Auch das gemäss der Formulierung $H_9O_4^+.H_2O$ verbleibende Wassermolekül $H_2O(5)$ ist tetraedrisch von seinen nächsten Nachbarn umgeben. Fig. 1 illustriert, wie die $H_9O_4^+$-Ionen einerseits durch Vermittlung dieses 'fünften' Wassermoleküls (linke Bildhälfte) und andererseits über direkte Kontakte (rechte Bildhälfte) zu wasserstoffverbrückten Verbänden zusammentreten. Indem sich Cl(2) in die Mulde schiebt, die ihm das $H_9O_4^+$-Ion auf seiner 'Unterseite' bietet, resultieren deutlich gewellte Schichten, die entlang der Ebene (001) zwischen den $SnCl_6^{2-}$-Oktaedern verlaufen. Dass gerade Cl(2) den kürzesten Sn—Cl-Abstand besitzt, hängt mit der reduzierten Stärke der einzigen auf Cl(2) weisenden Wasserstoffbrücke zusammen [Kontakt $O(4)-Cl(2^{vi})$ in Tabelle 2].

Doch scheint ganz generell die Kation/Anion-Wechselwirkung über gerichtete Wasserstoffbrücken keine wichtige Rolle zu spielen, da letztere mit 3,24 bis 3,36 Å relativ lang sind. Vereinfacht dargestellt entspricht die Anordnung der $SnCl_6^{2-}$-Ionen in der Elementarzelle [mit dem Zinnatom in der Lage 2(a)] den Eckpunkten und der Mitte eines 'Würfels', der durch eingelagerte Hydratwasserschichten in der z-Richtung stark aufgetrieben ist (siehe Gitterkonstanten). Nirgends wird die Summe der van der Waals-Radien zweier Chloratome (ca 3,60 Å) unterschritten, sofern es um den Kontakt benachbarter $SnCl_6^{2-}$-Ionen geht. Der weitaus kürzeste Abstand beträgt 3,878 (2) Å zwischen Cl(3) und $Cl(3^{viii})$.

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Calcium Sodium Vanadate at 300 K: Structure Refinement by Powder Neutron Diffraction

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Abstract. $NaCaVO_4$, orthorhombic, *Cmcm*, $a = 5.8726$ (2), $b = 9.3028$ (3), $c = 7.1562$ (3) Å, $Z = 4$. The structure has been refined by profile analysis of powder neutron diffraction data at room temperature ($R_{nuclear} = 1.67$, $R_{profile} = 4.62$, $R_{weight} = 5.38$ for 58 reflections). It is of the $Na_2CrO_4(II)$ type and closely related to the structure of $CrVO_4$.

Introduction. Research in the field of halides with β-K_2SO_4-like structures (Vermin, Verschoor & IJdo, 1976; Zandbergen, Verschoor & IJdo, 1979) led to the problem of ordering in the related $Na_2CrO_4(II)$ (<694 K) structure (Miller, 1936; Niggli, 1954; Nimmo, 1981). $NaCaVO_4$ seems a good example. Klement & Kresse (1961) report a low-temperature phase with

β-K$_2$SO$_4$ structure but Le Flem & Olazcuaga (1968) concluded from powder X-ray diffraction data that this compound has the Na$_2$CrO$_4$(II) structure. Paques-Ledent (1975) showed from vibrational analysis that the monovalent cations in a number of compounds with the Na$_2$CrO$_4$(II) structure are located on sites with C_{2v} symmetry instead of sites with C_{2h} symmetry as found by Le Flem & Olazcuaga (1968).

NaCaVO$_4$ was prepared by heating an appropriate mixture of sodium oxalate, CaCO$_3$ and V$_2$O$_5$, for 0·5 h at 600 K, for 2 d at 973 K and annealing for one week at 773 K. The X-ray powder-diffraction pattern was obtained with a Philips PW 1050 diffractometer. The symmetry and the systematic absences indicated space group $Cmcm$, $Cmc2_1$ or $C2cm$, in agreement with the work of Le Flem & Olazcuaga (1968). No single crystals were available, so we decided to use the neutron powder-profile-refinement technique (Rietveld, 1969; modified by Hewat, 1973) in order to obtain precise structural information. The neutron data were collected at 300 K on the powder diffractometer at the Petten High Flux reactor as described by van Laar, Rietveld & IJdo (1971). A wavelength of 2·5921 (3) Å was used. Data in the range $5·4 < 2\theta < 151·2°$ were used, in steps of 0·144°. Absorption and extinction effects were small and no corrections were made.

The structure of Le Flem & Olazcuaga (1968) was used as the trial model, but this model did not refine to reasonable R values. By changing the Na and Ca positions we obtained a better trial model, space group $Cmcm$, with the atoms as follows: Na in 4(c) (0,y,$\frac{1}{4}$); Ca in 4(b) (0,$\frac{1}{2}$,0); V in 4(c); O(1) in 8(g) (x,y,$\frac{1}{4}$); and O(2) in 8(f) (0,y,z). The parameters in the refinement were: a scale factor, three half-width parameters defining the Gaussian line shape, the counter zero error, the unit-cell parameters, the atomic positional parameters, both isotropic and anisotropic temperature factors and an asymmetry parameter below $2\theta = 38°$. The coherent scattering lengths assumed were: Ca 4·7, Na 3·6, V −0·5 and O 5·8 fm (Bacon, 1972). The Rietveld program minimizes the function $\chi^2 = \sum_i w_i \times [y_i(\text{obs.}) - (1/c)y_i(\text{calc.})]^2$, where y(obs.) and y(calc.) are the observed and calculated profile data points, w is the statistical weight allotted to each data point and c is the scale factor. The following R factors were calculated:

$$R_{\text{nuclear}} = 100 \sum |I(\text{obs.}) - (1/c)I(\text{calc.})|/\sum I(\text{obs.})$$
$$= 1·67;$$

$$R_{\text{profile}} = 100 \sum |y(\text{obs.}) - (1/c)y(\text{calc.})|/\sum y(\text{obs.})$$
$$= 4·62;$$

$$R_{\text{weight}} = 100 \left[\sum w|y(\text{obs.}) - (1/c)y(\text{calc.})|^2 / \right.$$
$$\left. \sum w|y(\text{obs.})|^2\right]^{1/2} = 5·38;$$

where I(obs.) and I(calc.) are the observed and calculated integrated intensities of each reflection. Considerably better agreement between the observed

Table 1. *Lattice parameters* (Å)

	a	b	c	Reference
NaCaVO$_4$	5·860 (7)	9·255 (13)	7·124 (15)	Le Flem & Olazcuaga (1968)
NaCaVO$_4$*	5·8726 (2)	9·3028 (3)	7·1562 (3)	This work
Na$_2$CrO$_4$(II)	5·862 (2)	9·251 (5)	7·145 (3)	Nimmo (1981)
CrVO$_4$	5·579	8·224	5·989	Brandt (1943)
InVO$_4$	5·765 (4)	8·542 (5)	6·592 (4)	Touboul & Tolédano (1980)

* E.s.d.'s in the lattice parameters do not include errors in the neutron wavelength.

Table 2. *Fractional atomic coordinates and isotropic thermal parameters* (Å^2)

	x	y	z	B/B_{eq}
Na	0	0·1808 (4)	0·25	1·6 (3)†
Ca	0	0·5	0	0·7 (2)†
V	0	0·8621 (34)	0·25	2·5 (8)
O(1)	0·2599 (3)	0·4623 (2)	0·25	0·8 (1)†
O(2)	0	0·2533 (2)	0·5597 (2)	1·1 (1)†

† These are B_{eq} values; $B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

and calculated intensities of certain reflections was found when anisotropic temperature factors were included in the refinement. Lattice parameters are given in Table 1, atomic parameters in Table 2.*

Discussion. The present refinement confirms the conclusions of Le Flem & Olazcuaga (1968) and Paques-Ledent (1975) that the structure is of the Na$_2$CrO$_4$(II) type and with respect to the cation positions is in agreement with the vibrational analysis of Paques-Ledent.

The structural details of NaCaVO$_4$ (300 K) and Na$_2$CrO$_4$(II) (Nimmo, 1981) are very similar, as can be seen from Tables 2 and 3(a). This is consistent with the ionic radii for six coordination for Na$^+$ and Ca^{2+}, 1·02 and 1·00 Å respectively, and the ionic radii for V^{5+} and Cr^{6+} for four coordination, 0·355 and 0·30 Å respectively (Shannon & Prewitt, 1969). The structure can be described as built up from CaO$_6$ octahedra sharing parallel edges giving slightly staggered chains along [001]. The chains are arranged in parallel planes normal to [010] and are linked together by the VO$_4$ tetrahedra. In addition, Na has a very deformed tetrahedral coordination (Table 4). There is some anisotropy in the thermal ellipsoid for Na, and somewhat smaller anisotropy for O(2). These observations are compatible with the assumption of rigid CaO$_6$ octahedra and VO$_4$ tetrahedra.

Table 3. *Fractional atomic coordinates from the literature*

	x	y	z
(a) $Na_2CrO_4(II)$ (Nimmo, 1981)			
Na(1)	0	0·1882 (1)	0·25
Na(2)	0	0·5	0
Cr	0	0·85361 (9)	0·25
O(1)	0·27001 (7)	0·45757 (5)	0·25
O(2)	0	0·24929 (5)	0·56402 (7)
(b) $InVO_4$ (Touboul & Tolédano, 1980)*			
In	0	0·5	0
V	0	0·86258 (6)	0·25
O(1)	0·2407 (3)	0·4787 (2)	0·25
O(2)	0	0·2497 (2)	0·5434 (3)

* Transformed to another origin.

Table 4. *Interatomic distances (Å) and angles (°)*

Na—O(1)	2·474 (4)	O(1)—V—O(1)	113·1 (18)
Na—O(2)	2·317 (2)	O(1)—V—O(2)	110·0 (1)
		O(2)—V—O(2)	103·5 (17)
Ca—O(1)	2·378 (1)		
Ca—O(2)	2·334 (2)	O(1)—Ca—O(1)	100·1 (1)
		O(1)—Ca—O(2)	90·4 (1)
V—O(1)	1·690 (18)		
V—O(2)	1·734 (20)	O(1)—Na—O(1)	69·5 (1)
		O(1)—Na—O(2)	103·8 (1)
		O(2)—Na—O(2)	146·2 (2)

The $CrVO_4$ structure (Brandt, 1943), common among the compounds ABO_4 with B = S, Se, Cr, P, V, and A an intermediate-size cation, has the same space group and the same framework as the compounds mentioned above – only the low-coordinated Na is omitted. This is illustrated by the atomic parameters of $InVO_4$ (Touboul & Tolédano, 1980) (Table 3b).

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