and Mn were considered in order to keep the number of parameters as small as possible. The octahedrally coordinated Al position ($d_{\text{Al–O}}$ ranging from 188.1(3) to 190.8(3) pm) is not affected by mixed occupation. The three-coordinated X site assigned to F^- by Moore [10] is occupied by variable amounts of H_2O, as follows from our chemical and thermal analyses. The seven crystallographically independent M sites (coordination numbers from 5 for Mn(3) to 5+1 or 6 for the others) are occupied by either Fe^{2+} or Mn^{2+} cations. The lowest possible $R1$ value was achieved by the assignment shown in Table 2 which yields fully occupied sites for M(1)-M(6). The resulting Fe and Mn content is in accordance with the chemical analysis [14]. In both crystals investigated, the 4+2-coordinated Fe(7) site is occupied by 76 % and shows a very broad maximum in the electron density map. It was successfully matched applying an anharmonic 3rd order tensor. The unusual shapes of the electron density distribution at the positions of the atoms Na(2) and Fe(7) is a consequence of the special coordination situation in the channels (see text below and Fig. 1).

The two independent A sites (coordination numbers 6 and 7) are both fully occupied by Na cations

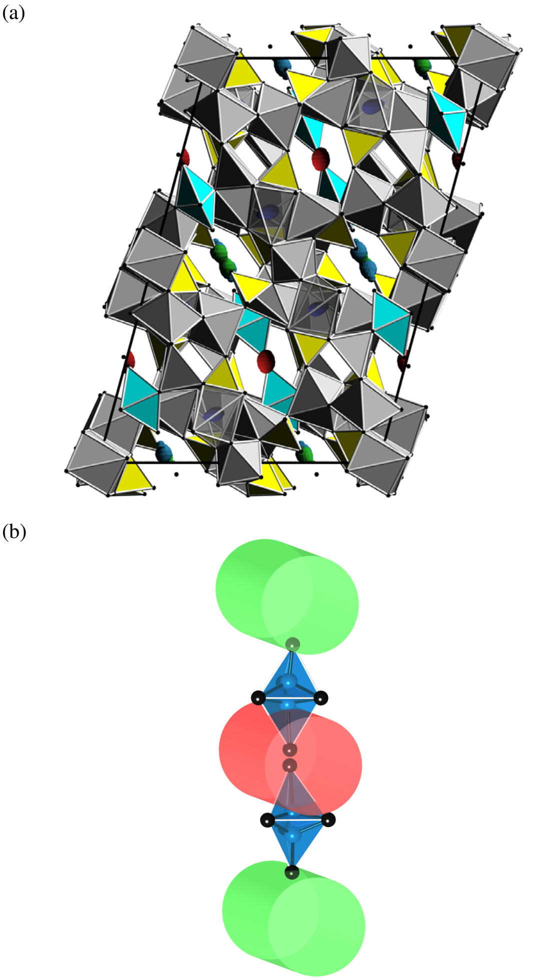

Fig. 2 (color online). a) Crystal structure of the HD arrojadite projected along [010]. Yellow polyhedra represent the ordered phosphate anions around P(1)-P(5), cyan tetrahedra depict the disordered phosphate anions around P(61) and P(62) (see text). Coordination polyhedra around the cations *A*, *B*, *C*, *M*, and Al are drawn light grey. The observed electron density distribution is drawn as isosurfaces at a value of 4.8×10^6 e^- pm^{-3} for the atoms Sr(1) (red, inside channels), "Cr(1)" (green, inside channels), and Fe(7) (light blue, inside channels). b) Enlarged view of the orientationally disordered phosphate anion described by two split positions around P(61) and P(62), respectively. The synoptic view of the two mutually exclusive orientations results in trigonal bipyramids with the apical oxygen atoms O(614) and O(624) protruding into the two channel types containing either the Sr(1) (red) or the "Cr(1)" and Fe(7) cations (green).

($d_{\text{Na–O}}$ ranging from 233.2(6) to 277.1(4) pm) in both NP and HD samples. Na(2) shows very large anisotropic displacement parameters and was successfully refined applying an anharmonic 3rd order tensor (Fig. 2). The coordination number and the Na-O distances are larger for Na(2) than for Na(1).

The *C* site in both NP and HD is situated close to the inversion center at 1/4, 1/4, 0 with a distance of about 100 pm between the two symmetry-related maxima. This site can therefore only be half-occupied. Based on the observed electron density and the geometrical parameters, Cr^{3+} was found to be suitable to occupy this position ($d_{\text{Cr–O}}$ ranging from 216.9(2) to 245.1(2) pm, fourfold coordination), but an appropriate statistically mixed occupation by primarily Fe^{3+} and some Al^{3+} is to be taken into account for chemical reasons [14]. However, Cr^{3+} was favored for the refinement on this position in order to keep the number of free variables as small as possible. The results of the refinements of HD and NP show a different occupation of the *C* site which can be interpreted by assuming a different ratio of Fe^{3+} and Al^{3+}.

The occupation of the eightfold-coordinated *B* site constitutes the main difference between the NP and HD crystal structures. In the HD crystal this site is fully occupied by Sr with $d_{\text{Sr–O}}$ ranging from 264.9(2) to 292.8(2) pm. In the case of the NP crystal this site shows two maxima in the electron density map. The main peak corresponds to a 100 % occupation by K(1), the small peak in direct vicinity ($d_{\text{K(1)–K(2)}}$ about 160 pm) can be correlated with the K(2) atom with an occupation of only 17 %. The occupation of two close lying positions by 17 % must be explained in terms of heavy scatterers being present ("wastebasket" site).

The $[AO_6]/[AO_7]$, $[CO_4]$, $[MO_6]$, $[AlO_6]$ and $[PO_4]$ units form a framework structure in which two kinds of channels oriented along [010] can be occupied by additional cations (Fig. 2a). In the first channel type the "wastebasket site" *C* occupied by "Cr(1)" and the Fe(7) site are located. The fourfold coordination environment allows an occupation by different cations and is completed by additional water molecules which do not show up as distinct maxima in the electron density map.

The second channel type is occupied by the *B* metals (Sr(1) in the HD crystal and K(1)/K(2) in the NP crystal). The oxygen atoms O(624) are protruding into this channel. Again, the coordination of the cations is most likely completed by additional water molecules. Distinct evidence for bonded water molecules has been provided by thermoanalytical investigations [15].

Some of the cation sites appear to be statistically occupied by different metals, and some of these are clearly occupied by only one kind of metal. The first type of cation sites is found not only inside the channels but also in large coordination polyhedra which contain more than six oxygen atoms (position of Na(2)). The second type are mainly the Al site, the Na(1) site and the Fe/Mn(1)-(6) sites. The "Cr" position is one of the most versatile sites in the structure. It is most probably occupied statistically by Fe^{3+}, Al^{3+}, Zn^{2+}, Ca^{2+}, and Mg^{2+}. Chemical analyses have proven the presence of those metals in appropriate amounts [14]. This statistical occupation by a number of different cations may be assumed for the underoccupied Fe(7) position as well. The K and/or Sr site shows large differences in the effective electron density depending on the location. Crystal structure descriptions reported for specimens of other locations show Ba on this position with Li atoms or split positions in its vicinity [10, 11, 13]. The occupation of this site seems to be correlated much more with the details of local chemism and paragenesis than that of the "Cr" site.

The Fe(7), Cr, K and/or Sr sites show incomplete coordination of the cations by oxide anions, and their coordination spheres most probably are completed by water molecules present inside the channels. The accessibility of these channels for small molecules can be demonstrated in an easy yet impressive way: a green arrojadite crystal becomes almost colorless when put into chloroform. The same effect is observed with acetonitrile, whereas in solvents like CS_2 and trichlorethylene a change to yellow/brown can be observed. Nonpolar solvents (*e. g.* CCl_4, cyclohexane) and poorly coordinating solvents like ethanol or dimethylformamide have no effect on the color. The original pale-green color returns when the solvent is removed by evacuating or warming the crystal in air. A preliminary TEM-EELS (*T*ransmission *E*lectron *M*icroscope with *E*lectron *E*nergy *L*oss *S*pectroscopy) study has proven the formation of charge-transfer complexes in arrojadite samples [16].

Conclusions

The crystallographic comparison of samples of NP and HD arrojadites clearly shows structural disorder with regard to a disordered phosphate anion described by two split orientations in positions centered by P(61) and P(62), respectively, and several of the cations inside the channels. Introducing anharmonic 3rd order tensors for some of the cations decreases the $R1$ value considerably. Whereas the disorder of the phosphate anion in both arrojadite samples, as well as the considerable anharmonic contributions to the electron density of Na(2) are similar, the occupation of sites close to the disordered phosphate anion by K(1) and K(2) and Sr(1), respectively, constitutes the main difference between the two investigated types of arrojadite minerals.

It would be very interesting to find out in further investigations whether transient arrojadites between NP and HD type exist or can be prepared synthetically following research initiated by Yakubovich *et al.* [5].

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