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A New Mixed-Valent Vanadium Phosphate with a Tunnel Structure: $Cd_5V_3P_6O_{25}$

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A new mixed-valent phosphate $Cd_5V_3P_6O_{25}$ was isolated and its structure was determined from single-crystal X-ray diffraction data. This phase crystallizes in the monoclinic space group $C2/c$ with a = 15.861(1) Å, b = 4.710(1) Å, c = 24.160(2) Å, β = 103.07(1)°, V = 1868.9(5) Å^3, $Z = 4$, $R = 0.029$, $R_w = 0.034$ for 2626 unique reflections with $I > 3\sigma(I)$. The structure consists of VO_5 pyramids and VO_6 octahedra occupied by V(IV) and V(III), respectively, and connected through monophosphate groups. The VO_5 pyramids exhibit one abnormally short V–O distance characteristic of the vanadyl ion and form columns parallel to **b**. The $[V_3P_6O_{25}]_\infty$ framework can be described as built up from mixed double chains $[V_2P_6O_{24}]_\infty$ of corner-sharing octahedra and PO_4 tetrahedra running along **b**; the latter are connected to each other through VO_5 pyramids, located in planes parallel to (001). This host lattice forms tunnels running along **b** where the cadmium ions are located. The latter exhibit a distorted octahedral coordination. © 1993 Academic Press, Inc.

Introduction

Numerous vanadium phosphates characterized by a tunnel or a layered structure have been discovered these last years. This exceptionally rich chemistry is easily explained by the great flexibility of vanadium coordination. Indeed this element may exhibit either a pyramidal or an octahedral coordination, but also all the intermediate configurations between the VO_5 and VO_6 polyhedra, with V–O distances ranging from 1.6 Å to 2.6 Å; this great adaptability of VO_6 or VO_5 polyhedra to the PO_4 tetrahedra is also favored by the fact that one of their corners is sometimes free, forming a vanadyl ion. This property, with the ability of vanadium to exhibit various oxidation states, mainly V(V), V(IV), and V(III), suggests that the crystal chemistry of vanadium is at its very beginning and that such compounds may be of interest for a variety of physical properties and particularly in redox catalysis. Nevertheless, a limited number of mixed valent vanadium phosphates have been isolated up to now. In the case of V(V)–V(IV) phosphates, only the compounds $RbV_3P_4O_{17+x}$ (*1*), $Rb_6V_6P_6O_{31}$ (*2*), $V_{12}P_3O_{34}$ (*3*), $Na_xV_{1+x}PO_5 \cdot (2-x)H_2O$ (*4*), $KV_3P_4O_{17}$ (*5*), $Ni_{0.5}VPO_5 \cdot 1.5H_2O$ (*6*), $Na(K)_{0.5}VPO_5 \cdot 2H_2O$ (*7*), and $AgV_2P_2O_{10}$ (*8*) have been synthesized, whereas the mixed valency V(III)–V(IV) has been observed in two oxides, $KV_3P_4O_{16}$ (*9*) and $V_3P_4O_{15}$ (*10*), and in three oxohydroxides, $V_4P_3H_2O_{15}$ (*11*), $Na_{2.44}V_4P_4O_{17}OH$ (*12*), and $V_4O(OH)_2(PO_4)_3$ (*13*). We report here on the synthesis and on the original crystal structure of the V(III)–V(IV) phosphate $Cd_5V_3P_6O_{25}$.

Experimental

Green-yellow single crystals of $Cd_5V_3P_6O_{25}$ were crystallized as a minor product in a nearly pure orthorhombic form of

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TABLE I

CRYSTAL DATA, INTENSITY MEASUREMENTS, AND STRUCTURE REFINEMENT PARAMETERS FOR $Cd_5V_3P_6O_{25}$

1. Crystal data	
Space group	$C2/c$
Cell dimensions	a = 16.861(1) Å b = 4.710(1) Å; β = 103.07(1)° c = 24.160(2) Å
Volume	1869 (2) Å^3
Z	4
2. Intensity measurement	
λ (Mo$K\alpha$)	0.71073
Scan mode	ω-$\frac{4}{3}$ θ
Scan width (°)	0.95 + 0.35 tanθ
Slit aperture (mm)	1.12 + tanθ
Max θ (°)	45
range of h	−32, +30
k	0, +9
l	0, +48
Measured reflections	8433
Reflections with $I > 3\sigma$	2626
Standard reflections	3 every 3000 seconds
μ (mm^{-1})	4.050
3. Structure solution and refinement	
Parameters refined	180
Agreement factors	R = 0.029, R_W = 0.034
Weighting scheme	$W = f(\sin\theta/\lambda)$
Δ/σ max.	0.01

$CdV_2P_2O_{10}$ prepared in the following way. First, an adequate mixture of CdO, V_2O_5, and $(NH_4)_2HPO_4$ was heated to 380°C in air in order to eliminate H_2O, and NH_3. In the second step, the finely ground product was mixed with an appropriate amount of vanadium and sealed in an evacuated silica ampoule. This sample was then heated at 800°C for 24 hr and slowly cooled at a rate of 1°C h^{-1} down to 600°C.

A green crystal of $Cd_5V_3P_6O_{25}$ with dimensions 0.090 × 0.064 × 0.039 mm was selected for the structure determination. The cell parameters reported in Table I were determined and refined by diffractometric techniques at 21°C with a least-squares refinement based upon 25 reflections with $18 < \theta < 22°$.

The systematic absence $h + k = 2n + 1$ for all the $h\ k\ l$, $l = 2n + 1$ for $h\ 0\ l$ and $k = 2n + 1$ for $0\ k\ 0$ are consistent with the space groups Cc and $C2/c$. The Patterson function shows $u0w$ and $u\frac{1}{2}w$ peaks which are only compatible with the $C2/c$ space group. The data were collected on a CAD-4 Enraf Nonius diffractometer with the data collection parameters reported in Table I. The reflections were corrected for Lorentz, polarization and secondary extinction effects. Analytic absorption correction was performed.

The structure was solved by the heavy atom method. The refinement of the coordinates and the anisotropic thermal factors of all the atoms led to $R = 0.029$, $R_w = 0.034$ and to the atomic parameters of Table II.

The scattering factors are taken from the International Tables for X-Ray Crystallography (*14*).

Description of the Structure and Discussion

The projection of the structure onto the (010) plane (Fig. 1) shows that the tridimensional framework $[V_3P_6O_{25}]_\infty$ is built up from single corner-sharing VO_5 pyramids, VO_6 octahedra, and PO_4 tetrahedra. This frame-

TABLE II

TABLE OF POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	x	y	z	B(Å^2)
Cd(1)	0.	0.	0.	0.628(7)
Cd(2)	0.16719(2)	0.4781(1)	0.20952(2)	0.760(5)
Cd(3)	0.44023(2)	−0.0237(1)	0.11704(2)	0.725(5)
V(1)	0.	−0.0605(3)	0.25	0.45(2)
V(2)	0.26883(4)	0.4943(2)	0.41304(3)	0.37(1)
P(1)	0.32368(7)	0.5112(4)	0.17458(5)	0.38(2)
P(2)	0.07178(8)	−0.0450(3)	0.14065(6)	0.41(2)
P(3)	0.15001(8)	0.4724(3)	0.00305(5)	0.40(2)
O(1)	0.	0.277(2)	0.25	1.2(1)
O(2)	0.0627(3)	−0.197(1)	0.1967(2)	0.58(6)
O(3)	0.0950(3)	−0.153(1)	0.3118(2)	0.71(6)
O(4)	0.1681(3)	0.271(1)	0.3622(2)	0.63(6)
O(5)	0.3653(3)	0.705(1)	0.4636(2)	0.61(6)
O(6)	0.2891(3)	0.1618(9)	0.4579(2)	0.65(6)
O(7)	0.3436(3)	0.360(1)	0.3644(2)	0.68(6)
O(8)	0.2452(3)	0.8139(9)	0.3538(2)	0.64(6)
O(9)	0.1834(3)	0.6242(9)	0.4512(2)	0.56(6)
O(10)	0.3005(3)	0.612(1)	0.2300(2)	0.71(6)
O(11)	0.0644(3)	0.2750(9)	0.1483(2)	0.63(6)
O(12)	0.0032(3)	−0.141(1)	0.0918(2)	0.83(6)
O(13)	0.0693(3)	0.625(1)	−0.0221(2)	0.78(6)

Note. Anisotropically refined atoms are given in the isotropic equivalent displacement parameter, defined as $B = \frac{4}{3}[\beta_{11} a^2 + \beta_{22} b^2 + \beta_{33} c^2 + \beta_{12} ab \cos\gamma + \beta_{13} ac \cos\beta + \beta_{23} bc \cos\alpha]$.

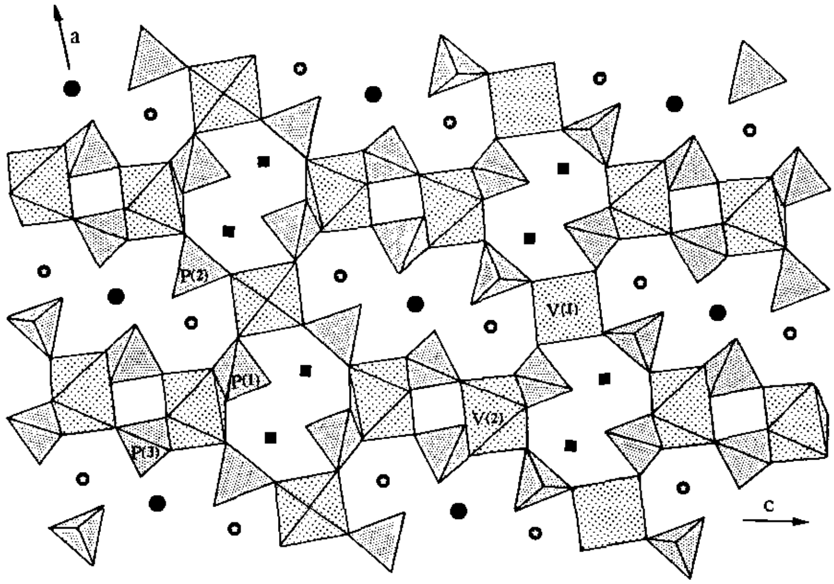

FIG. 1. Projection of the structure along **b** (● Cd(1), ■ Cd(2), ○ Cd(3)).

work delimits tunnels running along **b** where cadmium cations are located.

The two crystallographically independent vanadium atoms exhibit a pyramidal (V(1) site) and an octahedral (V(2) site) coordination, respectively. The V(1) pyramids share the four corners of their basal plane with PO_4 tetrahedra, leading to four almost equal equatorial V(1)–O distances (Table III) ranging from 1.951 to 1.973 Å; the fifth corner of the VO_5 pyramids is free, with an abnormally short V(1)–O(1) apical distance (1.589 Å) characteristic of the vanadyl group often observed in vanadium phosphates ($A_2VP_2O_8$ (A = K, Rb, Cs) (*15, 16*), $A_2V_3P_4O_{17}$ (A = K, Rb, Cs) (*17–20*), $Na_5V_2P_3O_{14} \cdot H_2O$ (*21*), ($AV_2P_2O_{10}$) (A = Ba, Pb, Ag) (*22, 23,* 8). the v(2) octahedra share their six apices with the PO_4 tetrahedra; the "O_6" octahedra are almost regular as shown for the O–O distances (Table III) but the V(2)–O distances vary significantly from 1.891 to 2.135 Å. The consideration of the charge balance in this phase, according to the formulation $Cd_5V_2^{III}V^{IV}P_6O_{25}$, and of the number of octahedral and pyramidal sites of 8 and 4 respectively per cell, suggests an ordering of the V(III) and V(IV) ions. Indeed the sum of the electrostatic valencies using the Brown and Altermatt curves (*24*) shows that the V(1) pyramidal sites are occupied by V(IV) ions, whereas the V(2) octahedral sites correspond to V(III).

The three independent PO_4 tetrahedra are characterized by an almost regular geometry (Table IV). One interesting feature, deals proceeds with the existence of free apices for each of them; one indeed observes one free apex for the P(1) and P(3) tetrahedra, corresponding to the O(10) and O(13) atoms respectively, whereas the P(2) tetrahedra exhibit two free apices corresponding to O(11) and O(12) respectively. In this framework, each P(1) tetrahedron shares its three other corners with two V(2) octahedra and one V(1) pyramid, whereas each P(2) tetrahedron is connected to one V(1) pyramid and one V(2) octahedron, and each P(3) tetrahedron to three V(2) octahedra. In spite of this "dissymmetry" in the mode of connection of the PO_4 tetrahedra, the P–O distances do not spread over a wide range, i.e., from 1.518 Å to 1.570 Å (Table IV). In fact the free apices of the PO_4 tetrahedra,

TABLE III

DISTANCES (Å) AND ANGLES (°) IN THE VO_6 OCTAHEDRA

V(1)	O(1)	O(2)	O(2$^{\mathrm{i}}$)	O(3)	O(3$^{\mathrm{i}}$)
O(1)	1.589(7)	2.895(7)	2.895(7)	2.797(7)	2.797(7)
O(2)	109.3(1)	1.951(4)	3.684(6)	2.719(6)	2.629(6)
O(2$^{\mathrm{i}}$)	109.3(1)	141.4(3)	1.951(4)	2.629(6)	2.719(6)
O(3)	102.8(1)	87.6(2)	84.0(2)	1.977(4)	3.856(6)
O(3$^{\mathrm{i}}$)	102.8(1)	84.0(2)	87.6(2)	154.4(3)	1.977(4)

V(2)	O(4)	O(5)	O(6)	O(7)	O(8)	O(9)
O(4)	2.135(4)	4.188(6)	2.762(6)	2.977(6)	2.898(6)	2.685(6)
O(5)	178.6(2)	2.054(4)	2.851(6)	2.848(6)	2.994(6)	3.037(6)
O(6)	86.4(2)	92.5(2)	1.891(4)	2.785(6)	3.932(6)	2.795(6)
O(7)	91.8(2)	89.0(2)	91.1(2)	2.010(4)	2.682(6)	3.976(6)
O(8)	87.6(2)	93.6(2)	171.2(2)	82.6(2)	2.053(4)	2.921(6)
O(9)	81.5(2)	97.8(2)	92.6(2)	172.1(2)	92.9(2)	1.975(4)

Note. The V–O distances are on the diagonals of the table. The values above the diagonals are the O–O distances and the values below them are the O–V–O angles. Symmetry codes: (i) $-x, y, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $x, -1 - y, z - \frac{1}{2}$; (v) $x - \frac{1}{2}, -y - \frac{3}{2}, z - \frac{1}{2}$; (vi) $-x, -y, -z$; (vii) $-x, -y - 1, -z$; (viii) $x, y - 1, z$; (ix) $x, y + 1, z$; (x) $x + \frac{1}{2}, y - \frac{1}{2}, z$; (xi) $x + \frac{1}{2}, y + \frac{1}{2}, z$; (xii) $x + \frac{3}{2}, y + \frac{3}{2}, z$.

can only be considered as free if one describes the structure in terms of a $[V_3P_6O_{25}]_\infty$ host lattice; in reality these apices are linked to cadmium atoms, which form rather short and more covalent Cd–O bonds, compared to larger univalent or divalent cations.

Considering the $[V_3P_6O_{25}]_\infty$ framework, the cadmium ions are located in two kinds of tunnels (Fig. 1). The Cd(1) and Cd(3) atoms are distributed in large 12-sided tunnels similar to those observed for $BaV_2P_2O_{10}$ *(20)*, whereas the Cd(2) atoms are located in smaller eight-sided tunnels. But the important feature deals with the six-fold coordination of Cd^{2+} in all cases (Table V). Indeed Cd(1) is characterized by an almost regular coordination with Cd–O distances from 2.24 Å to 2.44 Å, whereas Cd(2) and Cd(3) exhibit more strongly distorted CdO_6 octahedra with Cd-O distances ranging from 2.223 Å to 2.610 Å.

TABLE IV

DISTANCES (Å) AND ANGLES (°) IN THE PO_4 TETRAHEDRA

P(1)	O(3$^{\mathrm{ii}}$)	O(4$^{\mathrm{ii}}$)	O(8$^{\mathrm{iii}}$)	O(10)
O(3$^{\mathrm{ii}}$)	1.544(5)	2.512(6)	2.511(6)	2.546(6)
O(4$^{\mathrm{ii}}$)	109.3(3)	1.536(4)	2.545(6)	2.517(6)
O(8$^{\mathrm{iii}}$)	109.8(3)	112.5(2)	1.524(4)	2.440(6)
O(10)	110.8(2)	109.3(3)	105.0(3)	1.550(4)
P(2)	O(2)	O(7$^{\mathrm{iii}}$)	O(11)	O(12)
O(2)	1.570(4)	2.409(6)	2.516(6)	2.518(6)
O(7$^{\mathrm{iii}}$)	102.2(2)	1.526(4)	2.557(6)	2.560(6)
O(11)	108.7(3)	113.7(3)	1.527(4)	2.476(6)
O(12)	109.1(2)	114.2(3)	108.6(3)	1.522(5)
P(3)	O(5$^{\mathrm{iii}}$)	O(6$^{\mathrm{ii}}$)	O(9$^{\mathrm{iv}}$)	O(13)
O(5$^{\mathrm{iii}}$)	1.549(5)	2.495(6)	2.515(6)	2.535(6)
O(6$^{\mathrm{ii}}$)	108.9(2)	1.518(5)	2.528(6)	2.543(6)
O(9$^{\mathrm{iv}}$)	108.3(3)	110.8(2)	1.553(5)	2.460(6)
O(13)	110.5(3)	112.7(3)	105.5(2)	1.537(4)

Note. The P–O distances are on the diagonals of the table. The values above the diagonals are the O–O distances and the values below them are the O–P–O angles. See Note to Table III for symmetry codes.

Taking Cd^{2+} as an intercalated cation, the host lattice $[V_3P_6O_{25}]_\infty$ can be described in a very simple way as built up from double chains $[V_2P_6O_{24}]_\infty$ running along **b** (Fig. 2a); such chains consist of the corner-sharing VO_6 octahedra and PO_4 tetrahedra. These double chains result from the assemblage of two $[VP_3O_{15}]_\infty$ single chains (Fig. 2b) in which the VO_6 octahedra are connected through two PO_4 tetrahedra along **b**; two $[VP_3O_{15}]_\infty$ single chains are shifted by **b**/2 in such a way that the apical oxygen of one VO_6 octahedron of one chain be connected with the PO_4 tetrahedron of the other chain

TABLE V

OXYGEN ATOMS SURROUNDING Cd^{2+} WITH Cd–O < 2.5 Å

Cd(1)–O(5^{v})	2.441(4)
Cd(1)–O(5^{iii})	2.441(4)
Cd(1)–O(12^{vi})	2.305(4)
Cd(1)–O(12)	2.305(4)
Cd(1)–O(13^{vii})	2.249(5)
Cd(1)–O(13^{viii})	2.249(5)
Cd(2)–O(2^{ix})	2.300(4)
Cd(2)–O(7^{ii})	2.513(4)
Cd(2)–O(8^{iii})	2.479(5)
Cd(2)–O(10)	2.278(4)
Cd(2)–O(10^{iii})	2.248(5)
Cd(2)–O(11)	2.225(4)
Cd(3)–O(3^{ii})	2.610(6)
Cd(3)–O(4^{iii})	2.223(4)
Cd(3)–O(9^{iii})	2.448(4)
Cd(3)–O(11^{x})	2.266(4)
Cd(3)–O(12^{xi})	2.244(5)
Cd(3)–O(13^{xii})	2.312(5)

Note. See Note to Table III for symmetry codes.

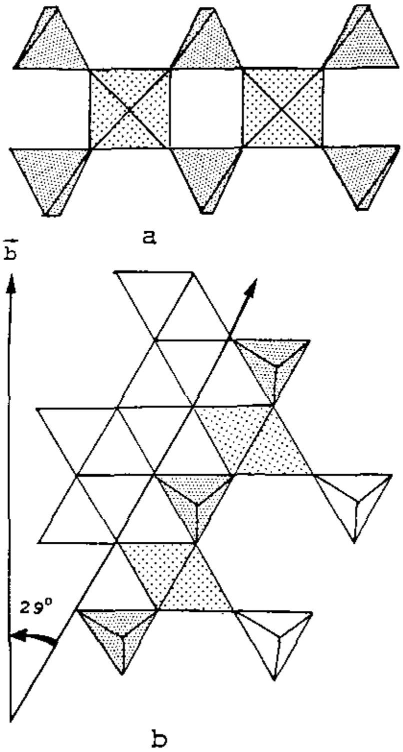

FIG. 3. (a) $V_2P_6O_{28}$ unit; (b) The orientation of $V_2P_6O_{28}$ units with respect to the **b** axis.

(Fig. 2a). The $[V_2P_6O_{24}]_\infty$ double chains can also be described by the stacking along **b** of $V_2P_6O_{28}$ units (Fig. 3). Such units are built up of two VO_6 octahedra linked through two PO_4 tetrahedra (Fig. 3a) with a geometry similar to that observed for the $[VP_3O_{15}]_\infty$ chains running along **b** (Fig. 2b); the mean plane of these structural units is approximately (011) so that two successive $V_2P_6O_{28}$ units are inclined by 29° with respect to **b** (Fig. 3b) and are connected in such a way that one PO_4 group of one unit be linked to one VO_6 octahedron of the next unit. Laterally in

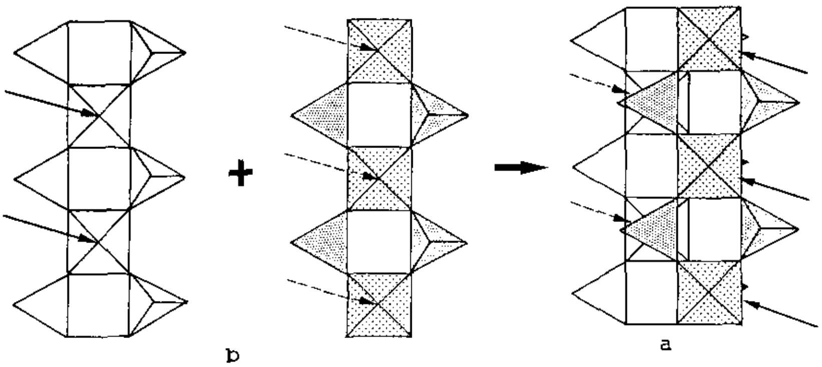

FIG. 2. The double $[V_2P_6O_{24}]_\infty$ chains (a) resulting from the assemblage of two $[VP_3O_{15}]_\infty$ single chains (b). Note that for clarity the PO_4 tetrahedra connected to the apical oxygen of the VO_6 octahedra above (full arrow) and below (discontinuous arrow).

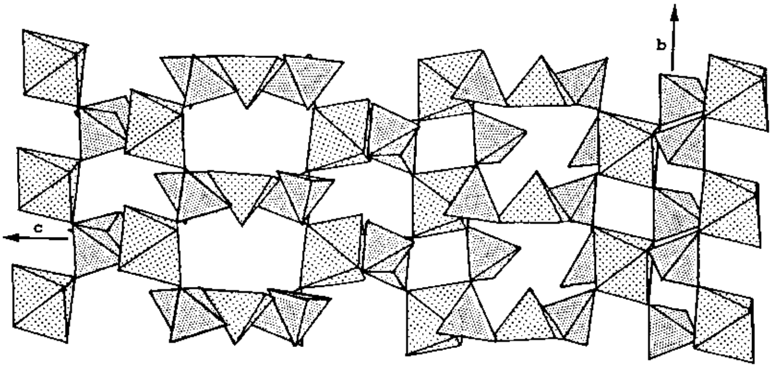

FIG. 4. Partial projection of the structure along **a** with $0 \leq x \leq \frac{1}{2}$.

the (010) plane, the $[V_2P_6O_{24}]_\infty$ double chains are connected to each other along **c**, through VO_5 pyramids (Fig. 1). In fact the VO_5 pyramids form columns running along **b** with the free apex alternately turned up and down from one column to the other along **c** as shown from the partial projection of the structure onto the (100) plane (Fig. 4). As a result, the structure consists of layers of $[V_3P_6O_{24}]_\infty$ double chains connected through single layers of VO_5 pyramids parallel to the (001) plane (Fig. 1 and 4).

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