

Crystal structure and properties of the new vanadyl(IV)phosphates $\text{Na}_2\text{MVO}(\text{PO}_4)_2$, $M = \text{Ca}$ and Sr

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Abstract

Two new complex vanadyl(IV)phosphates $\text{Na}_2\text{MVO}(\text{PO}_4)_2$ ($M = \text{Ca}$, Sr) were synthesized in evacuated quartz ampoules and investigated by means of X-ray diffraction, electron microscopy, DTA, ESR and magnetic susceptibility measurements. The crystal structure of $\text{Na}_2\text{SrVO}(\text{PO}_4)_2$ was solved ab initio from X-ray powder diffraction data. Both compounds are isostructural: $a = 10.5233(3) \text{ \AA}$, $b = 6.5578(2) \text{ \AA}$, $c = 10.0536(3) \text{ \AA}$ and $a = 10.6476(3) \text{ \AA}$, $b = 6.6224(2) \text{ \AA}$, $c = 10.2537(3) \text{ \AA}$ for Ca and Sr , respectively; S.G. *Pnma*, $Z = 4$. The compounds have a three-dimensional structure consisting of V^{4+}O_6 octahedra connected by PO_4 tetrahedra via five of the six vertexes forming a framework with cross-like channels. The strontium and sodium atoms are located in the channels in an ordered manner. Electron diffraction as well as high-resolution electron microscopy confirmed the structure solution. The new vanadylphosphates are Curie–Weiss paramagnets in a wide temperature range down to 2 K with $\theta = 12$ and 5 K for Ca and Sr phases, respectively.

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1. Introduction

Complex vanadium oxides and phosphates containing vanadium in a low oxidation state often demonstrate interesting magnetic properties and became an object of heightened attention of the investigators in the last few years. Among these compounds the so-called low-dimensional (i.e. chain-, layer- or pipe-like) structures look the most promising for discovering unusual phenomena [1,2].

Introduction of the tetrahedral groups XO_4 in the structure often leads to a low dimensionality [3]. So, for V^{4+} -compounds a presence of the $[\text{VO}(\text{X}^{5+}\text{O}_4)_2]^{4-}$ group often results in one- or two-dimensional struc-

tures. Two identical (e.g., Sr or Ba) or different (e.g., Ba and Zn) bivalent cations compensate the charge of the group where the tetrahedrally coordinated cations are V^{5+} , P^{5+} or As^{5+} . The atomic radii of P^{5+} and V^{5+} cations are close and, moreover, their typical oxygen coordination is a tetrahedron with an $\text{X}-\text{O}$ separation of 1.45–1.65 Å. The exchange of a tetrahedral VO_4 for a PO_4 group may or may not result in a change of the structure. For instance, $\text{Sr}_2\text{VO}(\text{VO}_4)_2$ and $\text{Sr}_2\text{VO}(\text{PO}_4)_2$ are isostructural and contain infinite chains of corner-shared VO_6 octahedra linked by phosphate (or vanadate) groups in layers [4,5]. However, $\text{Ba}_2\text{VO}(\text{VO}_4)_2$ and $\text{Ba}_2\text{VO}(\text{PO}_4)_2$ structures are quite different [6,7]. The first one contains isolated rutile-like chains of edge-shared VO_6 octahedra and in the latter structure chains are formed by VO_5 pyramids linked by two phosphate groups. The use of different bivalent cations in the *A*-framework in the $\text{MZnVO}(\text{PO}_4)_2$ ($M = \text{Sr}$, Ba) phases

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dramatically changes the structure resulting in layers of square pyramids linked by PO_4 groups [8,9].

Recently, we reported the synthesis and investigation of the new vanadylvanadates $\text{Na}_2M\text{VO}(\text{VO}_4)_2$ ($M = \text{Sr}, \text{Ca}$) [10]. This structure is somewhat similar to that of $\text{Ba}_2\text{VO}(\text{PO}_4)_2$ and the A -cations are orderly situated between the chains. $\text{Na}_2\text{SrVO}(\text{VO}_4)_2$ revealed a weak antiferromagnetic transition at about 80 K resulting from the superexchange interaction of the V^{4+} atoms via V^{5+}O_4 groups. One may expect that compounds with a similar structure may be formed during a $\text{V}^{5+} \rightarrow \text{P}^{5+}$ substitution.

Below we present the results of the synthesis and investigation of new complex vanadyl(IV)phosphates $\text{Na}_2M\text{VO}(\text{PO}_4)_2$ ($M = \text{Ca}, \text{Sr}$) by means of X-ray diffraction, electron microscopy, magnetic susceptibility and ESR measurements.

2. Experimental

Bulk samples of $\text{Na}_2\text{SrVO}(\text{PO}_4)_2$ and $\text{Na}_2\text{CaVO}(\text{PO}_4)_2$ were obtained by heating stoichiometric mixtures of $\text{Na}_4\text{P}_2\text{O}_7$, $\text{Sr}_2\text{P}_2\text{O}_7$ or $\text{Ca}_2\text{P}_2\text{O}_7$ and VO_2 in an evacuated and sealed silica tube for 36 h at 700°C . Reagents were thoroughly ground in an agate mortar under acetone, pressed into pellets and placed into silica tubes. $\text{Na}_4\text{P}_2\text{O}_7$ was obtained by heating Na_2HPO_4 in dynamic vacuum at 700°C for 24 h; $M_2\text{P}_2\text{O}_7$ ($M = \text{Ca}, \text{Sr}$) were synthesized by annealing a stoichiometric mixture of $M\text{CO}_3$ and $\text{NH}_4\text{H}_2\text{PO}_4$ at 800°C for 48 h in air.

The XRD patterns were indexed using the TREOR90 program [11]. Both $\text{Na}_2\text{CaVO}(\text{PO}_4)_2$ and $\text{Na}_2\text{SrVO}(\text{PO}_4)_2$ have an orthorhombic unit cell with lattice parameters $a = 10.5305(3) \text{ \AA}$, $b = 6.5617(2) \text{ \AA}$, $c = 10.0595(3) \text{ \AA}$ and $a = 10.6435(6) \text{ \AA}$, $b = 6.6194(4) \text{ \AA}$, $c = 10.2483(5) \text{ \AA}$ for Ca and Sr, respectively; $Z = 4$. In the X-ray pattern of the Sr-containing phase a few weak peaks were present (less than 5% of intensity) of an unknown admixture and a change of synthetic conditions did not result in the synthesis of a pure product. The Ca-containing sample was obtained as a single-phase material. We failed to obtain single crystals of the materials because both compounds melt with decomposition (at 730°C for $\text{Na}_2\text{CaVO}(\text{PO}_4)_2$ and at 800°C for $\text{Na}_2\text{SrVO}(\text{PO}_4)_2$) forming whitlockite-like phases. Therefore the structure solution was done using powder diffraction data.

X-ray powder diffraction (XPD) data for the structure solution and refinement were collected on a STOE diffractometer (transmission diffraction geometry, $\text{CuK}_{\alpha 1}$ -radiation, Ge-monochromator, linear-PSD). The WinCSD program package [12] was used for an ab initio structure solution. Finally, the full profile structure refinement was carried out with the GSAS [13,14] program package. Further details of the crystal

structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; <mailto:crysdata@fiz.karlsruhe.de>) on quoting the depository numbers CSD413693 and CSD413694.

Thermal analysis was performed on a NETZSCH STA 449C instrument in a purified Ar flow.

Electron diffraction (ED) and high-resolution electron microscopy (HREM) were performed with a JEOL 4000EX microscope. The image simulations were made using the MacTempas software.

Measurements of the ESR spectra have been performed on a conventional cw ESR spectrometer ADANI PS100.X at room temperature. Since all investigated compounds are dielectric we used bulk ceramic samples for ESR measurements.

Magnetic susceptibility measurements were performed on a Quantum Design MPMS SQUID magnetometer in the range between 2 and 400 K at fields of 0.1, 1 and 5 T.

3. Results and discussion

3.1. Crystal structure

The ab initio solution and following structure refinement for $\text{Na}_2\text{SrVO}(\text{PO}_4)_2$ were carried out using the WinCSD program package [12]. The larger difference in Z -number for Sr and V atoms (in comparison with that for Ca and V) allowed to distinguish uniquely these atoms inside the unit cell during the model construction. Since the reflections belonging to $\text{Na}_2\text{SrVO}(\text{PO}_4)_2$ mostly do not overlap with reflections of the unknown impurity, this phase was chosen for the structure solution. Integral intensities were extracted with the Win^XPow program package [15] and used for the further structure calculations and refinements. The $Pnma$ space group was chosen according to the electron diffraction data (see below). The coordinates of the heavy atoms were found from direct methods. The coordinates for the phosphorus and oxygen atoms were extracted from Fourier and difference Fourier maps. Finally, the Rietveld method refinement was used and ranges containing admixture peaks were excluded from the calculations. The thermal parameters for the oxygen atoms were constrained. The atomic coordinates found for $\text{Na}_2\text{SrVO}(\text{PO}_4)_2$ were taken as the initial ones for the refinement of the $\text{Na}_2\text{CaVO}(\text{PO}_4)_2$ structure. The experimental and structural parameters for $\text{Na}_2M\text{VO}(\text{PO}_4)_2$ ($M = \text{Ca}, \text{Sr}$) are listed in Table 1. The atomic coordinates, thermal parameters and main interatomic distances are presented in Tables 2 and 3, respectively. The experimental, calculated and difference X-ray patterns for $\text{Na}_2\text{CaVO}(\text{PO}_4)_2$ are shown in Fig. 1.

Table 1
Experimental conditions and structural parameters for Na₂MVO(PO₄)₂ (M = Ca, Sr)

	Na ₂ SrVO(PO ₄) ₂		Na ₂ CaVO(PO ₄) ₂
Space group		<i>Pnma</i> [62]	
<i>a</i> (Å)	10.6476(3)		10.5233(3)
<i>b</i> (Å)	6.6224(2)		6.5578(2)
<i>c</i> (Å)	10.2537(3)		10.0536(3)
<i>Z</i>		4	
<i>V</i> (Å ³)	723.02(5)		693.80(6)
Calculated density (g/cm ³)	3.587		3.283
Diffractometer		STOE STADI/P	
Radiation, wavelength		CuK _{α1} , 1.5406 Å	
Detector		linear PSD	
Number of atomic sites		12	
No. of variables		40	
2θ range, step	6.0–109.98, 0.01		5.0–95.17, 0.01
Total number of profile points	10399		9018
Total number of reflections	514		404
Reliability factors	<i>R</i> _{F2} = 0.079, <i>R</i> _P = 0.029, <i>R</i> _{wP} = 0.041, <i>χ</i> ² = 4.92		<i>R</i> _{F2} = 0.037, <i>R</i> _P = 0.017, <i>R</i> _{wP} = 0.021, <i>χ</i> ² = 1.13

Table 2
Atomic positions and thermal displacement parameters for Na₂SrVO(PO₄)₂ (upper rows) and Na₂CaVO(PO₄)₂ (lower rows)

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} × 100 (Å ²)
Sr	4 <i>c</i>	0.5573(1)	1/4	0.5970(2)	1.4(2)
(Ca)		0.5603(1)	1/4	0.5924(2)	1.3(1)
V	4 <i>c</i>	0.0268(2)	1/4	0.3113(2)	1.2(2)
		0.0331(1)	1/4	0.3072(1)	1.5(1)
P1	4 <i>c</i>	0.3142(3)	1/4	0.4161(4)	2.4(2)
		0.3218(2)	1/4	0.4180(2)	1.3(1)
P2	4 <i>c</i>	0.9161(3)	1/4	0.6304(3)	1.5(2)
		0.9090(2)	1/4	0.6366(2)	1.4(1)
Na	8 <i>d</i>	0.7868(3)	−0.0028(5)	0.3666(4)	2.5(2)
		0.7880(2)	−0.0055(2)	0.3674(2)	1.9(1)
O1	4 <i>c</i>	0.1746(6)	1/4	0.4291(6)	1.4(2)
		0.1762(3)	1/4	0.4350(4)	1.4(1)
O2	8 <i>d</i>	0.9888(4)	0.0586(7)	0.6773(4)	1.4
		0.9865(3)	0.0673(4)	0.6908(3)	1.4
O3	4 <i>c</i>	0.9011(6)	1/4	0.4876(6)	1.4
		0.9074(4)	1/4	0.4828(4)	1.4
O4	8 <i>d</i>	0.3654(4)	0.0507(8)	0.4832(4)	1.4
		0.3766(2)	0.0658(4)	0.4876(3)	1.4
O5	4 <i>c</i>	0.8536(6)	1/4	0.2270(7)	1.4
		0.8546(4)	1/4	0.2287(4)	1.4
O6	4 <i>c</i>	0.6011(6)	1/4	0.3295(6)	1.4
		0.6096(3)	1/4	0.3294(4)	1.4
O7	4 <i>c</i>	0.7875(6)	1/4	0.7065(7)	1.4
		0.7733(4)	1/4	0.6952(4)	1.4

The crystal structure of Na₂MVO(PO₄)₂ is shown in Fig. 2a. The structure is a three-dimensional framework formed by VO₆ octahedra linked with phosphate group tetrahedra by five of six vertexes. Formally, one may isolate pairs of chains consisting of octahedra linked to each other by PO₄ tetrahedra. Each octahedron in such “chain” is joined by three tetrahedra with the neighboring “chain”, forming a “ribbon” (Fig. 2b). Additionally, two tetrahedra link the octahedron with other “rib-

Table 3
Main interatomic distances (Å) for Na₂SrVO(PO₄)₂ (upper rows) and Na₂CaVO(PO₄)₂ (lower rows)

Sr–2 × O2	2.739(4)	V–O1	1.984(6)	Na–O1	2.691(6)
Ca–2 × O2	2.606(3)		1.980(4)		2.580(4)
Ca–2 × O4	2.697(4)	V–2 × O2	2.054(5)	Na–O2	2.459(5)
	2.512(3)		2.091(3)		2.477(3)
Ca–2 × O4	2.306(5)	V–O3	2.249(6)	Na–O3	2.413(5)
	2.319(3)		2.207(4)		2.394(3)
Ca–O6	2.780(6)	V–O5	2.036(7)	Na–O4	2.258(5)
	2.695(4)		2.036(4)		2.298(3)
Ca–O7	2.697(7)	V–O6	1.647(6)	Na–O5	2.314(5)
	2.468(4)		1.591(4)		2.290(3)
P1–O1	1.492(6)	P2–2 × O2	1.561(4)	Na–O6	2.618(6)
	1.542(4)		1.548(3)		2.546(3)
P1–2 × O4	1.585(5)	P2–O3	1.473(6)	Na–O7	2.450(6)
	1.510(3)		1.546(4)		2.446(3)
P1–O5	1.527(7)	P2–O7	1.577(7)		
	1.515(4)		1.545(4)		

bons”. One vertex remains unlinked. Three pairs of the “ribbons” form cross-like channels where large Na and M cations are situated in an ordered manner.

The vanadium octahedra are slightly distorted and the V atom is shifted from the equatorial plane toward the O(6) atom which is not bonded with phosphate tetrahedra (Fig. 3a). Therefore one short (≈ 1.6 Å) and one long (2.23 Å) V–O apical distances are formed. This indicates the presence of a vanadyl bond in the octahedron. All vanadyl bonds inside the “chain” are oriented in the same direction and inside the channels. The oxidation state of the vanadium atom in the compound calculated using BVS is 3.97 for Na₂CaVO(PO₄)₂ and agrees with that resulting from the chemical formula.

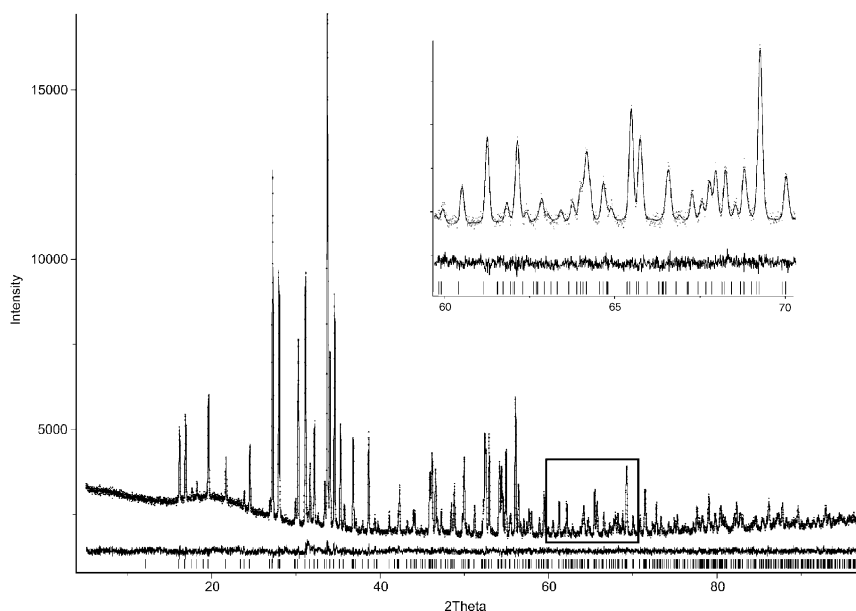


Fig. 1. Experimental, calculated and difference X-ray patterns for $\text{Na}_2\text{CaVO}(\text{PO}_4)_2$.

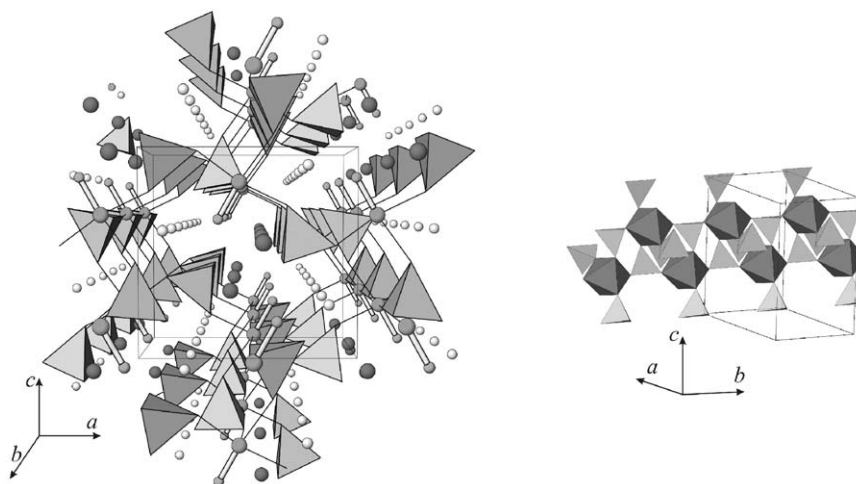


Fig. 2. (a) Crystal structure of $\text{Na}_2\text{MVO}(\text{PO}_4)_2$. Vanadyl bond in the VO_6 octahedra is shown by thick line and other V–O bonds by thin lines. (b) “Chains” and “ribbon” in the $\text{Na}_2\text{MVO}(\text{PO}_4)_2$ structure formed by VO_6 octahedra and PO_4 groups.

The sodium atoms are situated in a strongly distorted pentagonal bipyramid (Fig. 3c). These pyramids connected via triangular faces and opposite edges form infinite chains. The coordination polyhedra of the alkali-earth atoms may be considered as tetragonal antiprisms with non-equivalent distances $M\text{--O}4$ ($\times 2$), $M\text{--O}6$ and $M\text{--O}7$ forming the upper face while the bottom face is formed by nearly equal $M\text{--O}2$ ($\times 2$) and $M\text{--O}4$ ($\times 2$) bonds (Fig. 3b).

Contrary to our expectations a replacement of the vanadate group in the $\text{Na}_2\text{SrVO}(\text{VO}_4)_2$ vanadylvanadate for phosphate group resulted in a complete change of the structure. One can suggest that the size of the PO_4

group becomes too small to stabilize isolated chains. So, in the $\text{Na}_2\text{MVO}(\text{VO}_4)_2$ ($M=\text{Ca}, \text{Sr}$) compounds a presence of tetrahedral VO_4 groups results in a noticeable increase of the volume per large (A -cation and oxygen) atom: 19.3 and 20.0 \AA^3 for Ca and Sr compounds, respectively. In the $\text{Na}_2\text{MVO}(\text{PO}_4)_2$ these values are 17.4 (Ca) and 18.0 \AA^3 (Sr). At the same time, the average $A\text{--O}$ separations are very close in the both structures: 2.57 \AA for the vanadate and 2.51 \AA for the phosphate. The preservation of the chain structural motif for vanadylphosphates should result in essential shorter values of $A\text{--O}$ distances leading to mismatch between structural interstices and A -cations size. As a

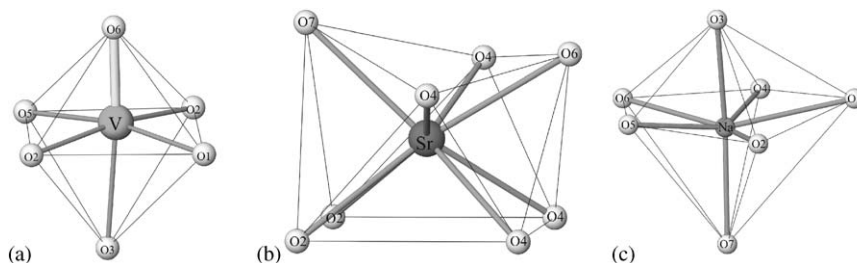


Fig. 3. Coordination polyhedra for vanadium (a), calcium (b) and sodium (c) atoms in the $\text{Na}_2\text{MVO}(\text{PO}_4)_2$ ($\text{M}=\text{Ca}, \text{Sr}$) structure.

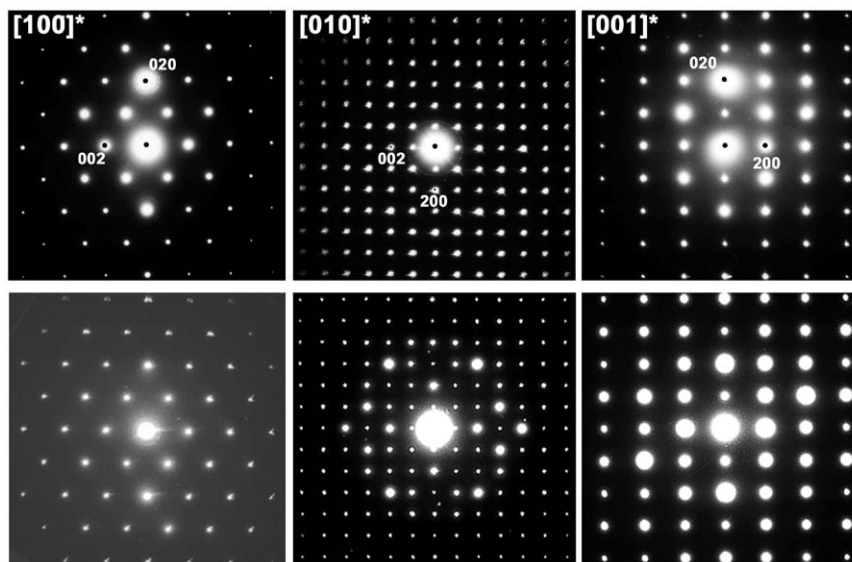


Fig. 4. Electron diffraction patterns of the $[100]^*$, $[010]^*$ and $[001]^*$ zones (from left to right) of $\text{Na}_2\text{SrVO}(\text{PO}_4)_2$ (top) and $\text{Na}_2\text{CaVO}(\text{PO}_4)_2$ (bottom).

consequence, a change of the coordination for the A-cations occurs and, simultaneously, the chains collapse forming a three dimensional framework.

3.2. ED and HREM study

Fig. 4 shows the ED patterns of the $[100]^*$, $[010]^*$ and $[001]^*$ zones of $\text{Na}_2\text{SrVO}(\text{PO}_4)_2$ and $\text{Na}_2\text{CaVO}(\text{PO}_4)_2$ as the top and bottom patterns, respectively. These patterns can be indexed using the cell parameters obtained from X-ray diffraction, and show the reflection conditions hkl : no conditions, $hk0$: $h = 2n$, $h0l$: no conditions and $0kl$: $k + l = 2n$. These reflection conditions correspond to the extinction symbol $Pn\bar{a}$, thus giving two possible space groups: $Pn2_1a$ and $Pnma$. The presence of the $h00$: $h = 2n + 1$ and the $00l$: $l = 2n + 1$ reflections on the $[010]^*$ ED pattern, and of the $0k0$: $k = 2n + 1$ reflections on the $[001]^*$ diffraction pattern is due to double diffraction as is clear by their absence on the other diffraction patterns in Fig. 4.

A HREM image of the $\text{Na}_2\text{SrVO}(\text{PO}_4)_2$ structure projected along the $[010]$ direction is shown in Fig. 5. A calculated image using the cell parameters and atomic coordinates obtained from the refinement of the XRD

data is shown in the image, within a white border. The calculated image has a width of 4 unit cells along a and along c , it has a defocus value of +2 nm and a thickness of 2.8 nm. In this image one can see pairs of white dots, which are the projection of the phosphorous columns, and in between two such pairs a separate bright dot, which is the projection of the columns of the Na atoms.

3.3. Magnetic susceptibility and ESR measurements

Both $\text{Na}_2\text{SrVO}(\text{PO}_4)_2$ and $\text{Na}_2\text{CaVO}(\text{PO}_4)_2$ compounds demonstrate Curie–Weiss (CW) behavior in a wide temperature range down to 2 K. The calculated effective magnetic moments are 1.69 and 1.76 μ_B for the Ca and Sr phases, respectively. The theoretical moment for the isolated V^{4+} cation (1.73 μ_B) is in good agreement with the observed values. CW temperatures $\theta = 12$ (Ca) and 5 K (Sr) indicate the absence of a noticeable magnetic interaction.

The ESR spectra of both $\text{Na}_2\text{CaVO}(\text{PO}_4)_2$ and $\text{Na}_2\text{SrVO}(\text{PO}_4)_2$ have almost symmetric powder line shape which is an evidence of low anisotropy of the g -factor reflecting almost isotropic magnetic interactions on V-site. The values of $g = 2.007(2)$ and $g = 2.009(2)$

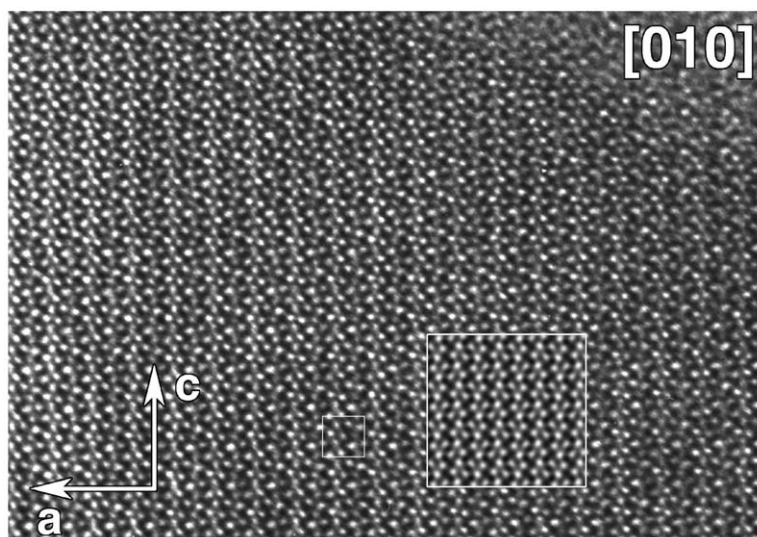


Fig. 5. HREM image of $\text{Na}_2\text{SrVO}(\text{PO}_4)_2$ projected along [010]. Unit cell and image simulation (size $4a \times 4c$, $\Delta f = +2 \text{ nm}$, $t = 2.8 \text{ nm}$) are both indicated by a white border.

for $\text{Na}_2\text{CaVO}(\text{PO}_4)_2$ and $\text{Na}_2\text{SrVO}(\text{PO}_4)_2$, respectively, are close to g -factor of the free electron (2.0023). The effective magnetic moment of the V^{4+} ion estimated from the ESR data is $\mu_{\text{eff}} = g\{S(S+1)\}^{1/2}\mu_{\text{B}} = 1.738 \mu_{\text{B}}$ for $\text{Na}_2\text{CaVO}(\text{PO}_4)_2$ and $1.740 \mu_{\text{B}}$ for $\text{Na}_2\text{SrVO}(\text{PO}_4)_2$.

This result is in a good agreement with the susceptibility data described above.

Acknowledgments

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