the presence of the heavy Hg atoms. The authors are convinced, however, that the distortion is at least to some extent real and due to the irregular coordination of the O atoms by one Ge and three Hg atoms. This effect, although less, is also visible in the ionic compounds Na_2SO_4 and Na_2SeO_4 (Mehrotra *et al.*, 1978). In addition, the differences between the observed and geometrically derived Hg—O distances (Table 2) are a consequence of the distortion of the $[GeO_4]$ tetrahedron.

Finally, it should be stated that the present results justify the geometrical method applied by Mehrotra *et al.* (1978) for rather detailed structure predictions of compounds with thenardite-type structures.

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References

BUSING, W. R. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 180–182.

GRDENIĆ, D. (1970). *Handbook of Geochemistry*, Section 80-A, edited by K. H. WEDEPOHL. Berlin: Springer.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

MEHROTRA, B. N., HAHN, TH., EYSEL, W., RÖPKE, H. & ILLGUTH, A. (1978). *Neues Jahrb. Mineral. Monatsh.* pp. 408–421.

RÖPKE, H. & EYSEL, W. (1978). *Neues Jahrb. Mineral. Monatsh.* pp. 1–9.

SHELDRICK, G. M. (1976). *SHELX* 76. A program for crystal structure determination. Univ. of Cambridge, England.

STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*. New York: Macmillan.

WITTMANN, A. (1969). *Handbook of Geochemistry*, Section 32-A, edited by K. H. WEDEPOHL. Berlin: Springer.

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Sodium Chromate (II) at 296 K (Neutron)

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Abstract. Na_2CrO_4 (II), orthorhombic, *Cmcm*, $a = 5{\cdot}862\ (2)$, $b = 9{\cdot}251\ (5)$, $c = 7{\cdot}145\ (3)$ Å at 296 K, $Z = 4$, $D_c = 2{\cdot}78$ Mg m^{-3}, λ (neutron) = 0·9884 Å; $R = 0{\cdot}03$; single crystal; source of material: BDH. The structure proposed by Niggli [*Acta Cryst.* (1954), **7**, 776] is confirmed.

Introduction. The present structure determination was made in the course of an investigation of thermal phase transitions in Na_2CrO_4 and Na_2SO_4 at atmospheric pressure. Whereas Na_2SO_4 undergoes a series of transitions, Na_2CrO_4 is only known to have one transition at 694 ± 4 K (Pistorius, 1965). However, Na_2CrO_4 (II) (<694 K) and Na_2SO_4 (III) (458–514 K and metastably at room temperature) are thought to be isostructural, as indeed are Na_2CrO_4 (I) (>694 K) and Na_2SO_4 (I) (>514 K) (Fischmeister, 1954; Eysel, 1973). Various orthorhombic and tetragonal space groups have been suggested for Na_2CrO_4 (II) and/or Na_2SO_4 (III):

Miller (1936):	Na_2CrO_4 (II), *Pbnn*, $Z = 4$
Frevel (1940):	Na_2SO_4 (III), *Pbnn*, $Z = 4$
Dasgupta (1953, 1954):	Na_2SO_4 (III), $I\bar{4}2d$, $Z = 16$
Niggli (1954):	Na_2CrO_4 (II), *Cmcm*, $Z = 4$
Fischmeister (1954):	Na_2SO_4 (III) and Na_2CrO_4 (II), *Cmcm*, $Z = 4$.

In view of this controversy and the fact that no accurate structure determination of either Na_2CrO_4 (II) or Na_2SO_4 (III) has been made, it was decided to investigate Na_2CrO_4 (II) with single-crystal neutron diffractometer data.

A crystal (42 mm^3) was grown by evaporation of an aqueous solution at 349 K. Above 343 K Na_2CrO_4 (II) crystallizes and there is no water of crystallization (Hartford, 1949). Data were collected on the Australian Institute of Nuclear Science and Engineering (AINSE) four-circle computer-controlled diffractometer located on the 2 TAN A facility at HIFAR, the research reactor of the Australian Atomic Energy Commission (AAEC) at Lucas Heights. ω–2θ scans were made for all Bragg intensity measurements, with a step size of 0·01° in 2θ. Background measurements were made for each Bragg reflexion. A standard reflexion was measured after every 25 reflexions to check stability of the specimen and the experimental system. Two equivalent sets of Bragg intensities ($2\theta <$ 75°) were collected. The neutron wavelength was 0·9884 Å.

From 443 relatively strong centered reflexions, the cell was determined by least squares to be orthorhombic. The conditions limiting possible reflexions were hkl: $h + k = 2n$, $h0l$: $l = 2n$, and the space group was deduced as *Cmcm*.

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The intensities were corrected for absorption by the crystal sample with a computer program which evaluates the correction for each reflexion from the linear absorption coefficient [0·0312 (2) mm^{-1}] and the shape and measured external dimensions of the sample. Also computed for each reflexion was the mean neutron-beam pathlength (appropriately corrected for absorption) in the crystal, for use in isotropic-extinction correction. An absorption-correction error term was calculated for each reflexion and incorporated into the e.s.d. of the reflexion intensity.

The consistency of the data was checked by comparing, for each set of equivalent reflexions, the variance from the mean intensity with the variance deduced from Poisson statistics. A standard F test at the 1% level was applied. One set of equivalents failed this test and was rejected from the data. Equivalent reflexions were then combined and the e.s.d. taken as the e.s.d. from the mean intensity, unless this e.s.d. was less than the e.s.d. from Poisson statistics, in which case the latter e.s.d. was assigned. The Lorentz correction was applied giving $|F_o|^2$ and $\sigma(|F_o|^2)$ for each combined reflexion. Systematically absent reflexions were removed from the data set leaving 298 reflexions, 69% of which had e.s.d.'s based on Poisson statistics.

The structure proposed by Niggli (1954) on the basis of Miller's (1936) results was used as an initial structure (Table 1) for least-squares refinement. The program used was *LINUS*, a version of *ORFLS* modified to allow extinction-correction refinement (Coppens & Hamilton, 1970). The scattering lengths were Na 3·51, Cr 3·52 and O 5·75 fm (*International Tables for X-ray Crystallography*, 1974). All refinements were based on comparison of $|F|^2$ values and all reflexions which were allowed by the space group and which passed the statistical test were retained in the data set. The weighting factors were $w = [\sigma(|F_o|^2)]^{-2}$. The discrepancy indices were $R_w = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(|F_o|^2)^2]^{1/2}$ and $R = \sum||F_o|^2 - |F_c|^2|/\sum|F_o|^2$.

A scale factor, the positional and anisotropic thermal parameters and an isotropic extinction parameter were varied. Refinement* converged to yield the parameters given in Table 1, with $R_w = R = 0·03$. Interatomic distances and angles are given in Table 2. The structure is illustrated in Fig. 1.

Table 2. *Interatomic distances* (Å) *and angles* (°) *for* Na_2CrO_4 (II)

The atoms are labelled as in Fig. 1.

$Na(1^{ii})\cdots O(2^{ii})$	2·3136 (9)	$Cr-O(2^{iii})$	1·6347 (8)
$Na(1^{ii})\cdots O(1^{i})$	2·524 (1)	$Cr-O(1^{iii})$	1·6560 (8)
$Na(1^{ii})\cdots O(1^{iii})$	2·952 (1)		
$Na(1^{ii})\cdots O(2^{iii})$	3·270 (1)	$O(2^{iii})-Cr-O(2^{v})$	108·77 (5)
$Na(2)\cdots O(2^{iii})$	2·3640 (7)	$O(1^{iii})-Cr-O(1^{iv})$	109·00 (5)
$Na(2)\cdots O(1^{i})$	2·4187 (8)	$O(1^{iii})-Cr-O(2^{iii})$	109·77 (1)
$Na(2)\cdots O(2^{iv})$	3·757 (1)		
$Na(2)\cdots O(2^{v})$	3·884 (1)		

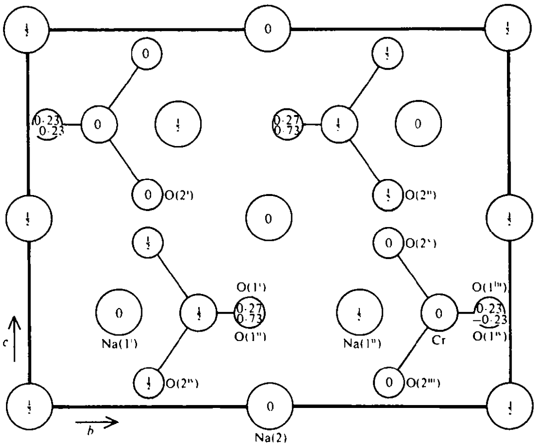

Fig. 1. Projection along **a** of the orthorhombic structure of Na_2CrO_4 (II).

Table 1. Na_2CrO_4 (II): *positional parameters and equivalent isotropic thermal parameters as determined in the present work, compared with those proposed by Niggli* (1954)

In the present work the extinction coefficient $g = 0·51$ (1).

	Na(1)	Na(2)	Cr	O(1)	O(2)
Present work					
x	0	0	0	0·27001 (7)	0
y	0·1882 (1)	$\frac{1}{2}$	0·85361 (9)	0·45757 (5)	0·24929 (5)
z	$\frac{1}{4}$	0	$\frac{1}{4}$	$\frac{1}{4}$	0·56402 (7)
U_{eq} (Å^2)*	0·0343 (3)	0·0197 (2)	0·0114 (2)	0·0238 (1)	0·0269 (1)
Niggli (1954)					
x	0	0	0	0·28	0
y	0·20	$\frac{1}{2}$	0·85	0·45	0·25
z	$\frac{1}{4}$	0	$\frac{1}{4}$	$\frac{1}{4}$	0·57

* $U_{eq} = 1/6\pi^2 \sum_i \sum_j \beta_{ij}\, \mathbf{a}_i . \mathbf{a}_j$.

Discussion. Miller (1936) proposed a structure for Na_2CrO_4 (II) on the basis of visually estimated X-ray single-crystal oscillation intensities. Niggli (1954) reconsidered Miller's work and proposed an alternative structure in a different space group, *Cmcm*, but with the same orthorhombic cell. The present analysis confirms Niggli's proposal and provides accurate positional and thermal parameters.

Prior to Fischmeister (1954), the various crystallographic studies of Na_2SO_4 (III) and Na_2CrO_4 (II) dealt

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35733 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

exclusively with only one of the compounds without mention of the other (Miller, 1936; Frevel, 1940; Dasgupta, 1953, 1954; Niggli, 1954). Although Fischmeister asserted, possibly quite correctly, that the two compounds are isomorphous, he did not present supporting evidence, and his claim that Frevel (1940) has shown this isomorphism is not strictly accurate. Frevel proposed a structure for Na_2SO_4 (III) which, as it happens, was isomorphous with the Miller (1936) proposal for Na_2CrO_4 (II) which was rejected by Niggli (1954) and by Fischmeister (1954) himself. Following Fischmeister it appears to have been generally accepted that Na_2SO_4 (III) and Na_2CrO_4 (II) are isomorphous (Wyckoff, 1964; Pistorius, 1965; Eysel, 1973), but evidence for this has not been published.

It would be useful to make a rigorous structure determination of Na_2SO_4 (III) and to check for isomorphism with Na_2CrO_4 (II). However, it may not be possible to obtain Na_2SO_4 (III) single-crystal data. Attempts to heat Na_2SO_4 (V) crystals for neutron diffraction through to phase III have resulted in destruction of the crystal. Probably it will be necessary to use a powder specimen.

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References

Coppens, P. & Hamilton, W. C. (1970). *Acta Cryst.* A**26**, 71–83.

Dasgupta, D. R. (1953). *J. Chem. Phys.* **21**, 2097.

Dasgupta, D. R. (1954). *Acta Cryst.* **7**, 275–276.

Eysel, W. (1973). *Am. Mineral.* **58**, 736–747.

Fischmeister, H. (1954). *Acta Cryst.* **7**, 776–777.

Frevel, L. K. (1940). *J. Chem. Phys.* **8**, 290.

Hartford, W. H. (1949). *Ind. Eng. Chem.* **41**, 1993–1997.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Miller, J. J. (1936). *Z. Kristallogr.* **94**, 131–136.

Niggli, A. (1954). *Acta Cryst.* **7**, 776.

Pistorius, C. W. F. T. (1965). *J. Chem. Phys.* **43**, 2895–2898.

Wyckoff, R. W. G. (1964). *Crystal Structures*, Vol. II, pp. 110–111. New York: Interscience.

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New Study of the Structure of $MnAl_6$

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Abstract. $MnAl_6$, orthorhombic, *Cmcm*, $a = 7{\cdot}5551\ (4)$, $b = 6{\cdot}4994\ (3)$, $c = 8{\cdot}8724\ (17)$ Å, $Z = 4$, $V = 435{\cdot}67$ Å^3, $D_c = 3{\cdot}31$ Mg m^{-3}, $R(F) = 0{\cdot}0209$ for 530 reflections refined. The structural parameters agree within experimental error with those of Nicol [*Acta Cryst.* (1953). **6**, 285–293] except for the Al(2)–Al(3) bond length which was erroneously reported previously. The structure consists of approximately planar layers of Mn and Al atoms with a spacing of about 2·6 Å. Short Mn–Al and Al–Al bond lengths are comparable to those observed in Mn_4Al_{11}.

Introduction. The structure of $MnAl_6$ has been determined by Nicol (1953) using two-dimensional Fourier methods, and investigated again by Forsyth (1959), measuring only a limited number of reflections in the [001] zone. In preparation for a possible electron density study the structure was redetermined from three-dimensional counter data.

Small single crystals were supplied by Dr J. B. Forsyth and Dr A. Harding. A nearly cubic crystal of approximate dimensions 0·09 × 0·10 × 0·10 mm was chosen for data collection at room temperature, using monochromatized Mo $K\bar{\alpha}$ radiation ($\lambda = 0{\cdot}71069$ Å). Cell dimensions were calculated by a least-squares refinement of the setting angles of 25 reflections with $\theta > 22°$. A quadrant of reflections ($\sin\theta/\lambda < 0{\cdot}8$ Å^{-1}) was measured with a θ–2θ scan. Each reflection was measured at three different values of the azimuthal angle ψ (0, 1·5, 3·0°). No large discrepancies were found between measurements at different ψ values.

3705 reflections were averaged after Lorentz–polarization and absorption corrections ($\mu = 3{\cdot}913$

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