*Acta Cryst.* (1972). B**28**, 1352

# The Crystal Structure of β-$Na_2Cr_2O_7$

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(*Received* 17 *August* 1971)

β-$Na_2Cr_2O_7$ is triclinic, $P\bar{1}$, with $a$ = 7·702 (10), $b$ = 10·380 (10), $c$ = 9·402 (10) Å, $\alpha$ = 89·41 (10), $\beta$ = 109·57 (10), $\gamma$ = 114·26 (10)°, $Z$ = 4, $D_m$ = 2·73 (1) g.cm$^{-3}$. The structure, which has been determined by X-ray diffraction (photographic methods) and refined to give $R_2$ = 0·09, is a superstructure derivative of the high-temperature α-$Na_2Cr_2O_7$, which in turn is probably isostructural with $Ag_2Cr_2O_7$. Part of the structure also shows strong similarities to the thortveitite-like α-$Mg_2P_2O_7$. The two dichromate ions are normal with Cr–O (bridging) = 1·78 (1) Å, Cr–O (terminal) = 1·61 (1) Å, O–Cr–O = 109 (1)° and Cr–O–Cr = 131 (1)°.

## Introduction

Most of the crystals with stoichiometry $X_2Y_2O_7$, where Y, the more electronegative metal, has an ionic radius of less than 0·4, have structures related either to that of thortveitite, if X has an ionic radius less than 1·0 Å, or to one of the 'dichromate' structures, if the ionic radius is larger (Brown & Calvo, 1970). Recently, the structures of several crystals in the border region between these two classes have been studied (Felsche, 1970). The structure of one of these, anhydrous $Na_2Cr_2O_7$, is reported here.

Vesnin & Khripin (1966) have examined the phase transitions in $Na_2Cr_2O_7$ using DTA and refractive index, and have identified four phases between room temperature and the melting point with transitions at 240, 290, and 330 °C. The phases above and below the 240 °C transition we designate (following Samuseva, Polataev & Plyushchev, 1962) α and β, respectively.

## Preliminary survey

Crystals of β-$Na_2Cr_2O_7$ are triclinic, space group $P\bar{1}$, with four molecules per unit cell and with the lattice parameters, at room temperature, given in Table 1. The density of 2·73 g.cm$^{-3}$ was measured by flotation in an equidensity mixture of $CH_3I$ and $CHBr_3$. From single-crystal photographs it is apparent that reflexions with $k+l$ odd are in general considerably weaker than those with $k+l$ even and on heating the odd reflexions become even weaker, disappearing at above 240 °C. The $k+l$ even reflexions change only slightly during this process. Above 240 °C, the crystal (now α-$Na_2Cr_2O_7$) is still single with a very similar unit cell to β-$Na_2Cr_2O_7$, but with space group $A\bar{1}$. The similarity between the crystal lattices of α-$Na_2Cr_2O_7$ and $Ag_2Cr_2O_7$ (Hazell, 1969) leads one to expect that they are probably isostructural. If this is so, then α-$Na_2Cr_2O_7$ has the 'dichromate' structure designated by Brown & Calvo (1970) as type I, and it is interesting to see how this becomes modified at lower temperatures.

## Experimental Procedure

Crystals of $Na_2Cr_2O_7$ were prepared by melting $Na_2Cr_2O_7.2H_2O$ (Shawinigan, reagent grade 99·5%) and cooling to room temperature. The X-ray powder pattern agreed with that given in the *ASTM Powder Data File* (1–0692). The infrared spectrum was similar to the spectra of other anhydrous dichromates and showed no bands that could be attributed to water of crystallization.

The crystals, which are hygroscopic, were sealed in thin-walled quartz capillary tubes in a nitrogen atmosphere. The cell constants given in Table 1 were obtained by least-squares refinement, using the angular settings of 15 reflexions measured on a Syntex automatic diffractometer with Mo $K\alpha$ radiation ($\lambda_{K\alpha}$ = 0·71069 Å).

Intensities were measured on a Joyce–Loebl microdensitometer from integrated precession photographs taken with Mo $K\alpha$ radiation. Two crystals were used. The first, 0·23 × 0·32 × 0·14 mm, was mounted with the reciprocal 011 axis parallel to the goniometer axis and was used to record layers with $h$ = 0, 1, and 2 and layers with $k = l-h-n$ where $n$ = 0, 1, 2, and 3. The second crystal, 0·31 × 0·35 × 0·22 mm, was mounted with the reciprocal [111] axis along the goniometer axis and was used to record the $h\bar{h}l$; $h,k,k$; $h,k,-(k+2h)$ layers. The intensities were corrected for Lorentz and polarization effects, but not for absorption which is effectively uniform over each precession photograph with the crystal settings used.

In all, 1181 independent observed reflexions were measured, but a further 557 unobserved reflexions were included in the refinement. Statistical tests on the $h\bar{h}l$ and $0kl$ intensities indicated centrosymmetric projections, and the space group $P\bar{1}$ was assumed. There were, of course, no systematic absences, but reflexions with $k+l$ odd were generally much weaker than those with $k+l$ even, and the fact that they disappeared at 240 °C suggested that the room-temperature structure is derived from the higher symmetry, high-temperature structure (space group $A\bar{1}$) by the loss of the $A$ centring.

The Patterson projections calculated with the $k+l$

even intensities gave positions for the chromium atoms that corresponded to the higher symmetry. The oxygen and sodium atoms were found from difference electron density projections and consideration of the likely conformation of the $Cr_2O_7$ groups. The structure was initially refined in the space group $A\bar{1}$ using all $k+l$ even reflexions to give $R_2\{=[\sum w(F_o-F_c)^2/\sum wF_o^2]^{1/2}\}=0{\cdot}10$. Deviations of the chromium atoms from these mean positions were postulated in the $P\bar{1}$ space group, using the Patterson function calculated with only the $k+l$ odd reflexions. In going from space group $A\bar{1}$ to $P\bar{1}$, one of the two sets of centres of symmetry is lost. Since it is not obvious which set is lost, two possible models for the superstructure must be tested. In addition, since the two $CrO_4$ tetrahedra in a single $Cr_2O_7$ group can be shifted from their $A\bar{1}$ positions in the same or in opposite directions, a total of four possible models have to be tested. Only one refined satisfactorily, giving $R_2=0{\cdot}12$ for the $k+l$ odd reflexions.

At this stage, anisotropic temperature factors were introduced, and the structure was refined further by full-matrix least-squares methods. Reflexions were weighted by the function $(3{\cdot}649-0{\cdot}083F_o+0{\cdot}0034F_o^2)^{-1}$ (Cruickshank, 1965), except that zero weight was given to unobserved reflexions for which $|F_c|<|F_{\min}|$ and to other reflexions for which measurements of $F_o$ were judged to be particularly unreliable. Scattering factors for $Na^+$, $Cr^{2+}$, and $O^-$ (O for the bridging oxygen atoms) were taken from *International Tables for X-ray Crystallography* (1962), and the final weighted agree-

Table 1. *Crystal data for* $Na_2Cr_2O_7$ *and related compounds*

Standard errors in the last figures quoted are given in parentheses.

| Compound | $\beta$-$Na_2Cr_2O_7$ | $\alpha$-$Na_2Cr_2O_7$ | $Ag_2Cr_2O_7$* | $\alpha$-$Mg_2P_2O_7$† |
|---|---|---|---|---|
| Space group | $P\bar{1}$ | $A\bar{1}$ | $A\bar{1}$ | $P2_1/c$ |
| $a$(Å) | 7·702 (10) | 7·82 (3) | 6·52 | 6·981 (5) |
| $b$ | 10·380 (10) | 10·36 (3) | 10·01 | 8·295 (5) |
| $c$ | 9·402 (10) | 9·54 (3) | 9·89 | 9·072 (5) |
| $\alpha$(°) | 89·41 (10) | 89·5 (3) | 88·78 | 90 |
| $\beta$ | 109·57 (10) | 110·1 (3) | 109·42 | 113·0(1) |
| $\gamma$ | 114·26 (10) | 113·4 (3) | 100·42 | 90 |
| $V$(Å$^3$) | 639 | 659 | – | – |
| $Z$ | 4 | 4 | – | – |
| $D_m$ | 2·73 (1) g.cm$^{-3}$ | – | – | – |
| $D_x$ | 2·72 g.cm$^{-3}$ | – | – | – |
| $\mu$(Mo $K\alpha$) | 3·67 mm$^{-1}$ | – | | – |

* From Hazell (1969), transformed from $P\bar{1}$.

† From Calvo (1967), transformed from $B2_1/c$

Table 2. *Atomic positional and thermal coordinates*

Standard errors in the last figures quoted, as given by the final round of least-squares analysis, are shown in parentheses. The temperature factors were calculated using the expression:

$$\exp[-2\pi^2 10^{-4}(u_{11}h^2a^{*2}+u_{22}k^2b^{*2}+u_{33}l^2c^{*2}+2u_{12}hka^*b^*+2u_{13}hla^*c^*+2u_{23}klb^*c^*)].$$

| | $x$ | $y$ | $z$ | $u_{11}$ | $u_{22}$ | $u_{33}$ | $u_{12}$ | $u_{13}$ | $u_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cr(1) | −0·1939 (3) | 0·0119 (2) | 0·1509 (2) | 215 (15) | 229 (9) | 225 (9) | 96 (11) | 51 (9) | 9 (7) |
| Cr(2) | 0·2488 (3) | 0·0803 (2) | 0·4091 (2) | 252 (15) | 249 (9) | 195 (8) | 135 (11) | 71 (9) | 30 (7) |
| O(11) | −0·3849 (15) | 0·0258 (11) | 0·1747 (9) | 195 (62) | 459 (53) | 309 (41) | 167 (54) | 124 (40) | 98 (37) |
| O(12) | −0·2380 (16) | −0·1542 (10) | 0·1238 (10) | 342 (72) | 299 (43) | 345 (43) | 141 (51) | 126 (43) | −9 (35) |
| O(13) | −0·1368 (16) | 0·0913 (10) | 0·0150 (9) | 273 (67) | 328 (45) | 335 (43) | 41 (51) | 128 (44) | 102 (35) |
| O(21) | 0·3598 (16) | 0·1634 (10) | 0·5812 (9) | 335 (71) | 341 (47) | 283 (39) | 161 (52) | 50 (42) | 29 (35) |
| O(22) | 0·3937 (18) | 0·1479 (12) | 0·3109 (10) | 469 (86) | 635 (68) | 304 (44) | 306 (69) | 199 (46) | 176 (43) |
| O(23) | 0·1992 (20) | −0·0871 (10) | 0·4072 (10) | 803 (104) | 285 (46) | 388 (47) | 321 (62) | 114 (55) | 117 (38) |
| O(*B*12) | 0·0188 (16) | 0·0999 (10) | 0·3237 (9) | 313 (69) | 364 (49) | 261 (39) | 124 (52) | −57 (42) | −89 (34) |
| Cr(3) | −0·1751 (3) | 0·5287 (2) | 0·6285 (2) | 220 (15) | 210 (9) | 193 (8) | 96 (10) | 56 (8) | 17 (6) |
| Cr(4) | 0·2332 (3) | 0·5588 (2) | 0·9095 (2) | 213 (15) | 240 (9) | 176 (8) | 107 (11) | 58 (8) | 31 (7) |
| O(31) | −0·3367 (19) | 0·5531 (11) | 0·6831 (11) | 524 (90) | 458 (58) | 548 (58) | 342 (67) | 336 (56) | 131 (47) |
| O(32) | −0·2299 (17) | 0·3606 (9) | 0·6031 (10) | 403 (81) | 265 (44) | 419 (48) | 94 (55) | 131 (49) | −43 (37) |
| O(33) | −0·1591 (17) | 0·5969 (11) | 0·4759 (9) | 430 (77) | 501 (54) | 231 (38) | 261 (58) | 91 (43) | 129 (37) |
| O(41) | 0·3167 (17) | 0·6520 (11) | 1·0729 (9) | 351 (73) | 460 (54) | 236 (37) | 186 (57) | 78 (41) | −8 (36) |
| O(42) | 0·4257 (17) | 0·5752 (12) | 0·8634 (10) | 345 (74) | 546 (64) | 344 (47) | 141 (63) | 170 (46) | −43 (43) |
| O(43) | 0·1086 (18) | 0·3916 (11) | 0·9152 (11) | 418 (83) | 367 (53) | 538 (57) | 180 (61) | 101 (55) | 170 (45) |
| O(*B*34) | 0·0762 (15) | 0·6217 (9) | 0·7693 (9) | 241 (63) | 256 (40) | 305 (40) | 72 (46) | −47 (41) | 30 (32) |
| Na(1) | 0·3744 (10) | 0·3511 (6) | 0·7359 (5) | 562 (48) | 336 (26) | 281 (23) | 251 (31) | 77 (26) | 43 (20) |
| Na(2) | −0·2391 (11) | 0·2267 (6) | 0·3930 (6) | 458 (53) | 400 (28) | 323 (24) | 106 (35) | 173 (28) | 32 (21) |
| Na(3) | 0·2941 (11) | 0·8263 (6) | 1·2146 (6) | 669 (53) | 480 (33) | 319 (25) | 380 (38) | 201 (28) | 85 (23) |
| Na(4) | −0·2334 (9) | 0·7414 (5) | 0·8979 (5) | 326 (43) | 338 (26) | 320 (23) | 141 (31) | 135 (24) | 61 (20) |

Table 3. *Observed and calculated structure factors for* $\beta$-$Na_2Cr_2O_7$

Unobserved reflexions are marked with an asterisk. *U* indicates an unreliable measurement which was given zero weight during refinements. Unobserved reflexions for which $F_c < F_o$ are not included.

| K | L | FO | FC |
|---|---|---|---|
| | | H=0 | |
| 0 | 2* | 2 | 3 |
| 0 | 3* | 2 | 3 |
| 0 | 4U | 155 | 124 |
| 0 | 5 | 13 | 16 |
| 0 | 6 | 48 | 46 |
| 0 | 8 | 19 | 17 |
| 0 | 9 | 12 | 13 |
| 0 | 10 | 18 | 17 |
| 0 | 12 | 11 | 11 |
| 1 | 0U | 6 | 0 |
| 1 | 1 | 47 | 34 |
| 1 | 2* | 3 | 4 |
| 1 | 3 | 71 | 69 |
| 1 | 4 | 19 | 20 |
| 1 | 5 | 89 | 84 |
| 1 | 6 | 31 | 33 |
| 1 | 7 | 70 | 70 |
| 1 | 8 | 19 | 17 |
| 1 | 11 | 36 | 34 |
| 1 | 12 | 9 | 10 |
| 1 | -1U | 5 | 7 |
| 1 | -2 | 49 | 54 |
| 1 | -3 | 12 | 11 |
| 1 | -4 | 17 | 19 |
| 1 | -5 | 32 | 33 |
| 1 | -6 | 31 | 37 |
| 1 | -7 | 49 | 54 |
| 1 | -8 | 18 | 17 |
| 1 | -9 | 15 | 15 |
| 1 | -11 | 30 | 29 |
| 2 | 0U | 92 | 114 |
| 2 | 2 | 59 | 57 |
| 2 | 3 | 17 | 16 |
| 2 | 4 | 64 | 63 |
| 2 | 5* | 4 | 6 |
| 2 | 6 | 23 | 25 |
| 2 | 7* | 5 | 5 |
| 2 | 8 | 21 | 20 |
| 2 | 9 | 11 | 9 |
| 2 | 10 | 7 | 6 |
| 2 | 11 | 8 | 9 |
| 2 | -1 | 8 | 9 |
| 2 | -2 | 51 | 51 |
| 2 | -4 | 51 | 53 |
| 2 | -5 | 26 | 25 |
| 2 | -6 | 16 | 15 |
| 2 | -7 | 19 | 19 |
| 2 | -8 | 38 | 39 |
| 2 | -9 | 21 | 18 |
| 2 | -10 | 7 | 7 |
| 3 | 0 | 14 | 15 |
| 3 | 1 | 13 | 13 |
| 3 | 2* | 4 | 4 |
| 3 | 3 | 66 | 69 |
| 3 | 4 | 17 | 16 |
| 3 | 5* | 5 | 6 |
| 3 | 7 | 31 | 32 |
| 3 | 8* | 6 | 6 |
| 3 | 10 | 21 | 18 |
| 3 | -1U | 95 | 107 |
| 3 | -2 | 18 | 16 |
| 3 | -3 | 42 | 41 |
| 3 | -4 | 28 | 29 |
| 3 | -5 | 25 | 26 |
| 3 | -6 | 22 | 21 |
| 3 | -7 | 25 | 26 |
| 3 | -9 | 26 | 27 |
| 3 | -10 | 14 | 13 |
| 3 | -11 | 9 | 10 |
| 3 | -12 | 10 | 9 |
| 4 | 0 | 22 | 21 |
| 4 | 1 | 34 | 34 |
| 4 | 2 | 6 | 6 |
| 4 | 3* | 4 | 5 |
| 4 | 6 | 29 | 29 |
| 4 | 7 | 19 | 13 |
| 4 | 8* | 6 | 6 |
| 4 | 9* | 6 | 7 |
| 4 | 10 | 32 | 29 |
| 4 | 11 | 12 | 11 |
| 4 | -1* | 4 | 0 |
| 4 | -2* | 4 | 4 |
| 4 | -3 | 38 | 39 |
| 4 | -4 | 114 | 119 |
| 4 | -5 | 13 | 14 |
| 4 | -6 | 31 | 30 |
| 4 | -7 | 16 | 15 |
| 4 | -8 | 38 | 36 |
| 4 | -9 | 15 | 13 |
| 4 | -10 | 10 | 10 |
| 4 | -11 | 8 | 9 |
| 4 | -12 | 15 | 14 |
| 5 | 0 | 21 | 20 |
| 5 | 1 | 46 | 48 |
| 5 | 2 | 31 | 31 |
| 5 | 3 | 131 | 131 |
| 5 | 5 | 10 | 10 |
| 5 | 6 | 5 | 5 |
| 5 | 7 | 38 | 37 |
| 5 | -1U | 121 | 149 |
| 5 | -2 | 9 | 9 |
| 5 | -3 | 16 | 15 |
| 5 | -4 | 5 | 7 |
| 5 | -5 | 35 | 32 |
| 5 | -6 | 23 | 21 |
| 5 | -7 | 43 | 41 |
| 5 | -9 | 6 | 8 |
| 5 | -10 | 28 | 24 |
| 6 | 0 | 11 | 10 |
| 6 | 1 | 38 | 37 |
| 6 | 2 | 51 | 53 |
| 6 | 3* | 5 | 5 |
| 6 | 4 | 44 | 41 |
| 6 | 5 | 8 | 7 |
| 6 | 6 | 31 | 30 |
| 6 | 7 | 11 | 9 |
| 6 | 8 | 8 | 10 |
| 6 | 9 | 13 | 11 |
| 6 | 10 | 25 | 29 |
| 6 | -1 | 16 | 15 |
| 6 | -2 | 34 | 35 |
| 6 | -3 | 49 | 47 |
| 6 | -4 | 32 | 32 |
| 6 | -6 | 31 | 29 |
| 6 | -7 | 17 | 15 |
| 6 | -8 | 30 | 29 |
| 6 | -10 | 11 | 11 |
| 6 | -11 | 5 | 4 |
| 7 | 1 | 43 | 44 |
| 7 | 2 | 6 | 6 |
| 7 | 3 | 50 | 50 |
| 7 | 4 | 16 | 16 |
| 7 | 5 | 14 | 15 |
| 7 | 6 | 17 | 15 |
| 7 | -1 | 62 | 60 |
| 7 | -2 | 5 | 6 |
| 7 | -3 | 19 | 19 |
| 7 | -5 | 71 | 70 |
| 7 | -6 | 26 | 25 |
| 7 | -8 | 11 | 11 |
| 7 | -9 | 23 | 21 |
| 7 | -10 | 25 | 26 |
| 7 | -11 | 6 | 5 |
| 8 | 1 | 15 | 15 |
| 8 | 2 | 51 | 49 |
| 8 | 3 | 18 | 17 |
| 8 | 6 | 34 | 31 |
| 8 | 7 | 6 | 3 |
| 8 | -1 | 9 | 6 |
| 8 | -2 | 26 | 25 |
| 8 | -3 | 43 | 40 |
| 8 | -7 | 24 | 24 |
| 8 | -8 | 15 | 14 |
| 8 | -10 | 15 | 14 |
| 9 | 0 | 23 | 20 |
| 9 | 4 | 14 | 13 |
| 9 | 5 | 8 | 7 |
| 9 | -1 | 23 | 23 |
| 9 | -2 | 8 | 6 |
| 9 | -4 | 20 | 18 |
| 9 | -5 | 34 | 32 |
| 9 | -6 | 6 | 9 |
| 9 | -7 | 8 | 9 |
| 9 | -8 | 8 | 7 |
| 9 | -9 | 7 | 7 |
| 9 | -10 | 11 | 11 |
| 10 | 0 | 8 | 8 |
| 10 | 1 | 9 | 9 |
| 10 | 2 | 28 | 27 |
| 10 | 5 | 13 | 12 |
| 10 | 6 | 26 | 25 |
| 10 | -2 | 31 | 29 |
| 10 | -3 | 12 | 11 |
| 10 | -5 | 14 | 13 |
| 10 | -7 | 20 | 19 |
| 11 | 0 | 35 | 31 |
| 11 | 1 | 8 | 7 |
| 11 | 2 | 5 | 7 |
| 11 | 4 | 5 | 5 |
| 11 | 5 | 15 | 15 |
| 11 | -1 | 12 | 12 |
| 11 | -2 | 6 | 6 |
| 11 | -3 | 9 | 9 |
| 11 | -4 | 26 | 23 |
| 11 | -5 | 8 | 6 |
| 11 | -7 | 7 | 7 |
| 11 | -8 | 9 | 10 |
| 12 | 0 | 13 | 10 |
| 12 | 2 | 24 | 21 |
| 12 | 3 | 13 | 10 |
| 12 | -2 | 32 | 31 |
| 12 | -4 | 17 | 17 |
| 13 | 0 | 18 | 15 |
| 13 | -4 | 14 | 18 |
| | | H=1 | |
| 0 | 0 | 39 | 26 |
| 0 | 2 | 199 | 170 |
| 0 | 3 | 6 | 2 |
| 0 | 4 | 12 | 12 |
| 0 | 6 | 41 | 39 |
| 0 | 8 | 10 | 8 |
| 0 | 9 | 13 | 12 |
| 0 | 10 | 7 | 7 |
| 0 | 11 | 7 | 4 |
| 0 | -2U | 127 | 125 |
| 0 | -3 | 23 | 20 |
| 0 | -4 | 18 | 21 |
| 0 | -5 | 13 | 12 |
| 0 | -6 | 63 | 61 |
| 0 | -7 | 28 | 28 |
| 0 | -8 | 11 | 12 |
| 0 | -9 | 12 | 14 |
| 0 | -10* | 7 | 7 |
| 0 | -11 | 13 | 14 |
| 1 | 1 | 36 | 35 |
| 1 | 5 | 64 | 61 |
| 1 | 6 | 13 | 15 |
| 1 | 7 | 33 | 31 |
| 1 | 8 | 12 | 11 |
| 1 | 9 | 32 | 32 |
| 1 | 10 | 12 | 12 |
| 1 | -3 | 5 | 5 |
| 1 | -4 | 15 | 16 |
| 1 | -5 | 119 | 106 |
| 1 | -6 | 5 | 9 |
| 1 | -7 | 29 | 31 |
| 1 | -8 | 24 | 24 |
| 1 | -9 | 46 | 39 |
| 1 | -12 | 7 | 7 |
| 2 | 1* | 3 | 5 |
| 2 | 2 | 123 | 111 |
| 2 | 3 | 16 | 11 |
| 2 | 4 | 39 | 42 |
| 2 | 5 | 15 | 17 |
| 2 | 9 | 7 | 7 |
| 2 | 10 | 19 | 20 |
| 2 | 12 | 10 | 10 |
| 2 | -1 | 40 | 38 |
| 2 | -3 | 52 | 49 |
| 2 | -4 | 23 | 22 |
| 2 | -5 | 9 | 8 |
| 2 | -6 | 86 | 76 |
| 2 | -7 | 17 | 20 |
| 2 | -8 | 42 | 41 |
| 2 | -10 | 12 | 12 |
| 2 | -11 | 21 | 20 |
| 2 | -12 | 14 | 17 |
| 3 | 1 | 154 | 137 |
| 3 | 2 | 15 | 15 |
| 3 | 3 | 76 | 70 |
| 3 | 4 | 20 | 21 |
| 3 | 5 | 66 | 66 |
| 3 | 7 | 11 | 12 |
| 3 | 9 | 34 | 35 |
| 3 | -1 | 56 | 55 |
| 3 | -2* | 4 | 5 |
| 3 | -3 | 11 | 13 |
| 3 | -4 | 31 | 32 |
| 3 | -5 | 12 | 14 |
| 3 | -7 | 15 | 17 |
| 3 | -8 | 20 | 22 |
| 3 | -12 | 14 | 15 |
| 4 | 1 | 16 | 12 |
| 4 | 2 | 13 | 15 |
| 4 | 3 | 28 | 25 |
| 4 | 4 | 45 | 49 |
| 4 | 6 | 43 | 43 |
| 4 | 7 | 7 | 7 |
| 4 | 8 | 30 | 30 |
| 4 | 9 | 24 | 22 |
| 4 | 10 | 16 | 17 |
| 4 | -1 | 22 | 26 |
| 4 | -4 | 37 | 39 |
| 4 | -5 | 16 | 17 |
| 4 | -6 | 28 | 29 |
| 4 | -7 | 8 | 11 |
| 4 | -8 | 9 | 11 |
| 4 | -10 | 25 | 27 |
| 4 | -11 | 10 | 11 |
| 5 | 1 | 107 | 101 |
| 5 | 4 | 16 | 16 |
| 5 | 5 | 36 | 35 |
| 5 | 6 | 7 | 8 |
| 5 | 8 | 9 | 11 |
| 5 | -1 | 14 | 16 |
| 5 | -3 | 94 | 87 |
| 5 | -4 | 39 | 40 |
| 5 | -5 | 34 | 35 |
| 5 | -7 | 32 | 34 |
| 5 | -8 | 26 | 26 |
| 5 | -11 | 10 | 10 |
| 5 | -12 | 24 | 19 |
| 6 | 0 | 11 | 11 |
| 6 | 1 | 6 | 7 |
| 6 | 2 | 18 | 20 |
| 6 | 3 | 21 | 19 |
| 6 | 4 | 51 | 50 |
| 6 | 5 | 7 | 9 |
| 6 | 6 | 11 | 8 |
| 6 | 8 | 34 | 33 |
| 6 | -1 | 33 | 34 |
| 6 | -2 | 9 | 11 |
| 6 | -3 | 27 | 29 |
| 6 | -4 | 16 | 11 |
| 6 | -5 | 50 | 48 |
| 6 | -6 | 46 | 40 |
| 6 | -7* | 6 | 8 |
| 6 | -8 | 10 | 12 |
| 6 | -9 | 16 | 11 |
| 6 | -10 | 20 | 20 |
| 7 | 1 | 59 | 55 |
| 7 | 2 | 12 | 15 |
| 7 | 3 | 24 | 25 |
| 7 | 6 | 9 | 11 |
| 7 | -1 | 13 | 13 |
| 7 | -2 | 11 | 12 |
| 7 | -3 | 82 | 77 |
| 7 | -4 | 9 | 14 |
| 7 | -5 | 17 | 19 |
| 7 | -7* | 6 | 9 |
| 7 | -8 | 17 | 19 |
| 7 | -9 | 13 | 14 |
| 8 | 0 | 20 | 24 |
| 8 | 1* | 7 | 7 |
| 8 | 2 | 33 | 33 |
| 8 | 3 | 7 | 10 |
| 8 | 4 | 24 | 25 |
| 8 | 6 | 9 | 10 |
| 8 | -1 | 30 | 31 |
| 8 | -5 | 27 | 27 |
| 8 | -8 | 7 | 11 |
| 8 | -9 | 15 | 20 |
| 8 | -10 | 7 | 11 |
| 9 | 2 | 18 | 20 |
| 9 | -1 | 13 | 14 |
| 9 | -2 | 13 | 14 |
| 9 | -3 | 21 | 22 |
| 9 | -4* | 7 | 7 |
| 9 | -5 | 13 | 16 |
| 9 | -7 | 16 | 19 |
| 9 | -8 | 9 | 10 |
| 10 | 0 | 41 | 40 |
| 10 | 4 | 24 | 25 |
| 10 | -1 | 5 | 11 |
| 10 | -4 | 15 | 22 |
| 10 | -5 | 11 | 14 |
| 10 | -6 | 11 | 12 |
| 10 | -9 | 15 | 21 |
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| 0 | 6 | 8 | 12 |
| 0 | -10 | 13 | 11 |
| 1 | 1 | 38 | 37 |
| 1 | 3 | 55 | 53 |
| 1 | 5 | 8 | 7 |
| 1 | 7 | 15 | 18 |
| 1 | -11 | 8 | 9 |
| 2 | 4 | 9 | 10 |
| 2 | 6 | 20 | 17 |
| 2 | -12 | 22 | 20 |
| 3 | 3 | 45 | 42 |
| 4 | 4* | 5 | 6 |
| 4 | 6 | 29 | 23 |
| -1 | 2 | 11 | 12 |
| -1 | 3 | 44 | 44 |
| -1 | 7 | 29 | 32 |
| -1 | -1 | 51 | 56 |
| -1 | -9 | 4 | 5 |
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| -3 | -7 | 33 | 33 |
| -4 | 0 | 120 | 112 |
| -4 | 1 | 8 | 10 |
| -4 | 2 | 14 | 19 |
| -4 | 4 | 57 | 58 |
| -4 | -1U | 19 | 19 |
| -4 | -2U | 70 | 69 |
| -4 | -4 | 53 | 55 |
| -4 | -6 | 21 | 22 |
| -5 | 1 | 33 | 36 |
| -5 | 4 | 5 | 6 |
| -5 | 5 | 8 | 10 |
| -5 | 6 | 5 | 8 |
| -5 | 7 | 8 | 10 |
| -5 | -1 | 30 | 29 |
| -5 | -2 | 2 | 6 |
| -5 | -3 | 87 | 82 |
| -5 | -4 | 15 | 17 |
| -5 | -5 | 22 | 23 |
| -5 | -6 | 12 | 12 |
| -5 | -7 | 91 | 81 |
| -5 | -8 | 20 | 19 |
| -5 | -9* | 4 | 5 |
| -5 | -10 | 10 | 9 |
| -5 | -11 | 13 | 16 |
| -6 | 0 | 23 | 26 |
| -6 | -1 | 9 | 12 |
| -6 | -2U | 5 | 7 |
| -6 | -3 | 10 | 12 |
| -6 | -4 | 9 | 10 |
| -6 | -6 | 20 | 22 |
| -7 | 0 | 32 | 30 |
| -7 | 1 | 70 | 70 |
| -7 | -3 | 72 | 69 |
| -7 | -4 | 12 | 14 |
| -7 | -5 | 13 | 16 |
| -7 | -7 | 32 | 30 |
| -8 | 0 | 17 | 20 |
| -8 | -2 | 22 | 22 |
| -8 | -3 | 14 | 16 |
| -8 | -4 | 17 | 15 |
| -8 | -6 | 17 | 18 |
| -8 | -8 | 5 | 7 |
| -9 | -1 | 22 | 21 |
| -9 | -2 | 9 | 9 |
| -9 | -3 | 77 | 77 |
| -9 | -5 | 15 | 15 |
| -9 | -9 | 17 | 14 |
| -10 | 0 | 11 | 12 |
| -10 | -2 | 25 | 27 |
| -10 | -4 | 15 | 15 |
| -10 | -5* | 6 | 7 |
| -10 | -6 | 36 | 39 |
| -10 | -8 | 10 | 12 |
| -11 | 1 | 22 | 20 |
| -11 | -4 | 8 | 11 |
| -12 | 2 | 32 | 30 |
| -12 | -5 | 9 | 10 |
| -12 | -6 | 25 | 25 |
| -12 | -8 | 10 | 7 |
| -13 | 3 | 12 | 11 |
| -13 | -5 | 10 | 11 |
| | | H=6 | |
| 0 | 0 | 17 | 15 |
| 0 | 3 | 9 | 8 |
| 0 | 6 | 19 | 16 |
| 0 | -12 | 10 | 11 |
| 1 | 1 | 49 | 47 |
| 1 | 4 | 14 | 13 |
| 1 | 5 | 20 | 21 |
| 2 | 2 | 13 | 13 |
| 2 | 6 | 10 | 12 |
| 3 | 3 | 13 | 13 |
| 3 | 6 | 9 | 7 |
| -1 | 3 | 23 | 23 |
| -1 | 5 | 45 | 40 |
| -1 | 7 | 9 | 13 |
| -1 | -1 | 45 | 45 |
| -1 | -11 | 8 | 7 |
| -2 | 2 | 60 | 59 |
| -2 | 3* | 6 | 6 |
| -2 | -2 | 84 | 84 |
| -2 | -10 | 9 | 9 |
| -3 | 0 | 11 | 12 |
| -3 | 1 | 19 | 21 |
| -3 | 3 | 19 | 19 |
| -3 | 4 | 14 | 13 |
| -3 | 5 | 30 | 32 |
| -3 | -3 | 16 | 18 |
| -3 | -9 | 34 | 31 |
| -4 | 0 | 17 | 19 |
| -4 | 2 | 43 | 40 |
| -4 | 3* | 6 | 8 |
| -4 | -4 | 16 | 16 |
| -4 | -8 | 9 | 9 |
| -5 | 0 | 29 | 27 |
| -5 | 3 | 17 | 19 |
| -5 | -1U | 42 | 43 |
| -5 | -2U | 29 | 30 |
| -5 | -5 | 36 | 37 |
| -6 | 0 | 33 | 29 |
| -6 | 1 | 17 | 17 |
| -6 | 2 | 57 | 53 |
| -6 | 4 | 24 | 23 |
| -6 | 5 | 5 | 3 |
| -6 | 6 | 48 | 43 |
| -6 | -1 | 7 | 8 |
| -6 | -2 | 40 | 39 |
| -6 | -3 | 5 | 7 |
| -6 | -4 | 12 | 15 |
| -6 | -6 | 18 | 18 |
| -6 | -7 | 5 | 7 |
| -6 | -8 | 3 | 4 |
| -6 | -11 | 13 | 13 |
| -7 | 1 | 10 | 11 |
| -7 | 2 | 8 | 8 |
| -7 | -1 | 78 | 76 |
| -7 | -2U | 6 | 1 |
| -7 | -3 | 25 | 26 |
| -7 | -4 | 29 | 29 |
| -7 | -5 | 73 | 71 |
| -7 | -7 | 22 | 20 |
| -8 | -3 | 7 | 9 |
| -8 | -4* | 5 | 6 |
| -8 | -8 | 34 | 33 |
| -9 | -1 | 36 | 35 |
| -9 | -3 | 25 | 26 |
| -9 | -4 | 11 | 8 |
| -9 | -5 | 7 | 9 |
| -10 | -1 | 9 | 11 |
| -10 | -4 | 23 | 25 |
| -10 | -5 | 12 | 12 |
| -10 | -7 | 10 | 7 |
| -11 | -1 | 32 | 30 |
| -11 | -2 | 11 | 10 |
| -11 | -6 | 10 | 10 |
| -12 | 0 | 18 | 16 |
| -12 | -3 | 9 | 10 |
| -12 | -4 | 39 | 38 |
| -12 | -7 | 15 | 14 |
| -12 | -8 | 16 | 18 |
| -13 | 1 | 10 | 10 |
| -13 | -5 | 7 | 6 |
| | | H=7 | |
| 0 | 0 | 22 | 19 |
| 1 | 1 | 31 | 28 |
| 2 | 2 | 7 | 6 |
| -1 | 3 | 32 | 32 |
| -1 | 5 | 14 | 12 |
| -1 | -1 | 22 | 22 |
| -2 | 3* | 7 | 10 |
| -2 | 4 | 9 | 7 |
| -2 | -2 | 6 | 7 |
| -3 | 1 | 22 | 25 |
| -3 | 3 | 25 | 21 |
| -3 | 5 | 25 | 33 |
| -3 | 7 | 14 | 16 |
| -3 | -3 | 11 | 11 |
| -3 | -11 | 15 | 14 |
| -4 | 0 | 46 | 46 |
| -4 | 2 | 22 | 20 |
| -4 | 4 | 29 | 35 |
| -4 | -4 | 20 | 19 |
| -4 | -10 | 11 | 11 |
| -5 | 0* | 7 | 7 |
| -5 | 1 | 8 | 8 |
| -5 | 2 | 7 | 5 |
| -5 | 3* | 6 | 8 |
| -5 | 5 | 20 | 22 |
| -5 | -1* | 8 | 9 |
| -5 | -5 | 5 | 3 |
| -5 | -9 | 28 | 26 |
| -6 | 0 | 28 | 28 |
| -6 | 1 | 6 | 7 |
| -6 | 2 | 20 | 22 |
| -6 | 4 | 26 | 29 |
| -6 | -1U | 6 | 5 |
| -6 | -2U | 31 | 24 |
| -6 | -6 | 5 | 5 |
| -7 | 0* | 4 | 6 |
| -7 | 1 | 18 | 21 |
| -7 | 4 | 3 | 4 |
| -7 | 5 | 4 | 5 |
| -7 | -1 | 16 | 17 |
| -7 | -2 | 5 | 5 |
| -7 | -3 | 31 | 30 |
| -7 | -4 | 8 | 9 |
| -7 | -5 | 21 | 22 |
| -7 | -6 | 12 | 12 |
| -7 | -7 | 17 | 17 |
| -7 | -8* | 4 | 5 |
| -7 | -9 | 25 | 27 |
| -7 | -10 | 17 | 15 |
| -8 | 0 | 16 | 15 |
| -8 | 2 | 31 | 35 |
| -8 | -2U | 8 | 6 |
| -8 | -4U | 9 | 4 |
| -8 | -6 | 5 | 6 |
| -8 | -8 | 10 | 9 |
| -9 | 1 | 34 | 37 |
| -9 | -1 | 29 | 26 |
| -9 | -2 | 7 | 9 |
| -9 | -3U | 34 | 32 |
| -9 | -5 | 36 | 36 |
| -9 | -9 | 16 | 17 |
| -10 | 0 | 11 | 16 |
| -10 | -1* | 7 | 7 |
| -10 | -4 | 4 | 3 |
| -10 | -5 | 5 | 11 |
| -10 | -6 | 25 | 26 |
| -11 | -1 | 15 | 18 |
| -11 | -3 | 4 | 4 |
| -11 | -5 | 18 | 20 |
| -12 | -2 | 18 | 20 |
| -12 | -4 | 14 | 16 |
| -12 | -6 | 12 | 11 |
| -12 | -8 | 19 | 20 |
| -13 | -1 | 13 | 11 |
| -14 | -4 | 15 | 17 |
| | | H=8 | |
| 0 | 0 | 5 | 5 |
| 1 | 1 | 11 | 11 |
| -1 | 5 | 8 | 14 |
| -1 | -1 | 33 | 30 |
| -2 | -2 | 30 | 27 |
| -3 | 2 | 9 | 8 |
| -3 | 3 | 26 | 26 |
| -3 | -3 | 8 | 8 |
| -4 | 2 | 14 | 17 |
| -4 | 4 | 7 | 11 |
| -4 | -4 | 27 | 26 |
| -5 | 3 | 12 | 14 |
| -5 | -5 | 15 | 13 |
| -5 | -11 | 20 | 19 |
| -6 | 0U | 35 | 36 |
| -6 | 1 | 10 | 11 |
| -6 | 2 | 14 | 19 |
| -6 | 4 | 26 | 24 |
| -7 | 2 | 13 | 12 |
| -7 | 3* | 7 | 8 |
| -7 | -1U | 31 | 31 |
| -7 | -2U | 9 | 2 |
| -7 | -7 | 40 | 37 |
| -7 | -9 | 9 | 9 |
| -8 | 0 | 27 | 27 |
| -8 | 4 | 30 | 27 |
| -8 | -2 | 3 | 6 |
| -8 | -3 | 5 | 10 |
| -8 | -4 | 11 | 13 |
| -8 | -5 | 12 | 12 |
| -8 | -7 | 7 | 8 |
| -8 | -8 | 19 | 17 |
| -8 | -9* | 3 | 5 |
| -9 | 1 | 20 | 21 |
| -9 | -1 | 14 | 15 |
| -9 | -2U | 13 | 11 |
| -9 | -3U | 36 | 37 |
| -9 | -4U | 9 | 2 |
| -9 | -7 | 34 | 30 |
| -10 | -2 | 7 | 7 |
| -10 | -6 | 13 | 12 |
| -11 | -2* | 6 | 8 |
| -11 | -3 | 22 | 24 |
| -12 | -2* | 7 | 8 |
| -12 | -3 | 9 | 8 |
| -12 | -4 | 17 | 18 |
| -12 | -6 | 19 | 22 |
| -12 | -7 | 10 | 11 |
| -13 | -3 | 20 | 16 |
| | | H=9 | |
| -2 | -2 | 14 | 15 |
| -3 | -3 | 15 | 14 |
| -4 | 2 | 22 | 21 |
| -5 | 3 | 14 | 11 |
| -5 | -5 | 10 | 14 |
| -6 | 2 | 31 | 27 |
| -6 | -6 | 13 | 12 |
| -7 | 1 | 9 | 6 |
| -7 | -1 | 18 | 17 |
| -7 | -7 | 18 | 10 |
| -8 | 2 | 22 | 24 |
| -8 | -1U | 9 | 10 |
| -8 | -2U | 31 | 25 |
| -8 | -8 | 6 | 8 |
| -9 | 1 | 8 | 7 |
| -9 | -1 | 36 | 31 |
| -9 | -2 | 5 | 7 |
| -9 | -3 | 4 | 5 |
| -9 | -4 | 4 | 6 |
| -9 | -5 | 42 | 37 |
| -9 | -6 | 7 | 7 |
| -10 | -4U | 10 | 2 |
| -11 | -1 | 24 | 28 |
| -11 | -5U | 22 | 25 |
| -12 | -4 | 23 | 21 |
| | | H=10 | |
| -4 | -4 | 30 | 26 |
| -5 | -5 | 6 | 7 |
| -7 | -7 | 33 | 29 |

ment index, $R_2, = 0{\cdot}089$ and unweighted agreement index, $R_1 (= \sum|F_o - F_c|/\sum|F_o|), = 0{\cdot}078$. For the $k+l$ odd reflexions, $R_2 = 0{\cdot}109$ and $R_1 = 0{\cdot}104$. In the final round of refinement, 751 observed $k+l$ even and 430 observed $k+l$ odd reflexions were used. In addition, the 24 of the 201 unobserved $k+l$ even and the 61 of the 356 unobserved $k+l$ odd reflexions for which $|F_c| > |F_{\text{min}}|$ were also included. Final parameter shifts were of the order of $0{\cdot}1\sigma$, none being larger than $0{\cdot}5\sigma$. The final atomic position and temperature coordinates are given in Table 2, and the structure factors are listed in Table 3.

## Discussion

The vibrations of the Cr atoms are essentially isotropic, but those of the oxygen and sodium atoms are not. The former are arranged with their minima along the direction of the Cr–O bonds and their maxima in a direction roughly perpendicular to the Cr–Cr vector. Such an arrangement is consistent with a model in which the whole $Cr_2O_7$ group undergoes isotropic translation vibrations with a root-mean-square amplitude of about 0·15 Å, and librational oscillations about the center of mass with an r.m.s. amplitude of about 8°. Although other models would be equally consistent with the observed motions, this one has been used as the basis for the corrections made to the bond lengths quoted in Table 4. Because of the uncertainly in the nature of the true molecular motions, the thermal corrections to the bond lengths are uncertain to 0·01 Å.

The dichromate ions in $\beta$-$Na_2Cr_2O_7$ consist of two $CrO_4$ tetrahedra having one apical oxygen atom in common, and apart from the relative configurations of the two tetrahedra both independent $Cr_2O_7$ ions are iden-

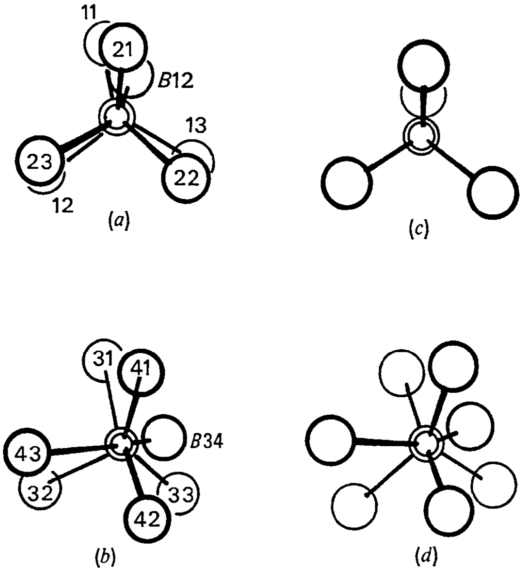

Fig. 1. Configuration of $Cr_2O_7$ ions projected down the Cr–Cr vector. (*a*) $\beta$-$Na_2Cr_2O_7$ layer I. (*b*) $\beta$-$Na_2Cr_2O_7$ layer II. (*c*) Idealized $Cr_2O_7$ in 'dichromate' structures. In most dichromate structures the ions do not show exact $C_{2v}$ symmetry. (*d*) $\alpha$-$Mg_2P_2O_7$.

tical. The Cr–O (bridging) distances do not differ significantly from 1·79 Å, nor the Cr–O (terminal) distances from 1·63 Å after correction for thermal motion. The angles are all effectively tetrahedral, the differences probably not being significant. In these respects, the dichromate ions are identical to other dichromate ions whose structures have already been determined (Brandon & Brown, 1968; Panagiotopoulos & Brown, 1970; Kharitanov, Kuz'min & Belov, 1970; Lofgren & Waltersson, 1971; and Lofgren, 1971). The two bridging Cr–O–Cr angles are identical (131 °) and are well within the ranges of values (122–138 °) found in other dichromates. The relative configuration of the two dichromate ions are, however, different as can be seen in Fig. 1, where they are shown in projection down the Cr–Cr vector. One of the ions [Fig. 1(*a*)] has the conformation found in most other 'dichromate' crystals [Figure 1(*c*)] (Brown & Calvo, 1970), while the other [Figure 1(*b*)] has a conformation not unlike that of the $P_2O_7$ group in $\alpha$-$Mg_2P_2O_7$ [Figure 1(*d*)] (Calvo, 1967). Three of the sodium atoms are in more or less octahedral coordination, with Na–O distances of 2·46 ± 0·07 Å* and angles of 90 ± 14 °*. The fourth sodium atom [Na(3)] has an irregular pentagonal bipyramidal coordination, with Na–O distances in the range 2·35–2·82 Å and O–O distances between adjacent ligands in the range 2·6 to 3·8 Å.

A scheme by which the structures of most of the alkali metal dichromates can be simply described has been given by Brown & Calvo (1970). According to this scheme $\alpha$-$Na_2Cr_2O_7$ is expected to have a type I structure† since it is probably isostructural with $Ag_2Cr_2O_7$ (Hazell, 1969). In this structure, (100) sheets of the kind illustrated in Fig. 2(*b*) are related to each other by the **a** translation vector of about 7 Å. The lattice parameters of $Ag_2Cr_2O_7$ and $\alpha$-$Na_2Cr_2O_7$ are compared in Table 1.

Table 4. *Interatomic distances*

| | | Uncorrected distance | Corrected* distance | Angles | | |
|---|---|---|---|---|---|---|
| | | | | O(12) | O(13) | O(*B*12) |
| Cr(1) | O(11) | 1·622 Å | 1·63 Å | 111° | 113° | 106° |
| | O(12) | 1·620 | 1·63 | | 110 | 110 |
| | O(13) | 1·601 | 1·61 | | | 108 |
| | O(*B*12) | 1·782 | 1·79 | | | |
| | | | | O(22) | O(23) | O(*B*12) |
| Cr(2) | O(21) | 1·609 | 1·62 | 111 | 111 | 108 |
| | O(22) | 1·620 | 1·64 | | 108 | 109 |
| | O(23) | 1·618 | 1·64 | | | 110 |
| | O(*B*12) | 1·778 | 1·79 | | | |
| | | Cr(1)–O(*B*12)–Cr(2) | | 131·3° | | |
| | | | | O(32) | O(33) | O(*B*34) |
| Cr(3) | O(31) | 1·602 | 1·62 | 111 | 112 | 110 |
| | O(32) | 1·618 | 1·63 | | 110 | 109 |
| | O(33) | 1·612 | 1·63 | | | 104 |
| | O(*B*34) | 1·790 | 1·80 | | | |
| | | | | O(42) | O(43) | O(*B*34) |
| Cr(4) | O(41) | 1·602 | 1·61 | 109 | 111 | 110 |
| | O(42) | 1·624 | 1·64 | | 107 | 109 |
| | O(43) | 1·612 | 1·63 | | | 111 |
| | O(*B*34) | 1·786 | 1·80 | | | |
| | | Cr(3)–O(*B*34)–Cr(4) | | 131·3° | | |

* Correction for thermal motion, see text.

Table 4 (*cont.*)

| | | | | | |
|---|---|---|---|---|---|
| Na(1) | O(33) | 2·347 Å | Na(3) | O(41) | 2·355 Å |
| | O(21) | 2·385 | | O(13) | 2·433 |
| | O(42) | 2·447 | | O(23) | 2·466 |
| | O(41) | 2·467 | | O(32) | 2·580 |
| | O(12) | 2·476 | | O(11) | 2·634 |
| | O(31) | 2·545 | | O(21) | 2·673 |
| | | | | O(43) | 2·825 |
| Na(2) | O(23) | 2·375 | Na(4) | O(42) | 2·386 |
| | O(32) | 2·391 | | O(12) | 2·411 |
| | O(22) | 2·432 | | O(43) | 2·414 |
| | O(*B*34) | 2·448 | | O(22) | 2·489 |
| | O(11) | 2·538 | | O(13) | 2·492 |
| | O(33) | 2·678 | | O(31) | 2·502 |

Standard errors derived from least-squares refinement:
Cr–O = 0·011 Å; Na–O = 0·013 Å;
O–Cr–O = 1°; Cr–O–Cr = 0·4°.

At 240 °C, $\alpha$-$Na_2Cr_2O_7$ undergoes a phase transition in which it looses the face-centring translation or, what is equivalent, all the centres of symmetry at $y=\frac{1}{4}$ and $\frac{3}{4}$ [Fig. 2(*a*)].

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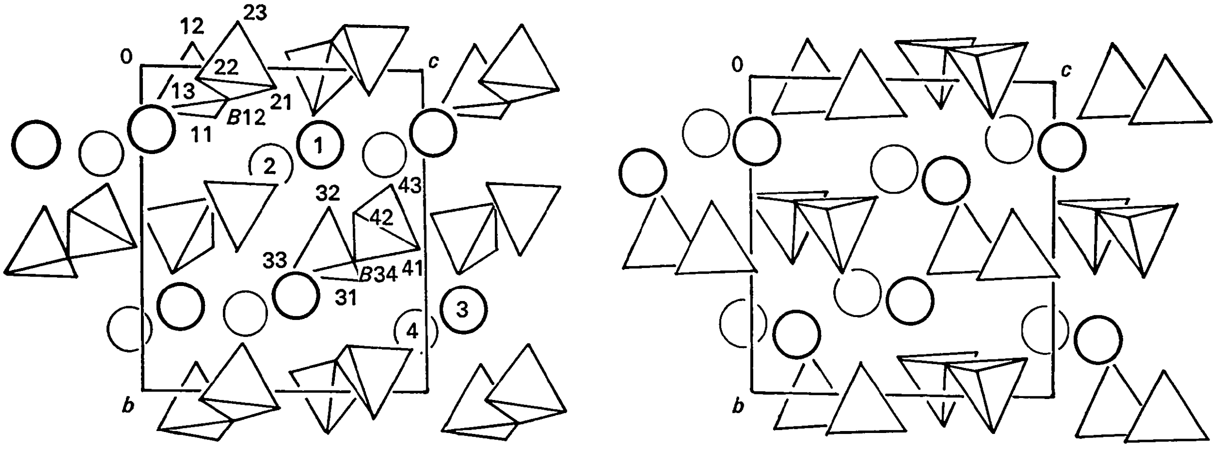
* Mean ± standard deviation.

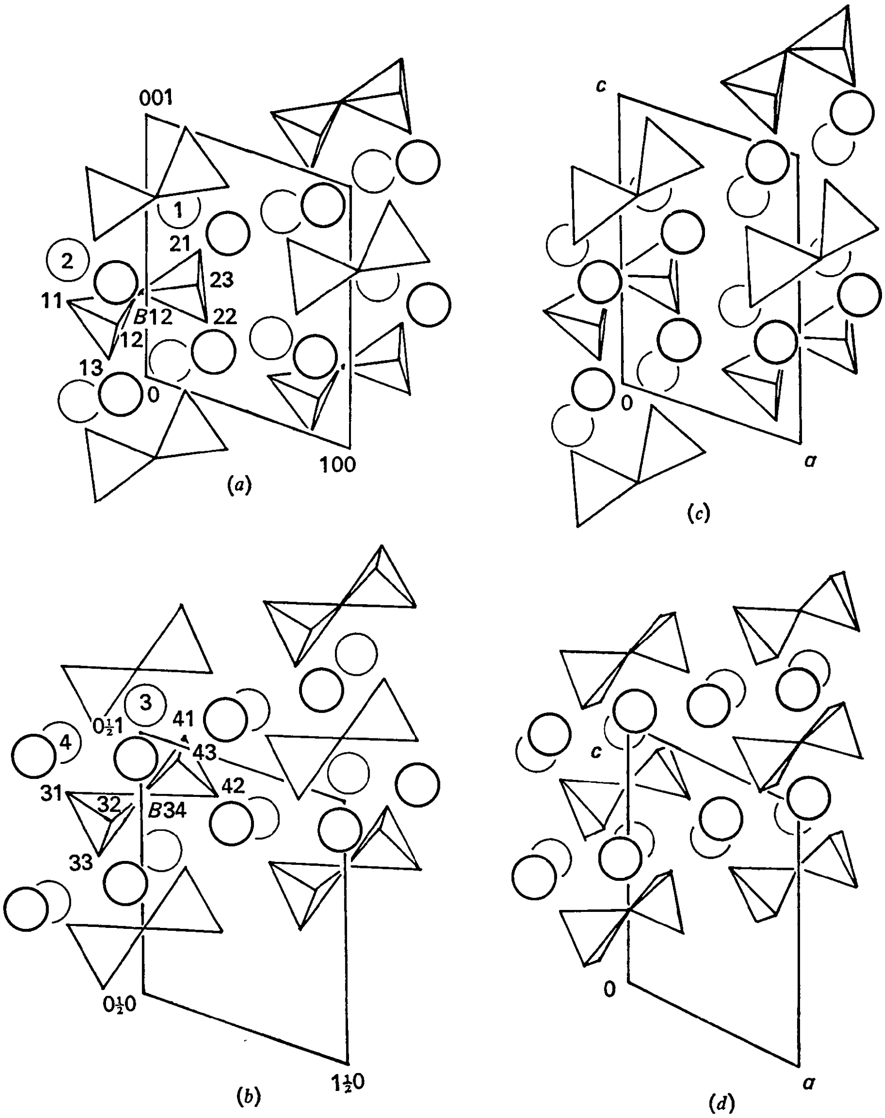
† Brown & Calvo (1970) have chosen the *b* and *c* axes to give a primitive cell. The transformation between the primitive cell, $C_P$, and the *A* centred cell, $C_A$, used here is $C_A = M\ C_P$ where

$$M=\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & -1\\ 0 & 1 & 1\end{pmatrix}$$



(a) (b)

Fig. 2. Projection of (a) $\beta$-$Na_2Cr_2O_7$ perpendicular to (100) and (b) $Ag_2Cr_2O_7$ perpendicular to (100). Oxygen atoms are at the apices of the tetrahedra, the Cr atoms are at the centers of the tetrahedra, and Na and Ag are shown as circles.



(a) (c) (b) (d)

Fig. 3. Projection of (a) layer I of $\beta$-$Na_2Cr_2O_7$ perpendicular to (010), (b) layer II of $\beta$-$Na_2Cr_2O_7$ perpendicular to (010), (c) $Ag_2Cr_2O_7$ perpendicular to (010) and (d) $\alpha$-$Mg_2P_2O_7$ perpendicular to (010). The atoms are indicated in the same way as in Fig. 2.

The effect of this transition can best be considered in terms of the (010) layers illustrated in Fig. 3. In $\alpha$-$Na_2Cr_2O_7$, these layers are identical and presumably similar to the corresponding (010) layer in $Ag_2Cr_2O_7$ [see Fig. 3(*c*)]. In $\beta$-$Na_2Cr_2O_7$, the two layers are different [see Fig. 3(*a*) and (*b*)]. Apart from small shifts in the cation, the most notable difference between the two layers lies in the configuration of the $Cr_2O_7$ ion. In layer I [Fig. 3(*a*)], the bridging oxygen atom lies directly between two opposite terminal oxygen atoms [O(11) and O(21)], the configuration found in most other 'dichromate' structures [see Fig. 1(*a*) and (*c*)]. In layer II, the bridging oxygen lies close to the plane of four terminal oxygen atoms [O(31), O(33), O(41), and O(42)]. The terminal oxygen atoms are also twisted slightly from the eclipsed configuration, so that layer II shows a strong similarity to the (010) layers in $\alpha$-$Mg_2P_2O_7$ (Calvo, 1967) [Fig. 3(*d*)],* a derivative of the thortveitite structure. It would thus appear that at high temperatures, $Na_2Cr_2O_7$ has a type I 'dichromate' structure but that on reducing the temperature alternate (010) layers transform into a configuration similar to that found in the thortveitite-like $\alpha$-$Mg_2P_2O_7$. We are presently studying the structure of $\alpha$-$Na_2Cr_2O_7$ and the phase transition in more detail.

We wish to thank Dr Calvo for helpful discussions and the National Research Council of Canada for financial assistance.

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* The unit cell of $\alpha$-$Mg_2P_2O_7$ has been transformed from the space group $B2_1/c$ reported by Calvo (1967) to $P2_1/c$ to facilitate comparison.

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*Acta Cryst.* (1972). B**28**, 1357

# The Structure of Ammonium Nitrate (IV)

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(*Received* 13 *August* 1971)

The structure of ammonium nitrate (IV), the phase which is stable between −18 and 32·3°C, has been refined by least-squares methods with three-dimensional neutron diffraction data. 188 independent reflections were observed on a four-circle diffractometer with a neutron wavelength of 1·232 Å and a limiting $2\theta$ angle of 100°. The refinement, using anisotropic temperature factors and an isotropic secondary extinction parameter, gave a final weighted $R$ index of 0·028. The structure is orthorhombic, space group *Pmmn*, with two $NH_4NO_3$ formula units per unit cell. A two-dimensional network of hydrogen bonds between the nitrogen atoms of the ammonium group and the oxygen atoms at one corner of the nitrate groups forms infinite sheets parallel to the (001) planes of the crystal. Adjacent sheets are bound together by van der Waals forces. This structure is simply related to the structures of the higher temperature phases.

## Introduction

Ammonium nitrate, $NH_4NO_3$, crystallizes in several polymorphic forms. The structure of the room-temperature phase, designated phase IV, was determined by West (1932), and by Hendricks, Posnjak & Kracek (1932) who also proposed possible structures for the higher temperature phases. The room-temperature phase is orthorhombic, space group *Pmmn*, with the cell constants (Swanson, Gilfrich, & Cook, 1957) $a=$

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