CRYSTALLOGRAPHIC STUDY

OF

ALKALI METAL DICHROMATES

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ALKALI METAL DICHROMATES

by

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SCOPE AND CONTENTS:

The alkali metal dichromates show extensive polymorphism. The crystal structures of the polymorphs α-$Na_2Cr_2O_7$, β-$Na_2Cr_2O_7$, β1-$Rb_2Cr_2O_7$ and $P2_1/c$ $NaRbCr_2O_7$ have been determined with x-ray methods. Crystal data were determined for β2-$Rb_2Cr_2O_7$, $P\bar{1}$ $Cs_2Cr_2O_7$ and the $P2_1/c$ $NaCsCr_2O_7$.

The dichromate ions found in this work have been compared with the dichromate ions found in other crystal structure determinations. The anions are described in terms of the bridging oxygen angles b and the torsion angles α_1 and α_2. Many of the dichromate ions are close to having C_{2v} symmetry with values for α_1 and α_2 close to zero and bridging angles of around 124°. But there is a number of dichromates with $\alpha_1 = -\alpha_2$ and $0° < |\alpha| < 60°$ for which the bridging angle varies between 131° to 141°.

The structures determined in this work are discussed as part of a unified description of thortveitite like and dichromate

like structures in terms of layers of Y_2O_7 anions. In terms of this description and Brown and Calvo's classification a structure is proposed for the $\beta 2Rb_2Cr_2O_7$, while for the structure of $NaCsCr_2O_7$ it is suggested that it is isostructural to that of $P2_1/c$ $NaRbCr_2O_7$. The phase transition of α-$Na_2Cr_2O_7$ to β-$Na_2Cr_2O_7$ is considered and it is suggested that a twisting thermal mode plays an important role in this as well as in other transitions.

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CHAPTER 1

INTRODUCTION: SURVEY OF THE POLYMORPHISM OF ALKALI METAL DICHROMATES

The alkali metal dichromates show extensive polymorphism. Though all of them melt at around 400° they show two or three phase transitions between room temperature and the melting point. A knowledge of the structure of the various polymorphs is necessary in order to understand the nature of the phase transitions between them. When this work started only two structures had been reported, those of $(NH_4)_2Cr_2O_7$ (1) and triclinic $K_2Cr_2O_7$ (2).

We have summarized in table 1.1 the cell constants and space groups of phases for which they are known, and in figure 1.1 the phase transitions of the various compounds.

$K_2Cr_2O_7$ and $Rb_2Cr_2O_7$ have more than one phase stable at room temperature. We will distinguish these by calling them as the β1, β2, ... phase while we will use the letters α, c and d for the higher temperature phases. Alternatively we will take advantage of the classification scheme of dichromate like structures proposed by Brown and Calvo (3) and call the phases as I, II, ... the number

Table 1.1 Cell constants and space groups of the dichromates

Compound	Phase	Type of Structure	Space Group	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)	V(Å^3)	Reference
$Na_2Cr_2O_7$	α	I	A$\bar{1}$	7.82	10.36	9.54	89.5	110.1	113.4	659	This Work
	β	I	P$\bar{1}$	7.70	10.38	9.40	89.41	109.57	114.26	639	This Work
$K_2Cr_2O_7$	β1	V	P$\bar{1}$	13.37	7.38	7.44	90.75	96.21	97.96	722	(2)
	α	VII(†)	$P2_1/n$	13.45	7.52	7.55		91.68		763	(6)
		X(†)	C2/c	13.06	7.37	7.43		91.85		715	(6)
$Rb_2Cr_2O_7$	β1	VIII	P$\bar{1}$	13.55	7.64	7.74	93.64	98.52	88.80	790	This Work
	β2	I(†)	P$\bar{1}$	7.60	7.39	7.85	90.2	70.0	70.5	387	This Work
		VII	$P2_1/n$	13.71	7.60	7.70		93.35		802	(11)
		X	C2/c	13.33	7.55	7.73		92.04		778	(10)
$Cs_2Cr_2O_7$	β		P$\bar{1}$	7.8	7.9	8.5	110.5	98.3	95.7	482	This Work
$(NH_4)_2Cr_2O_7$	α	X	C2/c	13.26	7.54	7.74		93.2		776	(1)
$NaRbCr_2O_7$			$P2_1/c$	12.95	11.13	10.04		93.42		1444	This Work
$NaCsCr_2O_7$			$P2_1/c$	12.98	11.58	10.10		93.8		1514	This Work

†Probable structural type

Figure 1.1

Phase transformations in alkali metal dichromates

$Na_2Cr_2O_7$

20°C —β(P$\bar{1}$)— 240°C —α(A$\bar{1}$)— 295°C —c— 330°C —d—

$K_2Cr_2O_7$

i) 20°C —β1(P$\bar{1}$) / V— 270°C —┐

—β2(=β1?)— 250°C —┘ —α(P2_1/n) / VII— 345°C —c— 380°C —d—

ii) 20°C —X(C2/c)— ?

$Rb_2Cr_2O_7$

i) 20°C —β1(P$\bar{1}$) / VIII— 318°C —┐

20°C —β2(P$\bar{1}$)— 260°C —┘ —α— 337°C —c—

ii) 20°C — VII (P2_1/n) — ?

iii) 20°C — X (C2/c) — ?

$Cs_2Cr_2O_7$

—β(P$\bar{1}$)— 347°C —α— 362°C —c—

$(NH_4)Cr_2O_7$

—γ— - 150°C —β— -2°C —α(C2/c) / X— 20°C —— decompose at 170°

indicating the structural group to which they belong.

Our present knowledge of the polymorphism is summarized below.

$Na_2Cr_2O_7$

Vesnin and Khripin (4) have studied the phase transformations of the anhydrous $Na_2Cr_2O_7$ with differential thermal analysis, measurements of refractive indices and x-ray powder patterns and have identified four phases between room temperature and the melting point. The phase transitions are reversible transformations and occur at 240, 295 and 330°C. Following Samuseva et al. (5) who examined the crystals using DTA we designate the phases above and below 240°C as α and β. In the present work we determined the structure of the α and β phase. The results are given in Chapter 3.1. Nothing is known about the structures of the other phases.

$K_2Cr_2O_7$

$K_2Cr_2O_7$ exists in two forms at room temperatures, a triclinic phase β1(V) and a metastable monoclinic phase (X), space group C2/c. Klement and Schwab (6) report that the single crystals of the β1 transform irreversibly but without destruction of the crystal at 270° to a monoclinic form α(VII), space group $P2_1/n$. On cooling a reversible transition occurs around 250°C but there is a dispute as to whether the structure formed below this transition (β2) is the original triclinic phase (4,6,7). According to Vesnin and Khripin (4) there are two more reversible phase transitions at 345°C and 380°C. The only phase whose structure has been determined so far is the triclinic phase (2).

$Rb_2Cr_2O_7$

Rubidium dichromate grown from aqueous solution at room temperatures forms three phases, one triclinic β1(VIII) and two monoclinic, VII, space group $P2_1/n$ and X, space group C2/c (6,8). We have determined the structure of β1 (9). Löfgren and Walterson (10) have determined the structure of X and Löfgren (11) the structure of VII.

On heating crystals of the triclinic phase two transformations take place, an irreversible transition at 318° and a reversible one at 337°. On cooling a reversible endothermic effect is observed at 260° (4). The phase formed before this transition is designated β2.

We grew crystals of β2-$Rb_2Cr_2O_7$ from the melt and found that they are twinned belonging to the triclinic class . An account of them is given in Chapter 3.2.2.

$Cs_2Cr_2O_7$

For the $Cs_2Cr_2O_7$ two reversible phase transitions have been reported at 347°, Samuseva (5) and at 362°, Vesnin (6). We looked at crystals grown from aqueous solutions and we found that they are triclinic but disordered and twinned. These results are discussed in Chapter 3.3.

$(NH_4)_2Cr_2O_7$

Jaffray (12,13) reports two phase transitions at -2°C and -150°C for the $(NH_4)_2Cr_2O_7$ but the phases are unidentified. The room temperature structure belongs to the space group C2/c and has been shown by Byström and Wilhelmi (1) to be of type X.

Binary Systems

Binary systems of the alkali dichromates have been studied by Lehrman (14) $K_2Cr_2O_7$-$Na_2Cr_2O_7$; and Samuseva (15) $K_2Cr_2O_7$-$Rb_2Cr_2O_7$, $K_2Cr_2O_7$-$Cs_2Cr_2O_7$, $Rb_2Cr_2O_7$-$Cs_2Cr_2O_7$. All these have been found to form a continous series of solid solutions, except for the systems of $Na_2Cr_2O_7$-$Rb_2Cr_2O_7$ and $Na_2Cr_2O_7$-$Cs_2Cr_2O_7$ where congruently melting compounds in the molar ratio 1:1 have been found (5). We studied single crystals of both of these compounds and determined the structure of $NaRbCr_2O_7$. This work is reported in Chapter 3.4.

Lately Hazell (16) reported the structure of $Ag_2Cr_2O_7$ which is triclinic at room temperature with structure I.

The structure of hydrated sodium dichromate $Na_2Cr_2O_7 \cdot 2H_2O$ has been determined recently by Kharitonov et al. (17) and Datt et al. (18) have given the results of a preliminary investigation of $Li_2Cr_2O_7$ $2H_2O$. These structures and that of $(NH_4)_2Cr_2O_7$ are not very accurate and will not be discussed further in this thesis.

CHAPTER 2

METHODS OF CRYSTAL STRUCTURE ANALYSIS

The purpose of this section is to define some of the nomenclature of the crystal structure determination methods used in this thesis.

Crystals are known to be homogeneous, symmetric and generally anisotropic solids. These properties are consequences of the periodic nature of the crystal, that is the electron density is a triply periodic function such that:

$$\rho(\underline{r}) = \rho(\underline{r}+\underline{r}_\ell) \qquad [1]$$

$$\underline{r}_\ell = u\underline{a} + v\underline{b} + w\underline{c} \qquad [2]$$

where u, v, w are integers and $\underline{a}$, $\underline{b}$, $\underline{c}$ are three non coplanar vectors usually selected so that they are the three smallest non coplanar translations in the crystal. They are called the lattice constants or lattice parameters. The set of points defined by equation [2] is called a lattice and the set of $\underline{r}_\ell$ are called the lattice vectors.

In diffraction of x-rays by an arbitrary object the radiation interacts with the electrons. If $\underline{k}_o$ is the wave vector of the incident radiation and $\underline{k}$ that of the scattered radiation the phase difference between the two waves scattered by two points separated by $\underline{r}$ is $2\pi(\underline{k}_o-\underline{k})\underline{r}$. Thus the resultant amplitude of the scattered radiation summed over the whole object is

$$F(\underline{r}^*) = \int \rho(\underline{r}) \exp(2\pi i \underline{r}^* \cdot \underline{r}) dv \qquad [3]$$

where

$$\underline{r}^* = \underline{k}_o - \underline{k}. \qquad [4]$$

If the scatterer is an ideal crystal, e.g. has perfect periodicity then from [1] and [3]

$$F(\underline{r}^*) = \sum_{uvw} \int_{\text{unit cell}} \rho(\underline{r}) \exp(2\pi i \underline{r}^* \cdot (\underline{r} + \underline{r}_\ell)) dv$$

$$= \int \rho(\underline{r}) \exp(2\pi i \underline{r}^* \cdot \underline{r}) dv \sum_{uvw} \exp(2\pi i \underline{r}^* \cdot \underline{r}_\ell)$$

and the amplitude has discrete values only at points

$$\underline{r}^* = \underline{h} = h\underline{a}^* + k\underline{b}^* + \ell\underline{c}^* \qquad [5]$$

where h, k, ℓ are integers, everywhere else the amplitude is zero. The three non coplanar vectors $\underline{a}^*$, $\underline{b}^*$, $\underline{c}^*$ (reciprocal lattice constants) satisfy the relations

$$\begin{aligned} &\underline{a} \cdot \underline{a}^* = 1,\ \underline{b} \cdot \underline{b}^* = 1,\ \underline{c} \cdot \underline{c}^* = 1 \\ &\underline{a} \cdot \underline{b}^* = 0,\ \underline{a} \cdot \underline{c}^* = 0 \quad \text{etc.} \end{aligned} \qquad [6]$$

So from [5]:

$$\underline{h} \cdot \underline{a} = h,\ \underline{h} \cdot \underline{b} = k,\ \underline{h} \cdot \underline{c} = \ell \qquad [7]$$

which are called the Laue equations and from equation [4]

$$|\underline{h}| = |\underline{k}_o - \underline{k}| = 2\sin\theta/\lambda \qquad [8]$$

which is the Bragg's law.

The intensity is given by $I(\underline{h}) = F(\underline{h})F^*(\underline{h})$. The intensity measured experimentally depends on the atoms present in the unit cell, their position and a number of additional factors

$$I(\underline{h}) = CLp\, A_{\underline{h}} |F(\underline{h})|^2 \ .$$

C is a constant which depends on the volume and density of the crystal irradiated and the intensity of the incident beam. L represents the dependence of the intensity on the diffraction geometry and it is called the Lorentz factor. p is equal to $(1+\cos^2 2\theta)/2$ and arises from the unpolarized nature of the x-ray beam and the manner in which its reflection efficiency varies with reflection angle.

When x-rays pass through the crystal their intensity is attenuated by absorption. This effect is represented by the factor $A_{\underline{h}}$ which is called the transmission coefficient

$$A_{\underline{h}} = \frac{1}{v} \int_{v} \exp(-\mu(p+q)dv$$

where v is the volume of the crystal, μ is the linear absorption coefficient and p and q are the path lengths of the radiation before and after scattering.

The Fourier transform of the electron density of a single atom is denoted by $f(\underline{h})$ and is called the atomic scattering factor. For a crystal with N atoms per unit cell equation [3] becomes

$$F(\underline{h}) = V \sum_{i=1}^{N} f_i(\underline{h})\exp(2\pi i\underline{h}\cdot\underline{r}_i). \qquad [9]$$

$F(\underline{h})$ is called the Structure Factor.

But the atoms in a crystal undergo thermal motion which reduces the amplitude of the structure factor F. This effect could be taken into account as Debye has shown (19) by multiplying $f_i(\underline{h})$ by $\exp(-2\pi^2 \sum_{j,k} U(i)_{jk} h_j h_k$. Where the matrix $U(i)_{jk}$ represents the thermal motion of the i atom and is called the anisotropic temperature factor.

Since the structure factor F is the Fourier transform of the electron density the electron density is the inverse Fourier transform of the structure factor and

$$\rho(\underline{r}) = \frac{1}{V} \sum_{\underline{h}} F(\underline{h})\exp(-2\pi i\underline{h}\cdot\underline{r}). \qquad [10]$$

From a diffraction experiment which measures the intensity we can deduce FF* but the information about the phase of F, in general a complex quantity, is not measurable. The problem of crystal structure determination is to find the phase of each of the structure factors. The methods which have been applied in this thesis for the solution of this problem are Patterson method and one of the direct methods.

The intensity is the Fourier transform of the convolution (or correlation) of the electron density with itself. From [3]

$$F(r^*)F^*(r^*) = \int \rho(r)\exp(2\pi i\underline{r}^*\cdot\underline{r})dv_r \int \rho(\underline{r}')\exp(-2\pi i\underline{r}^*\cdot\underline{r}')dv_r.$$

$$= \int \rho(\underline{r})\rho(\underline{r}+\underline{u})\exp(-2\pi i\underline{r}^*\cdot\underline{u})dv_r dv_u$$

where $\underline{u} = \underline{r}'-\underline{r}$. The inverse Fourier transform of the intensity is called in crystallography the Patterson function:

$$P(\underline{r}) = \frac{1}{V} \sum_{\underline{h}} FF^{*}\exp(-2\pi i\underline{h}\cdot\underline{r}) \ . \qquad [11]$$

It contains the image of the electron density convoluted with itself and it is a vector map whose peaks are weighted according to the number of electrons of the correlated atoms. The problem is to deduce the positions of the atoms from it. $P(\underline{r})$ is usually poorly resolved and the complexity of its interpretation becomes more involved with an increase in the number of atoms to be determined. If heavy and light atoms are present in the structure the heavy atoms dominate the Patterson function and their positions can be determined.

These positions determine the probable sign of a number of structure factors. Then the positions of the light atoms can be found from a difference synthesis $\Delta\rho$ which is equal to the difference between ρ_o, which is an "ideal" electron density corresponding to the F_o's (observed structure factors) and the "proposed" electron density ρ_c which corresponds to the F_c's (calculated structure factors).

$$\Delta\rho(\underline{r}) = \sum_{\underline{h}} (|F_o(\underline{h})| - |F_c(\underline{h})|)e^{i\alpha_c}e^{-2\pi i\underline{h}\cdot\underline{r}} \qquad [12]$$

α_c is the phase of F_c. $\Delta\rho(\underline{r})$ has peaks which should correspond to the positions of the light atoms.

There is a variety of methods, the direct methods (20), in which the determination of the phases of the F's is attempted by considering solely the structure factor amplitudes. These methods are based on the fundamental principle that the electron density has to be everywhere non-negative.

The method employed here (Chapter 3.4.1) applies in centrosymmetric structures where the phases are 0° or 180°. For this the normalized structure factors $E_{\underline{h}}$, defined by $E^2_{\underline{h}} = |F_{\underline{h}}|^2 / \sum_{i=1}^{N} f_i^2$ is introduced. In 1952 Sayre showed that for any equal-atom structure

$$F_{\underline{h}} = \phi_{\underline{h}} \Sigma F_{\underline{h}'} F_{\underline{h}-\underline{h}'}$$

where $\phi_{\underline{h}}$ is a scaling term. If the structure factors involved are sufficiently large then this equation shows that $F_{\underline{h}} F_{\underline{h}'} F_{\underline{h}+\underline{h}'}$ is positive. Even if the structure factors are not large enough there may be a strong probability that the following relationship is true

$$s(\underline{h})s(\underline{h}')s(\underline{h}+\underline{h}') \sim 1 \qquad [13]$$

where $s(\underline{h})$ means the sign of $F_{\underline{h}}$ and $\sim$ means is probably equal to. The probability that [13] is true is

$$P = \frac{1}{2} + \frac{1}{2} \tanh\{\frac{1}{N}|E_{\underline{h}} E_{\underline{h}'} E_{\underline{h}-\underline{h}'}|\}. \qquad [14]$$

In general an algorithim is set up by assigning symbolic phases to reflections with sufficiently large values of $|E|$ ($\geq$ 1.5 usually) (21). All the symbolic phases are not independent and their number is reduced to a minimum with the help of the relationships [13] (which are called "sigma two relationships") and relationships derived by forming products between the relationships [13] which have a common factor. The probability for these relationships of being correct has to be high ($P > 0.97$) if the method is to work. Then the origin is specified by assigning actual phases (0° or 180°) to a properly chosen set of symbolic phases. The remaining symbolic phases are then found from the relationships derived above. Sometimes no additional symbols need be specified. This is more likely to happen in space groups of higher symmetry and when heavy atoms are present.

With the signs of a few hundred reflections determined it is useful to compute a Fourier map with the E structure factors as coefficients (E map). This will give peaks at the positions of the atoms if the solution is correct.

Once the positions of the atoms are known either from Patterson or direct methods they can be further refined either with difference Fourier synthesis or by least squares.

In the difference Fourier synthesis the atoms are moved from areas where the synthesis is negative towards areas where it is positive.

In least squares small shifts of the atoms are calculated so as to minimize the numerator of the quantity.

$$R_2 = \left[\frac{\sum_{\underline{h}} w(\underline{h}) \left(|F_o(\underline{h})| - |F_c(\underline{h})| \right)^2}{\sum_{\underline{h}} w(\underline{h}) |F_o(\underline{h})|^2} \right]^{1/2}$$

called the weighted R factor. The weight w is to be taken as $w(\underline{h}) = 1/\sigma(\underline{h})$ where $\sigma(\underline{h})$ is the standard error of the corresponding observation. Usually it is not feasible in routine structure determinations involving large numbers of reflections to obtain reliable estimates of σ. Cruickshank et al. (22) suggest that $w(\underline{h}) = (a + b|F_o(\underline{h})| + c|F_o(\underline{h})|^2)^{-1}$. It is then possible to account for systematic unknown errors if $w(\underline{h})\cdot(|F_o(\underline{h})|-|F_c(\underline{h})|)^2$ is not a function of $|F_o(\underline{h})|$.

In the past, before the advent of the use of computers, it was more convenient to use

$$R_1 = \sum_{\underline{h}} (|F_o(\underline{h})| - |F_c(\underline{h})|)/\sum_{\underline{h}} F_o(\underline{h})$$

which is called the unweighted R factor or agreement index.

CHAPTER 3

EXPERIMENTAL PROCEDURES AND CRYSTAL STRUCTURE DETERMINATION

3.1.0 α and β $Na_2Cr_2O_7$. Introduction and Preliminary Survey

Vesnin and Khripin (4) 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°, 270° and 330°. The phases above and below the 240°C transition we will designate, following Samuseve, Palataev and Plyschev (5), as α and β respectively.

As is shown in the following paragraphs the 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 3.1. From single crystal photographs it is apparent that reflections with $k+\ell$ odd are in general considerably weaker than those with $k+\ell$ even and, on heating, the odd reflections become even weaker, disappearing at around 240°C. The $k+\ell$ even reflections 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 $A\bar{1}$.

Table 3.1 Crystal data for α and β $Na_2Cr_2O_7$. Standard errors in the last figures quoted are given in parentheses

Compound	β-$Na_2Cr_2O_7$	α-$Na_2Cr_2O_7$
Space group	$P\bar{1}$	$A\bar{1}$
a (Å)	7.702(10)	7.82(3)
b (Å)	10.380(10)	10.36(3)
c (Å)	9.402(10)	9.54(3)
α	89.41 (10)°	89.5 (3)°
β	109.57 (10)°	110.1 (3)°
γ	114.26 (10)°	113.4 (3)°
V ($Å^3$)	639	659
Z	4	4
D_m	2.73 (1)	
D_x	2.72	2.64
μ(MoKα)	3.67 mm^{-1}	3.56 mm^{-1}

3.1.1a β-$Na_2Cr_2O_7$. Experimental Procedure Sample preparation and crystal data

Crystals of sodium dichromate were grown from melt in an open furnace. The hydrated $Na_2Cr_2O_7 \cdot 2H_2O$ (Shawinigan Reagent, grade 99.5) was heated up to 180°C and kept at this temperature for 24 hours as the crystals lose the water of hydration at 130°C. The anhydrous sample was then heated 20 degrees above the melting point (360°C) and kept at this temperature for a few hours. The sample then was cooled gradually and at around 200°C it was transferred to a dry box containing a dry nitrogen atmosphere.

Powder photographs of the sample sealed in capillary tubes are the same as the powder pattern given for $Na_2Cr_2O_7$ in ASTM x-ray powder data file (23).

The crystals were selected and sealed in thin walled quartz capillary tubes inside the dry box in nitrogen atmosphere. From x-ray precession photographs it was found that the crystals of the room temperature phase belong to the triclinic class. From these precession photographs preliminary cell constants were measured which were used throughout the analysis. In order to determine accurate bond lengths, accurate cell constants were determined from a least squares refinement of the angular settings of 15 reflections, Table 3.2, of a crystal mounted on a Syntex diffractometer. They are given in Table 3.1. The density of 2.73 gm/cm^3 was measured by

Table 3.2 β-$Na_2Cr_2O_7$ Angular settings for 15 reflections.

*hkℓ**	2θ	ω	φ	χ
200	8.69	.01	84.79	48.37
312	17.78	359.93	144.59	76.95
$1\bar{1}4$	19.53	.04	292.77	65.32
$2\bar{1}3$	18.06	359.97	328.44	73.54
$4\bar{1}1$	20.75	360.00	48.83	53.70
$50\bar{1}$	21.72	.01	78.57	36.46
112	12.97	359.99	219.47	55.27
$1\bar{3}0$	19.31	.07	26.52	8.54
$\bar{2}\bar{4}2$	21.32	.11	347.89	.25
$\bar{1}\bar{1}2$	13.17	.09	241.62	18.41
$31\bar{2}$	13.48	.08	109.46	11.60
611	26.73	359.98	86.17	63.82
130	16.94	.08	190.69	12.88
$1\bar{3}0$	19.27	.13	26.61	8.43
224	26.14	.02	207.34	56.88

*The indices are given in the cell a = 10.067, b = 7.702 c = 9.401, α = 109.575, β = 104.225, γ = 70.040.

flotation in an equidensity mixture of CH_3I and $CHBr_3$ and corresponds to four $Na_2Cr_2O_7$ units per unit cell.

Intensity measurements

Intensities were measured with two crystals mounted on precession cameras with MoKα radiation. The first crystal of dimensions 0.23×0.32×0.14 mm was mounted along its [011]* reciprocal axis and was used to record the layers with h = 0,1,2 and layers with k = ℓ-h-n where n = 0,1,2 and 3. The second crystal, 0.31×0.35×0.22 mm, mounted along the [111]* axis was used to record the layers $h,\bar{h},\ell;h,k,k;$ $h,k,-(k+2h)$.

The intensities measured with Joyce-Loebl[1] micro-densitometer were corrected for Lorentz and polarization effect but not for absorption which is effectively uniform over each precession photograph with the crystal settings used.

In all 1181 unique observed reflections were measured. Another 557 unobserved reflections were included in the final set of data plus 64 reflections which were considered as unreliable either because they were too strong to be measured or because they were behind the backstop.

3.1.1b Structure Determination

The N(z) statistical test of Howells, Phillips and Rogers (20) was applied to the intensity measurements of the ($\bar{1}$10) and (010) projections and showed centrosymmetric in-

intensity distribution for the (010) and a hypercentric intensity distribution for ($\bar{1}$10) so the space group P$\bar{1}$ was assumed. The hypercentric distribution suggests noncrystallographic centers of symmetry such as would occur if two parallel noncentrosymmetric motifs are related by a noncrystallographic translation consistent with the supposition of a superstructure.

The structure was initially determined in the space group A$\bar{1}$. The ($\bar{1}$10) and (010) Patterson projections calculated with the $k+\ell$ even intensities gave positions for the chromium atoms which corresponded to the higher symmetry A$\bar{1}$. The Cr-Cr intramolecular vectors were identified in the peaks around the origin of these projections and a model was constructed for the Cr atom positions. Least squares refinement of the scale factors gave an agreement index $R_1 = 0.55$. It was assumed at this stage that the dichromate ion had a confirmation similar to that found in P$\bar{1}$ $Rb_2Cr_2O_7$. With the positions of the Cr atoms roughly known all that was needed for the determination of the oxygen positions was the determination of an azimuthal angle around each Cr-Cr axis to give the orientation of the Cr_2O_7 ion. This was found by considering the packing of the ions and the resultant model gave R = 0.40 for the $h+k$ even reflections. Difference synthesis maps for the (010) and ($\bar{1}$10) projections gave the positions of the Na atoms. This model was then refined by least squares in the space group A$\bar{1}$ using all the $k+\ell$ even reflections to give $R_1 = 0.08$. 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 $k+\ell$ odd reflections (24). In going from space group $A\bar{1}$ to $P\bar{1}$, one of the two sets of centers 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 $R_2 = 0.12$ for the $k+\ell$ odd reflections.

At this stage anisotropic temperature factors were introduced, and the structure was refined further by full matrix least squares. Reflections were weighted by the function $(3.649 - 0.083|F_o|+0.0034|F_o|^2)^{-1}$ (22) except that zero weight was given to unobserved reflections for which $|F_c|<|F_{min}|$ and other reflections for which measurements of F_o were judged to be particularly unreliable. Scattering factors for Na^+, Cr^{++} and O^- (O for the bridging oxygen atoms) were taken from International Tables for X-ray Crystallography (25) and the final weighted agreement index, R_2 was 0.089 and unweighted agreement index R_1 was 0.078. For the $k+\ell$ odd reflections R_2 was 0.109 and R_1 was 0.104. In the final round of refinement 751 observed $k+\ell$ odd reflections were used. In addition the 24 of the 201 unobserved

$k+\ell$ odd reflections for which $|F_c|>|F_{min}|$ were also included. Final parameter shifts were of the order of 0.1σ, none being larger than 0.5σ. The final atomic positions and temperature factors are given in Table 3.3 and the structure factors in Table 3.4.

3.1.2a α-$Na_2Cr_2O_7$. Experimental Procedure

Specimen heating

Air at constant pressure was passed through a tubular electric furnace and was directed from above onto the crystal. The temperature was controlled by adjusting the electric current in the furnace with a potentiometer. No special attempt was made to stabilize the temperature. A Chromel Alumel thermocouple set close above the crystal was used to record the temperature on a chart recorder. The temperature fluctuation never exceeded ±2.5°C during a 60 hour exposure.

Crystal data

The single crystal of β-$Na_2Cr_2O_7$ used for this work was sealed in a thin walled quartz capillary tube in nitrogen atmosphere.

The cell constants were measured from three precession photographs of the (110), ($\bar{1}$01) and (21$\bar{1}$) projections. The crystal was mounted along the [1$\bar{1}$1]* reciprocal axis. For each projection the same reciprocal plane of the room and the high temperature phase was photographed on the same film. The cell constants of the α phase, given in Table 3.1, were

Table 3.3 β-$Na_2Cr_2O_7$ Atomic positional and thermal coordinates

	x	y	z	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Cr1	-0.1939(3)	0.0119(2)	0.1509(2)	215(15)	229(9)	225(9)	96(11)	51(9)	9(7)
Cr2	0.2488(3)	0.0803(2)	0.4091(2)	252(15)	249(9)	195(8)	135(11)	71(9)	30(7)
O11	-0.3849(15)	0.0258(1)	0.1747(9)	195(62)	459(53)	309(41)	167(54)	124(40)	98(37)
O12	-0.2380(16)	-0.1542(10)	0.1238(10)	342(72)	299(43)	345(43)	141(51)	126(43)	-9(35)
O13	-0.1368(16)	0.0913(10)	0.0150(9)	273(67)	328(45)	335(43)	41(51)	128(44)	102(35)
O21	0.3598(16)	0.1634(10)	0.5812(9)	335(71)	341(47)	283(39)	161(52)	50(42)	29(35)
O22	0.3937(18)	0.1479(12)	0.3109(10)	469(86)	635(68)	304(44)	306(69)	199(46)	176(43)
O23	0.1992(20)	-0.0871(10)	0.4072(10)	803(104)	285(46)	388(47)	321(62)	114(55)	117(38)
B12	0.0188(16)	0.0999(10)	0.3237(9)	313(69)	364(49)	261(39)	124(52)	-57(42)	-89(34)
Cr3	-0.1751(3)	0.5287(2)	0.6285(2)	220(15)	210(9)	193(8)	96(10)	56(8)	17(6)
Cr4	0.2332(3)	0.5588(2)	0.9095(2)	213(15)	240(9)	176(8)	107(11)	58(8)	31(7)
O31	-0.3367(19)	0.5531(11)	0.6831(11)	524(90)	458(58)	545(58)	342(67)	336(56)	131(47)
O32	-0.2299(17)	0.3606(9)	0.6031(10)	403(81)	265(44)	419(48)	94(55)	131(49)	-43(37)
O33	-0.1591(17)	0.5969(11)	0.4759(9)	430(77)	501(54)	231(38)	261(58)	91(43)	129(37)
O41	0.3167(17)	0.6520(11)	1.0729(9)	351(73)	460(54)	236(37)	186(57)	78(41)	-8(36)
O42	0.4257(17)	0.5752(12)	0.8634(10)	345(74)	546(64)	344(47)	141(63)	170(46)	-43(43)
O43	0.1086(18)	0.3916(11)	0.9152(11)	418(83)	367(53)	538(57)	180(61)	101(55)	170(45)
B34	0.0762(15)	0.6217(9)	0.7693(9)	241(63)	256(40)	305(40)	72(46)	-47(41)	30(32)
Na1	0.3744(10)	0.3511(6)	0.7359(5)	562(48)	336(26)	281(23)	251(31)	77(26)	43(20)
Na2	-0.2391(11)	0.2267(6)	0.3930(6)	458(53)	400(28)	323(24)	106(35)	173(28)	32(21)
Na3	0.2941(11)	0.8263(6)	1.2146(6)	669(53)	480(33)	319(25)	380(38)	201(28)	85(23)
Na4	-0.2334(9)	0.7414(5)	0.8979(5)	326(43)	338(26)	320(23)	141(31)	135(24)	61(20)

cont'd...

Table 3.3 (cont'd)

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

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

Table 3.4 Observed and calculated structure factors for β-$Na_2Cr_2O_7$

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

Table 3.4 β-$Na_2Cr_2O_7$ (continued)

[illegible]

measured from these films relative to the known cell constants of the β phase. The difference,in spacing and in the angles between rows of reflections of the room and the high temperature phase, was used to calculate the cell constants from the accurately known β cell constants.

Intensity measurements

Intensities were measured from integrated precession photographs taken, with MoKα radiation, from a single crystal mounted along the [1$\bar{1}$1]* reciprocal axis on a precession camera. The crystal had an irregular shape which would be approximated with a spheroid of 0.29 mm height, along [1$\bar{1}$1]*, and a base with 0.19 mm length parallel to the (01$\bar{1}$)* reciprocal plane and 0.15 mm length normal to it. Integrated intensity photographs were taken of the layers $h,-h,\ell$; $h,-(h+1),\ell$; $h,-(h+2),\ell$; $h,k,-k$; $h,k,-(k+2)$; h,k,h; $h,k,h+1$ at an estimated temperature of 260 (±10)°C. The intensities were measured with a Joyce-Loebel microdensitometer and were corrected for Lorentz and polarization effects.

In all 820 reflections were measured. After averaging of the common reflections (see in the next paragraph) a set of 512 observed reflections and 202 unobserved reflections was obtained. Absorption correction was not considered necessary.

3.1.2b Structure Determination

The atomic coordinates obtained during the refinement of the structure of the β phase in space group $A\bar{1}$ were used as the initial coordinates of the α phase structure. This model was refined with isotropic temperature factors, individual scale factors for each layer and unit weights. After three cycles the agreement factor was $R_1 = 0.09$. At this stage the common reflections were averaged. Further refinement was attempted with a Cruickshank weighting scheme and one overall scale but failed to give any significant improvement. The value of the weighted agreement index R_2 was 0.11 and R_1 0.09.

When anisotropic temperature factors for the chromium and sodium atoms were introduced and refined the weighted and unweighted agreement indices dropped to 0.088 and 0.071 respectively.

Finally anisotropic temperature factors were introduced for all atoms and the model refined further. With 100 parameters the agreement indices dropped to $R_2 = 0.054$ and $R_1 = 0.043$. In the final cycle of the refinement 18 unobserved reflections, with calculated structure factors lower than the observed, were included. The reflections were weighted with the function $w = (3.17-0.111|F_o|+0.0025|F_o|^2)^{-1}$. The scattering factors used for the Na^+, Cr^{++}, O^- and O for the bridging oxygen atoms were those given in the

International Tables (25).

The final atomic positions and temperature factors are given in Table 3.5 and the observed and final calculated structure factors in Table 3.6.

3.1.2c Possible Disorder in α-$Na_2Cr_2O_7$

Although the geometry of the dichromate ion in the α-$Na_2Cr_2O_7$ shows bond lengths and angles close to the ones found in the other dichromates the temperature factors of the atoms of the anion are of the order of magnitude of the maximum values found in the other dichromates. Particularly the atoms 022, 023 and B12 have exceptionally large temperature factors. There are two alternative interpretations of these temperature factors, either they represent real thermal effects or the structure is disordered.

In the rest of this section we will examine the possibility of disorder in the α phase. This will be done in terms of certain artificial models:

1) The ordered model refined with structure factors measured above the phase transition (α ordered structure) or refined with $k+\ell$ even structure factors measured at room temperature (β ordered structure).
2) The disordered model, Figure 3.1a, which is generated from the β-$Na_2Cr_2O_7$ structure by a superposition of the β structure and the β structure translated by $(\underline{b}+\underline{c})/2$,

Table 3.5 α-$Na_2Cr_2O_7$. Atomic positional and thermal coordinates

	x	y	z	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Cr1	-0.1842(2)	0.0204(2)	0.1397(2)	362(8)	420(12)	390(8)	164(7)	92(6)	25(7)
Cr2	0.2391(2)	0.0680(2)	0.4086(2)	427(9)	438(13)	336(7)	206(8)	74(7)	21(8)
O11	-0.3569(12)	0.0439(9)	0.1782(8)	649(45)	747(72)	693(45)	366(44)	340(43)	106(47)
O12	-0.2347(11)	-0.1456(9)	0.1159(9)	619(46)	589(61)	759(49)	208(41)	250(41)	-39(43)
O13	-0.1536(12)	0.0891(10)	-0.0088(8)	784(52)	867(73)	565(42)	310(48)	385(44)	269(46)
O21	0.3338(11)	0.1541(9)	0.5757(7)	691(47)	783(69)	466(37)	336(45)	134(38)	-3(43)
O22	0.4107(14)	0.1128(15)	0.3367(10)	633(55)	1820(137)	852(60)	98(69)	425(56)	-310(76)
O23	0.1523(18)	-0.0981(12)	0.4107(11)	1693(99)	641(74)	826(59)	769(72)	-22(65)	22(65)
B12	0.0504(11)	0.1137(9)	0.2914(9)	667(46)	450(52)	896(55)	238(39)	-210(41)	33(45)
Na1	0.3377(8)	0.3429(6)	0.7265(5)	1021(36)	798(44)	586(25)	540(31)	275(27)	168(28)
Na2	-0.2351(7)	0.2382(6)	0.3934(5)	690(27)	697(37)	608(25)	93(24)	302(24)	95(23)

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 given in Table 3.3.

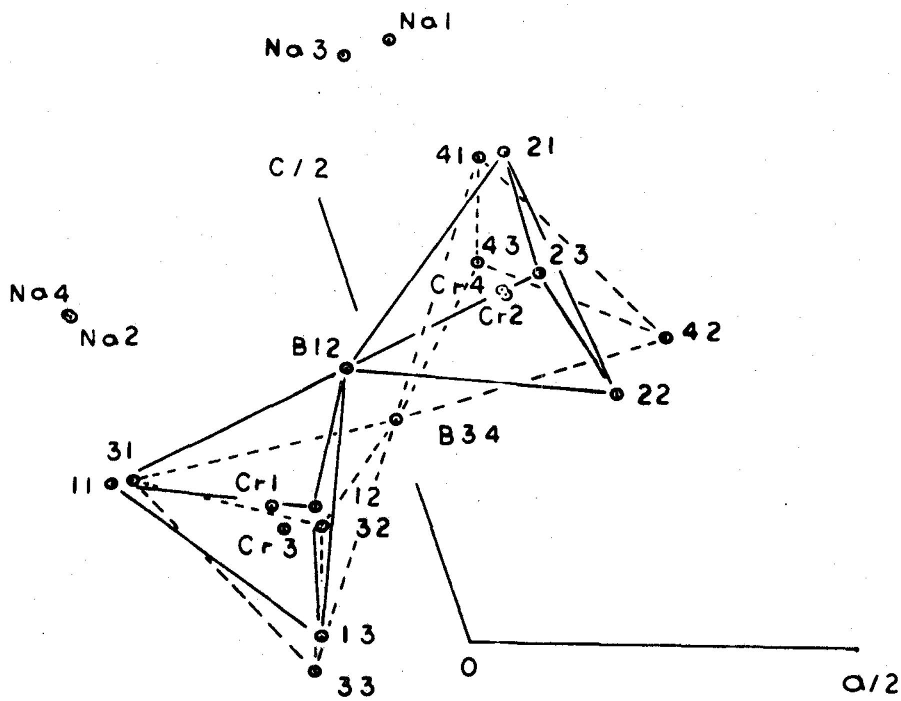
Table 3.6 α-$Na_2Cr_2O_7$. Observed and calculated structure factors.

Unobserved reflections are marked with an asterisk. U indicates unreliable measurement which was given zero weight during refinements.

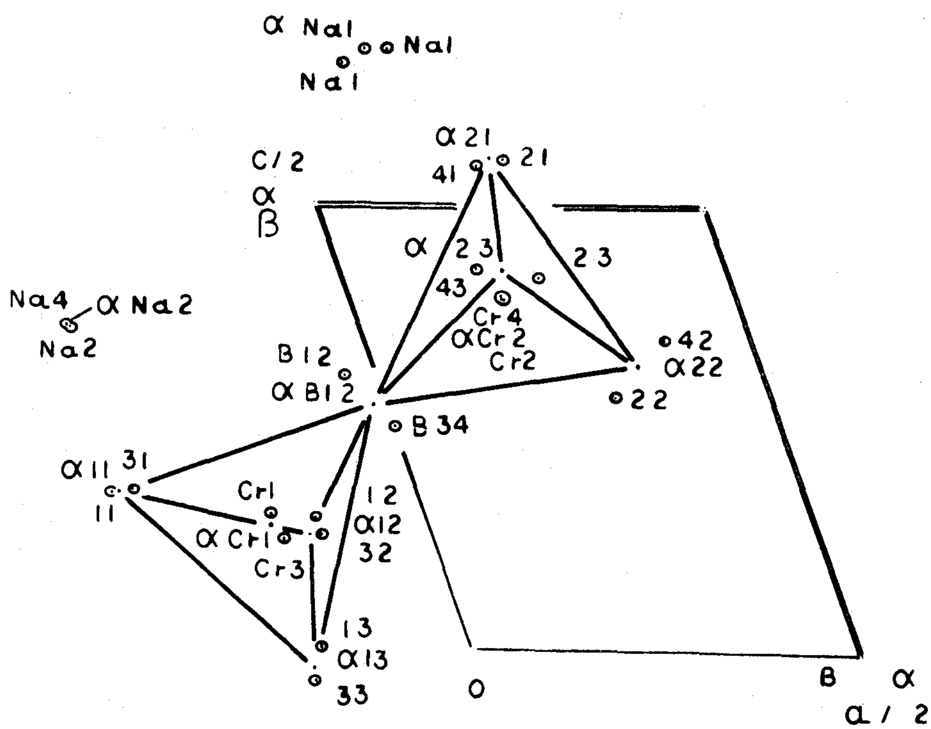
K	L	FO	FC
H=0			
0	2*	4	0
0	4	115	116
0	6	33	34
0	8	18	19
0	10*	8	9
1	3	65	66
1	5	76	77
1	7	65	62
1	9*	9	1
1	-3	13	12
1	-5	24	24
1	-7	49	50
1	-9	11	10
1	11	24	23
1	-11	23	20
2	0	123	117
2	4	60	59
2	6	19	20
2	8	13	14
2	-2	53	48
2	-4	50	52
2	-6	18	11
2	-8	32	35
2	10*	9	4
2	-10*	9	4
2	-12*	9	3
3	-1	105	104
3	-3	43	41
3	-5	25	25
4	0	22	21
4	-2*	6	0
4	-4	120	112
4	-6	20	19
5	1	41	40

Table 3.1 $Na_2Cr_2O_7$ β disordered structure and α ordered structure.

a) $Na_2Cr_2O_7$ β disordered structure (orthogonal projection).



b) $Na_2Cr_2O_7$. Superposition of the orthogonal projections of the α ordered structure and the β disordered structure.



the A centering symmetry operation. In this model atoms which in the β-$Na_2Cr_2O_7$ were related by the A pseudo-centering are in the β disordered model very close to each other. The distance between them will be called the "disorder separation". This model corresponds to a disorder structure, space group $A\bar{1}$, in which each dichromate ion has two possible conformations similar to the ones found in β-$Na_2Cr_2O_7$, each possible conformation occurring with equal probability. This model can be refined using the structure factors measured above the phase transition (α-disordered structure) or using the $k+\ell$ even structure factors measured at room temperature (β-disordered structure).

All these structures with the exception of the β disordered structure have been refined.

From the experimental evidence of only small changes in the intensities of even reflections and small changes in volume, we expect that the structure of the α phase will differ very little either from the β ordered structure if the α structure is ordered or from the β disordered structure if the α structure is disordered.

The α disordered structure with isotropic temperature factors, 89 variables, gave final agreement indices $R_1 = 0.051$ and $R_2 = 0.063$. In this structure it is not possible to identify two dichromate ions with interatomic distances and angles close to those found in other dichromate structures. Bond lengths for the terminal oxygen atoms deviate up to 0.1 Å from the usual values of 1.60 to 1.63 Å. The disorder separations in this structure, Table 3.7, when compared with those of the β disordered structure show no difference except for the Cr1, O32 and B12 for which the separation has decreased and the Na_2 for which it has increased. This indicates that if the α structure is disordered the Cr_2O_7 ions are closer to their mean positions than they are in the β phase.

The β ordered structure with anisotropic temperature factors, 100 variables, gave an agreement index $R_1 = 0.081$, using unit weights. The geometry for the dichromate ion is similar to that found in the α ordered model, Table 3.8, but the Cr-O bond lengths are rather short, especially the Cr2-B12 distance of 1.71 Å. In Table 3.9 we compare the temperature factors of the α and β ordered structures with those found in β-$Na_2Cr_2O_7$. The temperature factors of the a ordered structure have been corrected to room temperature by reducing them by the empirical factor of 0.3. The temperature factors which are starred (*) are for those atoms which show significant deviations from room temperature values. The atoms marked in Table 3.9 with a dagger (†) show significant deviations only in the β ordered structure. For these atoms the true disorder separation should be zero in the

Table 3.7 Disorder separations in α and β disordered structures

	Disorder separation in Å	
	β disordered structure	α disordered structure
Cr1-Cr3	0.31 Å	0.19 Å
Cr2-Cr4	0.21	0.25
O11-O31	0.35	0.28
O12-O32	0.26	0.27
O13-O33	0.37	0.34
O21-O41	0.28	0.30
O22-O42	0.97	0.71
O23-O43	0.67	0.65
B12-B34	0.76	0.58
Na1-Na3	0.53	0.40
Na2-Na4	0.14	0.40

Table 3.8 Geometry of the dichromate ion in α and β ordered structure

	Distances in Å angles in degrees α sodium ordered structure	β sodium ordered structure
	Distances and Angles	
Cr1-O11	1.620 Å	1.598 Å
-O12	1.604	1.607
-O13	1.627	1.586
B12	1.785	1.779
O11-Cr1-O12	110.6°	110.1°
O13	112.3	112.1
B12	108.7	109.2
O12 O13	109.6	110.4
B12	110.3	109.4
O13 B12	105.2	105.4
Cr2-O21	1.604 Å	1.595 Å
O22	1.618	1.554
O23	1.583	1.590
B12	1.750	1.712
O21-Cr1-O22	109.2°	109.7°
O23	111.2	111.7
B12	110.4	110.6
O22 O23	109.1	108.3
B12	106.7	107.1
O23 B12	110.0	109.3
Cr1-B12-Cr2	135.1°	136.6°
Cr1-Cr2	3.27 Å	3.24 Å

Table 3.9 Principal axes of thermal ellipsoids in β-$Na_2Cr_2O_7$ and in α and β ordered structures

Atom	Cr1			Cr2			O11			O12			O13			O21		
β1	16	15	14	17	14	14	22	17	12	20	18	16	22	18	14	20	18	16
β2	16	14	14	16	15	13	26	21	14	22	21	15	23	20	14	22	19	15
β ord.str.	23*	16	15†	20*	16	14†	26	20	16	25*	19	17†	26*	23*	18*	26*	21	17†
α ord. str.	17	16	15	18	16	14	22	21	17	23	20	18	24	22	15	23	21	17

Atom	O22			O23			B12			Na1			Na2		
β1	26	20	16	30	20	13	24	20	12	25	17	16	24	19	17
β2	26	19	16	26	20	17	23	16	13	26	18	17	18	18	17
β ord. str.	62*	21	13*	45*	22	15	52*	17	14	40*	19	17	22	20	18
α ord. str.	39*	21	17	37*	22	15	32*	17	15	26	20	18	25	20	17

The axes are given in 10^{-2} Å. The α and β ordered structure axes have been corrected to room temperature.

* Atoms which show significant deviations from room temperature values.

† Atoms which show significant deviations only in the β ordered structure.

β2 Signifies that the temperature factor belongs to the atom related by a pseudotranslation with the one named in the table.

disordered α structure and for all practical purposes they can be considered ordered[†] In almost all cases the major axis in the β ordered refinement is larger, as one expects from the disorder separation in this model, but the temperature factors for the α ordered structure are normal except for the 022, 023 and B12 atoms which show significantly large deviations both in α and β ordered structures. The major axes in the α phase are all the same size as in the β phase (except for the three anomalous ones) and almost all are smaller than temperature factors of the β ordered structure.

Hamilton's statistical test (26) applied to the α ordered structure (R_1 = 0.043, R_2 = 0.054, 100 variables) and the α disordered structure (R_1 = 0.051, R_2 = 0.063, 89 variables) shows that the α disordered structure must be rejected at the 0.005 significance level.

The geometry of the dichromate ion in the α ordered structure has bond lengths and angles very similar to those found in the other dichromates while the geometry of the anions of the α disordered structure is much less reasonable.

[†]The disorder separation calculated for these atoms, α ordered structure, arises because the α disordered structure has been calculated with isotropic temperature factors. The real anisotropy of the temperature factors is fitted by separating the atoms by about 0.2 Å .

As was mentioned in section 3.1.0 the intensities of the reflections of a single crystal of $Na_2Cr_2O_7$ have been observed as a function of temperature from a series of precession photographs. Reflections with $k+\ell$ = odd become weaker as the temperature is raised, becoming zero above the transition temperature while reflections with $k+\ell$ even change only slightly. No diffuse scattering was observed around the positions of the $k+\ell$ odd reflections either below or above the transition and their shape remained sharp up to the transition, further indicating that the phase transition does not involve disorder.

From the discussion above the only feature which suggests that the α phase is disordered is the anomalously large temperature factors of the atoms 022, 023 and B12. On the other hand, the statistical test, the molecular geometry, the general reduction of the disorder separations or anisotropic temperature factors and the absence of any diffuse reflections in the x-ray photographs all suggest that the structure is ordered.

If this is the case, the atoms 022, 023 and B12 must have large real thermal motions and this effect will be discussed in Chapter 4.

3.2.0 $Rb_2Cr_2O_7$.Introduction

$Rb_2Cr_2O_7$ is polymorphic. At room temperatures it has been observed in four forms two monoclinic VII $P2_{1/n}$ and X C2/c and two triclinic β1(VIII)$P\bar{1}$ and β2$P\bar{1}$. The VII, X and β1 are grown from aqueous solutions (8), the β2$P\bar{1}$ is obtained by cooling from a high polymorph. The VII ($P2_1/n$) phase is metastable (27,28,29) however its stability differs only slightly from that of α$P\bar{1}$ and the two forms may exist in contact for a long period (29). β1$P\bar{1}$ $Rb_2Cr_2O_7$ undergoes an irreversible transition to an unknown structure at 318°C. This transition takes place slowly and with a well-defined boundary (6), on further heating a reversible transition occurs at 337°C. On cooling the 318° effect disappears and is replaced by a reversible phase transition at 260°C to a new triclinic phase, the β2 $P\bar{1}$ $Rb_2Cr_2O_7$.

A knowledge of the structure of the various polymorphous is necessary in order to understand the nature of phase transitions between them. We have determined the structure of β1(VIII) $P\bar{1}$ $Rb_2Cr_2O_7$ (see also (9)). During the course of our work we learned of the work of P. Löfgren and K. Waltersson (10) and P. Löfgren (11) who have determined the C2/c and $P2_1/n$ structures. We have also briefly examined the β2 $P\bar{1}$ phase.

3.2.1a <u>β1(VIII) P$\bar{1}$ $Rb_2Cr_2O_7$. Experimental Procedure</u>

<u>Sample preparation and crystal data</u>

An ion exchange column was prepared in the Rb salt form through treatment with RbI. The column was then treated with $Na_2Cr_2O_7$. Crystals were obtained by slow evaporation of the solution at 42°C.

Originally the crystals studied from this sample were monoclinic space group $P2_1/n$. After six months only triclinic (β1) could be found.

Preliminary studies of the triclinic single crystals using precession and Weissenberg photographs showed that the cell constants agreed with those given by Klement and Schwab (6). Accurate cell constants were measured from Weissenberg photographs calibrated with rutile (a = 4.59369, c = 2,95814 Å (30) by mounting first the rutile crystal and then the $Rb_2Cr_2O_7$ on the same camera and recording their diffraction patterns on the same film. The density of 3.12 gr. cm^{-3} given in (31) corresponds to four $Rb_2Cr_2O_7$ units per unit cell. The crystal data are listed in Table 3.10.

<u>Intensity measurements</u>

Intensities were measured on a Joyce-Loebel microdensitometer from integrated Weissenberg photographs of the layers with k = 0, 1, 2, 3, 4 taken with CuKα radiation using a crystal of dimensions 0.06×0.20×0.06 mm with the long edge along the <u>b</u> and integrated precession photographs

Table 3.10 Crystal data for β1 and β2 $Rb_2Cr_2O_7$. Standard errors in the last figures quoted are given in parentheses.

Compound	β1 $Rb_2Cr_2O_7$	β2 $Rb_2Cr_2O_7$
System	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	13.554 (1)	7.60 (3)
b (Å)	7.640 (3)	7.39 (3)
c (Å)	7.735 (2)	7.85 (3)
α	93.64 (20)°	90.2 (4)°
β	98.52 (1)°	70.0 (4)°
γ	88.80 (4)°	70.5 (4)°
V(Å^3)	790	387
Z	4	2
D_m	3.12	
D_x	3.25	
μ(MoKα)	15.78 mm^{-1}	
μ(CuKα)	40.44 mm^{-1}	

of the layers with ℓ = 0, 1, 2 and h = 0, 1, 2 taken with MoKα radiation using a second crystal with dimensions 0.09×0.30×0.09 mm with the long edge along the b.

The intensities were corrected for Lorentz and polarization effects but not for absorption. A standard error (σ) was estimated for each intensity measurement for use in weighting the observed structure factors during the least-squares refinement. Each unobserved reflection was assigned the value of the local minimum observed intensity. In all 3221 measurements were made of 2881 independent reflections, of which 1618 were observed and 1263 unobserved.

3.2.1b Structure Determination

It was assumed that the structure of triclinic $Rb_2Cr_2O_7$ would be related to that of triclinic $K_2Cr_2O_7$ (2) since it had a similar unit cell and therefore it was assumed that the space group was also $P\bar{1}$. The structure was solved from the (010) and the (001) Patterson projections. In the (001) projection the Rb-Rb and Rb-Cr peaks were concentrated in a few regions in the map giving big peaks with the individual Rb-Rb or Rb-Cr vectors completely unresolved. Nevertheless this helped to give a rough estimate of the Rb x,y coordinates, which were refined by difference Fourier synthesis. Positions for the Cr atoms were determined from the difference synthesis and with successive difference syntheses the x and y coordinates of the oxygen atoms were found. The z coordinates were determined from the (010) Patterson projection for the Rb and Cr atoms and from the (010) difference synthesis for the oxygen atoms.

This model was refined with isotropic temperature factors with a full matrix least-squares program to an agreement index of $R_2 = 0.08$. At this stage anisotropic temperature factors were introduced and the model was refined further. Throughout the refinement a scale factor for each of the 11 independently measured layers was used. The scattering factors used for Rb^+, Cr^{++}, O (bridging oxygen) and O^- (terminal oxygen atoms) were those given in the International Tables (25) corrected for dispersion using the mean value of the real parts of the corrections for CuKα and MoKα radiations (25). In the refinement the weight used was $1/\sigma^2$. Comparison between F_o and F_c for the largest values of F_o at small 2θ, showed that systematically F_o was less than F_c indicating secondary extinction. The effect was appreciable for the 400 and 102 reflections only and their weight was set to zero. The weight was set to zero also for all unobserved reflections with $F_c<F_o$ and for 43 other reflections judged a priori to be unreliable. The final weighted agreement index R_2 was 0.058 and the unweighted agreement index R_1 0.063. The mean value of $w(|F_o|-|F_c|)^2$ plotted as a function of F_o showed no systematic variation which would indicate that the

weighting scheme was inadequate.

The final atomic coordinates and temperature factors are given in Table 3.11. The observed and final calculated structure factors are given in Table 3.12.

3.2.2 β2 P$\bar{1}$ $Rb_2Cr_2O_7$. Experimental Procedure

Sample preparation and crystal data

Crystals of $Rb_2Cr_2O_7$ in powder form were heated above the melting point (390°C) and then they were gradually cooled. Crystals from the sample were mounted on a precession camera. The x-ray photographs showed that the crystals were twinned and belonged to the triclinic crystal class. The existence of centers of symmetry in β1 $Rb_2Cr_2O_7$ and in β1 $K_2Cr_2O_7$ to whose structures the β2$Rb_2Cr_2O_7$ probably is similar suggest as P$\bar{1}$ the most probable space group of the β2$Rb_2Cr_2O_7$. The cell constants measured from uncalibrated precession photographs are given in Table 3.10.

The volume of 387 $Å^3$ corresponds to two units of $Rb_2Cr_2O_7$ per unit cell.

It was found that the twins were related by a mirror plane parallel to the a,b axis (twinning plane).

The structure of the phase is discussed in Chapter 5.6.

Table 3.11 β1 $P\bar{1}$ $Rb_2Cr_2O_7$ atomic positional and thermal coordinates.*

Atom	x	y	z	Temperature factor components					
				β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rb1	0.13528	0.11118	0.87628	37	91	106	-12	20	-18
Rb2	-0.15303	0.22589	0.62431	32	122	73	-8	6	16
Rb3	0.34205	0.55555	0.80287	24	102	88	-2	8	12
Rb4	0.62878	0.78601	0.70265	37	131	86	-7	14	6
σ(Rb)	0.00011	0.00019	0.00016	1	4	3	2	1	3
Cr1	0.1107	0.2853	0.3915	24	73	73	-16	4	-7
Cr2	-0.0853	0.3531	0.1361	26	71	79	-2	13	7
Cr3	0.3883	0.0613	0.7559	28	93	84	-8	13	1
Cr4	0.5826	0.3022	0.7157	26	85	78	-12	13	-0
σ(Cr)	0.0002	0.0003	0.0003	2	6	4	3	2	4
B12	0.0238	0.4283	0.2734	50	59	105	0	10	-10
O11	0.1994	0.4025	0.4953	23	117	193	9	-13	-67
O12	0.1543	0.1463	0.2571	46	168	93	28	11	-27
O13	0.0546	0.1833	0.5225	40	267	122	2	25	49
O21	-0.1478	0.5180	0.0506	21	73	192	15	15	54
O22	-0.1528	0.2493	0.2534	44	91	80	-20	13	-2
O23	-0.0546	0.2166	-0.0158	46	128	80	23	14	-13
B34	0.4712	0.1857	0.6530	37	111	127	-41	15	32
O31	0.2966	0.0102	0.6072	35	135	142	-5	16	24
O32	0.3496	0.1818	0.9121	29	151	97	8	21	-22
O33	0.4430	-0.1138	0.8289	48	140	156	-7	-14	4
O41	0.6197	0.3717	0.5466	69	115	103	1	55	31
O42	0.6678	0.1800	0.8150	34	129	191	16	27	39
O43	0.5604	0.4666	0.8438	48	118	104	6	34	-17
σ(O)	0.0007	0.0013	0.0012	8	26	20	11	10	17

*The standard errors are those indicated by the least-squares refinement. The temperature factors appear in the structure factor calculation as exp $(-10^{-4}\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell))$.

Table 3.12 β1-$Rb_2Cr_2O_7$. Observed and calculated structure factors

Unobserved reflections are marked with an asterisk. U indivates an unreliable measurement and X indicates a reflection believed to show extinction effects. S is the estimated standard error of FO.

H	L	FO	FC	S
		K= 0		
1	0*	4	1	2
2	0	20	17	8
3	0*	7	7	4
4	0X	268	333	268
5	0	14	7	14
6	0	60	54	3
7	0*	12	15	6
8	0	71	66	4
9	0*	15	5	7
10	0	60	56	4
11	0*	17	13	8
12	0*	17	5	8
13	0*	17	10	8
14	0	45	31	6
15	0*	14	8	7
16	0	16	23	16
0	1	19	14	19
-1	1*	6	4	3
1	1	21	22	1
-2	1	16	14	16
2	1	10	20	10
-3	1	44	42	3
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Table 3.12 β1-$Rb_2Cr_2O_7$ (continued)

		FO	FC	S
1	1	160	158	24
-1	1	230	267	77
1	-1*	6	6	3
-1	-1	164	171	16
2	1	14	15	2
-2	1	6	9	6
2	-1	185	165	19
-2	-1	181	183	16
3	1	37	39	2
-3	1	194	188	20
3	-1	123	112	13
-3	-1	16	16	6
4	1	15	17	3
-4	1	25	23	2
4	-1	137	136	15
-4	-1	142	151	15
5	1	100	101	9
-5	1	231	241	23
5	-1*	9	1	5
-5	-1	119	126	6
6	1	13	18	4
6	-1*	10	7	5
-6	-1	131	130	9
7	1*	12	8	6
7	-1	39	34	3
-7	-1*	12	7	6
8	1*	13	5	6
8	-1U	46	30	46
-8	-1	93	88	28
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

		FO	FC	S
-5	-3	101	103	7
6	-3	66	78	3
-6	3	47	46	2
6	-3	71	70	3
-6	-3	137	138	16
7	3*	14	5	7
-7	3	74	70	8
7	-3	20	24	4
-7	-3	47	43	3
8	3*	15	7	7
-8	3	89	83	4
8	-3	32	34	3
-8	-3*	15	4	7
9	3*	15	9	8
9	-3	25	29	4
-9	-3	26	32	4
10	3	42	40	4
10	-3*	15	6	8
11	3	24	23	5
11	-3*	15	8	8
12	3*	14	6	7
12	-3*	15	18	8
13	-3*	15	12	7
0	4	99	101	6
0	-4*	[illegible]	7	6
-1	4	25	25	3
-1	-4	51	49	2
1	-4	50	50	3
1	4	18	20	4
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

		FO	FC	S
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

H	L	K=-3		
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

		FO	FC	S
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

		FC	FC	S
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Table 3.12 β1-$Rb_2Cr_2O_7$ (continued)

H	L	FO	FC	S
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Table 3.12 β1-$Rb_2Cr_2O_7$ (continued)

H	K	FO	FC	S
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

L = 2

H	K	FC	FC	S
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Table 3.12 β1-$Rb_2Cr_2O_7$ (continued)

K	L	FO	FC	S
-7	4*	28	10	14
7	4	64	60	6
-7	-5*	30	2	15
7	-5	81	81	6
-7	5*	30	4	15
7	5*	31	[illegible]	15
-7	-6	32	33	8
7	-6*	33	34	16
-7	6*	33	21	16
7	6	80	81	13
-7	-7*	14	14	17
7	-7*	45	4	17
-8	0	37	38	5
8	0	33	38	16
-8	-1	143	147	5
8	-1	41	50	3
-8	1	27	24	9
8	1	77	79	15
-8	-2*	23	14	12
8	-2	95	36	7
-8	2	71	68	4
8	2*	25	6	13
-8	-3	115	115	6
8	-3	66	70	5
-8	3*	26	7	13
8	3	43	43	6
-8	-4	67	77	7
8	-4*	29	10	14
-8	4*	29	2	14
8	4*	29	[illegible]	15
-8	-5*	30	6	15
8	-5*	31	4	16
-8	5	80	52	6
8	5*	32	10	16
-8	-6	60	50	5
8	-6*	33	18	17
-8	6*	33	1	17
8	6*	34	2	17
-8	-7	45	55	6
8	-7*	35	7	18
-9	0	66	63	2
9	0	50	55	2
-9	-1*	24	20	12
9	-1*	25	[illegible]	13
-9	1*	24	[illegible]	12
9	1	127	14[illegible]	10
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

K	L	FC	FC	S
-11	-4*	31	7	15
11	-4*	32	12	16
-11	4*	32	10	16
11	-5	74	78	8
-11	-6*	35	17	17
11	-6*	35	2	18
-11	-7*	36	8	18
11	-7*	36	2	18
-12	0*	26	16	14
-12	-1	102	107	7
12	-1U	52	71	52
-12	1*	29	5	14
12	1	50	51	15
-12	-2*	29	14	15
12	2*	31	4	15
-12	-3	41	54	5
12	3*	32	17	16
-12	-6*	35	20	18
12	-6*	36	4	18
-12	-7	51	61	6
12	-7*	37	2	18
13	1	92	103	46
-13	-3	56	48	4
13	3	67	68	7

K L H= 0

K	L	FO	FC	S
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

K L H=-1

K	L	FO	FC	S
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

K L H=-2

K	L	FO	FC	S
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

3.3 $Cs_2Cr_2O_7$. Experimental Procedure

Crystal data

Crystals of $Cs_2Cr_2O_7$ were grown from aqueous solutions prepared from $Cs_2Cr_2O_7$ Alfa Inorganics, Reagent, 99.9%. The crystals obtained were needle like thin ($\sim$ 0.02 mm) plates of orange colour. The crystals examined with a polarizing microscope showed very sharp extinction. Preliminary studies with Weissenberg and precession cameras showed that the crystals were triclinic and twinned. Diffuse streaks indicated that the crystals were disordered as well. The photograph given in Figure 3.2 was obtained with a Weissenberg camera. The crystal was mounted with its needle axis lying approximately along the spindle axis of the camera. The photographs, Figures 3.3 and 3.4, were obtained with a precession camera from the same crystal. Because the 3.3 and 3.4 photographs show diffuse streaks it was not possible to determine the position of these planes accurately enough. The cell constants given in Table 3.13 should only be regarded as approximate.

Figure 3.2 $Cs_2Cr_2O_7$ $h0\ell$ Weissenberg photograph. Cu unfiltered radiation

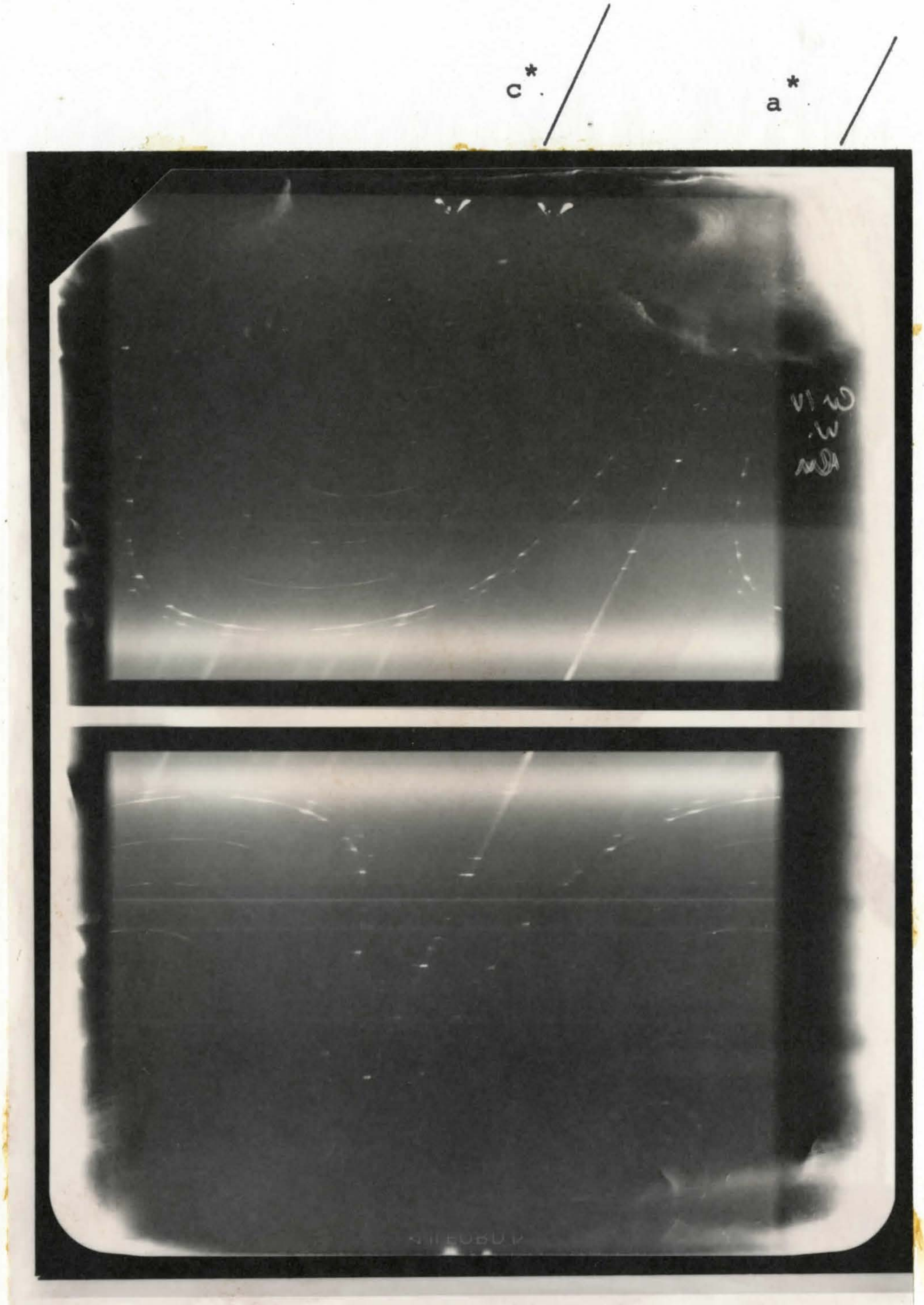


Figure 3.3 $Cs_2Cr_2O_7$ *hk0* precession photograph.
(Mo radiation, spindle axis 18°15')

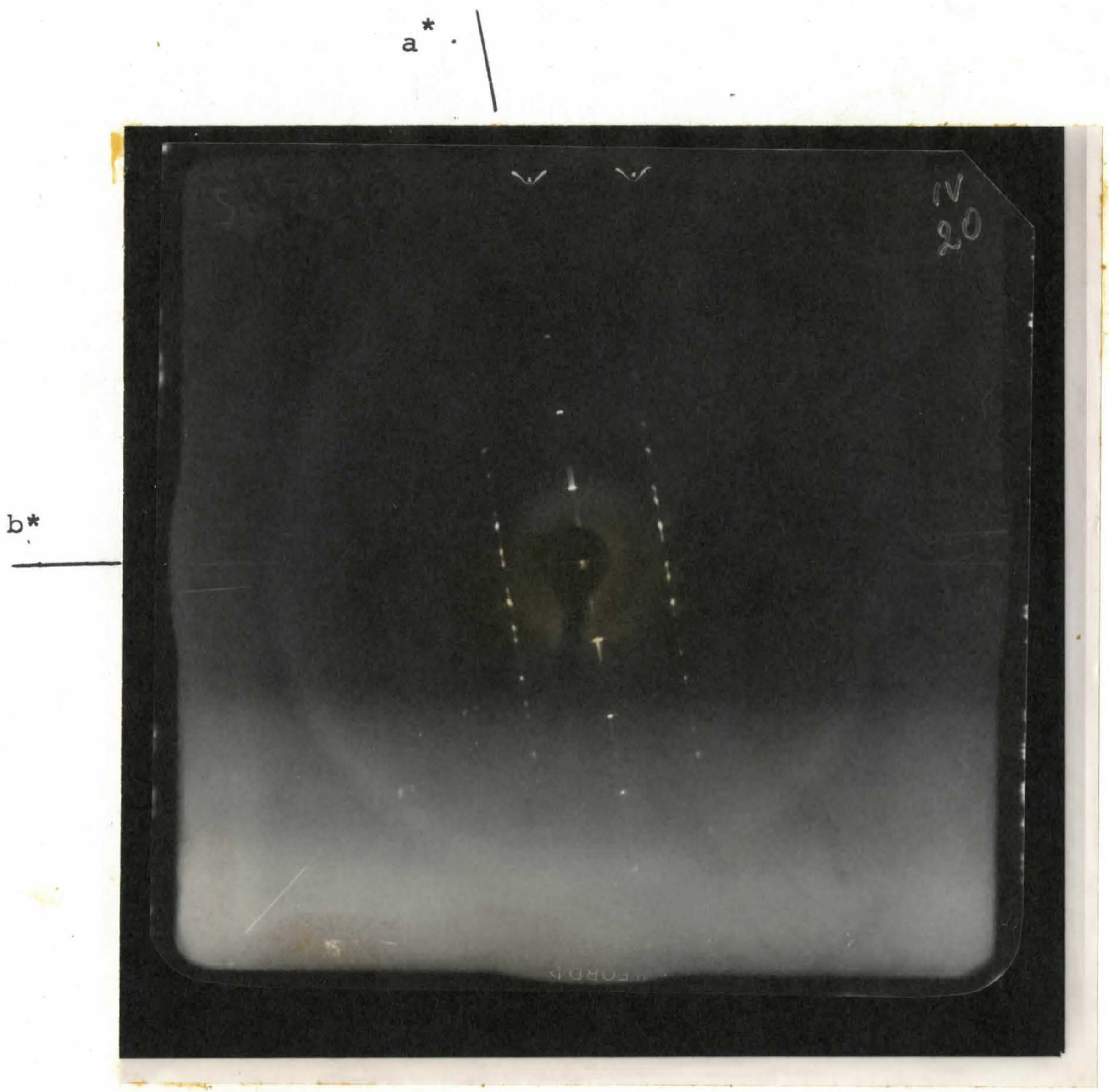


Figure 3.4 $Cs_2Cr_2O_7$ *0kℓ* precession photograph. (Mo radiation, spindle axis 99°35')

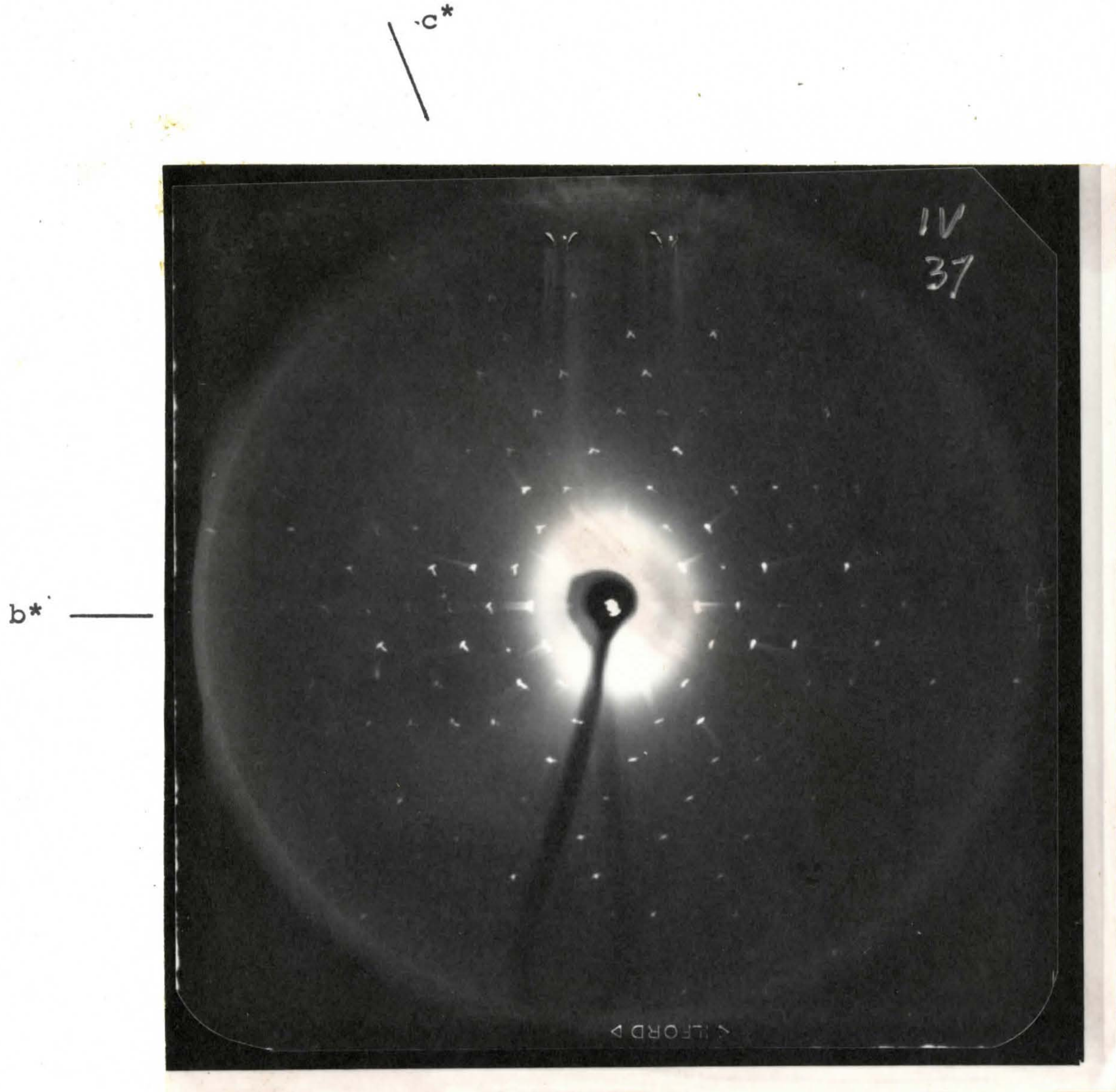


Table 3.13 $Cs_2Cr_2O_7$. Crystal data*

Compound	$Cs_2Cr_2O_7$
Space group	$P\bar{1}$
a (Å)	7.8
b (Å)	7.9
c (Å)	8.5
α	110.5°
β	98.3°
γ	95.7°
V ($Å^3$)	482
Z	2

*These cell constant should be regarded as approximate. See text.

3.4.0 $NaRbCr_2O_7$ and $NaCsCr_2O_7$. Introduction

The only congruently melting compounds found so far in the binary systems of alkali metal dichromates are $NaRbCr_2O_7$ and $NaCsCr_2O_7$, Samuseva, Poletaev and Plyushev (5).

We undertook the determination of the $NaRbCr_2O_7$ structure since the presence of Cs in $NaCsCr_2O_7$ would have resulted in a less accurate determination of the Cr_2O_7 ion.

3.4.1a $NaRbCr_2O_7$. Sample Preparation

A mixture of powdered anhydrous $Na_2Cr_2O_7$ prepared from $Na_2Cr_2O_7 2H_2O$ (Shawinigan, Reagent 99.5%) and powdered $Rb_2Cr_2O_7$ (Alfa Inorganics) in molecular ratio 1:1 was heated 20° above the melting point (362°) and kept at this temperature for a few hours, then it was cooled gradually and at around 200°C was transferred to a dry box with nitrogen atmosphere.

The crystals selected from the sample were hygroscopic and were sealed in thin walled quartz capillary tubes in a dry nitrogen atmosphere. Under examination with a polarizing microscope the crystals showed poor extinction so the final selection of good crystals was made with a precession camera.

3.4.1b $NaRbCr_2O_7$ Preliminary Investigation and Determination of the Structure with Precession Photographs

Preliminary studies of single crystals using a precession camera showed that the crystals were monoclinic with approximate cell constants close to those given in Table 3.14. The $h0\ell$, $h1\ell$, and $hk0$ layer photographs showed systematic absences for $h0\ell$ reflection with ℓ odd and for $0k0$ reflections with k odd. These systematic absences identify the space group uniquely as $P2_1/c$. The volume of the unit cell corresponds to 8 $NaRbCr_2O_7$ units per unit cell. The structure was solved and refined initially from photographic measurements but was later refined using diffractometer measured intensities.

Intensities were measured from integrated precession photographs of the layers $hk0$, $hk1$, $h0\ell$, $h1\ell$. The crystal was mounted on the precession camera with its a* axis along the spindle axis. MoKα radiation was used. The intensities were corrected for Lorentz and polarization effects and were scaled with a least squares program written by Dr. J. S. Stephens. Averaging the common reflections gave 600 unique observed reflections.

A three dimensional Patterson function calculated with these reflections showed a well defined peak, which was attributed to a Rb-Rb vector, in the $z = \frac{1}{2}$ Harker section.

From this Rb coordinates were chosen and these gave a

Table 3.14 Crystal data for $NaRbCr_2O_7$ and $NaCsCr_2O_7$. Standard errors in the last figures quoted are given in parentheses

Compound	$NaRbCr_2O_7$*	$NaCsCr_2O_7$†
Space group	$P2_1/c$	$P2_1/c$
a (Å)	12.947 (15)	12.98 (2)
b (Å)	11.133 (11)	11.58 (2)
c (Å)	10.037 (18)	10.10 (2)
β	93.42 (8)	93.8 (2)
V ($Å^3$)	1444	1514
Z	8	8
D_x	2.98	
μ(MoKα)	10.25 mm^{-1}	

*measured on diffractometer

†measured from film, may be systematically too small by one standard deviation.

satisfactory agreement between observed and calculated structure factors (R_1 = 55%).

Concurrently a solution was attempted with sign determining relationships (Chapter 2). The x-ray 67 programs were used for this. There were 215 reflections with normalized structure factors $E \geq 1.2$ but only 110 reflections with $E \geq 1.5$. The largest E value was 3.13. The sigma two relationships were calculated for the set of reflections with $E \geq 1.2$ and a solution of the phase problem was attempted with 80 of the highest E values in the fundamental set.

After two cycles the signs of 190 reflections with $E \geq 1.2$ were determined. An E map of the $h0\ell$ projection was calculated and showed Rb peaks at the same positions as were determined from the Patterson synthesis.

Additional strong peaks separated by about 2 Å in projection were suspected of being Cr atoms. A three dimensional E map showed that such an interpretation was consistent with the 3 Å intramolecular Cr-Cr distance found in the Cr_2O_7 ion in other structures. A least squares refinement of these positions gave a satisfactory agreement index of 0.42.

The remaining Na and O atoms were determined from successive 3-dimensional difference synthesis. The model , refined with a full matrix least squares program and with isotropic temperature factors and unit weights, gave R_1 = 0.10.

3.4.1c <u>Crystal Data and Intensities Measured on the Diffractometer</u>

A single crystal sealed in a thin walled quartz capillary tube was selected for cell constant and intensity measurements with the Syntex diffractometer. The crystal had an irregular shape which was approximated by 12 bounded planes. The Miller indices of the bounded planes and their distance from the center of the crystal are given in Table 3.15. The approximate volume of the crystal was 6×10^{-3} mm^3. The crystal was mounted on the diffractometer with the [563]* reciprocal axis close to the ϕ axis. Accurate cell constants measured from the angular settings of 14 low angle reflections, Table 3.16, MoKα radiation (λ = 0.71069 Å) are given in Table 3.14.

The intensities were measured with MoKα in the range $5<2\theta<55°$ and a limited number up to $2\theta = 65°$ for the quadrant of the reciprocal space with ℓ and $k \geq 0$. In all 3200 unique reflections were measured. The intensities were corrected for absorption with the ABSORP program (32). This program calculates the transmission coefficient $A_{\underline{h}}$ for each reflection with a numerical integration from the shape of the crystal defined as in Table 3.15,the linear absorption coefficient and the orientation of the crystal in the Eulerian cradle. The transmission coefficient calculated for the reflections

Table 3.15 $NaRbCr_2O_7$. Crystal Shape

Crystal faces	d(10^{-1} mm)†
(1 4 5)	0.80
($\bar{9}$ $\bar{8}$ 10)	0.97
(0 $\bar{1}$ 5)	0.80
($\bar{1}$ $\bar{4}$ $\bar{5}$)	1.29
(3 $\bar{2}$ 1)	0.80
($\bar{6}$ 1 0)	0.97
($\bar{5}$ $\bar{6}$ 3)	1.29
(5 6 $\bar{3}$)	1.29
(0 0 $\bar{7}$)	0.97
($\bar{1}$ 0 $\bar{1}$)	0.97
(1 0 1)	0.97
($\bar{3}$ 3 2)	0.97

†Distances of the crystal faces from the center of the crystal.

Tabl3 3.16 $NaRbCr_2O_7$. Angular settings for 14 reflections

h k ℓ	2θ	ω	φ	χ
$\bar{2}$ $\bar{3}$ 1	13.22	359.93	90.69	85.70
$\bar{1}$ $\bar{3}$ 1	12.08	359.96	167.54	72.48
$\bar{2}$ $\bar{3}$ 0	12.69	359.96	101.72	66.57
$\bar{3}$ $\bar{1}$ 1	10.73	.00	2.31	59.32
0 $\bar{2}$ 2	10.98	.07	235.88	51.91
$\bar{3}$ 0 2	12.12	.06	332.50	41.33
1 $\bar{2}$ 2	11.53	.10	228.41	37.36
$\bar{3}$ 1 2	12.67	.19	334.80	24.31
$\bar{4}$ 1 1	13.53	.14	359.55	23.29
$\bar{3}$ $\bar{1}$ $\bar{2}$	13.39	.07	69.96	20.47
3 $\bar{3}$ 1	15.21	.11	197.55	19.18
3 $\bar{1}$ 2	13.39	.08	229.31	4.13
$\bar{3}$ $\bar{3}$ $\bar{1}$	15.26	.06	83.91	50.69
1 $\bar{3}$ 2	14.15	.09	213.27	43.80

varied between 0.22 and 0.28. Because of the complicated shape of the crystal a very accurate identification of the Miller indices was not possible, so the bounding planes defined in Table 3.15 are only approximate. As a result the applied absorption correction was also only approximate.

After the absorption correction intensities less than three times the standard deviation calculated from counting statistics were characterized as unobserved. The number of observed reflections thus left was 1406. The intensities were then corrected for Lorentz and polarization effects.

3.4.1d Refinement with the Diffractometer Measurements

The model refined with the measurement from the precession photographs was further refined with the diffractometer measurements and with anisotropic temperature factors to a final agreement indices $R_1 = 0.046$, $R_2 = 0.058$. A Cruickshank weighting scheme was used with w = (17.10 $w = (17.710-0.3817|F_o| + 0.0042|F_o|^2)^{-1}$. The scattering curves of Rb^+, Cr^{++}, O^-, O (for the bridging oxygen) and Na^+ (25) were used. The Rb^+ and Cr^{++} curves were corrected for the real and imaginary parts of dispersion for MoKα radiation. The final atomic and thermal coordinates are given in Table 3.17. The values of F_o and F_c are given in Table 3.18

Table 3.17 $P2_1/c$ $NaRbCr_2O_7$. Atomic positional and thermal coordinates

	x	y	z	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Cr1	0.1579(1)	0.1037(2)	0.3862(2)	215(9)	199(11)	197(10)	-34(9)	10(7)	-18(8)
Cr2	-0.0032(1)	-0.0952(2)	0.2545(2)	146(8)	280(11)	209(9)	-15(9)	-19(7)	-9(9)
O11	0.1294(8)	0.2195(9)	0.4705(10)	446(57)	340(58)	393(58)	5(48)	48(45)	-133(49)
O12	0.2025(7)	0.1393(10)	0.2450(9)	379(53)	573(68)	202(47)	-102(51)	29(40)	72(49)
O13	0.2424(8)	0.0265(9)	0.4705(10)	420(57)	398(64)	375(53)	58(50)	-49(43)	244(50)
O21	-0.1275(7)	-0.0812(9)	0.2396(10)	203(42)	398(58)	402(56)	-73(44)	17(37)	2(50)
O22	0.0314(8)	-0.2247(9)	0.3155(10)	435(57)	401(60)	360(55)	151(51)	3(44)	91(48)
O23	0.0441(7)	-0.0781(9)	0.1099(9)	332(52)	356(58)	329(55)	-60(46)	58(42)	14(48)
B12	0.0432(8)	0.0178(11)	0.3644(9)	353(54)	762(82)	267(49)	-288(58)	72(41)	-223(56)
Cr3	0.4398(1)	0.2710(2)	0.4696(2)	182(9)	243(11)	200(10)	-1(9)	-34(7)	14(9)
Cr4	0.6642(1)	0.3644(2)	0.6089(2)	192(9)	246(11)	284(11)	-36(9)	-28(8)	-12(9)
O31	0.3332(7)	0.3204(10)	0.5189(11)	331(52)	537(70)	545(66)	-7(50)	135(48)	67(59)
O32	0.4592(8)	0.1341(9)	0.5228(10)	531(62)	210(50)	348(55)	-122(49)	-134(46)	31(46)
O33	0.4354(8)	0.2717(11)	0.3069(9)	567(65)	628(76)	186(46)	86(59)	-17(43)	77(50)
O41	0.6671(9)	0.4575(10)	0.7315(11)	686(73)	334(61)	456(63)	-31(57)	-90(54)	-185(54)
O42	0.7408(8)	0.4056(11)	0.4972(11)	508(65)	524(74)	452(69)	56(58)	230(53)	3(58)
O43	0.6960(8)	0.2321(9)	0.6596(12)	424(55)	307(56)	617(72)	-15(49)	28(50)	201(57)
B34	0.5364(8)	0.3666(10)	0.5368(12)	361(56)	304(59)	798(85)	-19(49)	-321(55)	56(60)
Na1	0.1521(4)	0.0765(5)	0.0161(5)	345(27)	264(29)	291(27)	18(24)	-64(21)	33(24)
Na2	0.2817(4)	0.3440(5)	0.1800(5)	343(27)	308(30)	344(29)	98(24)	12(22)	7(25)
Rb1	0.1483(1)	0.6833(1)	0.0862(1)	369(7)	274(7)	338(7)	12(6)	24(5)	-36(6)
Rb2	0.4171(1)	-0.0087(1)	0.2603(1)	329(6)	275(7)	338(7)	36(6)	14(5)	3(6)

Standard errors in the last figures quoted as given by final round of least squares analysis are shown in parentheses. The temperature factors were calculated using the expression given in Table 3.3.

Table 3.18 $NaRbCr_2O_7$. Observed and calculated structure factors

Only reflections characterized as observed (see text) are given here. The unobserved reflections were given zero weight during refinement.

H	K	FO	FC
L = 0			
0	-4	42	44
0	-8	79	82
0	-10	85	86
0	-12	48	46
-1	-2	23	26
-1	-3	49	48
-1	-4	158	166
-1	-5	46	48
-1	-6	117	121
-1	-7	82	88
-1	-8	140	142
-1	-10	57	57
-1	-14	56	54
-2	0	62	64
-2	-1	29	34
-2	-2	40	34
-2	-3	243	265
-2	-4	114	120
-2	-5	42	37
-2	-6	62	68
-2	-7	94	96
-2	-8	60	60
-2	-9	66	67
-2	-10	35	41
-2	-11	39	39
-3	0	39	37
-3	-1	65	61
-3	-2	95	87
-3	-3	76	75
-3	-5	79	80
-3	-7	113	116
-3	-8	61	60
-3	-9	26	21
-3	-10	48	52
-3	-11	35	27
-4	0	107	114
-4	-1	168	164
-4	-2	27	28
-4	-3	22	23
-4	-4	29	29
-4	-5	65	69
-4	-6	81	84
-4	-7	151	156
-4	-8	29	26
-4	-9	32	28
-4	-10	34	34
-4	-11	38	39
-5	0	113	107
-5	-1	126	121
-5	-2	124	121
-5	-3	155	145
-5	-4	72	74
-5	-5	57	61
-5	-7	80	86
-5	-8	45	48
-5	-9	45	45
-5	-10	69	75
-6	0	142	151
-6	-1	57	61
-6	-2	78	75
-6	-4	263	251
-6	-5	60	60
-6	-6	69	71
-6	-7	67	69
-6	-8	62	67
-7	0	338	338
-7	-2	24	25
-7	-4	47	46
-7	-5	35	37
-7	-6	25	25
-7	-10	80	85
-7	-12	51	58
-8	-1	51	48
-8	-2	38	36
-8	-3	117	117
-8	-4	89	91
-8	-5	29	28
-8	-6	42	36
-8	-7	96	94
-8	-8	66	71
-9	0	71	70
-9	-1	48	46
-9	-2	32	35
-9	-3	64	63
-9	-4	63	60
-9	-6	33	33
-9	-8	59	56
-10	0	130	129
-10	-1	72	74
-10	-2	48	48
-10	-4	29	24
-10	-5	43	42
-11	0	56	55
-11	-1	38	38
-11	-2	29	29
-11	-4	53	55
-11	-5	67	67
-11	-6	79	74
-11	-7	57	56
-12	0	109	108
-12	-1	62	64
-12	-2	56	66
-12	-3	61	62
-12	-7	37	34
-12	-8	35	35
-13	-1	36	37
-13	-2	30	27
-13	-4	65	64
-13	-6	45	47
-13	-8	44	39
-13	-9	44	44
-14	0	79	79
-14	-1	38	37
-14	-3	40	42
-14	-7	42	39
-15	-3	41	39
-15	-4	52	54
-17	-2	57	52
L = 1			
0	-1	26	23
0	-2	26	26
0	-4	70	73
0	-5	94	90
0	-6	49	52
0	-8	46	46
0	-11	77	76
0	-13	51	51
0	-14	35	33
-1	-1	46	51
-1	-3	244	261
-1	-4	28	28
-1	-5	88	90
-1	-6	49	53
-1	-7	38	34
-1	-8	60	63
-1	-10	86	82
-1	-11	37	36
1	-1	113	101
1	-2	108	114
1	-4	175	188
1	-5	85	85
1	-6	172	183
1	-8	45	44
1	-9	108	115
-2	-1	19	14
-2	-2	220	243
-2	-3	139	133
-2	-5	92	89
-2	-6	33	35
-2	-7	65	67
-2	-8	31	29
-2	-10	37	39
-2	-11	68	72
-2	-12	42	40
2	-1	35	32
2	-2	77	80
2	-3	81	81
2	-4	106	109
2	-5	185	194
2	-8	129	130
2	-10	67	71
2	-14	55	58
-3	-1	27	22
-3	-2	173	167
-3	-3	27	26
-3	-4	51	53
-3	-5	82	83
-3	-6	54	55
-3	-7	120	123
-3	-8	90	88
-3	-9	34	32
-3	-10	35	32
-3	-11	68	73
-3	-12	44	45
3	-2	108	103
3	-3	288	287
3	-5	71	73
3	-6	80	82
3	-7	96	96
3	-8	30	33
3	-9	49	48
3	-10	43	38
3	-13	74	67
-4	-1	133	137
-4	-2	95	99
-4	-4	147	140
-4	-5	46	46
-4	-6	93	96
-4	-7	145	150
-4	-8	44	46
-4	-10	32	27
-4	-12	41	41
-4	-13	40	37
4	-1	149	155
4	-2	211	211
4	-4	77	78
4	-7	74	76
4	-8	51	52
4	-9	47	48
-5	-1	71	68
-5	-3	33	31
-5	-4	72	66
-5	-5	126	119
-5	-8	71	72
-5	-10	109	110
5	-1	134	132
5	-2	98	95
5	-3	46	43
5	-4	38	41
5	-5	59	58
5	-6	56	58
5	-7	69	74
5	-8	43	47
-6	-1	67	64
-6	-2	96	92
-6	-4	71	71
-6	-6	94	93
-6	-7	67	67
-6	-8	38	41
-6	-9	47	50
-6	-11	34	30
6	-1	54	52
6	-2	63	63
6	-3	108	104
6	-5	60	61
6	-6	54	54
6	-7	64	67
6	-8	72	76
-7	-1	84	88
-7	-2	35	32
-7	-3	78	79
-7	-5	53	51
-7	-6	73	69
-7	-7	87	86
7	-2	105	107
7	-3	114	117
7	-4	83	83
7	-5	31	31
7	-6	94	98
-8	-1	70	72
-8	-2	106	104
-8	-3	145	136
-8	-5	57	52
-8	-6	44	38
-8	-7	67	64
-8	-9	56	55
8	-1	123	120
8	-3	27	23
8	-4	108	107
8	-5	46	51
8	-6	59	60
8	-8	53	58
-9	-3	119	118
-9	-5	37	37
-9	-7	41	36
-9	-8	51	50
-9	-10	62	64
-9	-11	49	49
9	-1	121	128
9	-2	38	42
9	-3	61	59
9	-4	77	73
9	-5	88	88
9	-6	29	23
9	-7	47	47
-10	-2	109	110
-10	-3	42	43
-10	-5	91	93
-10	-7	51	51
-10	-8	32	34
-10	-11	62	60
10	-2	81	78
10	-3	68	69
10	-4	29	31
10	-5	43	46
10	-6	32	29
-11	-2	55	55
-11	-3	66	66
-11	-4	37	34
-11	-5	67	64
-11	-6	90	85
-11	-7	31	27
11	-1	40	39
11	-2	47	48
11	-3	33	34
11	-4	59	61
-12	-2	34	32
-12	-4	39	43
-12	-5	36	32
-13	-2	36	34
-13	-3	54	59
13	-1	46	44
13	-2	41	37
13	-3	33	35
-14	-1	29	28
-14	-2	38	41
-14	-2	46	46
14	-3	63	63
14	-4	60	53
14	-5	40	41
-15	-1	33	38
15	-3	44	45
15	-4	37	46
16	-1	49	47
16	-2	43	42
L = 2			
0	-1	81	71
0	-2	235	224
0	-4	67	61
0	-5	63	60
0	-6	41	42
0	-8	69	69
0	-9	94	95
0	-10	46	45
0	-12	41	42
0	-13	50	53
-1	0	130	135
-1	-1	88	93
-1	-2	80	74
-1	-3	86	87
-1	-4	151	158
-1	-5	41	40
-1	-6	203	217
-1	-8	115	118
-1	-10	30	25
-1	-11	31	32
-1	-12	46	48
1	0	49	48
1	-1	130	114
1	-2	180	177
1	-3	150	141
1	-4	128	118
1	-5	185	190
1	-6	51	54
1	-7	27	27
1	-8	101	100
1	-9	32	35
-2	0	30	21
-2	-1	48	47
-2	-2	219	239
-2	-6	85	87
-2	-7	61	65
-2	-10	100	96
-2	-11	48	45
-2	-13	47	48
2	0	267	253
2	-1	125	118
2	-2	38	38
2	-3	29	34
2	-4	34	31
2	-5	36	34
2	-6	76	72
2	-7	54	56
2	-8	36	36
2	-9	53	50
2	-10	49	56
-3	0	275	278
-3	-1	159	159
-3	-2	31	32
-3	-3	30	31
-3	-4	22	18
-3	-5	106	112
-3	-6	66	67
-3	-9	51	50
3	0	178	166
3	-1	340	[illegible]
3	-1	340	322
3	-4	37	38
3	-5	47	47
3	-6	52	55
3	-8	57	59
3	-9	29	31
3	-10	35	33
-4	0	78	83
-4	-1	127	125
-4	-2	147	152
-4	-4	87	90
-4	-8	67	71
-4	-13	40	41
4	0	50	48
4	-1	88	81
4	-2	83	75
4	-3	46	46
4	-4	79	62
4	-5	84	83
4	-6	119	122
4	-7	43	47
4	-8	32	32
4	-9	80	84
-5	0	158	166
-5	-1	105	107
-5	-3	62	64
-5	-4	142	143
-5	-6	95	98
-5	-9	43	45
-5	-10	67	70
-5	-12	45	43
5	0	146	145
5	-1	22	18
5	-2	161	161
5	-3	98	101
5	-4	134	135
5	-5	28	31
5	-6	34	33
5	-7	36	37
5	-8	151	152
-6	-2	52	52
-6	-3	45	42
-6	-4	67	64
-6	-5	54	50
-6	-6	55	54
-6	-7	72	74
-6	-8	41	47
-6	-9	78	75
-6	-13	54	53
6	0	68	65
6	-1	22	32
6	-2	45	40
6	-4	41	40
6	-5	27	30
6	-6	199	205
6	-9	31	31
-7	0	117	121
-7	-1	141	143
-7	-2	105	118
-7	-4	34	32
-7	-7	34	30
-7	-8	98	102
-7	-9	40	41
7	0	43	41
7	-1	60	63
7	-2	150	144
7	-3	26	24
7	-4	36	38
7	-5	57	56
7	-6	46	45
-8	0	41	37
-8	-3	34	31
-8	-6	159	152
-8	-8	32	33
-8	-9	37	35
8	0	81	80
8	-1	45	41
8	-2	112	103
8	-4	87	88
8	-5	62	63
8	-7	45	47
-9	-1	77	78
-9	-2	107	107
-9	-3	77	78
-9	-4	78	78
-9	-5	38	38
-9	-6	68	66
9	0	45	44
9	-1	33	30
9	-2	43	37
9	-3	68	65
9	-5	56	57
-10	0	222	223
-10	-1	40	40
-10	-3	32	30
-10	-8	46	39
-10	-9	67	61
10	0	127	132
10	-1	97	96
10	-3	44	40
10	-5	32	33
-11	0	49	50
-11	-1	48	46
-11	-2	51	52
-11	-8	101	96
11	0	39	44
11	-4	108	111
-12	0	74	75
-12	-3	58	55
-12	-4	49	51
-12	-6	30	27
-12	-7	77	81
-13	-1	34	33
-13	-3	38	39
-13	-4	76	73
-13	-5	48	51
13	0	78	73
13	-1	57	60
13	-2	32	28
13	-6	68	71
-14	0	28	27
-14	-1	50	51
14	-2	41	44
14	0	34	34
14	-2	45	44
14	-6	36	40
-15	-1	47	51
15	0	40	42
15	-3	44	44
17	0	82	82
L = 3			
0	-1	92	95
0	-2	293	277
0	-3	47	44
0	-7	43	45
0	-9	42	38
0	-12	84	88
-1	-2	33	37
-1	-3	90	85
-1	-5	180	175
-1	-6	65	61
-1	-7	58	55
-1	-8	94	96
1	-1	72	64
1	-2	203	186
1	-3	88	85
1	-4	22	17
1	-5	61	58
1	-7	88	90
1	-8	91	94
1	-10	51	50
-2	-1	157	158
-2	-3	173	167
-2	-4	25	21
-2	-7	61	64
-2	-9	137	145
-2	-11	40	40
-2	-13	45	50
2	-1	169	158
2	-3	57	57
2	-4	163	161
2	-5	139	133
2	-6	39	34
2	-7	63	64
2	-8	33	28
2	-9	80	87
2	-13	43	45
-3	-1	117	133
-3	-2	24	22
-3	-3	54	55
-3	-5	71	66
-3	-6	115	113
-3	-7	57	57
-3	-8	53	45
-3	-9	52	51
-3	-10	40	44
-3	-12	39	42
3	-1	56	45
3	-3	50	45
3	-4	78	75
3	-5	203	203
3	-6	49	51
3	-7	62	65
3	-8	35	34
-4	-1	94	94
-4	-2	131	133
-4	-4	87	95
-4	-5	163	166
-4	-8	109	107
4	-1	127	116
4	-2	55	56
4	-3	94	93
4	-4	63	62
4	-5	138	135
4	-6	64	64
4	-8	60	58
-5	-2	103	107
-5	-3	85	86
-5	-4	127	128
-5	-5	41	44
-5	-6	32	36
-5	-9	55	52
-5	-12	58	65
5	-1	49	49
5	-2	74	71
5	-3	128	127
5	-4	27	28
5	-5	39	40
5	-6	69	73
5	-8	33	30
5	-9	96	102
-6	-1	23	22
-6	-2	178	188
-6	-4	56	53
-6	-6	49	46
-6	-7	40	46
-6	-8	82	83
-6	-11	38	42
6	-2	176	176
6	-3	26	27
6	-5	90	92
6	-6	75	77
6	-8	68	59
-7	-1	105	111
-7	-2	85	84
-7	-3	55	58
-7	-5	40	46
-7	-10	44	47
-7	-12	66	66
7	-1	48	48
7	-2	184	176
7	-3	123	120
7	-4	52	55
-8	-2	41	39
-8	-3	61	57
-8	-4	[illegible]	[illegible]
-8	-5	202	203
-8	-6	37	39
-8	-8	42	42
8	-2	110	106
8	-3	52	53
8	-4	42	42
8	-5	58	[illegible]
-9	-1	29	28
-9	-3	118	119
-9	-5	34	27
-9	-6	45	44
-9	-9	65	62
9	-1	124	120
9	-3	83	83
9	-4	61	61
9	-5	40	39
9	-6	50	51
-10	-1	69	69
-10	-2	50	53
-10	-4	68	70
-10	-5	51	49
10	-1	44	40
10	-2	43	39
10	-4	48	44
10	-5	35	39
-11	-1	30	35
-11	-3	41	44
-11	-4	37	39
-11	-5	50	51
-11	-6	36	39
-11	-8	65	66
11	-1	34	31
11	-2	33	31
-12	-2	62	61
-12	-4	45	46
-12	-6	48	44
12	-2	62	61
12	-3	33	34
-13	-2	47	49
-13	-3	37	37
-14	-2	54	55
-14	-1	59	61
-14	-2	40	35
14	-1	35	31
14	-2	42	44
14	-8	44	41
-15	-1	35	38
15	-2	50	54
15	-5	48	46
16	-3	42	44
L = 4			
0	0	153	158
0	-1	142	146
0	-2	121	112
0	-3	68	70
0	-4	140	131
0	-5	29	28
0	-6	36	33
0	-7	40	40
0	-8	45	42
0	-12	36	36
-1	0	102	108
-1	-1	190	156
-1	-2	49	48
-1	-3	40	37
-1	-4	104	95
-1	-5	111	98
-1	-6	70	67
-1	-7	48	46
-1	-8	57	65
1	0	164	164
1	-1	40	41
1	-3	62	61
1	-4	186	175
1	-6	120	113
-2	0	214	230
-2	-1	38	43
-2	-2	97	105
-2	-4	64	61
-2	-5	97	61
-2	-7	68	70
-2	-9	34	35
-2	-10	35	35

Table 3.18 $NaRbCr_2O_7$ (continued)

H	K	FC	FC
2	0	70	71
2	-2	53	51
2	-3	43	37
2	-6	37	39
2	-7	141	137
2	-8	109	110
2	-9	30	33
-3	0	75	81
-3	-2	54	61
-3	-4	43	48
-3	-5	46	46
-3	-6	44	43
-3	-7	79	76
-3	-8	62	61
-3	-10	82	87
-3	-11	47	47
-3	-12	37	38
3	0	61	55
3	-1	139	132
3	-2	26	20
3	-3	64	61
3	-4	27	28
3	-5	34	33
3	-6	86	86
3	-8	30	31
3	-9	64	66
-4	0	76	80
-4	-1	36	25
-4	-2	63	64
-4	-3	106	110
-4	-4	91	100
-4	-6	118	114
-4	-7	67	61
-4	-9	48	47
4	-2	117	113
4	-3	27	23
4	[illegible]	[illegible]	[illegible]
-5	0	71	73
-5	-1	34	32
-5	-2	111	113
-5	-3	68	68
-5	-4	97	98
-5	[illegible]	118	113
5	0	210	203
5	-1	30	31
5	-3	33	29
5	-4	41	40
5	-5	54	54
5	-6	62	61
5	[illegible]	63	58
-6	0	140	142
-6	-1	29	27
-6	-3	50	46
-6	-4	33	30
-6	-5	45	43
-6	-6	103	106
-6	-8	43	43
-6	-9	35	36
-6	-10	45	41
6	0	166	157
6	-1	64	60
6	-2	79	71
6	-3	55	55
6	-5	57	55
6	-6	38	39
6	-8	100	104
-7	0	115	118
-7	-1	174	173
-7	-2	62	62
-7	-3	30	36
-7	-4	74	[illegible]
-7	-5	41	45
7	0	107	103
7	-1	56	50
7	-2	91	80
7	-3	31	29
7	-5	35	34
7	-6	87	88
-8	0	39	37
-8	-1	59	59
-8	-2	37	38
-8	-3	64	60
-8	-9	71	65
8	-9	61	60
8	-1	29	29
8	-2	56	57
8	-3	72	65
8	-4	99	98
8	-5	59	59
8	-6	84	82
-9	0	147	144
-9	-1	48	47
-9	-5	58	63
-9	-6	38	35
-9	-8	46	44
-9	-10	52	46
9	0	90	91
9	-1	52	46
9	-3	37	35
9	-4	45	43
9	-5	43	44
-10	0	113	117
-10	-1	60	57
-10	-3	50	48
-10	-4	62	58
-10	-6	38	38

H	K	FO	FC
-10	-7	53	57
-10	-10	55	52
10	0	75	73
10	-1	99	97
10	-4	56	59
-11	-1	40	38
-11	-2	44	46
-11	-3	45	49
-11	-4	54	53
-11	-6	70	75
-11	-7	49	48
11	0	41	41
11	-2	36	39
11	-3	34	35
11	-4	65	64
-12	-2	97	97
-12	-4	54	51
12	0	68	66
12	-4	59	65
-13	-5	47	44
-13	-6	45	44
13	-1	34	38
13	-4	62	66
-14	-1	36	68
-14	-3	33	36
14	0	41	42
14	-1	37	37
14	-5	47	51
14	-6	41	34
15	-4	41	43
16	0	61	62

H	K	L = 5	
0	-1	29	28
0	-2	37	34
0	-3	62	62
0	-4	91	[illegible]
0	-6	34	32
0	-7	100	97
0	-8	47	46
0	-10	41	46
0	-11	39	34
-1	-1	108	113
-1	-3	58	[illegible]
-1	-4	149	145
-1	-6	137	129
-1	-7	139	126
-1	-8	73	69
-1	-11	44	39
1	-1	44	44
1	-3	69	66
1	[illegible]	34	33
1	-13	43	37
-2	-1	131	147
-2	-2	61	61
-2	-3	39	42
-2	-4	159	154
-2	-7	47	38
-2	-8	60	56
-2	-11	111	106
2	-1	62	57
2	-2	121	115
2	-3	25	23
2	-4	131	123
2	-5	68	67
2	-6	84	79
2	-7	90	85
-3	-1	106	113
-3	-2	90	96
-3	-3	233	236
-3	-4	34	35
-3	[illegible]	74	[illegible]
-3	-7	69	61
3	-1	150	140
3	-2	27	30
3	-3	31	25
3	-4	34	26
3	-6	44	39
-4	-1	113	113
-4	-2	55	52
-4	-3	62	60
-4	-4	45	48
-4	-5	49	51
-4	-10	66	71
-4	-11	193	183
4	-3	54	53
4	-4	35	34
4	-5	79	79
4	-7	85	85
4	-8	33	35
-5	-6	127	123
-5	-7	39	36
5	-1	44	39
5	-2	124	118
5	-3	94	89
5	-4	117	116
5	-5	48	46
5	-6	100	95
-6	-1	48	68
-6	-2	72	73
-6	-3	36	35
-6	-5	37	41
-6	-6	70	72
-6	-10	36	37

H	K	FC	FC
-6	-11	56	54
6	-1	47	41
6	-3	94	92
6	-4	94	91
6	-6	73	74
6	-11	72	76
-7	-2	106	111
-7	-3	112	111
-7	-4	70	74
-7	-5	47	50
-7	-9	31	28
-7	-7	36	37
-7	-8	50	58
-7	-9	34	31
-7	-10	41	43
7	-1	116	110
7	-3	59	61
7	-4	80	49
7	-5	39	39
7	-6	40	47
-8	-1	144	137
-8	-3	41	45
-8	-5	35	60
-8	-7	38	59
-8	-8	51	47
-8	-2	74	70
8	-3	43	46
8	-4	35	38
-9	-1	125	127
-9	-3	35	36
-9	-7	63	60
-9	-8	48	48
9	-1	56	58
9	-2	51	49
9	-3	57	54
9	-4	66	67
9	-5	65	60
-10	-1	69	73
-10	-2	81	75
10	-1	48	46
10	-4	37	41
10	-5	39	39
-11	-3	74	57
-11	-5	52	47
-11	[illegible]	38	29
-12	-1	59	60
-12	[illegible]	60	58
-13	-1	43	43
-13	-3	33	34
13	-5	44	44
14	-1	45	45
17	-2	43	39

H	K	L = 6	
-0	0	156	158
0	-2	95	92
0	-3	120	117
0	-4	42	41
0	-5	30	23
0	-6	71	70
0	-9	38	34
0	-10	70	75
-1	0	33	31
-1	-2	96	99
-1	-5	59	57
-1	-6	36	53
-1	-7	133	129
-1	-8	68	64
1	0	104	102
1	-1	168	166
1	-2	94	87
1	-4	208	198
1	-6	74	75
1	-7	33	27
1	-8	33	35
-2	-2	44	49
-2	-3	89	94
-2	-4	55	54
-2	-7	34	32
-2	-9	83	78
2	0	91	95
2	-2	121	118
2	-4	49	46
2	-5	36	36
2	-6	62	57
2	-7	67	64
2	-8	34	35
2	-12	45	44
-3	0	57	62
-3	-1	68	75
-3	-3	66	69
-3	-4	31	28
-3	-5	41	40
-3	-6	91	84
-3	-8	64	62
3	0	95	92
3	-1	28	26
3	-2	120	120
3	-3	98	95
3	-4	86	80
3	-5	96	90
3	-6	61	61
3	-7	44	46

H	K	FC	FC
-4	0	170	176
-4	-1	49	48
-4	-2	94	95
-4	-3	71	72
-4	-4	83	86
4	-6	134	135
4	[illegible]	27	28
4	[illegible]	41	42
4	[illegible]	34	42
4	[illegible]	68	67
4	[illegible]	44	45
-5	0	221	236
-5	-1	59	62
-5	-2	38	41
-5	-3	29	28
-5	-4	48	48
-5	-6	31	28
-5	-7	34	38
-5	-8	82	78
-5	-10	58	52
5	-1	50	46
5	-3	39	40
5	[illegible]	38	76
5	[illegible]	78	28
6	[illegible]	107	105
6	[illegible]	102	103
6	[illegible]	41	[illegible]
6	[illegible]	66	[illegible]
6	[illegible]	46	44
6	[illegible]	34	37
6	-4	69	71
6	[illegible]	47	46
6	[illegible]	30	28
-7	[illegible]	122	124
7	[illegible]	87	87
7	[illegible]	85	[illegible]
7	[illegible]	30	[illegible]
7	[illegible]	62	60
7	[illegible]	53	54
-8	0	36	36
-8	-1	37	36
8	[illegible]	85	85
8	[illegible]	60	61
8	[illegible]	57	58
8	[illegible]	33	34
8	[illegible]	54	45
8	[illegible]	38	37
8	[illegible]	75	78
-9	-1	103	[illegible]
-9	-4	53	48
9	0	51	51
9	-1	48	44
9	-2	58	61
9	-4	41	38
-10	0	54	54
-10	-2	52	49
-10	-3	29	35
-10	-4	58	52
-10	-6	52	51
10	-2	39	45
-11	0	30	32
-11	-1	47	45
-11	-4	91	86
-11	-6	63	67
11	0	49	51
11	-1	56	53
11	-6	49	46
-12	0	113	104
12	0	50	49
12	-2	46	43
12	-5	37	34
-13	-1	52	45
13	0	54	52
13	-2	58	60
13	-3	42	39
13	-6	49	41
14	-2	44	43
15	0	63	62

H	K	L = 7	
0	-1	45	44
0	-2	80	79
0	-3	29	31
0	-4	124	117
0	-5	53	51
0	-11	38	39
-1	-2	90	91
-1	-3	87	88
-1	-7	43	40
-1	-8	46	48
-1	-9	69	70
1	-4	50	48
-2	-1	30	30

H	K	FC	FC
-2	-2	137	138
-2	-3	50	54
-2	[illegible]	121	115
-2	[illegible]	36	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]
3	-5	91	87
3	[illegible]	119	116
3	-6	85	81
3	[illegible]	72	75
3	[illegible]	68	70
[illegible]	[illegible]	104	107
[illegible]	[illegible]	40	40
[illegible]	[illegible]	37	36
[illegible]	[illegible]	48	47
[illegible]	[illegible]	38	42
[illegible]	[illegible]	80	78
[illegible]	[illegible]	[illegible]	[illegible]
5	-4	48	[illegible]
5	-5	66	64
-10	-2	70	66
-10	-5	65	66
10	-2	68	67
10	-3	76	84
-11	-3	38	38
11	-2	40	37
-12	-1	28	25
12	-5	54	54

H	K	L = 8	
-0	0	151	150
0	-2	117	118
0	-4	44	45
0	-5	43	49
0	-8	58	53
0	-9	66	64
0	-10	48	45
-1	-1	48	48
-1	-2	61	62
-1	-4	102	107
-1	-6	93	93
1	-1	77	78
1	-2	60	60
1	-6	71	66
1	-8	55	53
-2	0	31	27
-2	-1	105	113
-2	-2	39	40
-2	-6	70	74
2	0	96	92
-3	-1	33	33
-3	-2	35	40
-3	-3	81	78
-3	-5	32	32
-3	-6	101	105
3	-1	68	71
3	-2	69	69
3	-3	64	67
3	-5	61	62
3	-6	38	37
3	-9	41	40
3	0	47	45

H	K	FO	FC
3	0	47	45
3	-1	38	41
3	-2	79	76
3	-3	58	56
3	-8	33	30
-4	-2	30	36
-4	-3	30	34
-4	-5	33	38
-4	-7	36	38
-4	-8	42	41
4	0	56	56
4	-1	75	72
4	-2	57	61
4	-3	55	56
4	-5	37	38
-5	-10	38	31
-5	0	43	43
-5	-2	37	36
-5	-6	77	74
-5	-10	48	45
5	0	113	113
5	-1	43	45
5	-2	37	39
5	-6	86	[illegible]
5	-8	64	55
-6	0	60	64
-6	-1	56	45
-6	-2	74	72
-6	-4	58	62
-6	-6	55	54
-6	-9	30	37
6	-1	40	41
6	-2	41	43
6	-3	31	34
6	-4	115	126
6	-6	69	65
-7	[illegible]	39	37
-7	-2	78	81
-7	[illegible]	[illegible]	[illegible]
-7	-5	52	[illegible]
-7	-6	34	31
7	0	47	47
7	-1	35	38
7	-2	49	51
7	-3	39	40
7	-4	35	37
7	-5	36	38
-8	-2	45	38
-8	-3	45	40
-8	-6	74	74
8	-1	60	64
8	-2	40	42
8	-4	37	42
-9	-1	83	86
-9	-4	41	43
-9	-6	38	30
9	0	53	61
9	-6	46	51
-10	-6	36	38
10	-3	43	43
-11	-2	54	58
11	-4	51	55
-12	0	71	66
12	0	67	70
13	-4	41	41
13	-6	42	35
14	0	48	52

H	K	L = 9	
0	-2	48	46
0	-9	38	33
-1	-1	35	35
-1	-3	79	76
-1	-10	67	67
1	-1	58	56
1	-2	65	62
1	-3	61	60
1	-6	48	55
-2	-2	45	47
-2	-3	67	70
-2	-7	63	61
2	-2	38	37
2	-3	69	72
2	-4	43	44
2	-8	37	38
-3	-1	73	72
-3	-4	77	76
-3	-7	47	48
3	-3	88	86
3	-4	52	53
3	-5	48	45
3	-6	50	52
3	-8	39	34
-4	-4	43	46
-4	-6	40	35
-4	-8	72	63
4	-1	52	48
4	-4	46	42
-5	-1	42	48
-5	-2	59	57
-5	-3	77	76
5	-1	34	37
5	-3	72	75
5	-9	39	40
5	-7	56	52
-6	-2	32	23

H	K	FO	FC
-6	-3	41	42
-6	-7	42	34
6	-2	32	36
6	-5	41	44
-7	-1	50	53
-7	-6	42	40
7	-2	78	82
-8	-1	48	47
-8	-5	43	52
8	-1	43	42
-9	-3	57	56
9	-1	35	35
9	-2	59	40
-10	-4	61	65
-11	-2	40	39

H	K	L = 10	
6	-1	37	35
6	-2	38	40
6	-6	42	44
-7	-7	47	45
7	-2	41	43
-8	0	44	42
-8	-3	46	47
8	-4	38	31
-9	0	46	44
9	-3	39	49
-10	0	63	67
-11	0	40	42
0	-2	51	49
0	-4	58	53
0	-7	39	44
-1	0	51	49
-1	-1	45	43
-1	-3	44	42
-1	-4	38	45
1	0	52	50
1	-4	41	40
1	-5	38	38
1	-6	53	52
-2	0	66	64
-2	-4	51	49
-2	-7	38	38
2	0	66	70
2	-2	35	44
2	-3	58	44
2	-7	48	43
2	-8	42	41
-3	0	87	86
-3	-7	43	41
3	-3	35	34
3	-4	50	51
-4	-3	53	52
-4	-4	76	82
-4	-7	48	35
4	0	101	101
-5	0	35	26
-5	-2	44	42
-5	-4	51	45
5	0	72	70
5	-4	55	58
-6	0	51	55
-6	-1	43	36
-6	-6	27	40

H	K	L = 11	
0	-2	55	52
0	-3	56	53
0	-4	48	47
0	-6	42	38
-1	-5	51	49
-1	-7	48	44
-2	-1	77	83
-2	-2	43	35
-2	-4	38	41
2	-1	43	42
-3	-3	45	49
3	-1	35	37
3	-4	37	39
-4	-5	43	42
4	-3	27	40
4	-5	40	37
5	-1	32	50
5	-4	40	49
-6	-2	56	57
6	-2	44	48
-7	-3	44	47
-7	-4	38	39
-8	-3	41	43
-9	-1	44	41

H	K	L = 12	
-0	0	39	34
1	0	44	37
1	-2	52	48
2	-2	55	58
-3	-1	54	54
-3	-2	62	54
-5	0	39	35
-5	-2	51	48
-6	-2	36	35

3.4.2 $NaCsCr_2O_7$. Experimental Procedure

Crystals of $NaCsCr_2O_7$ were obtained by slow cooling of the congruently melting (362°C) 1:1 mixture of anhydrous sodium and cesium dichromate. The powdered $Na_2Cr_2O_7$ was prepared from $Na_2Cr_2O_7$ $2H_2O$ Shawinigan, Reagent, 99.5% and the powdered cesium dichromate was obtained from Alfa Inorganic, 99.9%.

Single crystal precession photographs of the $hk0$, $h0\ell$, $h1\ell$, and $hk1$ layer were taken and showed systematic absences of ℓ odd for the $h0\ell$ reflections and k odd for the $0k0$ reflections in a monoclinic unit cell. The space group is thus uniquely determined as $P2_1/c$. The cell constants measured from uncalibrated photographs are given in Table 3.14. Since the cell constants of $NaRbCr_2O_7$ measured in the same way were systematically smaller than those measured with the Syntex diffractometer, the values of $NaCsCr_2O_7$ cell constants given in Table 3.14 might also be systematically smaller by about one standard deviation. The volume of 1514 $Å^3$ corresponds to eight $NaCsCr_2O_7$ units per unit cell.

The similarity of the unit cells and the intensities of the $h0\ell$, $hk0$, $h1\ell$ layers of $NaCsCr_2O_7$ with those of $NaRbCr_2O_7$ indicates that these two compounds are probably isostructural.

CHAPTER 4

THE DICHROMATE ION

4.1 The Geometry of the Dichromate Ion

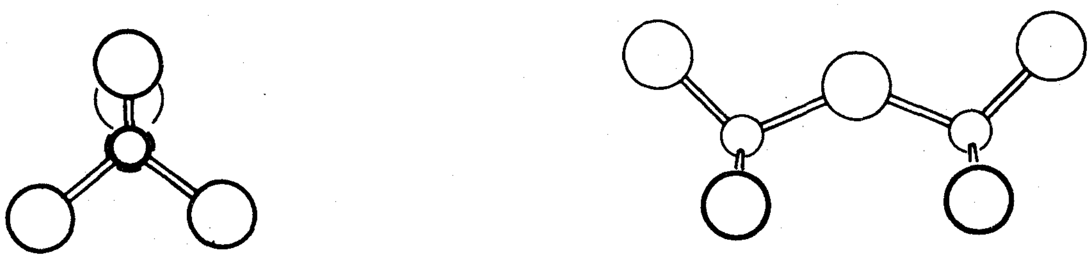
The dichromate anion $Cr_2O_7^{2-}$ consists of two CrO_4 tetrahedra sharing one oxygen atom. We will call the shared oxygen the bridging oxygen atom and the other oxygens as the terminal ones.

In all dichromate ions whose structures have so far been determined the bridging oxygen angle (Cr-B (bridging oxygen)-Cr) varies between 121 to 141 degrees, while the O-Cr-O angles are very close to the tetrahedral angle which is 109.5°. The Cr-O terminal distances are all equal (1.62 Å) but the Cr-B distances are somewhat larger (1.79 Å).

For a Y_2O_7 molecule with the above geometry and with a bridging angle different from 180° there are three special symmetric conformations. Two eclipsed conformations have symmetry C_{2v}(mm) and one staggered conformation has symmetry C_s(m), (Figure 4.1 a,b,c). We shall call the staggered conformation C and the two eclipsed conformations A or B depending on whether the bridging oxygen lies inside or outside respectively of the quadrilateral defined by

Figure 4.1 Special symmetric conformations of Y_2O_7 ions.

a) Conformation $A(C_{2v})$. From $SrCr_2O_7$.



b) Conformation $B(C_{2v})$. From $SrCr_2O_7$.

c) Conformation $C(C_s)$. From α-$Mg_2P_2O_7$.

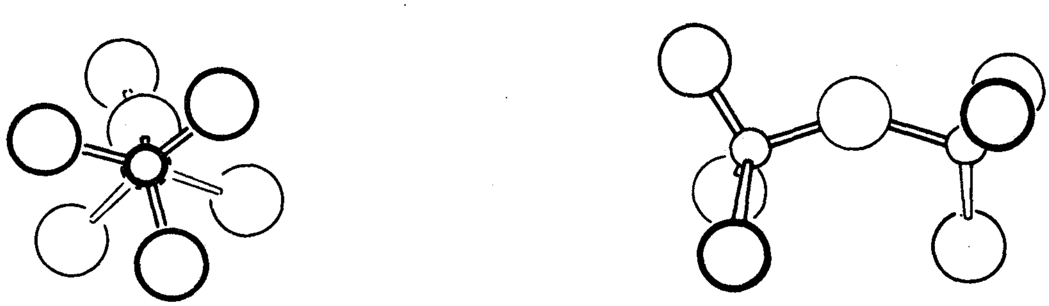
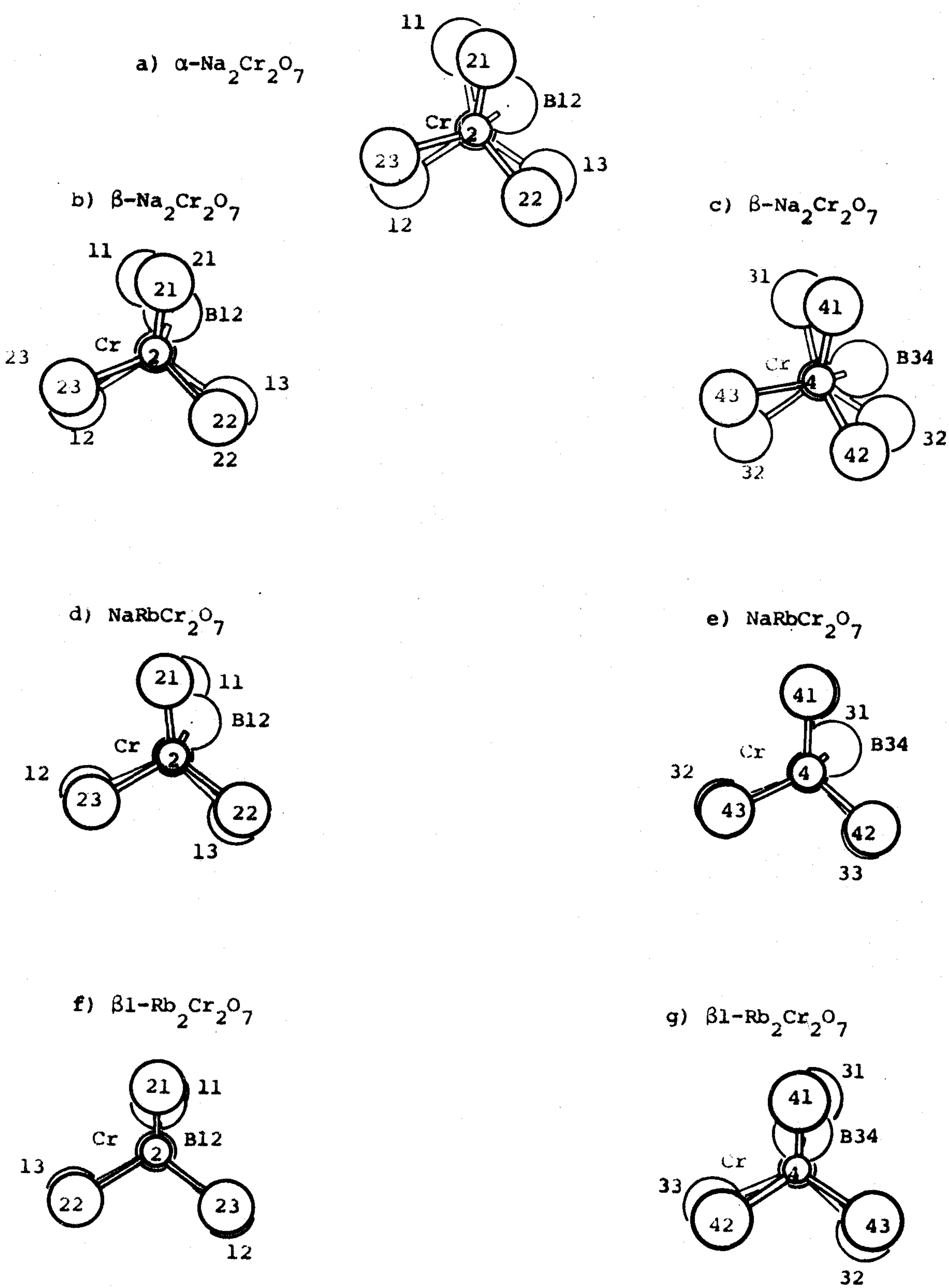


Figure 4.2 The dichromate ions found in this work. (Viewed along the Cr-Cr axis)



the two Cr and the two oxygen atoms lying on the plane of symmetry.

Both the A and B conformations have been found in $SrCr_2O_7$ (8) but the staggered conformation has not yet been found in the dichromates, although it is frequently found in other groups such as $P_2O_7^{4-}$.

The Cr_2O_7 ion normally has symmetry lower than C_{2v}. In one possible conformation the anion loses the planes of symmetry but it retains the twofold axis (symmetry C_2). Such a dichromate anion with crystallographic C_2 symmetry and a conformation very close to that of A has been found in the type X C2/c structures of $Rb_2Cr_2O_7$ and $(NH_4)_2Cr_2O_7$. In all the other known dichromate structures the anion has no crystallographic symmetry, though sometimes the deviations from the C2v or C2 symmetry are rather small.

The conformation of the dichromate ion can be described by three angles: the bridging oxygen angle (Cr-B-Cr), b, and the angles α_1 and α_2 which define the rotations of each of the two tetrahedra around the Cr-B (bridging atom) bond†.

4.2 Analysis of the Temperature Factors

For the structures determined in this work the anisotropic temperature factors have been analysed to determine the

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†An exact definition of α_1, α_2 is given in p 91.

magnitude and the directions of the principle axes of the thermal ellipsoids and are given in Tables 4.1, 4.2, 4.3, 4.4.

As can be seen from these tables, the thermal motion of the Cr atoms is nearly isotropic while that of the oxygen atoms is anisotropic with the minor axes of the ellipsoids lying within 20° of the direction of the Cr-O bonds and the major and intermediate axes approximately normal to it.

The information contained in the temperature factors is insufficient to account for the modes of vibration that are important in the thermal motion of the Cr_2O_7 ion. Luu and Lafont (33) in a Raman study of β1 $K_2Cr_2O_7$ assign to the various modes the frequences given in Table 4.5. From the 27 modes of the Cr_2O_7 ion only the 8 lowest modes are likely to be important at room temperatures. The remaining one bending and two stretching modes of the Cr-B-Cr as well as the 16 internal bonding modes, while consistent with the observed temperature factors, can be discarded on the grounds of too high an energy.

The eight lowest modes are the three translational, the three librational around the principal axes of inertia of the ion and the two torsional. The normal coordinates for the torsion modes are the angles α_1 and α_2 defined in the previous section. These two modes are degenerate and therefore mix to give the A_2 symmetric torsion mode $\alpha_1-\alpha_2$ and the B_2 antisymmetric torsion mode $\alpha_1+\alpha_2$.

Table 4.1 β-$Na_2Cr_2O_7$. Principal axes of anisotropic temperature factors

Atom	rms Displacements (Å)	Angles in degrees with respect to bond		Angles in degrees with respect to a	b	c
	0.16			122	109	34
Cr1	0.15			45	159	103
	0.14			61	81	59
	0.17			128	118	72
Cr2	0.14			39	150	109
	0.14			97	81	153
		Cr1-O11				
	0.217	105		82	156	102
O11	0.171	98		92	73	156
	0.121	17		22	105	110
		Cr1-O12				
	0.22	119		94	55	143
O12	0.17	84		151	91	83
	0.12	30		62	145	126
		Cr1-O13				
	0.22	83		43	150	115
O13	0.18	128		111	81	138
	0.14	39		126	118	59
		Cr2-O21				
	0.20	103		143	96	46
O21	0.18	126		66	167	103
	0.16	39		117	78	133
		Cr2-O22				
	0.26	73		86	35	79
O22	0.20	59		24	123	94
	0.16	144		107	101	11
		Cr2-O23				
	0.30	82		27	96	115
O23	0.20	69		88	108	148
	0.13	157		109	19	109
		Cr1-OB12	Cr2-OB12			
	0.24	89	104	129	105	39
OB12	0.20	86	140	46	160	94
	0.12	5	127	71	77	51
	0.16			143	98	51
Cr3	0.14			125	17	96
	0.14			82	76	39

(continued next page)

Table 4.1 β-$Na_2Cr_2O_7$ (continued)

Atom	rms Displacements (Å)	Angles in degrees with respect to bond		Angles in degrees with respect to a	b	c
	0.16			143	98	51
Cr3	0.14			125	17	96
	0.14			82	76	39
	0.16			104	142	80
Cr4	0.15			19	126	121
	0.13			103	79	147
		Cr3-O31				
	0.26	84		64	77	59
O31	0.21	106		100	132	46
	0.14	17		28	135	120
		Cr3-O32				
	0.22	112		113	56	133
O32	0.21	99		23	99	129
	0.15	24		86	145	111
		Cr3-O33				
	0.23	72		75	42	87
O33	0.20	69		19	123	123
	0.14	152		101	67	147
		Cr4-O41				
	0.22	76		94	151	72
O41	0.19	81		16	117	103
	0.15	163		84	102	157
		Cr4-O42				
	0.26	86		109	22	111
O42	0.19	63		60	78	72
	0.16	28		43	108	152
		Cr4-O43				
	0.26	91		51	115	153
O43	0.20	137		46	77	85
	0.17	47		110	29	117
		Cr3-OB34	Cr4-OB34			
	0.23	86	92	38	110	146
OB34	0.16	102	127	97	20	105
	0.13	12	143	127	88	119
	0.25			155	90	64
Na1	0.17			77	131	133
	0.16			111	41	126

(continued next page)

Table 4.1 β-$Na_2Cr_2O_7$ (continued)

Atom	rms Displacements (Å)	Angles in degrees with respect to bond	Angles in degrees with respect to a	b	c
	0.24		149	41	92
Na2	0.19		68	49	90
	0.17		69	92	178
	0.27		138	106	83
Na3	0.18		112	40	124
	0.17		56	125	145
	0.19		82	150	110
Na4	0.18		138	61	112
	0.17		131	97	30

Table 4.2 α-$Na_2Cr_2O_7$. Principal axes of anisotropic temperature factors

Atom	rms Displace-ments (Å)	Angles in degrees with respect to bond		Angles in degrees with respect to a	b	c
	0.22			117	116	37
Cr1	0.20			51	154	115
	0.18			129	88	116
	0.23			134	109	53
Cr2	0.20			50	161	104
	0.18			107	88	140
		Cr1-O11				
	0.28	86		72	49	80
O11	0.27	88		104	56	139
	0.21	5		23	120	130
		Cr1-O12				
	0.29	116		96	57	144
O12	0.25	27		82	103	113
	0.23	27		82	144	117
		Cr1-O13				
	0.31	85		65	163	107
O13	0.29	97		143	83	103
	0.20	171		115	105	21
		Cr2-O21				
	0.29	83		111	134	65
O21	0.26	76		21	134	102
	0.21	165		89	80	28
		Cr2-O21				
	0.49	95		113	19	107
O22	0.27	89		72	73	52
	0.21	5		29	98	137
		Cr2-O23				
	0.47	65		152	91	54
O23	0.27	76		80	82	37
	0.19	150		116	8	95
		Cr1-OB12	Cr2-OB12			
	0.40	90	84	41	99	151
OB12	0.21	133	92	82	39	79
	0.19	137	7	130	52	116

(continued next page)

Table 4.2 α-$Na_2Cr_2O_7$ (continued)

Atom	rms Displacements (Å)	Angles in degrees with respect to bond	Angles in degrees with respect to a	b	c
	0.33		141	104	78
Na1	0.25		55	141	129
	0.23		104	55	138
	0.32		37	148	93
Na2	0.25		81	70	45
	0.22		125	113	45

Table 4.3 β1-$Rb_2Cr_2O_7$. Principal axes of anisotropic temperature factors

Atom	rms Displacements (Å)	Angles in degrees with respect to bond		Angles in degrees with respect to a	b	c
	0.17			132	45	99
Cr1	0.15			114	96	16
	0.11			51	45	78
	0.16			132	85	129
CR2	0.15			72	150	112
	0.14			133	120	47
		Cr1-O11				
	0.28	84		109	122	31
O11	0.15	61		74	148	115
	0.14	150		25	85	74
		Cr1-O12				
	0.26	97		125	144	72
O12	0.19	81		134	69	122
	0.14	169		65	118	142
		Cr1-O13				
	0.28	56		87	16	78
O13	0.20	47		138	78	122
	0.16	62		132	101	35
		Cr2-O21				
	0.25	99		88	73	23
O21	0.15	79		143	126	69
	0.11	166		127	41	100
		Cr2-O22				
	0.21	102		149	62	95
O22	0.15	52		80	93	173
	0.15	139		119	152	85
		Cr2-O23				
	0.23	97		139	133	80
O23	0.18	85		122	55	125
	0.14	172		67	118	143
		Cr1-OB12	Cr2-OB12			
	0.21	56	141	178	93	83
OB12	0.18	47	117	91	109	17
	0.13	62	64	88	161	105
	0.18			125	45	110
Cr3	0.16			78	53	46
	0.15			142	112	51

(continued next page)

Table 4.3 β1-$Rb_2Cr_2O_7$ (continued)

Atom	rms Displace-ments (Å)	Angles in degrees with respect to bond		Angles in degrees with respect to a	b	c
	0.18			128	47	108
Cr4	0.15			89	62	33
	0.13			142	124	64
		Cr3-O31				
	0.21	134		90	54	41
O31	0.20	56		120	46	118
	0.17	117		150	114	63
		Cr3-O32				
	0.22	94		98	159	66
O32	0.18	16		47	80	53
	0.13	106		44	108	134
		Cr3-O33				
	0.25	101		43	90	141
O33	0.21	109		100	16	104
	0.18	22		49	74	55
		Cr4-O41				
	0.27	92		32	85	67
O41	0.19	87		77	159	103
	0.11	4		119	110	27
		Cr4-O42				
	0.25	85		75	68	35
O42	0.19	64		115	143	57
	0.16	154		30	118	98
		Cr4-O43				
	0.22	69		143	85	119
O43	0.20	115		108	157	69
	0.13	34		59	113	143
		Cr3-OB34	Cr4-OB34			
	0.23	81	99	48	134	105
OB34	0.20	101	121	73	89	26
	0.09	15	147	133	136	69
	0.21			128	60	123
Rb1	0.16			142	109	48
	0.15			85	36	59
	0.20			65	152	101
Rb2	0.17			27	68	84
	0.14			100	106	13
	0.18			84	157	109
Rb3	0.16			98	69	155
	0.15			170	99	75
	0.20			115	27	94
Rb4	0.18			36	64	74
	0.15			114	97	16

Table 4.4 $P2_1/c$ $NaRbCr_2O_7$. Principal axes of anisotropic temperature factors

Atom	rms Displacements (Å)	Angles in degrees with respect to bond		Angles in degrees with respect to a	b	c
	0.16			34	122	103
Cr1	0.15			101	123	35
	0.12			58	50	59
	0.17			95	7	94
Cr2	0.15			66	92	160
	0.12			24	83	70
		Cr1-O11				
	0.23	82		100	52	139
O11	0.21	83		168	102	83
	0.15	170		83	140	130
		Cr1-O12				
	0.25	93		68	156	99
O12	0.19	78		26	71	77
	0.14	167		103	103	16
		Cr1-O13				
	0.25	86		85	135	135
O13	0.21	116		164	104	80
	0.11	26		105	49	134
		Cr2-O21				
	0.21	112		72	158	103
O21	0.20	82		92	78	167
	0.13	24		162	108	88
		Cr2-O22				
	0.24	69		47	46	79
O22	0.20	88		59	104	148
	0.15	159		121	47	119
		Cr2-O23				
	0.20	88		131	43	99
O23	0.19	53		75	63	33
	0.16	143		135	121	58
		Cr1-OB12	Cr2-OB12			
	0.31	95	72	114	31	106
OB12	0.16	130	93	141	98	48
	0.13	139	18	61	61	46
	0.16			67	139	124
Cr3	0.15			123	131	56
	0.12			138	85	128

(continued next page)

Table 4.4 $P2_1/c$ $NaRbCr_2O_7$. (continued)

Atom	rms Displacements (Å)	Angles in degrees with respect to bond		Angles in degrees with respect to a	b	c
	0.17			66	94	159
Cr4	0.16			110	24	101
	0.13			32	66	73
		Cr3-O31				
	0.25	103		76	55	40
O31	0.22	66		109	36	118
	0.17	28		156	98	64
		Cr3-O32				
	0.26	78		31	105	119
O32	0.17	53		112	73	150
	0.13	140		69	23	83
		Cr3-O33				
	0.26	95		57	34	86
O33	0.23	78		34	122	104
	0.13	167		96	79	166
		Cr4-O41				
	0.28	105		152	99	61
O41	0.23	84		116	52	130
	0.14	16		80	39	54
		Cr4-O42				
	0.26	84		44	75	54
O42	0.23	67		96	17	106
	0.16	24		47	98	139
		Cr4-O43				
	0.27	82		86	116	154
O43	0.21	109		173	87	92
	0.14	20		96	153	64
		Cr3-OB34	Cr4-OB34			
	0.32	89	83	59	95	152
OB34	0.17	132	86	96	173	88
	0.14	137	8	148	85	118
	0.20			35	92	128
Na1	0.17			70	34	65
	0.15			117	56	132
	0.21			140	130	86
Na2	0.19			88	95	175
	0.15			130	40	93

(continued next page)

Table 4.4 $P2_1/c$ $NaRbCr_2O_7$ (continued)

Atom	rms Displacements (Å)	Angles in degrees with respect to bond	Angles in degrees with respect to		
			a	b	c
	0.19		169	100	82
Rb1	0.19		79	67	154
	0.16		83	155	115
	0.19		147	113	65
Rb2	0.18		72	77	25
	0.16		116	27	92

Table 4.5 Raman spectra of β1 $K_2Cr_2O_7$ according to Luu and Lafont (33).

			Assignment
41 cm^{-1}		34 cm^{-1}	
48		44	libration
60		55	
78		87	
83		71	translation
105		120	
133		127	A_2 } torsion of Cr_2O_7
146		150	B_2 }
240		225	A_1 Cr-O-Cr bending
	280		
	290		
	300		$A_1+A_2+B_1+B_2$
	320		CrO_3 rocking
	335		
	340		
	367		A_1 } CrO_3 symmetric bend
	390		B_1 }
	377		A_2 }
	380		B_2 } CrO_3 antisymmetric bend
	390		B_1 }
	394		A_1 }
450-476-502-525			? Very weak
562		572	A_1 (O_3Cr)-O symmetric stretch
	605-650-694		? Very weak
755		743	B_1 (O_3Cr)-O antisymmetric stretch
	826		?
917		916	A_1 } Cr-O symmetric stretch
	891		B_1 }
962		962	A_1 }
926		930	A_2 } Cr-O antisymmetric stretch
945		948	B_1 }
954		956	B_2 }

Estimates of the rms amplitudes for the libration around the minor (Cr-Cr) axis and for the two torsion, Table 4.6, have been calculated from the temperature factors after the subtraction of the translational motion. Usually it is assumed (34) that the translational and librational modes only are important. In this case the bridging oxygen atom should show librational amplitude around the Cr-Cr axis of the same size as the other oxygen atoms but the bridging oxygen atoms show systematically larger libration than the terminal oxygen atoms. Such an apparent libration can be explained if the antisymmetric torsion mode $(\alpha_1+\alpha_2)$ is active. The bridging oxygen appears to have a larger vibration because of the coupling between the libration mode (around Cr-Cr) and the antisymmetric torsion mode which allows the terminal oxygens to remain relatively fixed in the crystal.

One consequence of the thermal motion is that the Cr-O bonds calculated from the atomic coordinates appear shorter than they really are (35). These bond lengths have been corrected using the method of Busing and Levy (36) and the corrected, together with the uncorrected bond lengths are given in Tables 4.7, 4.8, 4.9, 4.10. It is assumed that the oxygen atoms are riding on chromium atoms, an assumption that is in reasonable agreement with the proposed motion of the dichromate groups. As the Busing and Levy correction applies for small vibrations only bond lengths for some of the

Table 4.6 Estimates of libration and torsion amplitudes. Rms values in degrees

	α-$Na_2Cr_2O_7$	β-$Na_2Cr_2O_7$		β1-$K_2Cr_2O_7$		β1-$Rb_2Cr_2O_7$		$NaRbCr_2O_7$	
*	1 Cr1,Cr2	2 Cr1,Cr2	3 Cr3,Cr4	4 Cr1,Cr2	5 Cr3,Cr4	6 Cr1,Cr2	7 Cr3,Cr4	10 Cr1,Cr2	11 Cr3,Cr4
Libration of Cr_2O_7 around Cr-Cr	8	6	7	7	7	7	5	6	6
OB libration around Cr-Cr	27	13	14	9	12	8	14	21	25
† B_2 torsion	7	6	6	6	7	6	6	7	9
*† A_2 torsion	8	6	6	6	6	6	4	6	7

*The numbers are used to identify the anions in Figure 4.3.
The atoms in parentheses belong to the anion.

†Estimated from the apparent libration of CrO_4 groups around an axis parallel to the line from the middle of the Cr-Cr distance to the bridging oxygen

*†Estimated from the apparent libration of CrO_4 around the Cr-OB axis.

Table 4.7 β-$Na_2Cr_2O_7$. Interatomic Distances

		Uncorrected Distance (Å)	Corrected* Distance (Å)	Angles (in degrees)		
				O12	O13	OB12
Cr1	O11	1.622	1.63	111	113	106
	O12	1.620	1.63		110	110
	O13	1.601	1.61			108
	OB12	1.782	1.79			
				O22	O23	OB12
Cr2	O21	1.609	1.62	111	111	108
	O22	1.620	1.64		108	109
	O23	1.618	1.64			110
	OB12	1.778	1.79			
		Cr1 - OB12 - Cr2	131.3°			
				O32	O33	OB34
Cr3	O31	1.602	1.62	111	112	110
	O32	1.618	1.63		110	109
	O33	1.612	1.63			104
	OB34	1.790	1.80			
				O42	O43	OB34
Cr4	O41	1.602	1.61	109	111	110
	O42	1.624	1.64		107	109
	O43	1.612	1.63			111
	OB34	1.786	1.80			
		Cr3 - OB34 - Cr4	131.3°			

*Correction for thermal motion, see text.

Na-O distances less than 3.3 Å

Na1-O33	2.347	Na2-O23	2.375	Na3-O41	2.355	Na4-O42	2.386
O21	2.385	O32	2.391	O13	2.433	O12	2.411
O42	2.447	O22	2.432	O23	2.466	O43	2.414
O41	2.467	OB34	2.448	O32	2.580	O22	2.489
O12	2.476	O11	2.538	O11	2.634	O13	2.492
O31	2.545	O33	2.678	O21	2.673	O31	2.502
				O43	2.825		

Standard errors derived from least squares refinement:

Cr-O = 0.011Å; Na-O = 0.013Å; O-Cr-O = 1°; Cr-O-Cr = 0.4°

Table 4.8 α-$Na_2Cr_2O_7$. Interatomic Distances

		Uncorrected Distance (Å)	Corrected* Distance (Å)	Angles (in degrees) O12	O13	OB12
Cr1	O11	1.620	1.64	111	112	109
	O12	1.604	1.62		110	110
	O13	1.627	1.66			105
	OB12	1.785	1.82			
				O22	O23	OB12
Cr2	O21	1.604	1.62	109	111	110
	O22	1.618	1.69		109	107
	O23	1.583	1.64			110
	OB12	1.750	1.78			

Cr1 - OB12 - Cr2 135.1°

Na-O Distances less than 3.3 Å

		Distance (Å)			Distance (Å)
Na1	O13	2.367	Na2	O22	2.405
	O21	2.423		O23	2.425
	O12	2.561		O12	2.448
	O21	2.601		O11	2.526
	O11	2.654		O13	2.660
	O22	2.762		OB12	2.736
	O23	2.835		O22	2.939

Standard errors derived from least squares refinement:
Cr-O = 0.010 Å, Na-O = 0.012 Å, O-Cr-O = 1°, Cr-O-Cr = 0.6°

*Correction for thermal motion, see text.

Table 4.9 β1-$Rb_2Cr_2O_7$. Interatomic Distances

		Uncorrected Distance (Å)	Corrected* Distance (Å)	Angles (in degrees)		
				O12	O13	OB12
Cr1	O11	1.600	1.61	110	112	108
	O12	1.604	1.62		109	110
	O13	1.602	1.62			109
	OB12	1.780	1.79			
				O22	O23	OB12
Cr2	O21	1.624	1.64	110	110	110
	O22	1.630	1.64		108	109
	O23	1.616	1.63			109
	OB12	1.772	1.78			
		Cr1 - OB12 - Cr2 = 123.0°				
				O32	O33	OB34
Cr3	O31	1.600	1.61	110	110	106
	O32	1.615	1.62		111	109
	O33	1.609	1.62			111
	OB34	1.789	1.80			
				O42	O43	OB34
Cr4	O41	1.593	1.61	110	109	110
	O42	1.606	1.62		110	111
	O43	1.602	1.61			108
	OB34	1.759	1.77			
		Cr3 - OB34 - Cr4 = 137.5°				

*Correction for thermal motion, see text.

Rb-O Distances less than 3.31 Å

Rb1-O21	2.86	Rb2-O22	2.89	Rb3-O43	2.87	Rb4-OB34	2.90
O13	2.87	O23	2.91	O33	2.88	O33	2.90
O22	2.89	O31	2.99	O41	2.92	O32	2.94
O23	2.90	O12	3.04	O22	2.93	O12	2.96
O12	2.91	O13	3.04	O43	3.00	O43	2.96
O32	2.93	O42	3.06	O11	3.02	O42	3.11
O23	3.07	O11	3.07	O32	3.02	O31	3.23
O31	3.28	OB12	3.19	O21	3.09	O11	3.24
		O41	3.24			O41	3.31

Standard errors derived from least squares refinement:

Cr-O = 0.01 Å , Rb-O = 0.01 Å , O-Cr-O = 1°.

Table 4.10 NaRb Cr_2O_7. Interatomic Distances

		Uncorrected (Distance (Å)	Corrected* Distance (Å)	Angles (in degrees)		
				O12	O13	OB12
Cr1	O11	1.597	1.61	112	109	106
	O12	1.611	1.63		109	112
	O13	1.593	1.61			109
	OB12	1.769	1.79			
				O22	O23	OB12
Cr2	O21	1.615	1.62	112	110	107
	O22	1.618	1.64		109	109
	O23	1.620	1.63			110
	OB12	1.755	1.78			

Cr1 - OB12 - Cr2 = 135.9°

				O32	O33	OB34
Cr3	O31	1.593	1.61	110	109	106
	O32	1.630	1.64		109	111
	O33	1.630	1.65			111
	OB34	1.746	1.77			
				O42	O43	OB34
Cr4	O41	1.607	1.63	111	111	106
	O42	1.608	1.63		109	108
	O43	1.604	1.62			111
	OB34	1.767	1.79			

Cr3 - OB34 - Cr4 = 141.4°

*Correction for thermal motion, see text.

Na-O Distances less than 3.0 Å				Rb-O Distances less than 3.4 Å			
Na1-O11	2.332	Na2-O21	2.351	Rb1-O13	2.908	Rb2-O32	2.972
O42	2.362	O33	2.434	O23	2.994	O43	3.019
O23	2.442	O41	2.458	O42	3.004	O32	3.097
O12	2.452	O31	2.556	O22	3.008	O33	3.164
O21	2.568	O13	2.576	O22	3.065	O33	3.198
O31	2.608	O12	2.598	OB12	3.152	O13	3.208
O23	2.770	O32	2.874	O43	3.293	OB34	3.214
		O11	2.884	O41	3.316	O12	3.226
				O43	3.323	O41	3.316
				OB12	3.385	O31	3.337
						O42	3.338
						OB34	3.377

Standard errors indicated by the leat squares refinement
Cr-O = 0.010 Å, Na-O = 0.010 Å, Rb-O = 0.010 Å, O-Cr-O = 1°
Cr-O-Cr = 0.6°.

α-$Na_2Cr_2O_7$ bonds which have large temperature factors are somewhat uncertain.

4.3 Discussion on the Conformations of the Dichromate Ion

The main features of dichromate ions found in the various structures are summarised in Table 4.11. The mean bond lengths of the terminal oxygen atoms of the various conformations vary between 1.60 to 1.63 Å. The Cr-OB bond length varies between 1.76 to 1.80 Å. The mean O-Cr-O angle in all structures is very close to the tetrahedral value of 109.47°. What varies significantly from structure to structure is the bridging oxygen angle which ranges from 121° to 141° and the two torsion angles α_1 and α_2. These angles are taken to be zero when a terminal oxygen atom lies in the Cr-B-Cr plane (A conformation), and are otherwise taken to be the smallest angle between this plane and the projection of one of the Cr-O (terminal) bonds on the plane perpendicular to Cr-B (bridging oxygen). The sense of the rotation is taken as positive if the terminal oxygen atom lies to the left of the Cr-B-Cr plane when viewed from the bridging oxygen.

The torsion angles found in a variety of dichromate ions are plotted against each other in Figure 4.3. Since the CrO_4 tetrahedra of the anions have almost exact C_{3v} symmetry with the Cr-B bond as the threefold axis it is sufficient to consider values of α_1 and α_2 only in the -60 to +60 degrees. On the other hand in all of these structures two dichromate

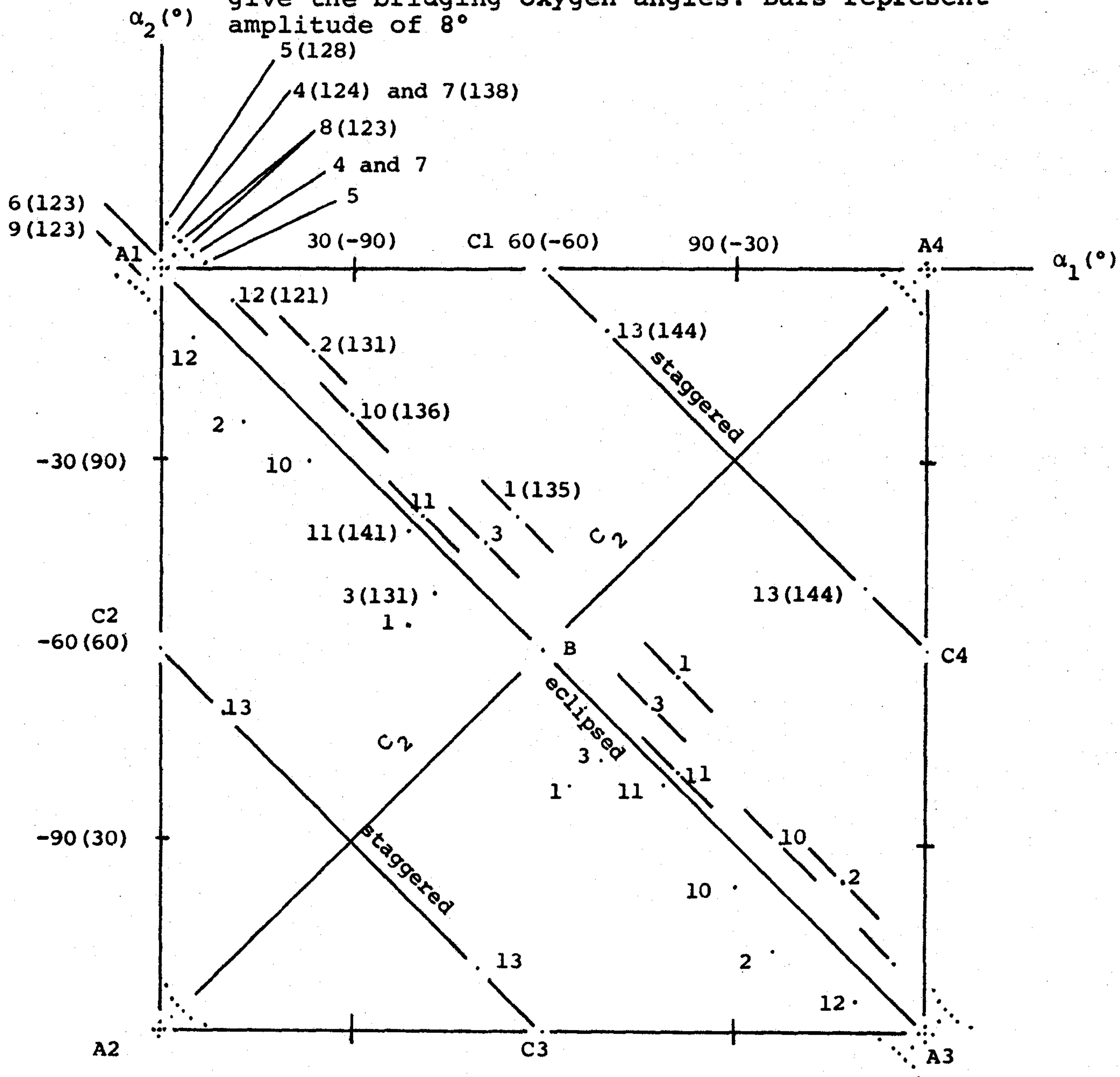
Table 4.11 Geometry of the dichromate ion

	$Na_2Cr_2O_7$			$K_2Cr_2O_7$		$Rb_2Cr_2O_7$				$NaRbCr_2O_7$		$Ag_2Cr_2O_7$	$Mg_2P_2O_7$
Phase	α	β		β1		β1		VII	X	$P2_1/c$		$P\bar{1}$	α
Dichromate ion Number †	1	2	3	4	5	6	7	8	9	10	11	12	13
Symmetry	*	*	*	*	*	*	*	*	C_2	*	*	*	
Mean Cr-OB (Å)	1.77	1.79	1.80	1.78	1.78	1.78	1.78	1.80	1.77	1.76	1.76	1.78	
Mean Cr-O (terminal (Å)	1.61	1.63	1.63	1.63	1.60	1.63	1.62	1.60	1.62	1.61	1.61	1.62	
Cr-Cr (Å)	3.27	3.24	3.26	3.14	3.19	3.12	3.31	3.16	3.12	3.27	3.32		
Mean O-Cr-O (degrees)	109.4	109.5	109.4	109.6	109.4	109.6	109.7	109.4	109.3	109.5	109.5		
Cr-Ob-Cr (degrees)	135	131.3	131.3	124.0	127.6	123.0	137.5	122.9	122.9	135.9	141.4	121.0	144.
α_1 (degrees)	56	24	51	5	7	1	5	4	2	30	41	11	-50
α_2 (degrees	-39	-13	-43	2	1	0	2	3	2	-23	-39	-5	-10

† The number given in Figure 4.3

* Exact symmetry C_1

Figure 4.3 Conformations of the dichromate ion. The anions are numbered as in Table 4.11. Numbers in parentheses give the bridging oxygen angles. Bars represent amplitude of 8°



ions are related by centers of symmetry so each ion is accompanied by its enantiomorph, with $\alpha_1 = -\alpha_1$ and $\alpha_2 = \alpha_2$. In addition the assignment of α_1 or α_2 to a particular end of the dichromate ion is arbitrary so α_1 and α_2 can be interchanged. These symmetries generate for each point on the graph a further three points.

The origin A1 (with $\alpha_1 = 0$, $\alpha_2 = 0$) corresponds to the conformation A with C2v symmetry, the points A2, A3, A4, each represent also the A conformation. The point B represents the B conformation with C2v symmetry and the points C1, C2, C3, C4 represent staggered conformations with C_1 symmetry. The line $\alpha_1 = \alpha_2$ (A2A4) represents conformations with C_2 symmetry while the line $\alpha_1 = -\alpha_2$ (A1A3) represents conformations where the terminal oxygens are eclipsed. The lines C1C2 and C3C4 represent conformations in which the terminal oxygens are in a staggered conformation.

All the conformations so far found in anhydrous dichromates† are concentrated around the $\alpha_1 = -\alpha_2$ axis. Close to the origin the bridging angle lies between 121° to 128°††. For conformations with $|\alpha| > 15°$ the bridging angle is normally

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†The anions in $Na_2Cr_2O_7 \cdot 2H_2O$ have conformations with bridge angle b=126°, α_1=21°, α_2=13° and b = 122°, α_1=12°, α_2=3°. We do not consider these anions because of the hydrogen bonding between the water molecules and the anions.

††The only exception is the angle 138° found in one of the ions in β1(VIII) $Rb_2Cr_2O_7$.

larger than 130 degrees. These larger values for conformations close to B can be understood in terms of the repulsion of the two terminal oxygen atoms which lie on the mirror plane. If the bridging angle were to be 125° the O-O distance would be around 2.6 Å. With a bridging angle of 130° this distance increases to 3.2 Å (Van der Waals O-O separation 2.8(37)).

The different conformations arising from different values of the torsion angles are related to the two torsion modes of vibration. The antisymmetric torsion mode corresponds to line segments parallel to the $\alpha_1 = -\alpha_2$ line, the symmetric torsion mode to line segments parallel to the $\alpha_1 = \alpha_2$ line.

The torsional motions can thus be displaced on the α_1, α_2 graph by a line of 6° length corresponding to the rms torsional libration. If there is an appropriate change in the environment the dichromate ion can easily adopt a neighbouring conformation. All the conformations are connected by the antisymmetric torsion to form a continuous line. Thus the anion may readily undergo a continuous deformation from the configuration A1 to B and vice versa. As the terminal oxygen atoms are more or less fixed by adjacent atoms in the structure the antisymmetric torsion mode appears in the crystal as a libration of the bridging oxygen around the Cr-Cr axis. In the crystal frame of reference the transitions between conformations parallel to the $\alpha_1 = -\alpha_2$ line appears as a rotation of the bridging oxygen around the Cr-Cr axis . The position of the terminal oxygen atoms in this picture change by small amounts.

Since most dichromates have conformations lying close to the $\alpha_1 = -\alpha_2$ line and that in the crystal a change of conformation along this line can be achieved by rotation of only the bridging oxygen atom, leaving the other atoms relatively unchanged, it can be seen that transformations involving such conformation changes might easily occur.

4.4 The α to β Phase Transition in $Na_2Cr_2O_7$

As the temperature of the α phase of $Na_2Cr_2O_7$ is lowered the torsional $(\alpha_1+\alpha_2)$ and one of the librational oscillations around the mirror axis of the moment of inertia becomes large. The particular lattice mode is one in which Cr_2O_7 ions in different layers† move in opposite directions. At the phase transitions these motions freeze out so that layers become different. As the temperature is decreased further the layers differ more and more from each other, an effect that continues to room temperature and probably below.

It is interesting to note that the same sort of torsional mode is invoked by Brown and Calvo (3) to explain

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†Layers of dichromate ions parallel to the (010) plane, related above the transition temperature with the A face centering symmetry operation. A description of these layers is given in Chapter 5.

the $\beta_1 \rightarrow \alpha$ phase transition in $K_2Cr_2O_7$ but in this case there is a sudden flipping of half the bridging oxygen atoms through 120° with a corresponding transformation of half the sheets.

CHAPTER 5

LAYERS IN THORTVEITITE AND DICHROMATE LIKE STRUCTURES

5.1 Introduction. Description of the Layers

Compounds with stoichiometry $X_2Y_2O_7$ where the ionic radius of the Y atom is less than 0.60 Å usually crystallize either in structures related to thortveitite if the ionic radius of X is less than 0.97 Å or in one of a series of related structures typical of those found among the alkali metal dichromates if the ionic radius of X is greater than 0.97 Å.

Thortveitite like structures are found for many pyrophosphates (38-40) and pyroarsenates (41). They usually have a high temperature β phase which is isomorphous with the mineral thortveitite ($Sc_2Si_2O_7$, (42)) and show a bridging angle Y-O-Y of 180° and a low temperature α phase which have a bridging angle of less than 180°. The α phases show great diversity in their structures although all similar to thortveitite.

Crystals which adopt one of dichromate structures include alkali dichromates, $Ag_2Cr_2O_7$, $\beta Ca_2P_2O_7$, $\beta Sr_2V_2O_7$, $Pb_2V_2O_7$, Brown and Calvo (3) have developed a general scheme for classifying dichromate like structures by considering the various stacking arrangements of sheets of dichromate ions. Their scheme does not extend to the thortveitite like structures nor does it include that of $NaRbCr_2O_7$ or $\alpha\ Ca_2P_2O_7$.

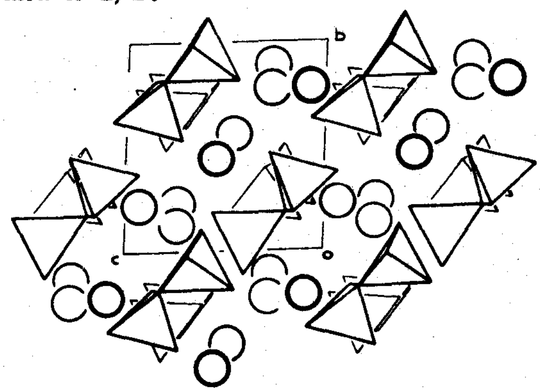
An alternative description can be used to describe both thortveitie and dichromate like structures. Both types of structures are built up from layers of Y_2O_7 ions with the cations sandwiched between them, Figure 5.1a, b, the Y-Y vectors lie in the plane of the layer.

Orthogonal projections of the layers of a few structures are given in Figures 5.1c, 5.2, 5.3 and 5.4. The A and C axes lie in the plane of the layer and are chosen to give a B centered cell. The Y-Y vectors are roughly parallel to the A axis and perpendicular to C. We shall call the rows of anions parallel to the C axis C rows and the rows parallel to the A axis A rows.

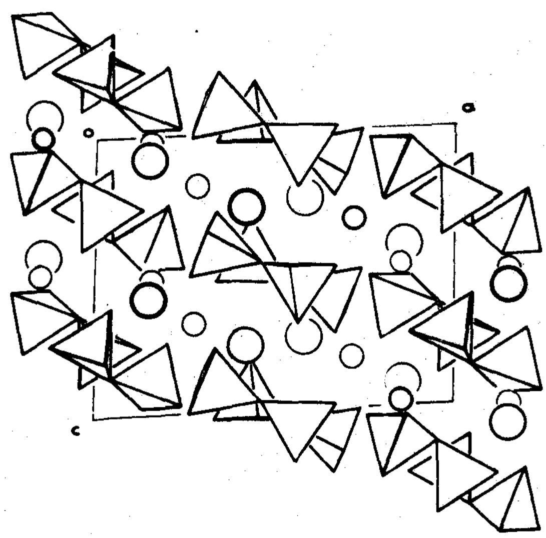
The Y_2O_7 anions of the C rows are related in the thortveitite structures by a glide plane lying in the plane of the layer and in the dichromate structures by centers of symmetry. Both of these symmetry elements are present in thortveitite itself. With the exception of the α-$Mg_2P_2O_7$ (39) layer all the other layers of Figures 5.2 to 5.4 have the A row anions related by centers of symmetry, with the result that the unit cell defined by the A and C axes is B face centered, i.e. adjacent C rows are related to each other by a translation and there is only one crystallographically

Figure 5.1 Layers in $\beta1\text{-}Rb_2Cr_2O_7$, $NaRbCr_2O_7$ and $Sc_2Si_2O_7$

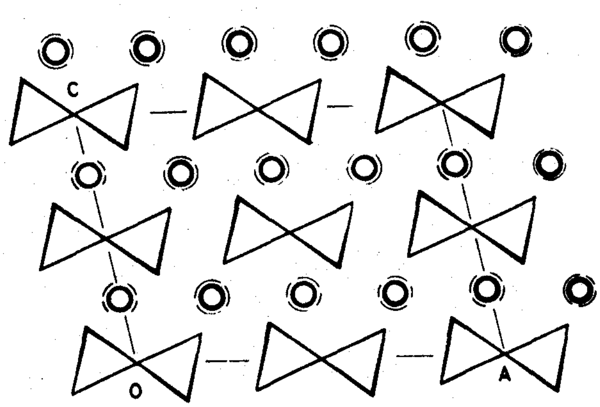
a) $\beta1\text{-}Rb_2Cr_2O_7$ ($P\bar{1}$). Viewed down the [101] axis, atoms around x=0 and x=1/2.



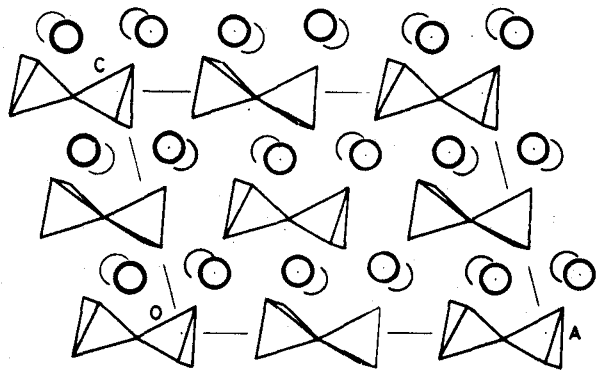
b) $NaRbCr_2O_7$ ($P2_1/c$). Viewed down the b axis, atoms around y = 0 and y = $\frac{1}{2}$.



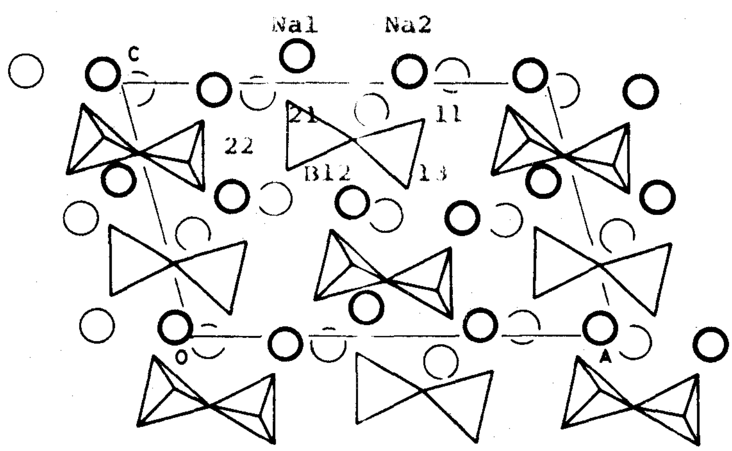
c) $Sc_2Si_2O_7$ (C2/m) Plane (010) viewed down the [010]*; O = 0,0,0; A = 2,0,0; C = 0,0,2.



a) α-$Mg_2P_2O_7$ ($B2_1/c$). Plane $(0\bar{1}0)$, viewed down the $[0\bar{1}0]^*$;
$O = 0,\frac{1}{4},0$; $A = 1,\frac{1}{4},0$; $C = 0,\frac{1}{4},1$.



b) α-$Na_2Cr_2O_7$ ($A\bar{1}$). Plane (010) viewed down the $[010]^*$;
$O = 1,0,0$; $A = \bar{1},0,\bar{1}$; $C = 1,0,1$.



c) X-$Rb_2Cr_2O_7$ ($C2/c$) Plane $(\bar{1}11)$ viewed down the $[\bar{1}11]^*$
$O = 0,0,\frac{1}{2}$; $A = 1,0,1\frac{1}{2}$; $C = 0,1,\frac{\bar{1}}{2}$.

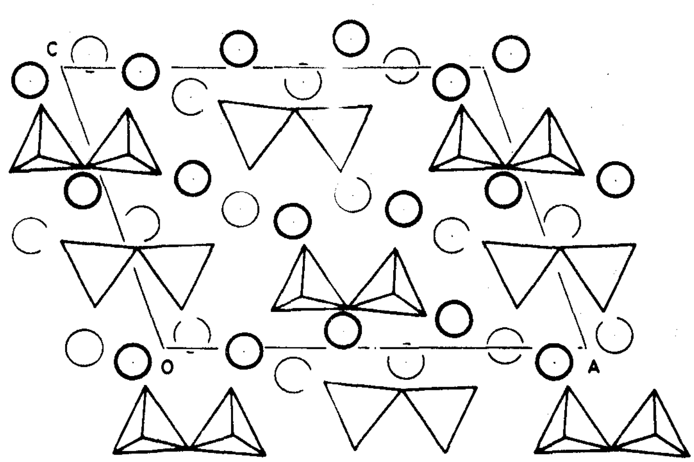
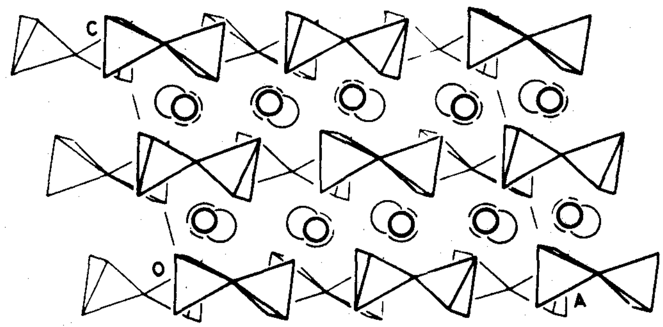


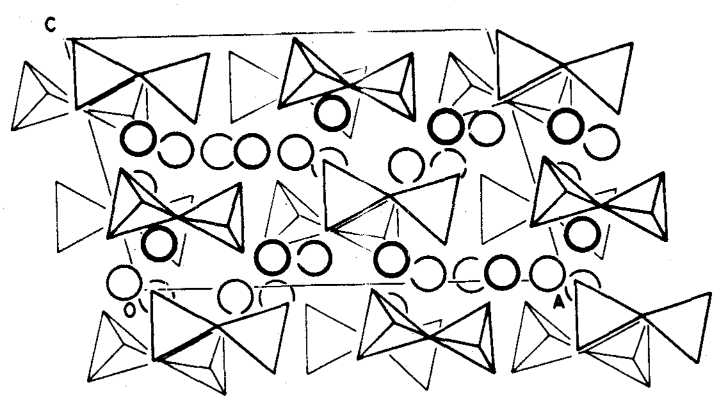
Figure 5.2 Layers of α-$Mg_2P_2O_7$, α-$Na_2Cr_2O_7$ and X-$Rb_2Cr_2O_7$

Figure 5.3 Packing of the layers in α-$Mg_2P_2O_7$, α-$Na_2Cr_2O_7$ and X-$Rb_2Cr_2O_7$. The layers of Figure 5.2 and the next higher layer.

a) α-$Mg_2P_2O_7$



b) α-$Na_2Cr_2O_7$



c) X-$Rb_2Cr_2O_7$

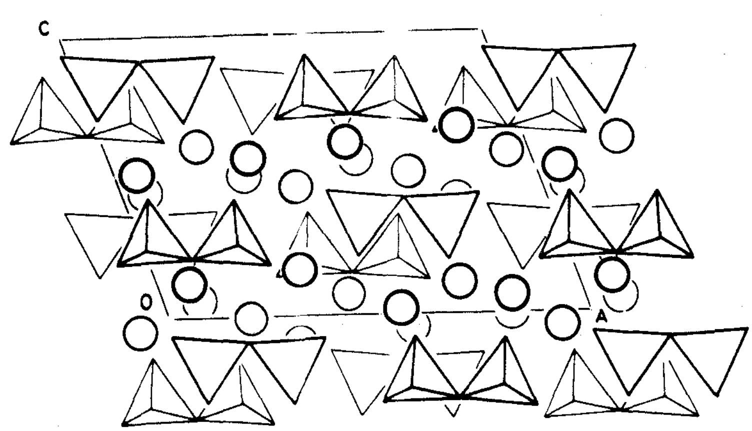
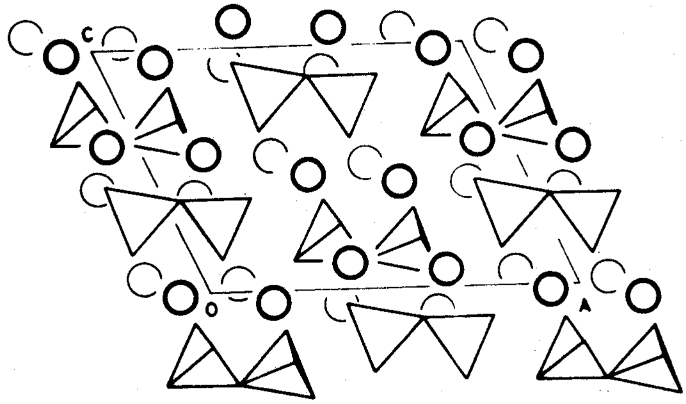
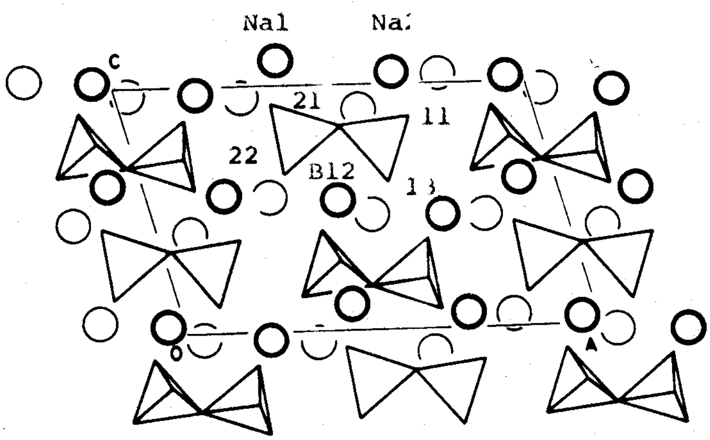


Figure 5.4 Layers of $Ag_2Cr_2O_7$ and β-$Na_2Cr_2O_7$

a) $Ag_2Cr_2O_7$ ($P\bar{1}$). Plane (100) viewed down the [$\bar{1}$00]*;
O = $1,0,0$; A = $\bar{1},0,\bar{1}$; C = $1,0,1$



b) β-$Na_2Cr_2O_7$ ($P\bar{1}$). Plane (010) viewed down the [010]*;
O = $1,0,0$; A = $\bar{1},0,\bar{1}$; C = $1,0,1$



c) β-$Na_2Cr_2O_7$ ($P\bar{1}$). Plane (010) viewed down the [010]*;
O = $1,\frac{1}{2},\frac{1}{2}$; A = $\bar{1},\frac{1}{2},\frac{\bar{1}}{2}$ C = $1,\frac{1}{2},1\frac{1}{2}$.

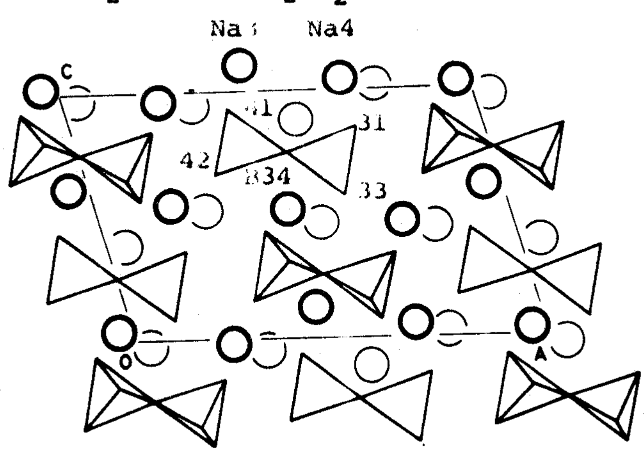
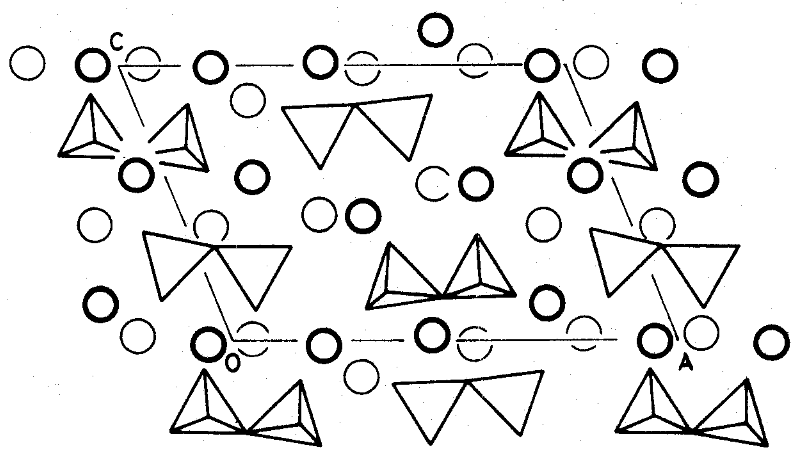
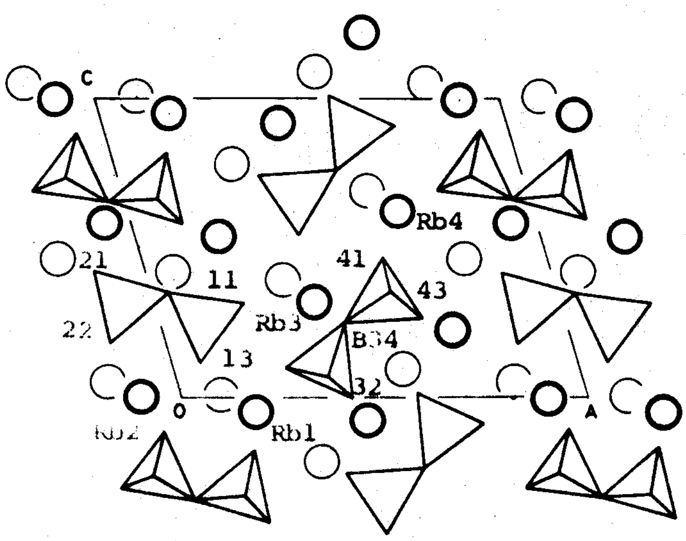


Figure 5.5 Layers of VII-$Rb_2Cr_2O_7$ and β1-$Rb_2Cr_2O_7$

a) VII-$Rb_2Cr_2O_7$ ($P2_1/n$). Plane (111) viewed down the $[\bar{1}\bar{1}\bar{1}]^*$; O = 0,1,0; A = 1,1,$\bar{1}$; C = 0,0,1.



b) β1-$Rb_2Cr_2O_7$ ($P\bar{1}$). Plane $(11\bar{1})$ viewed down the $[\bar{1}\bar{1}1]^*$; O = 0,0,$\frac{1}{2}$; A = 1,0,1$\frac{1}{2}$; C = 0,1,$-\frac{1}{2}$.



distinct anion.

In $Sc_2Si_2O_7$ thortveitite the C glide becomes a mirror plane and there are additional centers of symmetry on the bridging oxygen, relating the two halves of the Si_2O_7 anion and imposing a bridging oxygen angle of 180° and a staggered conformation to the anion.

In α-$Mg_2P_2O_7$ the A,C cell is B face centered but with the exception of the C glide there is no other symmetry element that relates anions of the A or C rows. With no restriction on its symmetry, the anion has a distorted staggered conformation similar to the anion in $Sc_2Si_2O_7$ but with a bridging angle different from 180°. Though the centers of symmetry are lost, the differences from the $Sc_2Si_2O_7$ layer are small and one can identify pseudocenters of symmetry that relate the A row anions.

5.2 The Structure and Packing of Typical Layers (α-$Mg_2P_2O_7$, α-$Na_2Cr_2O_7$, X C2/c$Rb_2Cr_2O_7$)

The layers

We will examine the structure of the layers by concentrating on three typical structures only, α-$Mg_2P_2O_7$, α-$Na_2Cr_2O_7$ and type X C2/c $Rb_2Cr_2O_7$, Figures 5.2, 5.3, representing structures with small ($r<0.95$ Å), intermediate ($0.95<r<1.05$ Å) and large ($r>1.05$ Å) cation respectively.

In both $Sc_2Si_2O_7$ and α-$Mg_2P_2O_7$ the c glide has as a consequence that the bridging oxygens lie on the C axis while in α-$Na_2Cr_2O_7$ and C2/c $Rb_2Cr_2O_7$ the C glide is lost and the A rows are shifted in the A direction relative to each other by small amounts. In these layers the Cr_2O_7 ions have eclipsed conformations for the terminal oxygens and the cations have moved from the positions they occupied in α-$Mg_2P_2O_7$.

In α-$Na_2Cr_2O_7$ this shift is appreciable for the two cations which lie in the middle of the first C row, but the layer is still rather similar to that of α-$Mg_2P_2O_7$. In going from α-$Na_2Cr_2O_7$ to X $Rb_2Cr_2O_7$ the shifts become larger for all the cations and the layer differs more from that in α-$Mg_2P_2O_7$. In X $Rb_2Cr_2O_7$ there are crystallographic twofold axes running through the bridging oxygen atom at an angle of about 45° to the normal to the layers and a glide plane normal to this axis relating ions along the A rows.

Packing of the layers

In α-$Mg_2P_2O_7$ neighbouring layers, are related with a 2_1 axis perpendicular to the layer in a way that the layer above is not only rotated in relation to the layer below by 180° but also is shifted by 1/4 A. As a result the C rows of the layer above lie in the middle of two C rows of the layer below and are related by a pseudotranslation of $\frac{1}{4}A + \frac{1}{2}C$, Figure 5.3a.

In α-$Na_2Cr_2O_7$ where a simple translation relates neighbouring layers there is a shift of the centers of symmetry of the two layers by about $1/6A + \frac{1}{2}C$, Figure 5.3b.

In X-$Rb_2Cr_2O_7$ neighbouring layers are related with a translation of 1/5A + 1/2C, Figure 5.3c. Thus the relative shift between neighbouring layers decreases as the ionic radius of the cation increases.

In general in thortveitite like structures with a small cation radius there are symmetry elements such as two-fold axes or twofold screw axes normal to the layer. In structures with intermediate radii the layers are related only by translations and centers of symmetry while for cations of large ionic radius the symmetry elements lie at angles of 45° to the layer.

Because in most high symmetry dichromate like structures the layers are not parallel to the planes of symmetry the symmetry of the resulting structure is not apparent from the figures of the layers. For these structures the scheme proposed by Brown and Calvo (3) is more appropriate. In this classification the dichromate-like structures are described in terms of sheets corresponding to the C rows stacked in the A direction. These sheets are described in a system of axes in which a corresponds to the B centering translation described above and b and c lie on the plane of the sheet making angles of about 45° with the B and C axes described above. The symmetry elements in the larger cation alkali metal dichromate structures lie along the a, b and c axes of Brown and Calvo's classification.

5.3 Special Cases of Layers in Small Cation Structures (Thortveitite Like)

The layers described above are characterized by the fact that the Y-Y vectors are parallel to the A axis and the A, C cell is B centered. This type of layer can undergo certain transformations.

The low temperature pyrophosphate phases derived from the thortveitite structure, all differ from the parent structure in having a P-O-P angle of less than 180°. This is achieved by the bridging oxygen atom moving in a direction perpendicular to the layer either up or down. The variety of different structures that appear at low temperatures arise from different arrangements of bridging oxygen displacements.

In α-$Cu_2P_2O_7$ with C2/c symmetry (38), there are no centers of symmetry to relate neighbouring anions in the A rows. Instead they are related by twofold axes and translations while neighbouring A rows are related with a glide plane parallel to the layer.

In the I2/c α-$Zn_2P_2O_7$ (40) the structure is more complex. There are two anion conformations on each A row. Every third anion on the A row has a twofold axis passing through its bridging atom while the two anions in the middle are related to each other by a twofold axis.

5.4 Special Cases of Layers in Medium and Large Cation Structures

5.4.1 $Ag_2Cr_2O_7$

The layers in P$\bar{1}$ $Ag_2Cr_2O_7$, Figure 5.4a, have structures intermediate to that of α-$Na_2Cr_2O_7$ and X(C2/c) $Rb_2Cr_2O_7$. The layer is B centered and the anion has conformation close to that of the anion in X-$Rb_2Cr_2O_7$.

5.4.2 β-$Na_2Cr_2O_7$

β-$Na_2Cr_2O_7$ is a superstructure derivative of α-$Na_2Cr_2O_7$ and alternate layers differ from each other. The intermediate character of $Na_2Cr_2O_7$ in the series is rather strikingly illustrated by the fact that at low temperatures one of the two crystallographically distinct layers in β-$Na_2Cr_2O_7$ becomes similar to that in $Ag_2Cr_2O_7$. The other layer becomes similar to that in the α-$Mg_2P_2O_7$. In each case the conformation of the dichromate ion is like that of the anion in the layer it resembles. Thus β-$Na_2Cr_2O_7$ is composed of alternating α-$Mg_2P_2O_7$ like and $Ag_2Cr_2O_7$ layers.

5.4.3 $P2_1/n$ and β1 P$\bar{1}$ $Rb_2Cr_2O_7$

In $P2_1/n$ $Rb_2Cr_2O_7$ the centering of the A,C cell of X(C2/c) $Rb_2Cr_2O_7$ is lost but the n glide plane is retained, Figure 5.5a. However the differences between the $P2_1/n$ and the C2/c structure are small. The comparison of the $P2_1/n$ with the $C2_1/n$ have rotated around axes normal to the layer in relation to their positions in C2/c.

In β1 $P\bar{1}$ $Rb_2Cr_2O_7$ there is no symmetry element that relates adjacent C rows. One C row shows a small distortion the other a larger distortion from the C rows of C2/c $Rb_2Cr_2O_7$, Figures 5.2c and 5.5b. The relationship between them can best be understood in the scheme of Brown and Calvo where neighbouring C rows belong to different sheets and they are related by a non-crystallographic pseudoglide plane approximately perpendicular to C. As a result of the glide the role of b and c axes is interchanged between one sheet and the next. The slight inequalities in the lengths of b and c necessarily result in α distortion of the second sheet compared to the first. The small differences in environment of the dichromate ions result in differences of the angle at the bridging oxygen atom and the torsion angles α_1 and α_2.

5.4.4 β1(V) $P\bar{1}$ $K_2Cr_2O_7$

The layers of β1 $K_2Cr_2O_7$ are parallel to the $(11\bar{1})$ plane and show rather striking similarities with the β1(VIII) $P\bar{1}$ $Rb_2Cr_2O_7$ layer. The packing of the layers is similar in these two structures. The similarities between the layers of the β1 structures of K and Rb pose some interesting questions as to what extent the β1 → α → β2 phase transitions in K and Rb are similar or different. These questions can not be answered at present. Information on the symmetry of the α $Rb_2Cr_2O_7$ phase is needed.

5.4.5 $P2_1/c$ $NaRbCr_2O_7$

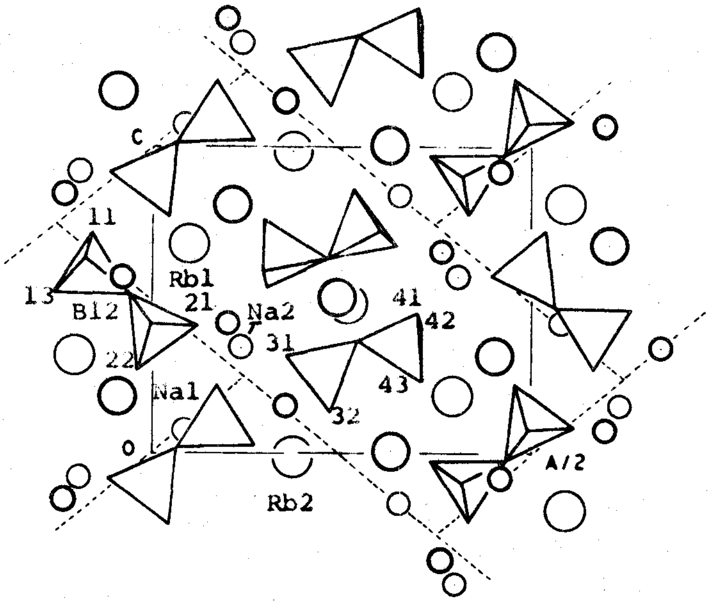
The structure of the $P2_1/c$ $NaRbCr_2O_7$ layer which is parallel to the $(20\bar{1})$ plane is appreciably different from that of the other dichromate layer, Figure 5.6. The A axis, parallel to the [201], has twice the length found in the other dichromates. The C axis is parallel to [010]. Parallel to the C axis there are twofold screw axes which alternate with rows of centers of symmetry. The Na atoms form bonds mainly with the oxygen atoms of the anion that contains Cr1 and Cr2 while the Rb atoms from bonds mainly with the anion that contains Cr3 and Cr4. The arrangement of the cations in the layer is such that rectangular regions of the layer, containing four dichromate ions and 8 rubidium atoms can be identified. Sodium atoms define the bounds of these rectangles. Each rectangle has a structure similar to that of a segment of a C row with a center of symmetry at its center. The rectangles are related by a twofold screw axis parallel to C resulting in a layer that resembles a parquet floor, Figure 5.6b. Neighbouring layers are related by glide planes, normal to the C axis at C = 1/4 and C = 3/4, Figure 5.6c.

5.4.6 α-$Ca_2P_2O_7$

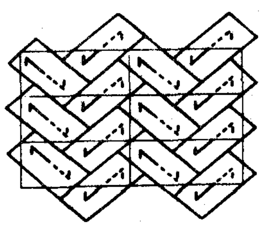
An extreme use of transformation of the layers is found in α-$Ca_2P_2O_7$ (43) in which the cations instead of lying above and below the Y_2O_7 layer nearly lie on the same plane that the Y-Y vectors lie, Figure 5.7. The Y-Y vectors have

Figure 5.6 The $NaRbCr_2O_7$ layer

a) $NaRbCr_2O_7$ ($P2_1/c$). Plane $(20\bar{1})$ viewed down the $[\bar{2}01]^*$;
O = $0,0,\frac{1}{4}$; A/2 = $1,0,\frac{3}{4}$; C = $0,1,\frac{1}{4}$.



b) The rectangles of the layer



c) Packing of layers

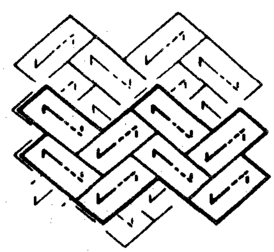
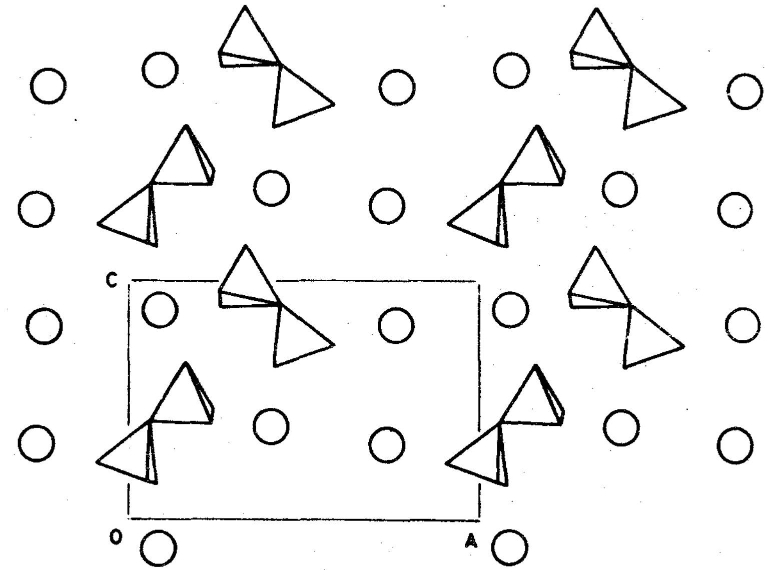


Figure 5.7 Layer of α-$Ca_2P_2O_7$

α-$Ca_2P_2O_7$ ($P2_1/n$) Plane (001) down the c axis;

O = $0,0,\frac{1}{4}$; A = $1,0,\frac{1}{4}$; C = $0,1,\frac{1}{4}$.



an angle of 45° with the A and C axes and there are twofold screw axes on the plane of the layer which relate neighbouring rows. α-$Sr_2P_2O_7$ (44) has a similar layer but the plane of the layer is a mirror plane so the cations lie onto the plane and the anion has an m symmetry.

5.6 The Structure of β2 $Rb_2Cr_2O_7$

The unit cell of β2 $Rb_2Cr_2O_7$, Table 3.10, corresponds to that expected for a type I structure.

Unfortunately since all the axes are of roughly the same length it is not immediately obvious what orientation a type I structure would have in the crystal.

The thickness of the sheets described by Brown and Calvo for the three known $Rb_2Cr_2O_7$ structures varies between 6.7 to 6.9 Å while the thickness of the layers described in the previous sections is around 5.0 Å.

The interplanar distances in the β2-$Rb_2Cr_2O_7$ lattice that are close to these values are:

$$d_{100} = 7.32 \qquad d_{10\bar{1}} = 5.4$$
$$d_{001} = 6.90 \quad (\text{Å}) \quad d_{110} = 4.7 \quad (\text{Å})$$
$$d_{010} = 6.67 \qquad d_{111} = 5.2\ .$$

From these it is apparent that the sheets are either parallel to the b,c, plane or parallel to the a,c, plane. Since the angle between the axes which lie in the sheets always is close to 90° the sheets are likely to be parallel to the b,c, plane.

The interplanar distances which are close to 5.0 Å are the d_{110} = 4.7 Å and the d_{111} = 5.2 Å both cut the b,c, plane in the $[01\bar{1}]$ direction which is the expected orientation between the sheets and the layers but it is not possible to decide which of these planes is in fact parallel to the layers.

The twin plane being parallel to the b,c, plane cuts both the sheets and the layers.

In conclusion the $\beta 2(P\bar{1})$ $Rb_2Cr_2O_7$ structure is probably a type I structure in the classification scheme of Brown and Calvo with the sheets parallel to the b,c plane. The axes have been chosen to conform with the convention of Brown and Calvo.

CHAPTER 6

SUMMARY

The alkali metal dichromates show extensive polymorphism. The structures of the polymorphs which have been determined so far belong to a large series of structures of the $X_2Y_2O_7$ compounds. This series includes dichromate like structures with medium and large cation radii and thortveitite like structures with small cation radii. All these structures are built from layers of Y_2O_7 ions with the cations sandwiched between them.

From the alkali metal dichromates $Na_2Cr_2O_7$ has four phases. We have determined the structure of the room temperature β and the next higher temperature α phase. These structures illustrate rather strikingly the intermediate character of the $Na_2Cr_2O_7$ in the series. α-$Na_2Cr_2O_7$ is built up from identical layers intermediate in structure between the large and small cation layers. β-$Na_2Cr_2O_7$ is built up from two crystallographically nonequivalent layers. One of them resembles the layers of the larger cation and the other the layers of the smaller cation structures. The phase transition $\alpha \rightarrow \beta$ is very close to a second order phase transition and probably it is triggered by a torsional mode of vibration of the dichromate ion. There is no information

on the higher temperature phases c and d. Probably the a → c transition is a first order transition as we have observed an abrupt change in the diffraction pattern at around 300°C.

$Rb_2Cr_2O_7$ has three phases growing from aqueous solutions β1, VII and X. On heating the β1 phase an irreversible transition occurs 318°C to an α phase of unknown symmetry and on further heating a transition to the c phase at 337°C. On cooling the α phase a reversible transition takes place at 260°C to a β2 phase whose cell constant we have determined and for which we have suggested a possible structure. We have determined the structure of the β1 phase, Löfgren and Walterson (10,11) the structures VII and X. The X-$Rb_2Cr_2O_7$ layer has a typical structure of a large cation layer. The VII-$Rb_2Cr_2O_7$ has layers which are a slightly distorted form of the X layer structures, while the layer of β1 $Rb_2Cr_2O_7$ is a further, very much distorted, form of the VII layer.

Cr_2O_7 has two phases grown from aqueous solutions β1 ($P\bar{1}$) and an unstable C2/c phase probably of type X structure. On heating β1 an irreversible transition takes place rapidly at 270°C to an α phase of P2/n symmetry and probably type VII structure. On further heating two transitions take place at 345°C and 380°C to phases c and d both of unknown symmetry.

On cooling the α phase a reversible transition takes place to a β2 phase. The existence of β2 phase is disputed. The only structure which has been determined is that of β1 whose layers look similar to those of β1 $Rb_2Cr_2O_7$.

The $Cs_2Cr_2O_7$ two phase transitions take place at 347° and 362°C. The only crystallographic information on this system is our work on the room temperature phase which shows that it belongs to the triclinic systems but is both disordered and twinned.

From the binary systems of dichromates the only compounds formed are those of $NaRbCr_2O_7$ and $P2_1/c$ $NaCsCr_2O_7$. In view of the large polymorphism of the dichromates it is rather surprising that all the other binary systems form solid solutions. We have determined the structure of $NaRbCr_2O_7$. The layer in this structure shows blocks of four dichromate ions similar in structure to regions found in the other $Rb_2Cr_2O_7$ layers.

$NaCsCr_2O_7$ is probably isostructural with $NaRbCr_2O_7$. No phase transitions have been determined for these two phases. It would be interesting to look for such transitions at lower temperatures. The fact that the bridging oxygen atoms show large librations around the Cr-Cr axis might indicate the existence of a lower temperature transition similar to the α-β transition in $Na_2Cr_2O_7$.

Although we have studied a few polymorphs and one phase transition in somewhat more detail there is a large number of questions which remain unanswered.

BIBLIOGRAPHY

1. A. Bystrom and K. Wilhelmi. Acta Chem. Scand. 5, 1003 (1951).

2. J. K. Brandon and I. D. Brown, Can. J. Chem. 46, 933 (1968)

3. I. D. Brown and C. Calvo. J. Solid State Chem. 1, 183 (1970).

4. Yu. I. Vesnin and L. A. Khripin. Zh. Neorg. Khim. 11, 2216 (1966) [English translation: Russ. J. Inorg. Chem. 11, 1188 (1966)].

5. R. G. Samuseva, I. F. Poletaev and V. F. Plyushchev. Zh. Neorg. Khim. 7, 1146 (1962) [English translation: Russ. J. Inorg. Chem. 7, 589 (1962)].

6. U. Klement and G. Schwab. Z. Krist. 114, 170 (1960).

7. J. Jaffray and A. Labavy, Compt. Rend. 242, 1421 (1956).

8. K. A. Wilhelmi. Arkiv. Kemi 26, 149 (1967).

9. N. Ch. Panagiotopoulos and I.D. Brown. Canad. J. Chem. 48, 537 (1970).

10. P. Löfgren and K. Waltersson. Acta Chem. Scand. 25, 35 (1971).

11. P. Löfgren. Acta Chem. Scand. 25, 44 (1971).

12. J. Jaffray. J. de Phys. 12, 565 (1951).

13. J. Jaffray. J. de Phys. 13, 430 (1952).

14. A. Lehrman. H. Selditsch and P. Skell. J. Am. Soc. 58, 1612 (1936).

15. R. G. Samuseva, Yu. A. Okanev and V. E. Plyuschev. Russ. J. Inorg. Chem. 12, 1489 (1967).

16. R. G. Hazell. Acta Cryst. A25, S116 (1969) and private communication.

17. Yu. A. Kharitonov, E. A. Kuzmin and N. V. Belov. Kristallografiya 15, 942 (1970). [English translation: Soviet Physics Crystallography 15, 820 (1971)].

18. I. D. Datt, N. V. Rannev, T. G. Balicheva and R. P. Ozerov. Kristallografiya 15, 949 (1970). [English translation: Soviet Physics Crystallography 15, 821 (1971)].

19. R. W. James. The Optical Principles of the Diffraction of X-rays. G. Bell and Sons Ltd., London. 1962.

20. H. Lipson and W. Cochran. The Determination of Crystal Structures. G. Bell and Sons Ltd., London 1962.

21. J. Karle and I. L. Karle. Acta Cryst. 21, 849 (1966).

22. D.W.J. Cruickshank, D.E. Pilling, A. Bujosa, F. M. Lovell and M. R. Truter: Computing Methods in the Phase Problem, Oxford: Pergamon Press (1961).

23. ASTM (American Society for Testing and Materials) Powder Diffraction File, Philadelphia, Pa. (1968).

24. K. Sakurai. Acta Cryst. 11, 840 (1958).

25. International Tables for X-ray Crystallography, Vol. III, Tables 3.3.1A, 3.3.2B, 3.3.2C, Birmingham: Kynoch Press (1962).

26. W. C. Hamilton. Acta Cryst., 18, 502 (1965).

27. J. Le Bel. Compt. Rend. 153, 1081 (1911).

28. W. Storhtenbekker. Rec. Trav. Chim. 26, 240 (1907).

29. G. N. Vyrubov. Bull. Soc. Chim. (France) [4], 3, 7 (1908).

30. M. E. Straumanis, T. Ejima and W. J. James. Acta Cryst. 14, 493 (1961).

31. Handbook of Chemistry and Physics 48th ed. The Chemical Rubber Co. p. B-215 (1967).

32. ABSORP a program from Cornell University.

33. D. V. Luu and R. Lafont. Journal de Phys. 31, 85 (1970).

34. H. Lynton and M. R. Truter. J. Chem. Soc. 5112 (1960).

35. D.W.J. Cruickshank. Acta Cryst. 9. 757 (1956).

36. W.R. Busing and H.A. Levy. Acta Cryst. 17, 142 (1964).

37. L. Pauling. The Nature of the Chemical Bond, p. 260, Cornell University Press, Ithaca,N. Y. (1960).

38. B.E. Robertson and C. Calvo. Acta Cryst. 22, 665 (1967).

39. C. Calvo. Acta Cryst. 23, 289 (1967).

40. B.E. Robertson and C. Calvo. J. of Solid State Chem. 1, 120 (1970).

41. C. Calvo and K. Neelakantan. Can. J. Chem. 48, 890, (1970).

42. D.W.J. Cruickshank, H. Lynton and G. A. Barclay. Acta Cryst. 15, 491 (1962).

43. C. Calvo. Inorg. Chem. 7, 1345 (1968).

44. L.H. Hagman, I. Jansson and C. Magneli. Acta Chem. Scand. 22, 1419 (1968).