

Fig. 1. Projection along the *b* axis of the average structure of incommensurate K₂MoO₄. The full circles show one specimen of a split-atom set, while the dashed circles show the other. K⁺ ions are hatched horizontally, Mo atoms vertically; the O atoms are shown by the open circles. The radii of the circles are chosen to show the 50% probability spheres.

are of course related by the *c* mirror plane of the average structure. This proves that a strong correlation must exist between the position of K(2) and the orientation of the MoO₄²⁻ ions above and below it (in the *z* direction) and *vice versa*. It should be pointed out here that moving from one orientation of the anion to the other can be performed by a rotation through only 60° around an axis roughly parallel to *b*.

The resulting overall isotropic temperature factor *B* is rather high. This can partly be attributed to the

relatively high temperature and the fact that two phase-transition temperatures are nearby. The high value of *B*, however, might well be an indication that the simple split-atom model is too crude. The latter is compatible only with a block-wave modulation. If the actual modulation waves for K(2) and O have a more continuous form, in addition to the split-atom positions intermediate positions would also be present, which in the split-atom model would lead to an increase of *B*.

It should be noted that the anionic tetrahedra have an orientation with respect to the *z* axis which quite closely resembles that of the low-temperature monoclinic phase.

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Reinvestigation of the Structure of Tetracadmium Sodium Orthovanadate, Cd₄Na(VO₄)₃

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Abstract. *M_r* = 817.407, orthorhombic, *Pnma*, *a* = 9.8189 (3), *b* = 7.0298 (2), *c* = 5.3610 (1) Å at 294 K, *V* = 370.04 (3) Å³, *Z* = 4(Cd_{4/3}Na_{1/3}VO₄), *D_m* = 4.71 (26), *D_x* = 4.890 g cm⁻³, λ(Mo *Kα*) = 0.71073 Å, μ = 99.387 cm⁻¹, *T* = 294 K. Final *R* = 0.0185 for 1289 unique reflections. Crystal growth from melt in oxygen atmosphere. Least-squares structural refinement and normal-probability-plot analyses confirm results of physical tests that structure is centrosymmetric, in contrast to previous report that space

group is *Pn2₁a*. One Cd atom per formula occupies an octahedron with ⟨Cd–O⟩ = 2.307 Å, one V atom a tetrahedron with ⟨V–O⟩ = 1.718 Å, remaining one-third Cd and one-third Na atom a distorted tetrahedron with ⟨Cd/Na–O⟩ = 2.374 Å. CdO₆ octahedra form infinite edge-sharing chains linked by corner sharing VO₄ and Cd/NaO₄ tetrahedra.

Introduction. The crystal structure of Cd₄Na(VO₄)₃ was reported by Ben Amara, Vlasse, Olazcuaga & Le

Flem (1979) to be polar, with no atomic coordinate displaced further than 0.21 Å from a centrosymmetric arrangement. Such a structure is expected to be ferroelectric with transition temperature not higher than 450 K (Abrahams, Kurtz & Jamieson, 1968). Recent studies of the physical properties of crystalline $\text{Cd}_4\text{Na}(\text{VO}_4)_3$ have shown (Abrahams, Nassau, Ravez, Simon & Olazcuaga, 1983) that it is without nonlinear optical properties or phase transition between room temperature and melting. Further refinement of the structure using the original 1241 measured reflections (Marsh, 1980) resulted in a significantly better fit by the centrosymmetric than by the polar atomic arrangement. The original set of reflections contains only positive or zero Miller indices. In view of the anomalous-scattering component in the structure factors as measured with Mo $K\alpha$ radiation it is probable that the assumed-polar y coordinates obtained by least-squares refinement with a data set that lacks Bijvoet or Friedel pairs would be subject to appreciable error: they would also be in error if the assumption were incorrect. Reinvestigation of the crystal structure of $\text{Cd}_4\text{Na}(\text{VO}_4)_3$ under improved experimental conditions is hence of considerable interest: the results of such a study are reported herein.

Experimental. Crystal growth as given by Abrahams *et al.* (1983), see also Ben Amara *et al.* (1979). Density from mass of ground spherical crystal with diameter 0.896 (17) mm; another ground sphere, radius 0.071 (2) mm, on CAD-4 diffractometer under control of PDP 11/40-8e minicomputer. Lattice parameters measured on Bond (1960) diffractometer, see Abrahams *et al.* (1983). Systematically absent reflections correspond to space groups $Pn2_1a$ or $Pnma$. Maximum transmission factor 39.45%, minimum 36.12%. Hemisphere of reciprocal space measured with graphite-mo. chromated Mo $K\alpha$ radiation, maximum $(\sin\theta)/\lambda = 1.03 \text{ \AA}^{-1}$ with $0 \leq h \leq 20$, $-14 \leq k \leq 14$, $-11 \leq l \leq 11$.

Each reflection measured with Poisson statistical precision of 2.0% or better. Six standard reflection (800, $\bar{8}00$, 080, $0\bar{8}0$, 006, $00\bar{6}$) intensities measured at 6h intervals. Small linear decline in intensity detected and corrected by equation $I_t = I_0 (1 - 0.000165t)$, with t in h. Average agreement factor for each intensity standard is 0.0151 before correction, 0.0066 afterward. Total of 7415 reflections measured (excluding standards), resulting in 1759 independent values for $Pnma$. Based on $F_m > 3\sigma F_m$ criterion (see below) remaining 1289 integrated intensity values corrected for Lorentz, polarization and absorption effects and used in following analyses. For the four octants measured, $R_{\text{int}} = 0.0184$. Paraelectric analog of atomic arrangement proposed by Ben Amara *et al.* (1979) taken as starting model for refinement by method of least squares.

Reciprocal of variance gave least-squares weight of each F_m , with variance in F_m^2 estimated by method of Abrahams, Bernstein & Keve (1971), i.e. $\sigma^2 F_m^2 =$

$V_1 + V_2 F_m^4 + \text{larger of } V_3 F_m^4 \text{ or } V_4$. Variance V_1 given by counting statistics, $V_2 = 16 \times 10^{-4}$, $V_3 = 6 \times 10^{-4}$ and V_4 is variance from differences among equivalent members before averaging. Refinement with isotropic temperature factors gave $R = 0.1358$, $wR = 0.2480$, $S = 7.629$; with anisotropic temperature factors, $R = 0.0302$, $wR = 0.0364$, $S = 1.131$. Hamilton (1965) ratio $\mathcal{R} = wR(\text{iso})/wR(\text{aniso}) = 6.813$ with $\mathcal{R}_{22,1249,0.005} = 1.0172$, hence isotropic model rejected at half-percent confidence level. Correction for isotropic extinction resulted in $R = 0.0185$, $wR = 0.0286$, $S = 0.889$: δR -plot (Abrahams & Keve, 1971) largely linear except for extrema, with slope of 0.725 and zero intercept indicative of minor remaining residual systematic error. Since $\mathcal{R}_{1,1248,0.005} = 1.0033$, hypothesis that F_m values not subject to extinction correction similarly rejected. Extinction factor $g = 4.3 (2) \times 10^{-3}$. Refinement of all models in $Pnma$ converged completely after several cycles, ratio of maximum least-squares shift to parameter-error less than 10^{-3} .

Possibility that atomic arrangement is noncentrosymmetric, as postulated by Ben Amara *et al.* (1979), investigated by refining their model with isotropic extinction correction included as additional variable (*cf.* Marsh, 1980). Refinement with 1289 independent reflections in $Pn2_1a$ failed to converge after many cycles, with oscillating parameter shifts as large as 1.2σ for position and 3.6σ for thermal parameters. Reaveraging structure factors in point group $m\bar{2}m$ gave 2393 independent $F(hkl)$ and $F(h\bar{k}l)$: refinement in $Pnma$ again rapidly converged whereas parameter shifts continued to oscillate ($>0.8\sigma$) in $Pn2_1a$. Failure to reach convergence in $Pn2_1a$ with either data set strongly indicates incorrect space group. Note, however, that $wR(Pnma)/wR(Pn2_1a) = 1.044$, 1.064 respectively for the two sets. Further model-dependent diffraction test for inversion centers made by refining in $Pn2_1a$ with all xyz coordinates replaced by $x\bar{y}z$ (reversed b axis), excluding strongest 25% data [$|F(hkl)|_{\text{max}} \leq 26.0$] for greatest sensitivity, resulted in parametric oscillations for both model senses and indistinguishable agreement factors.

The final diffraction test, not model dependent, compared Bijvoet pair $[F(hkl)]$ and $[F(h\bar{k}l)]$ magnitudes in δm normal probability plots (Abrahams & Keve, 1971). Random differences are expected in $Pnma$ leading to linear plot with unit slope and zero intercept. Systematic differences are expected in $Pn2_1a$ leading to significant nonlinearity with greater average slope. The experimental δm plot for all 1195 deviates was quite linear except for 23 extrema terms. The departures were small, the slope 0.85 with intercept of -0.29σ . Eliminating all Bijvoet pairs with $(\sin\theta)/\lambda < 0.80 \text{ \AA}^{-1}$ to enhance the test sensitivity, by increasing the relative anomalous-scattering component, the remaining 593 deviates form a linear array with only four departures in the extrema. Each is from a pair with magnitude less than 6% of maximum. The slope of 0.80 with intercept

of -0.22σ is strongly supportive of a normal distribution of deviates, *i.e.* as expected for the centrosymmetric space group. The δm plot has been deposited.

Effect of small departure from stoichiometric formula investigated by changing Cd/Na atomic scattering ratio in position 4(c) (with one-third occupancy by each atom) from unity to 1.05/0.90. Agreement indicators indistinguishable between stoichiometric and non-stoichiometric models, although all β_{ii} values for modified Cd/Na atom increased about 5σ as compared with the stoichiometric model.

All atomic scattering factors, including f' and f'' values, from *International Tables for X-ray Crystallography* (1974): linear interpolation used for composite Cd/Na atom of 19.667e, $F(000) = 491e$. *ORFLS4* and *ORFFE4* programs of Busing, Martin & Levy (1973) compiled and used on PDP 11/40 minicomputer. Final atomic coordinates in *Pnma* with e.s.d.'s are listed in Table 1 together with equivalent B values.*

Discussion. A principal conclusion drawn from the present study is that detection of inversion centers in materials with highly nonuniform atomic distributions may be ambiguous if diffraction methods only are used, and is most reliable if made by such physical tests as second harmonic generation [see, for example, Kurtz & Perry (1968)] or the piezoelectric development of electric charge [see, for example, Abrahams (1975)]. The tendency of many structural studies to depend exclusively on diffraction evidence has led to erroneous space-group assignments and hence incorrect structural determinations [see, for example, Marsh & Schomaker (1979, 1980), Schomaker & Marsh (1979) and Herstein & Marsh (1982) where several such errors have been detected and corrected].

A comparison of the atomic coordinates in Table 1 with those reported by Ben Amara *et al.* (1979) shows the greatest differences to be in the y coordinates, as expected for the change in space group from *Pn2₁a* to *Pnma*: that for O(1) of 0.232 Å is the largest, although differences as large as 0.087 Å are also found in the corresponding values of the O(1) z coordinate. The principal interatomic distances are listed in Table 2. Despite individual differences in interatomic metal–oxygen distances as large as 0.112 Å [for Cd/Na–O(1)], the average metal–oxygen distances in the two space groups do not differ by more than 0.004 Å (for $\langle\text{Cd–O}\rangle$).

* Lists of all 1759 structure factors and anisotropic thermal parameters in space group *Pnma* together with the δm normal probability plot have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38412 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic position coordinates and equivalent isotropic thermal parameters

	x	y	z	B_{eq}^*
Cd/Na	0.35336 (5)	$\frac{1}{4}$	0.99564 (6)	1.41 Å ²
Cd	0	0	0	1.07
V	0.18098 (3)	$\frac{1}{4}$	0.49293 (4)	0.74
O(1)	0.1175 (1)	0.0554 (2)	0.3507 (2)	1.35
O(2)	0.3583 (1)	$\frac{1}{4}$	0.4443 (4)	1.62
O(3)	0.1310 (1)	$\frac{1}{4}$	0.8038 (2)	1.56

* $\frac{1}{3}$ trace \bar{B} .

Table 2. Interatomic distances in Å for $\text{Cd}_4\text{Na}(\text{VO}_4)_3$

V–O(1)	1.686 (1) × 2	Cd–O(1)	2.240 (1) × 2
V–O(3)	1.737 (1)	Cd–O(2 ⁱⁱ)	2.261 (1) × 2
V–O(2)	1.761 (1)	Cd–O(3)	2.419 (1) × 2
Cd/Na–O(1 ⁱⁱⁱ)	2.301 (1) × 2	O(1)–O(3)	2.791 (2)
Cd/Na–O(2)	2.406 (2)	O(1)–O(1 ^{iv})	2.914 (2)
Cd/Na–O(3)	2.414 (2)	O(2)–O(3)	2.949 (2)
		O(2)–O(3 ⁱⁱ)	2.999 (2)
O(1)–O(1 ⁱ)	2.736 (2)	O(1)–O(2 ⁱⁱⁱ)	3.068 (2)
O(1)–O(2)	2.778 (2)		

Symmetry code: (i) $x, \frac{1}{2}-y, z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; (iv) $-x, -y, 1-z$.

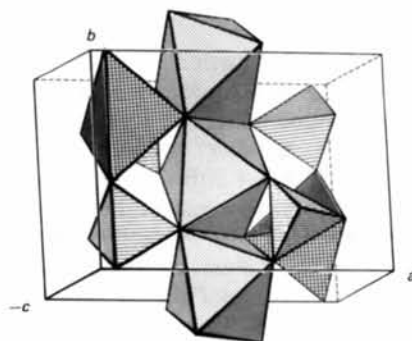


Fig. 1. Clinometric partial view of $\text{Cd}_4\text{Na}(\text{VO}_4)_3$ structure. CdO_6 octahedra (sharing edges) are shown with dotted faces, VO_4 tetrahedra (sharing corners) with hatched faces, and Cd/NaO_4 tetrahedra (sharing corners) with crosshatched faces, together with the unit-cell outline.

The structure of $\text{Cd}_4\text{Na}(\text{VO}_4)_3$ is characterized by edge-sharing CdO_6 octahedra that form infinite chains along [010] and that share corners with the VO_4 and Cd/NaO_4 tetrahedra. The VO_4 and Cd/NaO_4 tetrahedra also share corners, see Fig. 1. Each tetrahedron of O atoms occupied only by $\frac{1}{3}$ Cd and $\frac{1}{3}$ Na atom is highly distorted, with O–Cd/Na–O angles ranging from 137.8 to 88.2° for an average of 108.3°.

The 2.307 Å value of $\langle\text{Cd–O}\rangle$ from Table 2 is in good agreement with the distance of 2.32 Å predicted from Shannon's (1976) ionic radii, as is the experimental $\langle\text{V–O}\rangle$ distance of 1.718 Å with the predicted 1.725 Å. An average $\langle\text{V–O}\rangle$ distance of 1.721 (8) Å taken over 41 individually averaged values has been reported by Hawthorne & Faggiani (1979). By contrast, the 2.374 Å value of $\langle\text{Cd/Na–O}\rangle$ in the highly

distorted Cd/NaO₄ tetrahedron (see Table 2) considerably exceeds the predicted distance of 2.255 Å. The resulting 'loose' fit in this tetrahedron is reflected in the appreciably larger amplitudes of vibration of the Cd/Na composite atom as compared with the nearly equally massive V atom: the r.m.s. amplitudes of the former are 0.153, 0.141 and 0.122 Å along the crystal axes, the latter are 0.086, 0.115 and 0.088 Å.

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Structure Refinement of Hafnium Phosphide, Hf₃P

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Abstract. $M_r = 566.4$, Ti₃P-type tetragonal structure, $P4_2/n$, $a = 10.6654$ (4), $c = 5.2925$ (3) Å, $U = 602.02$ Å³, $Z = 8$, $D_x = 12.49$ Mg m⁻³, $\text{Mo } K\alpha$, $\lambda = 0.71069$ Å, $\mu = 109.3$ mm⁻¹, room temperature, $F(000) = 1848$. The crystal structure has been refined from visually estimated intensity data obtained from Weissenberg X-ray photographs [$R(F) = 0.072$ for 341 reflections]. The atomic coordination follows rules formulated earlier for representatives of the Fe₃P–Ti₃P–V₃S–Hf₃As family of structures.

Introduction. The atomic coordination in compounds crystallizing with the Fe₃P-, Ti₃P-, α -V₃S- and β -V₃S-type structures was thoroughly discussed by Rundqvist, Andersson & Pramatus (1979). Some interesting coordination trends were observed, suggesting an empirical rule for the coordination of metal neighbours about the non-metal atoms. Later, the structure of Hf₃As was determined by Willerström, Carlsson & Rundqvist (1980) and classified as a new member of the Fe₃P–Ti₃P–V₃S structure family. The atomic coordination in Hf₃As was consistent with the empirical coordination rule proposed, and more recent

structure refinements of Hf₃Sb and h -Ta₃Ge (Willerström & Rundqvist, 1981) and Tc₃P (Rühl, Jeitschko & Schwochau, 1982) also supported the validity of the rule. In connection with these studies it seemed worthwhile to refine the structure of Hf₃P. The occurrence of this compound was first reported by Ganglberger, Nowotny & Benesovsky (1966). They found that Hf₃P crystallizes with the Ti₃P-type structure, which was later confirmed by Lundström & Tansuriwongs (1968). In the present work, the Hf₃P structure was refined using a single crystal selected from material provided by Professor S. Rundqvist of the Inorganic Chemistry Department of Uppsala University, Sweden.

Experimental. An Hf₃P powder diffraction photograph obtained using a Guinier–Hägg-type focusing camera (Philips XDC-700), Cu $K\alpha_1$ radiation (Deslattes & Henins, 1973), silicon SRM-640 ($a = 5.43088$ Å) (Hubbard, Swanson & Mauer, 1975) as internal calibration standard; unit-cell dimensions refined by the least-squares method, the result being in satisfactory agreement with that reported by Lundström & Tan-