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Supporting information for article:

Vanadium clusters formation in geometrically frustrated spinel oxide AlV2O4

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Section S1

Table S1. Low-symmetry crystal phases induced by irrep $\mathbf{k}_9(\tau_4)$ of space group Fd$\bar{3}$m.

Designations for order parameters (OP): $\mathbf{k}_9 - \eta$; $\mathbf{k_{10}} - \varphi$, $\mathbf{k_{11}} - \xi$. The superscript index after the closing parenthesis is the irrep number according to Kovalev (Kovalev, 1993). The coefficients in front of some improper OP means the number of OP given type. V_0/V is the change of primitive cell volume as result of structural phase transition. The superscript index in the structural formula means the type of Wyckoff position according to International Tables for Crystallography.

№	Critical OP	Improper OP	Symbol of space group	V/V$_0$	Translations of primitive cell of the Fd$\bar{3}$m structure	Structural formula
1	$(\eta\,0\,0\,\eta)^4$	$(\xi\,0)^5$; $(\xi\,0\,0)^7$; $(0\,\eta\,0\,0\,0\,0\,0\,\eta)^6$; $(0\,0\,0\,0\,0\,\varphi)^3$	Cmcm (N63)	4	$2a_2+2a_3-2a_1$, $2a_3+2a_1-2a_2$, $2a_1+2a_2-2a_3$	$(A^c)^2 A^g_2 (B^g_2)^2 B^f_2 B^e_2 (X^g_2)^4 (X^f_2)^2 X^h$
2	$(\eta\,\eta\,\eta\,\eta)^4$	ξ^4; $(\eta\,\eta\,\eta\,\eta)^1$; $(\varphi\,\varphi\,\varphi\,\varphi\,\varphi\,\varphi)^3$	F$\bar{4}$3m (N216)	8	$2a_2+2a_3-2a_1$, $2a_3+2a_1-2a_2$, $2a_1+2a_2-2a_3$	$A^a (A^e_4)^2 A^g_6 A^b (B^e_4)^2 (B^h_{12})^2 (X^e_4)^4 (X^h_{12})^4$
3	$(\eta\,0\,0\,0)^4$	$(\xi\,\xi\,\xi)^7$	Rm (N166)	2	a_2-a_1, a_3-a_2, $2a_1+2a_2+2a_3$	$(A^c_{1/2})^2 B^a_{1/4} B^b_{1/4} B^h_{3/2} (X^c_{1/2})^2 (X^h_{3/2})^2$
4	$(\eta\,\eta\,0\,\eta)^4$	$(-\xi\,-\xi\,\xi)^7$; $(0\,0\,\eta\,0)^1$; $(0.866\eta,\,-0.500\eta\,0\,\eta\,0\,0\,-0.866\eta\,-0.500\eta)^6$ $(\varphi\,0\,0\,\varphi\,0\,\varphi)^3$; $(-\varphi\,\varphi\,-\varphi\,-\varphi\,\varphi\,\varphi)^1$	Rm (N166)	8	$2a_3$, $-2a_2$, $6a_2-2a_1-2a_3$	$(A^c_{1/8})^2 (A^h_{3/8})^2 (B^h_{3/8})^3 B^c_{1/8} B^g_{3/8} B^f_{3/8} (X^h_{3/8})^6 X^c_{1/8} X^c_{3/8} (X^i_{6/8})^2$
5	$(\eta_1\,\eta_2\,0\,\eta_1)^4$	$(\xi\,0)^5$; $(\xi\,\xi\,0)^9$; $2\,(-\xi_2\,\xi_1\,-\xi_1)^7$; $(0\,0\,\eta\,0)^1$; $(0\,0\,0\,0\,\eta\,0\,0\,0)^5$; $(-\eta\,0\,0\,\eta)^2$; $3(\eta_2\,\eta_3\,0\,\eta_1\,0\,0\,-\eta_2\,\eta_3)^6$; $2\,(\varphi_2\,0\,0\,\varphi_2\,0\,\varphi_1)^3$; $(\varphi\,0\,0\,-\varphi\,0\,0)^4$; $2(-\varphi_2\,\varphi_2\,-\varphi_2\,-\varphi_2\,\varphi_1\,\varphi_1)^1$; $(-\varphi\,\varphi\,-\varphi\,-\varphi\,0\,0)^2$	C2/m (N12)	8	$4a_2-2a_3$, $2a_3$, $2a_1-2a_2$	$(A^i_{1/8})^4 (A^j_{2/8})^2 (B^j_{2/8})^4 (B^i_{1/8})^4 B^h_{1/8} B^g_{1/8} (X^j_{2/8})^{12} (X^i_{1/8})^8$
6	$(\eta_1\,\eta_1\,\eta_2\,\eta_1)^4$	$(-\xi\,-\xi\,\xi)^7$; ξ^4; $(-\xi\,\xi\,-\xi)^{10}$; $2(\eta_1\,\eta_1\,\eta_2\,\eta_1)^1$;	R3m (N160)	8	$2a_1$, $2a_1-2a_3$,	$(A^a_{1/16})^4 (A^b_{3/16})^4 (B^b_{3/16})^6 (B^a_{1/16})^2 (B^c_{6/16})^2 (X^b_{3/16})^{12} (X^a_{1/16})^4 (X^c_{6/16})^4$

		$(-0.500\eta\ -0.866\eta\ \eta\ 0\ 0\ 0\ -0.500\eta\ 0.866\eta)^5$; $(0.866\eta\ -0.500\eta\ 0\ \eta\ 0\ 0\ -0.866\eta\ -0.500\eta)^6$; $2(\varphi_1\ \varphi_2\ \varphi_2\ \varphi_1\ \varphi_2\ \varphi_1)^3$ $(-\varphi\ \varphi\ -\varphi\ -\varphi\ \varphi\ \varphi)^1$; $(-\varphi\ -\varphi\ \varphi\ \varphi\ -\varphi\ -\varphi\ \varphi)^2$			$6a_2-2a_1-2a_3$	
7	$(\eta_1\ \eta_2\ \eta_2\ \eta_1)^4$	$(\xi 0)^5$; $(\xi 0\ 0)^7$; ξ^4; $(\xi 0)^6$; $(0\ 0\ \xi)^{10}$; $2(\eta_1\ \eta_2\ \eta_2\ \eta_1)^1$; $2(\eta_1\ 0\ \eta_2\ 0\ \eta_2\ 0\ \eta_1\ 0)^5$; $(\eta_1\ \eta_1\ \eta_2\ \eta_2)^4$; $2(0\ \eta_1\ 0\ \eta_2\ 0\ \eta_2\ 0\ \eta_1)^6$; $3(\varphi_3\ \varphi_3\ \varphi_3\ \varphi_3\ \varphi_1\ \varphi_2)^3$; $(-\varphi\ -\ \varphi\ \varphi\ \varphi\ 0\ 0)^4$; $(0\ \varphi\ -\varphi\ 0\ 0\ 0)^1$; $(-\varphi\ 0\ 0\ -\varphi\ 0\ 0)^2$	Imm2 (N44)	8	$2a_3$, $2a_1-2a_2$, $2a_1+2a_2-2a_3$	$(A^a_{1/16})^2(A^c_{2/16})^2 A^e_{4/16}(A^d_{2/16})^2(A^b_{1/16})^2(B^c_{2/16})^4(B^d_{2/16})^4$ $(B^e_{4/16})^4(X^c_{2/16})^8(X^d_{2/16})^8(X^e_{4/16})^8$
8	$(\eta_1\ 0\ 0\ \eta_2)^4$	$(\xi 0)^5$; $(\xi\ -\xi\ 0)^{10}$; $2(\xi_2\ \xi_1\ \xi_1)^7$; $2(0\ \eta_1\ 0\ 0\ 0\ 0\ \eta_2)^6$; $(0\ 0\ 0\ 0\ 0\ \varphi)^3$; $(0\ 0\ 0\ 0\ \varphi\ \varphi)^2$	C2₁/m (N11)	4	a_1+a_2, a_2-a_1, $2a_3-a_1-a_2$	$(A^e_{1/4})^4(B^e_{1/4})^4(B^f_{2/4})^2(X^e_{1/4})^8(X^f_{2/4})^4$
9	$(\eta_1\ \eta_2\ \eta_3\ \eta_1)^4$	$(\xi 0)^5$; $(\xi\ \xi\ 0)^9$; $2(-\xi_2\ \xi_1\ -\xi_1)^7$; ξ^4; $(\xi 0)^6$; $2(\xi_1\ -\xi_1\ -\xi_2)^{10}$; $(0\ \xi\ \xi)^8$; $3(\eta_1\ \eta_2\ \eta_3\ \eta_1)^1$; $(-\eta\ 0\ 0\ \eta)^3$; $4(\eta_2\ \eta_3\ \eta_1\ 0\ \eta_4\ 0\ \eta_2\ -\eta_3)^5$; $(-\eta\ 0\ 0\ \eta)^2$; $2(\eta_1\ \eta_2\ \eta_3\ \eta_1)^4$; $4(\eta_2\ \eta_3\ 0\ \eta_1\ 0\ \eta_4\ -\eta_2\ \eta_3)^6$; $4(\varphi_4\ \varphi_3\ \varphi_3\ \varphi_4\ \varphi_2\ \varphi_1)^3$; $2(\varphi_2\ \varphi_1\ -\varphi_1\ -\varphi_2\ 0\ 0)^4$; $3(\varphi_2\ -\varphi_3\ \varphi_3\ \varphi_2\ \varphi_1\ \varphi_1)^1$; $3(-\varphi_2\ \varphi_3\ -\varphi_3\ -\varphi_2\ \varphi_1\ -\varphi_1)^2$	Cm (N8)	8	$4a_2-2a_3$, $2a_3$, $2a_1-2a_2$	$(A^a_{1/16})^8(A^b_{2/16})^4(B^b_{2/16})^{12}(B^a_{1/16})^8(X^b_{2/16})^{24}(X^a_{1/16})^{16}$
10	$(\eta_1\ \eta_2\ 0\ \eta_3)^4$	ξ^3; $2\ (\xi_1\ \xi_2)^5$; $3\ (\xi_1\ \xi_2\ \xi_3)^9$; $3(\xi_1\ \xi_2\ \xi_3)^7$; $(0\ 0\ \eta\ 0)^1$; $(0\ 0\ \eta\ 0)^3$; $2(0\ 0\ 0\ 0\ \eta_1\ \eta_2\ 0\ 0)^5$; $3(\eta_1\ \eta_2\ 0\ \eta_3)^2$; $2(\eta_1\ \eta_2\ 0\ \eta_3)^4$; $6(\eta_1\ \eta_2\ \eta_3\ \eta_4\ 0\ 0\ \eta_5\ \eta_6)^6$; $3(\varphi_1\ 0\ 0\ \varphi_2\ 0\ \varphi_3)^3$; $3(\varphi_1\ 0\ 0\ \varphi_2\ 0\ \varphi_3)^4$; $3(-\varphi_1\ \varphi_1\ -\ \varphi_2\ -\ \varphi_2\ \varphi_3\ \varphi_3)^1$; $3(-\varphi_1\ \varphi_1\ \varphi_2\ \varphi_2\ -\varphi_3\ -\varphi_3)$	Pi (N2)	8	$2a_1$, $2a_2$, $2a_3$	$(A^i_{1/8})^8(B^i_{1/8})^{16}(X^i_{1/8})^{32}$

11	$(\eta_1\ \eta_2\ \eta_3\ \eta_4)^4$	ξ^3; 2 $(\xi_1\ \xi_2)^5$; 3 $(\xi_1\ \xi_2\ \xi_3)^9$; 3$(\xi_1\ \xi_2\ \xi_3)^7$; ξ^2; ξ^4; 2$(\xi_1\ \xi_2)^6$; 3$(\xi_1\ \xi_2\ \xi_3)^{10}$; 3$(\xi_1\ \xi_2\ \xi_3)^8$; 4$(\eta_1\ \eta_2\ \eta_3\ \eta_4)^1$; 4$(\eta_1\ \eta_2\ \eta_3\ \eta_4)^3$; 8$(\eta_1\ \eta_2\ \eta_3\ \eta_4\ \eta_5\ \eta_6\ \eta_7\ \eta_8)^5$; 4$(\eta_1\ \eta_2\ \eta_3\ \eta_4)^2$; 3$(\eta_1\ \eta_2\ \eta_3\ \eta_4)^4$; 8 $(\eta_1\ \eta_2\ \eta_3\ \eta_4\ \eta_5\ \eta_6\ \eta_7\ \eta_8)^6$; 6 $(\varphi_1\ \varphi_2\ \varphi_3\ \varphi_4\ \varphi_5\ \varphi_6)^3$; 6 $(\varphi_1\ \varphi_2\ \varphi_3\ \varphi_4\ \varphi_5\ \varphi_6)^4$; 6 $(\varphi_1\ \varphi_2\ \varphi_3\ \varphi_4\ \varphi_5\ \varphi_6)^1$; 6 $(\varphi_1\ \varphi_2\ \varphi_3\ \varphi_4\ \varphi_5\ \varphi_6)^2$	P1 (N1)	8	$2a_1$, $2a_2$, $2a_3$	$(A^a_{1/16})^{16}(B^a_{1/16})^{32}(X^a_{1/16})^{64}$

References

Kovalev, O. V. (1993) *Representations of Crystallographic Space Groups. Irreducible Representations, Induced Representations and Co-representations.* Taylor and Francis Ltd.

Section S2

The vectors of primitive cell translations of low-symmetry phases (a_1, a_2, a_3) have the following positions in the expanded $(2 \times 2 \times 2)$-cell of spinel: $a_1 = (0, 1, 1)$; $a_2 = (1, 0, 1)$ and $a_3 = (1, 1, 0)$. The basis vectors of $(2\times2\times2)$-spinel cell are of the form $A_1 = (2, 0, 0)$; $A_2 = (0, 2, 0)$; $A_3 = (0, 0, 2)$ or $A_1 = a_2 + a_3 - a_1$, $A_2 = a_1 + a_3 - a_2$, $A_3 = a_1 + a_2 - a_3$. The R3̄m-phase, generated by critical irrep $k_9(\tau_4)$ and corresponding to the direction $(\eta\,0\,0\,0)$ in OP space, has basis vectors $(1, -1, 0)$, $(0, 1, -1)$, $(4, 4, 4)$ or $(a_2 - a_1)$, $(a_3 - a_2)$, $2(a_1 + a_2 + a_3)$. The relationship between the basis vectors of the unit cell of low-symmetry R3̄m-phase ($A`_1$, $A`_2$ and $A`_3$), and the basis vectors of the unit cell of high-symmetry phase, $A_1$, $A_2$, and $A_3$, is indicated such expressions: $A`_1 = 1/2(A_1 - A_2)$, $A`_2 = 1/2(A_2 - A_3)$, $A`_3 = 2(A_1 + A_2 + A_3)$.

In the F-lattice of spinel structure we can choose two horizontal vectors $A`_1$ and $A`_2$ angled 120° to each other, and a vertical vector- $A`_3$ which can be directed along the axis of the third order structure of cubic spinel. At this, vector $A`_3$ can be chosen as equal to body diagonal of the initial $(2 \times 2 \times 2)$-cube. The obtained rhombohedral cell in such a way is shown in Fig. 1 (without taking into account displacement of rhombohedral cell relative to the initial cubic cell).
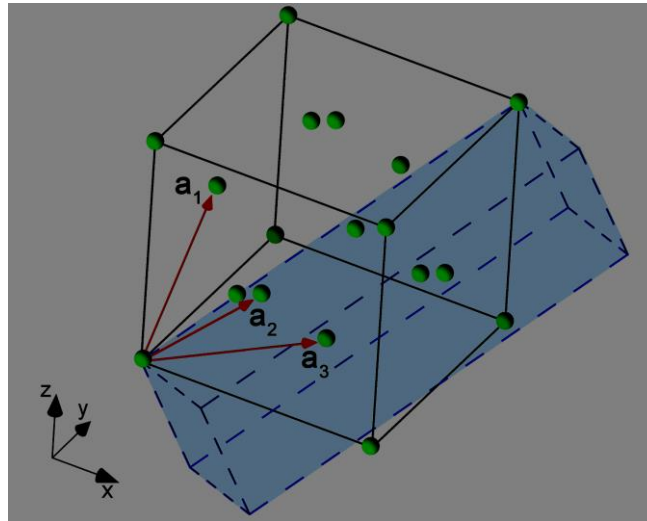

Fig. 1. The relationship between the face-centered cubic $(2\times2\times2)$-lattice and R-centred lattice in hexagonal representation for $(\eta\,0\,0\,0)$-domain of rhombohedral R3̄m-phase. Atoms of F-centered cubic cell are marked in green.

The structure of the low-symmetry R3̄m-phase can be oriented by eight different ways with respect to the initial high-symmetry Fd3̄m -spinel structure. These eight orientations or domains of R3̄m-phase correspond to the eight directions of the order parameter in the OP space: $(0\,0\,0\ \eta)$, $(0\,0\,0\ -\eta)$, $(0\,0\ \eta\ 0)$, $(0\,0\ -\eta\ 0)$, $(0\ \eta\,0\,0)$, $(0\ -\eta\,0\,0)$, $(\eta\,0\,0\,0)$, $(-\eta\,0\,0\,0)$.

Section S3

Consider the theoretical derivation of $R\bar{3}m$ -phase structure from the cubic spinel structure and evaluate the real role of noncritical coordinates in the formation of low-symmetry phase.

Wyckoff position 8*a*. Atom displacements in the positions (a) are generated by critical irrep $\mathbf{k}_9(\tau_4)$ (η_a) and noncritical irrep $\mathbf{k}_{11}(\tau_7)$ (ξ_a). Al-cations in cubic spinel structure have coordinates: (000) and (1/4, 1/4, 1/4). After displacements of the first (a_{1x}, a_{1x}, a_{1x}) and the second (a_{2x}, a_{2x}, a_{2x}) atoms their coordinates will become equal (a_{1x}, a_{1x}, a_{1x}) and ($1/4 - a_{2x}$, $1/4 - a_{2x}$, $1/4 - a_{2x}$). Additional indices x, y, z correspond to orientation of atom displacements in the low-symmetry phase relative to their positions in the high-symmetry phase.

After transformations (1), that is transition to hexagonal cell, atom coordinates will be equal to $(0, 0, 3/16 + a_{1x}/2)$ and $(0, 0, 5/16 - a_{2x}/2)$.

If we compare these coordinates with coordinates of Wyckoff position 6c of space group $R\bar{3}m$ (0, 0, z), then $z_a = 3/16 + a_{1x}/2$ and $z`_a = 5/16 - a_{2x}/2$ will be obtained. Al-atoms occupy the following positions in the $R\bar{3}m$-phase structure at room temperature: Al(1) $\rightarrow$ (0, 0, z) = (0, 0, 0.18298(3)) and Al(2) $\rightarrow$ (0, 0, z`) = (0, 0, 0.30931(3)). When comparing theoretical and experimental values z_a и $z`_a$, we will find $a_{1x} = -0.00903$ and $a_{2x} = 0.00637$.

The obtained values of Al-atom displacements allow us to find numerical estimations for η_a and ξ_a parameters. These parameters can be calculated by means of formula for symmetrical coordinates: $\eta_a = 2\sqrt{3}(a_{1x} - a_{2x})$ and $\xi_a = 2(a_{1x} + a_{2x})$. As a result of the calculations we receive $\eta_a = -0.05337$ and $\xi_a = -0.00532$. Thus the contribution of noncritical OP ξ_a into rhombohedral structure formation at room temperature appeared to be one order less than the contribution from critical OP η_a.

Wyckoff position 16d. Atom displacements in the positions (d) are generated by critical irrep $\mathbf{k}_9(\tau_4)$, which enters twice into mechanical representation of spinel structure (η_{1d}, η_{2d}). Consider V-cations with coordinates: (5/8, 9/8, 9/8), (5/8, 5/8, 5/8) and (1/8, 7/8, 3/8). The two first atoms are not displaced; only the third atom is displaced: ($1/8 - d_{2z}$, $7/8 - d_{1x}$, $3/8 - d_{1x}$). In the hexagonal system V-atoms coordinates are equal to (0, 0, 0), (0, 0, 1/2) and ($5/6 - 2/3d_{1x} + 2/3d_{2z}$, $1/6 + 2/3d_{1x} - 2/3d_{2z}$, $5/12 - 1/3d_{1x} - 1/6d_{2z}$). They will occupy by Wyckoff positions 3a, 3b and 18h respectively. For position 18h we will obtain $x = 5/6 - 2/3d_{1x} + 2/3d_{2z}$, $z = 5/12 - 1/3d_{1x} - 1/6d_{2z}$.

At room temperature in the AlV_2O_4 structure V-atoms occupy the following positions in the $R\bar{3}m$-phase structure (Horibe et al., 2006):

V(1) $\rightarrow$ (0, 0, 0);

V(2) $\rightarrow$ (0, 0, 1/2);

V(3) $\rightarrow$ (x, -x, z) = (0.84873(2), 0.15127, 0.41786(1)).

When comparing theoretical and experimental atom coordinates we will receive for V(3): $d_{1x} = -0.010$, $d_{2z} = 0.013$. The displacement values of V-cations along the x and z axes are of the same order, but have opposite directions. From expressions of symmetrical coordinates $\eta_{1d} = 4\sqrt{3}d_{1x}$, $\eta_{2d} = 2\sqrt{6}d_{2z}$ it follows the estimations for displacement contributions of V-cations into OP-value $\eta_{1d} = -0.070$, $\eta_{2d} = 0.064$.

Wyckoff position 32*e*. Atom displacements in the positions (e) are generated by critical irrep $\mathbf{k}_9(\tau_4)$, which enters three times into mechanical representation of spinel structure (η_{1e}, η_{2e}, η_{3e}), and are generated by noncritical irrep $\mathbf{k}_{11}(\tau_7)$, which enters twice into mechanical representation of spinel structure (ξ_{1e}, ξ_{2e}), and by unit irrep $\mathbf{k}_{11}(\tau_1)$ (λ_e). Spinel positions 32e in $R\bar{3}m$-structure are split into four nonequivalent positions. For O-coordinates in cubic spinel structure we have (with taking into account displacements e^i_j (i=1-4, j = x, z)):

O(1), 2c: $(u + e^1_x, 1/2 + u + e^1_x, 1/2 + u + e^1_x)$, $(7/4 - u - e^1_x, 3/4 - u - e^1_x, 9/4 - u - e^1_x)$;

O(2), 2c: $(u + e^2_x, u + e^2_x, u + e^2_x)$, $(9/4 - u - e^2_x, 3/4 - u - e^2_x, 3/4 - u - e^2_x)$;

O(3), 6h: $(u + e^3_z, 1 - u + e^3_x, 1 - u + e^3_x)$, $(1 - u + e^3_x, u + e^3_z, 1 - u + e^3_x)$,

$(1 - u + e^3_x, 1 - u + e^3_x, u + e^3_z)$, $(9/4 - u - e^3_z, 3/4 + u - e^3_x, 3/4 + u - e^3_x)$,
$(1/4 + u - e^3_x, 3/4 - u - e^3_z, 3/4 + u - e^3_x)$, $(1/4 + u - e^3_x, 3/4 + u - e^3_x, 3/4 - u - e^3_z)$;

O(4), 6h: $(u + e^4_z, 3/2 - u + e^4_x, 3/2 - u + e^4_x)$, $(3/2 - u + e^4_x, u + e^4_z, 3/2 - u + e^4_x)$,
$(3/2 - u + e^4_x, 3/2 - u + e^4_x, u + e^4_z)$, $(9/4 - u - e^4_z, 5/4 + u - e^4_x, 5/4 + u - e^4_x)$,
$(3/4 + u - e^4_x, 3/4 - u - e^4_z, 5/4 + u - e^4_x)$, $(3/4 + u - e^4_x, 5/4 + u - e^4_x, 3/4 - u - e^4_z)$,

where u is the free parameter of Wyckoff position 32e. In the above expressions, the atomic coordinates are recorded with exactness up to the primitive cell vectors determined by triple vectors (1/2, –1/2, 0), (1/2, 0, –1/2), (0, 1, 1).

In the hexagonal system the oxygen atom coordinates are equal respectively

O(1), 2c: $(0, 0, 11/16 + 1/2\,u + 1/2e^1_x)$, $(0, 0, 21/16 - 1/2\,u - 1/2e^1_x)$;

O(2), 2c: $(0, 0, 3/16 + 1/2\,u + 1/2e^2_x)$, $(0, 0, 13/16 - 1/2\,u - 1/2e^2_x)$;

O(3), 6h: $[4/3(1\text{-}u) + 2/3(e^3_x - e^3_z), -4/3(1 - u) - 2/3(e^3_x - e^3_z), 41/48 - 1/6u + 1/6(2e^3_x + e^3_z)]$,
$[-8/3(1 - u) - 4/3(e^3_x - e^3_z), -4/3(1 - u) - 2/3(e^3_x - e^3_z), 41/48 - 1/6u + 1/6(2e^3_x + e^3_z)]$,
$[4/3(1 - u) + 2/3(e^3_x - e^3_z), 8/3(1 - u) + 4/3(e^3_x - e^3_z), 41/48 - 1/6u + 1/6(2e^3_x + e^3_z)]$,
$[-1 + 4/3\,u - 2/3(e^3_x - e^3_z), -1 - 4/3\,u + 2/3(e^3_x - e^3_z), 13/16 + 1/6u - 1/6(2e^3_x + e^3_z)]$,
$[1/3 - 8/3\,u + 4/3(e^3_x - e^3_z), -1/3 - 4/3\,u + 2/3(e^3_x - e^3_z), 23/48 + 1/6u - 1/6(2e^3_x + e^3_z)]$,
$[1/3 + 4/3\,u - 2/3(e^3_x - e^3_z), -1/3 + 8/3\,u - 4/3(e^3_x - e^3_z), 23/48 + 1/6u - 1/6(2e^3_x + e^3_z)]$;

O(4), 6h: $[1 - 4/3\,u + 2/3(e^4_x - e^4_z), -1 + 4/3\,u - 2/3(e^4_x - e^4_z), 11/16 - 1/6u + 1/6(2e^4_x + e^4_z)]$,
$[-1 + 8/3\,u - 4/3(e^4_x - e^4_z), -1 + 4/3\,u - 2/3(e^4_x - e^4_z), 11/16 - 1/6u + 1/6(2e^4_x + e^4_z)]$,
$[1 - 4/3\,u + 2/3(e^4_x - e^4_z), 1 - 8/3\,u + 4/3(e^4_x - e^4_z), 11/16 - 1/6u + 1/6(2e^4_x + e^4_z)]$,
$[-2/3 + 4/3u - 2/3(e^4_x - e^4_z), 2/3 - 4/3u - 2/3(e^4_x - e^4_z), 47/48 + 1/6u - 1/6(2e^4_x + e^4_z)]$,
$[-1/3 - 8/3u - 4/3(e^4_x - e^4_z), -2/3 - 4/3u - 2/3(e^4_x - e^4_z), 31/48 + 1/6u - 1/6(2e^4_x + e^4_z)]$,
$[2/3 + 4/3u - 2/3(e^4_x - e^4_z), 1/3 + 8/3u - 4/3(e^4_x - e^4_z), 31/48 + 1/6u - 1/6(2e^4_x + e^4_z)]$.

The atom coordinates in hexagonal system are recorded with exactness up to the primitive cell vectors determined by three vectors (1, 0, 0), (0, 1, 0), (2/3, 1/3, 1/3). In the transition to the hexagonal system we used scale transformation, which transforms the vector (2, 2, 2) into the vector (0, 0, 1).

At room temperature, oxygen atoms occupy four Wyckoff positions in the AlV_2O_4 rhombohedral structure (Horibe et al., 2006):

O(1) → $(0, 0, z_1) = (0, 0, 0.12132(6))$;

O(2) → `$(0, 0, z_2) = (0, 0, 0.37045(6))$;

O(3) → $(x_1, -x_1, z_3) = (0.83153(8), 0.16847, 0.53921(4))$;

O(4) → $(x_2, -x_2, z_4) = (0.82972(8), 0.17028, 0.29034(4))$.

In the cubic phase u equal 0.376 (Reuter et al., 1983). Using this value of u the values of the displacements of oxygen atoms can be estimated:

O(1): $e^1_x = 0.0064$;

O(2): $e^2_x = -0.0101$;

O(3): $e^3_x = 0.0068$, $e^3_z = 0.0021$;

O(4): $e^4_x = -0.0035$, $e^4_z = -0.0000(4)$.

From symmetric coordinates the estimate of relative contributions of oxygen atom displacements into the critical and non-critical order parameters can be obtained:

$\eta_{1e} = 2\sqrt{3}(e^1_x - e^2_x) = -0.057$; $\eta_{2e} = 2\sqrt{6}(e^3_x - e^4_x) = 0.050$; $\eta_{3e} = 2\sqrt{3}(e^3_z - e^4_z) = 0.007$;

$\xi_{1e} = e^1_x + e^2_x + 2\,e^3_x + e^3_z + 2\,e^4_x + e^4_z = 0.005$;

$\xi_{2e} = \sqrt{2}(e^1_x + e^2_x - e^3_z - e^4_z) = 0.008$;

$\lambda_e = \sqrt{3}(e^1_x + e^2_x - 2e^3_x + e^3_z - 2\,e^4_x + e^4_z) = -0.015$.

Thus, we can say that the structure formation of the rhombohedral phase at room temperature is defined by critical irrep $\mathbf{k}_9(\tau_4) - \eta$, absolute value of which proved to be one order greater than non-critical parameter $\mathbf{k}_{11}(\tau_7) - \xi$. Note that unit irrep ($\mathbf{k}_{11}(\tau_1) - \lambda$) does not change the crystal symmetry. Besides, we would like to point out that the greatest contribution to the critical order parameter is caused by x- and z-displacements of vanadium, x-displacement of oxygen and x-displacement of aluminum.

References

Horibe, Y., Shingu, M., Kurushima, K., Ishibashi, H., Ikeda, N., Kato, K., Motome, Y., Furukawa, N., Mori, S. & Katsufuji, T. (2006). *Phys. Rev. Lett*. A**96**, 086406 (1-4).

Reuter, Von B., Aust, R., Colsmann, G. & Neuwald, Ch. (1983). *Z. anorg. allg. Chem*. A**500***, 188-198.

Section S4

Table S2. The nearest interatomic distances in vanadites $(A)[V_2]O_4$ $(A=$ Li, Al, Mg, Zn, Cd, Co, Fe, Mn) with the structure of cubic spinel

Вещество	a, Å	u	A-O, Å	V–O, Å	V`–O, Å	A–A, Å	V – V, Å	A- V, Å	O–O, Å	O–O`, Å
LiV_2O_4	8.2384(6) at 193(2) K (Das et al., 2007).	0.386	1.943	1.972	3.408	3.567	2.913	3.415	3.174	2.652
AlV_2O_4	8.192 (Reuter et al., 1983).	0.376	1.788	2.040	3.533	3.547	2.896	3.396	2.919	2.873
MgV_2O_4	8.4021(7) (Niitaka et al., 2014).	0.385	1.968	2.018	3.489	3.638	2.971	3.483	3.214	2.727
ZnV_2O_4	8.4028(4) at 60 K (Reehuis et al., 2003).	0.385	1.971	2.017	3.487	3.639	2.971	3.484	3.219	2.723
	8.4111 at 298 K (Ebbinghaus et al., 2004).	0.374	1.812	2.108	3.651	3.642	2.974	3.487	2.959	2.989
CdV_2O_4	8.6911 at t 299 K (Onoda & Hasegawa, 2003).	0.392	2.141	2.034	3.504	3.763	3.073	3.603	3.496	2.649
CoV_2O_4	8.4073(1) (Kismarahardja et al., 2011)	0.3648	1.672	2.191	3.789	3.640	2.972	3.485	2.730	3.215
FeV_2O_4	8.45547 at 200 K(MacDougall et al., 2012).	0.375	1.831	2.114	3.661	3.661	2.989	3.505	2.989	2.989
	8.4609 for $Fe_{1.2}V_{1.8}O_4$ (Zhang et al., 2012).	0.385	1.978	2.034	3.517	3.664	2.991	3.508	3.231	2.752
MnV_2O_4	8.5220(7) at 300 K (Shahi et al., 2014).	0.3875*	2.030	2.030 (Shahi et al., 2014).	3.506	3.690	3.0130(1) (Shahi et al., 2014).	3.533	3.314	2.712

Notes. Free parameter **u** defines the positions of the oxygen atoms (u, u, u) in Wyckoff position 32e. Sign * means the estimated value **u** according to the formula $d_{V-O} = a[3u^2 - (11/4)u +43/64]^{1/2}$. d_{A-O} and d_{V-O} are the shortest distances between atoms A and V and oxygen atoms respectively. O-O and O-O` are the shortest distance between oxygen atoms calculated according to the formulas: $a(2u-1/2)(2)^{1/2}$ and $a(1-2u)(2)^{1/2}$ respectively.

References

Das, S., Zong, X., Niazi, A., Ellern, A., Yan, J. Q. & Johnston, D. C. (2007). *Phys. Rev. B.* A**76**, 054418(1-6).

Ebbinghaus, S.G., Hanss, J., Klemm, M. & Horn, S. (2004). *J. All. Comp.* A**370**, 75-79.

Kismarahardja, A., Brooks, J. S., Kiswandhi, A., Matsubayashi, K., Yamanaka, R., Uwatoko, Y., Whalen, J., Siegrist, T. & Zhou, H. D. (2011). *Phys. Rev. Lett.* A**106**, 056602 (1-4).

MacDougall, G J., Garlea, V. O., Aczel, A. A., Zhou, H. D. & Nagler, S. E. (2012). *Phys. Rev. B.* A**86**, 060414(R) (1-5).

Niitaka, S., Lee, S., Oshima, Y., Kato, K., Hashizume, D., Takata, M. & Takagi, H. (2014). *J. Solid State Chem.* A**215**, 184-188.

Onoda, M. & Hasegawa, J. (2003). *J. Phys.: Condens. Matter.* A**15**, L95-L102.

Reehuis, M., Krimmel, A., Buttgen, N., Loidl, A. & Prokofiev, A. (2003). *Eur. Phys. J. B.* A**35**, 311-316.

Reuter, Von B., Aust, R., Colsmann, G. & Neuwald, Ch. (1983). *Z. anorg. allg. Chem.* A**500***,* 188-198.

Shahi, P., Kumar, S., Sharma, N., Singh, R., Sastry, P. U., Das, A., Kumar, A., Shukla, K. K., Ghosh, A. K., Nigam, A. K. & Chatterjee, S. (2014). *J. Mater. Sci.* A**49**, 7317-7324.

Zhang, Q., Singh, K., Guillou, F., Simon, C., Breard, Y., Caignaert, V. & Hardy, V. (2012). *Phys. Rev. B.* A**85**, 054405 (1-10).