

Table 4 (cont.)

<i>h</i>	<i>k</i>	<i>l</i>	$ F_o $	F_c	<i>h</i>	<i>k</i>	<i>l</i>	$ F_o $	F_c	<i>h</i>	<i>k</i>	<i>l</i>	$ F_o $	F_c	<i>h</i>	<i>k</i>	<i>l</i>	$ F_o $	F_c
	10		55	36		2		55	52		10		<54	-5		3		81	83
	11		75	96		3		<34	4		11		56	-53		4		<54	-42
	12		57	-49		4		83	94		12		<51	-10		5		57	-57
	13		54	-66		5		<38	18		13		51	-16		6		<54	-8
	14		55	21		6		106	-138							7		57	-24
						7		<50	-42		0 10	0	110	-121		8		<54	27
0	7	1	79	-54		8		55	83		1		<50	12		9		55	53
	2		82	-92		9		<54	-18		2		58	46					
	3		141	160		10		57	25		3		<51	-11		0 12	0	57	-73
	4		119	103		11		<54	32		4		55	30		1		73	81
	5		68	-67		12		74	-74		5		<53	-43		2		57	16
	6		36	-6		13		<51	-32		6		75	-75		3		<57	-16
	7		41	-16							7		<54	25		4		57	21
	8		66	-47		0 9	1	63	-59		8		57	22		5		<57	-34
	9		77	67		2		<38	-26		9		<54	-28		6		56	-39
	10		75	73		3		142	142		10		56	51		7		<55	52
	11		57	-60		4		<48	21		11		<51	-7					
	12		54	-8		5		72	-68		12		73	-63		0 13	1	57	-13
	13		55	-20		6		<51	-34		13		<46	4		2		<56	52
	14		50	-36		7		55	5							3		56	28
0	8	0	103	-105		8		<54	-21		0 11	1	78	-55		4		<56	-42
	1		74	-69		9		81	73		2		<53	29		5		55	-16

Reynolds who undertook most of the computing work, including the tedious task of finding the best positions for the light atoms.

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The Structure of the Intermetallic Phase θ (Cr-Al)

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The monoclinic θ -phase in the chromium-aluminium system has been shown to be isomorphous with α' (V-Al). The structure has been refined and the interatomic distances are discussed and compared with those in α' (V-Al) and with those in two ternary alloy phases containing chromium and aluminium.

1. Introduction

The chromium-aluminium system has been investigated by many workers and the composition of the θ -phase, which is in equilibrium with the primary solid solution, has been shown to be represented by the formula CrAl₇ (Raynor & Little, 1945). The phase forms monoclinic crystals and the unit cell given by Hofmann & Wiehr (1941) is:

$$a=20.43, b=7.62, c=25.31 \text{ \AA}; \beta=155^\circ 10'.$$

This unit cell corresponds to the morphology of the crystals.

The similarity of rotation photographs from θ (Cr-Al) and α' (V-Al) has been reported by Brown (1957). The present analysis of θ (Cr-Al) was undertaken to investigate the relationship between the two phases and in particular the nature of the chromium-aluminium

bonds, since interesting orientational properties have been observed in the abnormally short transition metal to aluminium bonds which occur in certain phases (Brown, 1957).

2. Material

The crystals used in this analysis were prepared from an aluminium-chromium alloy containing about 1% weight chromium. The alloy was cooled from 700 °C. to 500 °C. at a rate of 15° per hour, and then quenched rapidly. The crystals were extracted electrolytically and found to be in the form of plates and prisms. Many of the plates appeared to be twinned. A photograph of similar crystals is given by Hofmann & Wiehr. No difficulty was found in selecting single crystals for analysis.

3. Unit cell

Laue, oscillation and Weissenberg photographs confirmed that the unit cell is monoclinic and provided approximate values of the lattice parameters. The alternative unit cell given by Hofmann & Wiehr was used in this analysis since it has only one parameter greater than 11 Å and also corresponds to that of α' (V-Al) used by Brown (1959). It is related to the morphological unit cell by the matrix:

$$\begin{array}{c} 001 \\ 010 \\ \bar{1}0\bar{1} \end{array}$$

The transformation of the Hofmann & Wiehr cell gives the new unit cell:

$$a=25.31, b=7.62, c=10.92 \text{ \AA}; \beta=128^\circ 12'.$$

Accurate lattice parameters were determined by the θ -method described by Weisz, Cochran & Cole (1948), but using a Geiger Counter and linear ratemeter in place of the photographic film used by them. The values obtained were:

$$\begin{aligned} a &= 25.196 \pm 0.017, & b &= 7.574 \pm 0.003, \\ c &= 10.949 \pm 0.009 \text{ \AA}; & \beta &= 128^\circ 43' \pm 3'. \end{aligned}$$

The volume of the unit cell is therefore $1630 \pm 2 \text{ \AA}^3$. The density of the crystals, determined by the displacement method, was $3.18 \pm 0.05 \text{ g.cm.}^{-3}$ so that the mass content of the unit cell is $3060 \pm 50 \text{ A.M.U.}$

A sample of about 50 mg. of the crystals was chemically analysed by Messrs. Johnson, Matthey and Co. Ltd., giving 22.6% weight chromium and 77.6% weight aluminium. This corresponds to a ratio of one chromium atom to 6.6 aluminium atoms. The mass of the $\text{CrAl}_{6.6}$ unit is 230 A.M.U., so that there are 14 chromium atoms and approximately 90 aluminium atoms in the unit cell.

4. The space group

Laue and Weissenberg photographs indicated that the

unit cell is *C*-face centred and that the Laue symmetry group is $2/m$. The possible space groups are therefore $C2$, Cm and $C2/m$. These can be distinguished by the presence or absence of a centre of symmetry in the [010] and [001] projections, since $C2$ has a centre of symmetry in the [010] projection only, Cm has no centre of symmetry in either projection, and $C2/m$ has a centre of symmetry in both projections. A Wilson statistical test was therefore applied to intensities from Weissenberg photographs for the [010] and [001] zones, and the results of this are shown in Fig. 1. In both cases the points lie above the curve for a centro-symmetric distribution and the space group $C2/m$ was therefore chosen.

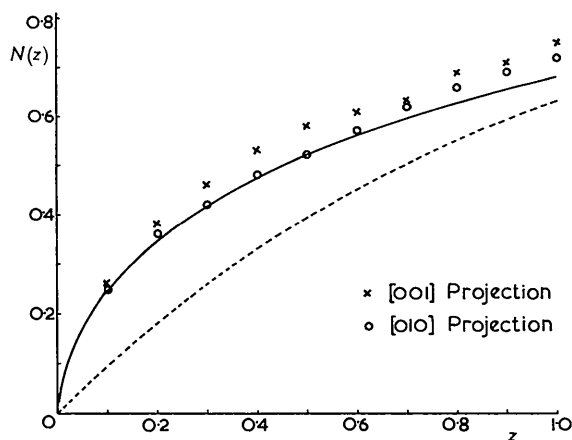


Fig. 1. Tests for centro-symmetry of the [001] and [010] zones.

5. Collection of intensities

The crystal used for the collection of intensity data was approximately cubic with edges about 0.1 mm. in length and was cut from one of the prismatic single crystals. For this size of crystal the correction of intensities for absorption of Mo $K\alpha$ radiation can be assumed to be a function of $\sin \theta/\lambda$ only, within the accuracy of the measurements.

Reflections of the form ($h0l$) were collected on a zero-layer normal-beam Weissenberg photograph using filtered Mo $K\alpha$ radiation and a multiple-film technique. An intensity scale was made using a reflection in this zone from the same crystal and intensities out to $\sin \theta/\lambda = 1.0$ were measured by visual comparison with this scale. The intensities were corrected for Lorentz and polarization factors and allowance was made for absorption and resolution of the $\alpha_1\alpha_2$ doublet by scaling F_o to F_c in regions of $\sin \theta/\lambda$. A rough correction for extinction was found to be necessary for the stronger reflections.

Reflections of the form $hk0$ were collected in a similar way. Due to the large amount of overlap in the [010] projection it was found necessary to collect reflections of the form $hk1$ and $hk2$ to complete the refinement of the structure. These were collected on

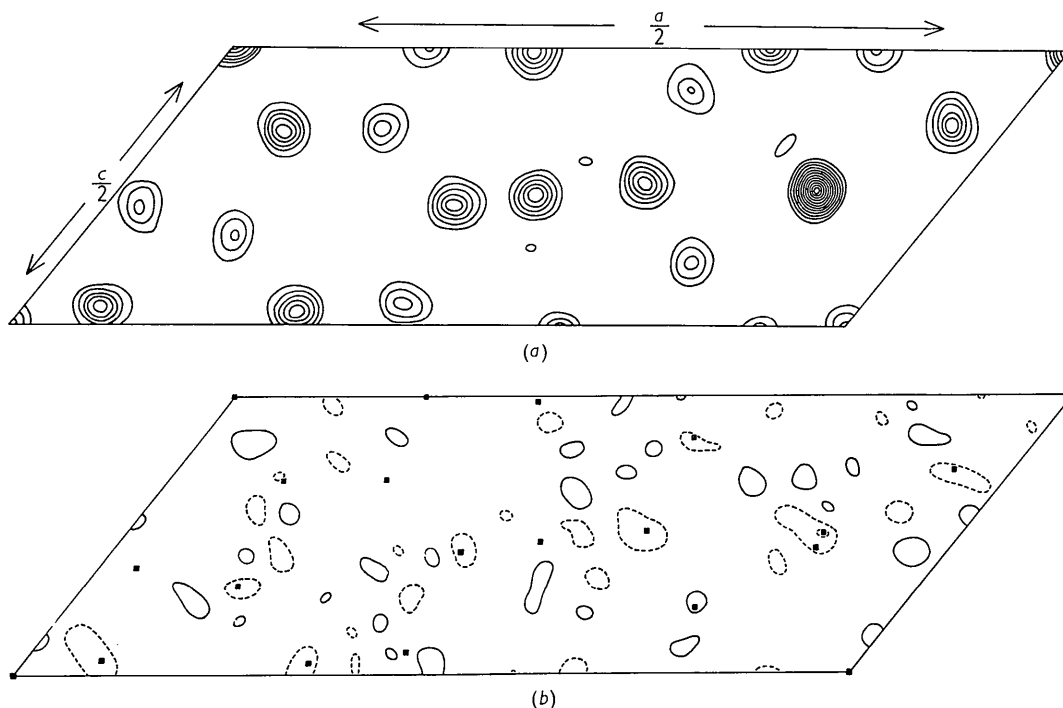


Fig. 2. Final F_o and $F_o - F_c$ [010] Fourier projections. (a) F_o . The contours are at equal arbitrary intervals. The $F(000)$ term is not included. (b) $F_o - F_c$. The contour intervals are one-fifth those of the F_o ; negative contours are shown as broken lines. Squares represent atomic sites.

two equi-inclination Weissenberg photographs and their intensities measured as before.

6. Isomorphism with $\alpha'(V-Al)$

The similarity of rotation photographs from $\theta(Cr-Al)$ and $\alpha'(V-Al)$ has been reported by Brown (1957). The similarity of the structures was also indicated by a comparison of the photographs obtained in this analysis and those obtained by Brown (1959) in the analysis of $\alpha'(V-Al)$. The cell dimensions and contents were also found to be very similar and the space group is the same. It was therefore decided to take the structure of $\alpha'(V-Al)$, which was then reasonably well refined, as a trial structure for $\theta(Cr-Al)$, replacing the vanadium atoms by chromium atoms. The values of F_o for reflections out to $\sin \theta/\lambda = 0.5$ in the [010] zone and to $\sin \theta/\lambda = 0.8$ in the [001] zone were scaled in regions of $\sin \theta/\lambda$ to the values of F_c from this trial structure and R -factors of 0.15 and 0.18 respectively were obtained, confirming the similarity of the structures.

The positions of the chromium atoms are 2 in 2(a), 4 in 4(i) and 8 in 8(j) and the positions of the aluminium atoms are 2 in 2(d), 8 sets of 4 in 4(i) and 7 sets of 8 in 8(j), making a total of 14 chromium and 90 aluminium atoms in the unit cell.

7. Refinement of the [010] projection

The refinement of the structure was carried out by

means of $F_o - F_c$ syntheses, using the atomic scattering factors given by Forsyth & Wells (1959). After a few cycles using reflections out to $\sin \theta/\lambda = 0.5$, the further reflections out to $\sin \theta/\lambda = 0.8$ were included. An additional isotropic temperature factor of $B = 0.40$ was applied to all the aluminium atoms in addition to the factor of 0.24 introduced by the scaling, which applies to all atoms. The final R factor was 0.060 for 350 measured reflections.

In this projection all atoms are well resolved with the exception of Cr_2 and Al_7 and since the contribution from the single Al_7 atom is much less than that from the double Cr_2 atom it is only for this atom that the x and z co-ordinates cannot be obtained with so much accuracy. The final F_o and $F_o - F_c$ syntheses are shown in Fig. 2.

8. Refinement of the [001] projection

While the [010] projection was being refined, the [001] projection was refined independently using reflections from the zero layer out to $\sin \theta/\lambda = 0.8$ and the R -factor was reduced to about 0.10. A large amount of overlap occurs in this projection and in order to overcome this intensities of reflections of the form $(hk1)$ and $(hk2)$ were collected.

For the space group $C2/m$, the structure factor for a reflection hkl is given by:

Table 1. Atomic co-ordinates for $\theta(\text{Cr-Al})$ and the corresponding values of $\cos 2\pi lz$ for the first and second layers

Atom	Final co-ordinates			$\cos 2\pi lz$	
	x	y	z	$l=1$	$l=2$
2 Cr ₀ in 2(a) (0, 0, 0)				1.000	1.000
4 Cr ₁ in 4(i) ($x_1, 0, z_1$)	0.2505 ± 0.0002		0.2630 ± 0.0004	-0.082	-0.987
8 Cr ₂ in 8(j) (x_2, y_2, z_2)	0.0854 ± 0.0001	0.3240 ± 0.0003	0.7525 ± 0.0002	0.054	-0.994
2 Al ₀ in 2(d) (0, $\frac{1}{2}, \frac{1}{2}$)				-1.000	-1.000
4 Al ₃ in 4(i) ($x_3, 0, z_3$)	0.6152 ± 0.0003		0.0005 ± 0.0006	1.000	1.000
4 Al ₄ in 4(i) ($x_4, 0, z_4$)	0.2932 ± 0.0003		0.0745 ± 0.0006	0.893	0.593
4 Al ₅ in 4(i) ($x_5, 0, z_5$)	0.3750 ± 0.0003		0.3840 ± 0.0006	-0.745	0.111
4 Al ₆ in 4(i) ($x_6, 0, z_6$)	0.5214 ± 0.0003		0.2870 ± 0.0006	-0.230	-0.894
4 Al ₇ in 4(i) ($x_7, 0, z_7$)	0.0810 ± 0.0006		0.7235 ± 0.0020	-0.165	-0.945
4 Al ₈ in 4(i) ($x_8, 0, z_8$)	0.1285 ± 0.0003		0.1445 ± 0.0006	0.616	-0.242
4 Al ₉ in 4(i) ($x_9, 0, z_9$)	0.0912 ± 0.0003		0.3410 ± 0.0006	-0.541	0.413
4 Al ₁₀ in 4(i) ($x_{10}, 0, z_{10}$)	0.2245 ± 0.0003		0.4575 ± 0.0006	-0.965	0.861
8 Al ₁₁ in 8(j) (x_{11}, y_{11}, z_{11})	0.1820 ± 0.0002	0.1850 ± 0.0004	0.0090 ± 0.0004	0.998	0.994
8 Al ₁₂ in 8(j) (x_{12}, y_{12}, z_{12})	0.0692 ± 0.0002	0.3205 ± 0.0004	0.1485 ± 0.0004	0.595	-0.291
8 Al ₁₃ in 8(j) (x_{13}, y_{13}, z_{13})	0.9643 ± 0.0002	0.1880 ± 0.0005	0.1330 ± 0.0004	0.670	-0.101
8 Al ₁₄ in 8(j) (x_{14}, y_{14}, z_{14})	0.3100 ± 0.0002	0.3155 ± 0.0005	0.2405 ± 0.0004	0.059	-0.993
8 Al ₁₅ in 8(j) (x_{15}, y_{15}, z_{15})	0.0456 ± 0.0002	0.1955 ± 0.0005	0.4695 ± 0.0004	-0.982	0.927
8 Al ₁₆ in 8(j) (x_{16}, y_{16}, z_{16})	0.1655 ± 0.0002	0.3070 ± 0.0004	0.4760 ± 0.0004	-0.978	0.915
8 Al ₁₇ in 8(j) (x_{17}, y_{17}, z_{17})	0.2065 ± 0.0002	0.3145 ± 0.0005	0.2780 ± 0.0004	-0.175	-0.938

$$F(hkl) = \sum_n f_n \cos 2\pi(hx + lz) \cos 2\pi ky$$

$$= \sum_n f_n (\cos 2\pi hx \cos 2\pi lz - \sin 2\pi hx \sin 2\pi lz)$$

$$\times \cos 2\pi ky$$

and for a reflection $\bar{h}kl$ by:

$$F(\bar{h}kl) = \sum_n f_n (\cos 2\pi hx \cos 2\pi lz + \sin 2\pi hx \sin 2\pi lz)$$

$$\times \cos 2\pi ky.$$

Therefore

$$F(hkl) + F(\bar{h}kl) = 2 \sum_n f_n \cos 2\pi hx \cos 2\pi ky \cos 2\pi lz.$$

The Fourier synthesis of $F(hkl) + F(\bar{h}kl)$ perpendicular to the c axis will therefore have peaks at the atomic positions weighted by the corresponding value of $f_n \cos 2\pi lz$. The values of $\cos 2\pi lz$ for the atoms for the first and second layers are given in Table 1. Only the y co-ordinates of the 8 sets of atoms in general positions remained to be determined from the [001] projection. Of these Cr₂, Al₁₄ and Al₁₇ do not contribute appreciably to the first layer synthesis and Al₁₂ and Al₁₃ do not contribute appreciably to the second layer synthesis, so that these two layers were sufficient to complete the refinement.

The final R -factors were as follows:

zero layer	110 measured reflections	$R = 0.092$
first layer	215 measured reflections	$R = 0.059$
second layer	220 measured reflections	$R = 0.057$

The final F_o and $F_o - F_c$ syntheses for the first and second layers are shown in Figs. 3 and 4.

The final R -factor for all measured reflections with $\sin \theta/\lambda$ less than 1.0 (1134 reflections) was 0.068. The final atomic co-ordinates with their standard deviations are given in Table 1. The standard deviations

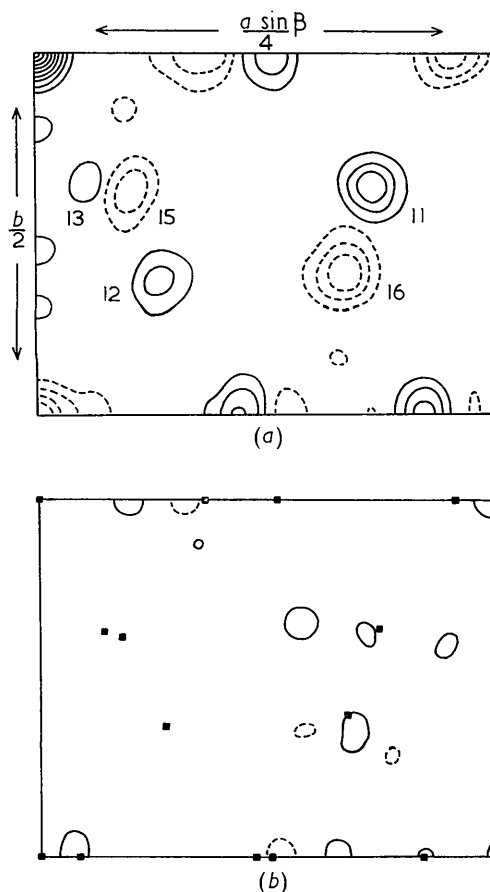


Fig. 3. Final F_o and $F_o - F_c(hkl)$ Fourier projections. Negative contours are shown as broken lines. (a) F_o . The contours are at equal arbitrary intervals. (b) $F_o - F_c$. The contour intervals are one-fifth those of the F_o . Squares represent sites of atoms which contribute appreciably to the (hkl) F_o synthesis.

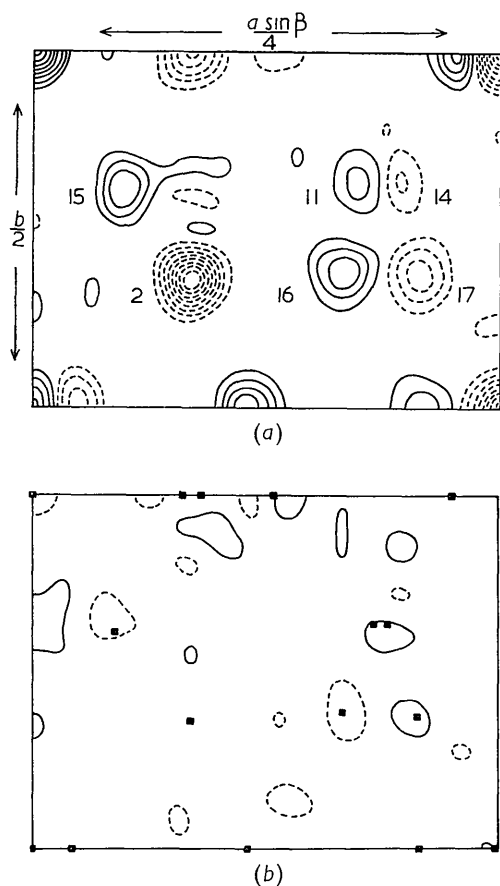


Fig. 4. Final F_o and $F_o - F_c(hk2)$ Fourier projections. Negative contours are shown as broken lines. (a) F_o . The contours are at equal arbitrary intervals. (b) $F_o - F_c$. The contour intervals are one-fifth those of the F_o . Squares represent sites of atoms which contribute appreciably to the $(hk2)$ F_o synthesis.

have been calculated from the final $F_o - F_c$ syntheses by the method suggested by Lipson & Cochran (1953). Tabulated values of F_o and F_c are available.

9. The interatomic distances

The structure is similar to that of $\alpha'(V-Al)$ and Fig. 5 shows several co-ordination groups in their appropriate orientation, indicating how these are linked.

A list of interatomic distances is given in Table 2, together with their standard deviations. The mean Al-Al distance is 2.84 Å, which is about normal for this type of compound. The Cr-Al distances can be divided into two groups having mean values of 2.53 Å and 2.74 Å. The first of these groups contains the bonds involved in the linkage between the co-ordination polyhedra. These are all the Cr-Al distances less than 2.59 Å, with the exception of the Cr₁-Al₅ distance (2.53 Å). In each case except Al₀ the aluminium atom has only two chromium neighbours and the Cr-Al-Cr bond angle is about 180°. Al₀ has four

chromium neighbours, with two pairs of 180° bonds. No bond angles near 180° occur in the second group. The sum of the twelve co-ordinated radii of chromium and aluminium is 2.71 Å, so that the value 2.53 Å for the first group is significantly shorter than this. The corresponding mean V-Al distances in the isomorphous $\alpha'(V-Al)$ are 2.56 Å and 2.79 Å respectively. The smaller values obtained for $\theta(Cr-Al)$ are as would be expected from the replacement of the vanadium atoms by the smaller chromium atoms.

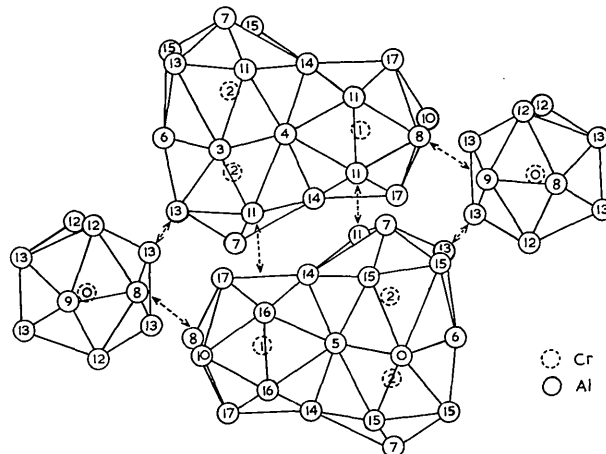


Fig. 5. Structural groups in $\theta(Cr-Al)$. The numbers of the atoms refer to those given in Table 1. The polyhedra are shown as if solid, with the chromium atoms added at their centres.

The distance between the Cr₂ atoms is 2.666 Å, which is larger than the corresponding V-V distance (2.636 Å) in $\alpha'(V-Al)$ and differs from it in being significantly larger than the closest distance of approach in the pure metal (2.50 Å). This would seem to emphasise the importance of the opposing short Cr-Al bonds.

The values of the Cr-Al distances may also be compared with those in Cr₄Si₄Al₁₃ (Robinson, 1953) and Mg₃Cr₂Al₁₈ (Samson, 1958). The occurrence of short Cr-Al distances in the former has been discussed by Taylor (1954) in connection with certain other alloy phases. The atomic co-ordinates given for these structures lead to the Cr-Al distances and inter-bond angles which are given in Table 3, together with those for $\theta(Cr-Al)$. The short distances again occur when the aluminium atom has only two chromium neighbours and the inter-bond angle is about 180°. In both these structures the chromium atoms are co-ordinated by twelve other atoms which lie at the vertices of nearly regular icosahedra. In Cr₄Si₄Al₁₃ these form groups of four inter-penetrating icosahedra, each chromium atom having three chromium neighbours, and these groups share corners with other groups. In Mg₃Cr₂Al₁₈ icosahedra share corners only, but in both cases the short distances are associated with the linkage between co-ordination polyhedra. The values of the short

Table 2. *Interatomic distances in $\theta(\text{Cr-Al})$*

Atom	Already quoted	Neigh- bours	Distance (Å)	Std. devn. (Å)	Atom	Already quoted	Neigh- bours	Distance (Å)	Std. devn. (Å)		
Cr ₀		2 Al ₈	2.570	0.007	Al ₈	1 Cr ₀ , 1 Cr ₁	1 Al ₉	2.834	0.010		
		2 Al ₉	2.922	0.007				1 Al ₁₀	2.696	0.010	
		4 Al ₁₂	2.836	0.005				2 Al ₁₁	2.910	0.009	
		4 Al ₁₃	2.567	0.005				2 Al ₁₂	2.865	0.006	
Cr ₁		1 Al ₄	2.860	0.009	Al ₉	1 Cr ₀ , 1 Al ₈	2 Al ₁₃	2.807	0.009		
		1 Al ₅	2.534	0.009				2 Al ₁₇	2.845	0.006	
		1 Al ₈	2.483	0.009				1 Al ₁₀	2.747	0.010	
		1 Al ₁₀	2.592	0.009				2 Al ₁₂	3.031	0.006	
		2 Al ₁₁	2.588	0.007				2 Al ₁₃	2.893	0.009	
		2 Al ₁₄	2.911	0.007				2 Al ₁₅	2.739	0.009	
		2 Al ₁₆	2.693	0.007				2 Al ₁₆	2.766	0.006	
		2 Al ₁₇	2.675	0.007							
Cr ₂		1 Cr ₂	2.666	0.005	Al ₁₀	1 Cr ₁ , 1 Al ₈	2 Al ₁₆	2.803	0.009		
		1 Al ₀	2.577	0.003			1 Al ₉	2 Al ₁₆	2.831	0.006	
		1 Al ₃	2.678	0.007				2 Al ₁₇	2.667	0.009	
		1 Al ₄	2.740	0.007				2 Al ₁₇	2.939	0.006	
		1 Al ₅	2.620	0.007		Al ₁₁	1 Cr ₁ , 1 Cr ₂	1 Al ₁₁	2.802	0.010	
		1 Al ₆	2.785	0.007				1 Al ₃ , 1 Al ₄	1 Al ₁₃	2.978	0.007
		1 Al ₇	2.468	0.003				1 Al ₄ , 1 Al ₇	1 Al ₁₄	2.761	0.007
		1 Al ₁₁	2.531	0.006				1 Al ₈	1 Al ₁₄	2.861	0.007
		1 Al ₁₃	2.481	0.006					1 Al ₁₇	2.784	0.007
		1 Al ₁₄	2.796	0.006		Al ₁₂	1 Cr ₀ , 1 Al ₃	1 Al ₁₂	2.719	0.007	
		1 Al ₁₅	2.772	0.006				1 Al ₆ , 1 Al ₈	1 Al ₁₂	2.935	0.010
	1 Al ₁₅	2.786	0.006		1 Al ₉		1 Al ₁₃	2.732	0.007		
							1 Al ₁₃	2.825	0.007		
Al ₀	4 Cr ₂	2 Al ₅	2.559	0.007			1 Al ₁₆	2.814	0.007		
		2 Al ₆	2.701	0.007			1 Al ₁₇	2.806	0.007		
		4 Al ₁₅	2.688	0.005							
Al ₃	2 Cr ₂	1 Al ₄	2.891	0.010	Al ₁₃	1 Cr ₀ , 1 Cr ₂	1 Al ₁₃	2.848	0.010		
		1 Al ₆	2.875	0.010			1 Al ₃ , 1 Al ₆	1 Al ₁₅	2.894	0.007	
		2 Al ₁₁	2.887	0.006			1 Al ₇ , 1 Al ₈				
		2 Al ₁₂	2.856	0.009			1 Al ₉ , 1 Al ₁₁				
		2 Al ₁₃	2.844	0.006			1 Al ₁₂ , 1 Al ₁₂				
		2 Al ₁₇	2.792	0.009							
Al ₄	1 Cr ₁ , 2 Cr ₂ , 1 Al ₃	1 Al ₅	2.652	0.010	Al ₁₄	1 Cr ₁ , 1 Cr ₂	1 Al ₁₄	2.794	0.010		
		2 Al ₁₁	2.762	0.006			1 Al ₄ , 1 Al ₄	1 Al ₁₅	2.990	0.007	
		2 Al ₁₁	2.797	0.009			1 Al ₅ , 1 Al ₇	1 Al ₁₆	2.914	0.007	
		2 Al ₁₄	2.869	0.006			1 Al ₁₁ , 1 Al ₁₁	1 Al ₁₇	2.881	0.007	
		2 Al ₁₄	3.073	0.009							
Al ₅	1 Cr ₁ , 2 Cr ₂ , 1 Al ₀ , 1 Al ₄	1 Al ₆	2.843	0.010	Al ₁₅	1 Cr ₂ , 1 Cr ₂	1 Al ₁₅	2.763	0.007		
		2 Al ₁₄	2.767	0.006			1 Al ₀ , 1 Al ₅	1 Al ₁₅	2.961	0.010	
		2 Al ₁₅	2.810	0.006			1 Al ₆ , 1 Al ₇	1 Al ₁₆	3.095	0.007	
		2 Al ₁₆	2.734	0.009			1 Al ₇ , 1 Al ₉				
Al ₆	2 Cr ₂ , 1 Al ₀ , 1 Al ₃ , 1 Al ₅	2 Al ₁₂	2.806	0.009	Al ₁₆	1 Cr ₁ , 1 Al ₅	1 Al ₁₆	2.923	0.010		
		2 Al ₁₃	2.734	0.006			1 Al ₆ , 1 Al ₉	1 Al ₁₇	2.772	0.007	
		2 Al ₁₅	2.857	0.006			1 Al ₁₀ , 1 Al ₁₀	1 Al ₁₇	2.925	0.007	
		2 Al ₁₆	3.201	0.009			1 Al ₁₂ , 1 Al ₁₄				
							1 Al ₁₅				
Al ₇	2 Cr ₂	2 Al ₁₁	2.882	0.020	Al ₁₇	1 Cr ₁ , 1 Al ₃	1 Al ₁₇	2.810	0.010		
		2 Al ₁₃	2.834	0.020			1 Al ₈ , 1 Al ₁₀				
		2 Al ₁₄	2.881	0.020			1 Al ₁₀ , 1 Al ₁₁				
		2 Al ₁₅	2.763	0.020			1 Al ₁₂ , 1 Al ₁₄				
		2 Al ₁₅	2.905	0.020			1 Al ₁₆ , 1 Al ₁₆				

Cr-Al distances are similar to values which occur in $\theta(\text{Cr-Al})$. The shorter (2.46 Å) occurs in $\text{Cr}_4\text{Si}_4\text{Al}_{13}$ where each chromium atom has three of these bonds all on the same side, making angles of 63° to each other. In $\theta(\text{Cr-Al})$ the two shortest bonds (2.468 Å, 2.481 Å) occur from the Cr₂ atom, which has three of its four short bonds on the same side, making angles of 70° , 70° and 73° to each other.

10. Summary

The structures of $\theta(\text{Cr-Al})$, $\text{Cr}_4\text{Si}_4\text{Al}_{13}$ and $\text{Mg}_3\text{Cr}_2\text{Al}_{18}$ all contain short transition metal to aluminium distances similar to those observed in certain other alloy phases and discussed by Taylor (1954) and Brown (1957). The chromium atoms are co-ordinated by nearly regular icosahedra which may interpenetrate, or share corners or faces with other icosahedra. The

Table 3. Cr-Al distances and inter-bond angles in $\text{Cr}_4\text{Si}_4\text{Al}_{13}$, $\text{Mg}_3\text{Cr}_2\text{Al}_{18}$ and $\theta(\text{Cr-Al})$

Phase	Al atom	Neigh- bours	Distances (Å)	Angle (°)
$\text{Cr}_4\text{Si}_4\text{Al}_{13}$	Al ₁	2 Cr	2.46 (2)	166.2
	Al ₂	2 Cr	2.77 (2)	60.5
$\text{Mg}_3\text{Cr}_2\text{Al}_{18}$	Al _f	2 Cr	2.58 (2)	173.2
	Al _g	1 Cr	2.81	—
$\theta(\text{Cr-Al})$	Al ₀	4 Cr	2.58 (4)	180 (2)
	Al ₇	2 Cr	2.47 (2)	167.9
	Al ₈	2 Cr	2.48, 2.57	175.0
	Al ₁₁	2 Cr	2.53, 2.59	162.7
	Al ₁₃	2 Cr	2.48, 2.57	169.4
	Al ₃	2 Cr	2.68 (2)	59.6
	Al ₆	2 Cr	2.78 (2)	57.2
	Al ₁₄	2 Cr	2.80, 2.91	102.4
	Al ₁₅	2 Cr	2.77, 2.79	104.9
	Al ₅	3 Cr	2.62 (2), 2.53	≤ 180
	Al ₄	3 Cr	2.74 (2), 2.86	≤ 180
	others	1 Cr	> 2.59	—

Cr-Al distances in the three phases fall into two groups, one of which is significantly shorter than the sum of the twelve-co-ordinated radii of the atoms. These short distances indicate a stronger Cr-Al interaction which is associated with the sharing of corners between the icosahedra when the Cr-Al-Cr bond angle

is near 180°. This suggests a directional character not usually associated with a purely metallic bond.

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The Crystal Structure of Sodium Triphosphate, $\text{Na}_5\text{P}_3\text{O}_{10}$, Phase I

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The crystal structure of the high-temperature form of sodium triphosphate, $\text{Na}_5\text{P}_3\text{O}_{10}$, Phase I, has been determined by Fourier methods. The unit cell is monoclinic with

$$a = 9.61, b = 5.34, c = 19.73 \text{ \AA}; \beta = 112^\circ.$$

The space group is $C2/c$ and the unit cell contains 4 units of $\text{Na}_5\text{P}_3\text{O}_{10}$. The triphosphate ions have twofold axial symmetry with the central phosphorus atoms lying on twofold axes of the unit cell. Bond lengths are P-O (chain) = 1.62 ± 0.03 (inner), 1.66 ± 0.03 (outer), P-O (mean, terminal) 1.48 ± 0.03 Å. The structure is generally more distorted than that found previously for the low-temperature form, Phase II. Some of the sodium ions are co-ordinated in distorted octahedral arrangements, while the remainder are involved in 4-fold co-ordination of an unusual type. A comparison of the structures of Phase I and Phase II suggests an explanation of some of their differences in properties.

Introduction

The crystalline forms of sodium triphosphate $\text{Na}_5\text{P}_3\text{O}_{10}$ and its hexahydrate are of theoretical interest and of importance in the production of modern detergent powders. A knowledge of the crystal structures of these salts is relevant to the explanation of many of the phenomena connected with their preparation, interconversion and hydration, which are at present

only partially understood (Raistrick, 1948; Van Wazer, 1958). In the present paper the structure of the high temperature anhydrous form, Phase I, is worked out and compared with that of the low temperature form, Phase II, which has been given previously (Davies & Corbridge, 1958).

Small crystals were obtained from a melt of composition 45% sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) and