

The Structure of $\alpha(\text{AlCrSi})\text{-Cr}_4\text{Si}_4\text{Al}_{13}$

BY KEITH ROBINSON*

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

(Received 23 June 1953)

The crystal structure of the intermetallic compound $\text{Cr}_4\text{Si}_4\text{Al}_{13}$ has been determined. The main framework of the structure is a network of linked tetrahedra of Cr, Si and Al atoms, the latter being in 4-coordination. The form of the first prominent Brillouin zone of the structure suggests that Cr has a negative 'effective valency' in this compound, and electron counts indicate a small excess of electrons in the Cr atoms. Unusually short interatomic distances between Cr and Al, similar to those previously reported for Mn and Al in Mn_3SiAl_9 , occur in the structure.

1. Introduction

The surfaces of primary separation in the aluminium-rich corner of the Al-Cr-Si system have been given by Mondolfo (1943) and by Pratt & Raynor (1951). Although their diagrams differ appreciably in detail, both record the presence of two ternary compounds, $\alpha(\text{AlCrSi})$ having the lower and $\beta(\text{AlCrSi})$ the higher chromium content. The author has recently shown (Robinson, 1953) that $\beta(\text{AlCrSi})$ is not in fact a new ternary compound but merely a solid solution of aluminium in the binary compound CrSi_2 . No detailed crystallographic data have previously been available for $\alpha(\text{AlCrSi})$, although it was suggested by Mondolfo that this phase might be hexagonal with a possible composition CrSiAl_6 . It has been found as a result of the present investigation that the structural formula of $\alpha(\text{AlCrSi})$ is $\text{Cr}_4\text{Si}_4\text{Al}_{13}$, i.e. the aluminium content is very much lower than that suggested by Mondolfo.

The work described here has been carried out in conjunction with a metallographic examination of the alloys in the Metallurgy Department of the University of Birmingham, England; the results of that examination have been reported by Pratt & Raynor (1951) and I am indebted to Dr Pratt and Prof. Raynor for kindly providing the specimens used.

2. Specimens

Single crystals of $\alpha(\text{AlCrSi})$ had been extracted electrolytically from slowly cooled alloys. Only crystals from one sample have been examined crystallogra-

phically, but the chemical composition of the extracts from other alloys does not differ appreciably from that of the chosen sample (see Table 1). The crystals examined came from the alloy referred to as (1/8), i.e. the melt contained 1% chromium and 8% silicon by weight.

The crystals, which frequently have a thick tabular habit and extend up to 2 mm. in linear dimensions, are hard and brittle; an estimate of the hardness is given by a Brinell hardness number of 407. Their shape suggests the presence of a trigonal axis perpendicular to the principal face.

3. Experimental data

(i) Powder photograph

A powder photograph of $\alpha(\text{AlCrSi})$ using crystal-reflected monochromatic Cu $K\beta$ radiation ($\lambda = 1.39217 \text{ \AA}$) in a 9 cm. diameter camera has been indexed in terms of a cubic unit cell. Extrapolation of the value of a_0 estimated from high angle reflexions as a function of $\frac{1}{2}(\cos^2 \theta / \sin \theta + \cos^2 \theta / \theta)$ to its value at $\theta = 90^\circ$ (Nelson & Riley, 1945) gives

$$a_0 = 10.917 \pm 0.001 \text{ \AA}.$$

For purposes of identification of the phase from X-ray powder photographs the data shown in Table 2 may be used. Included in this table are values of $\sin \theta / \lambda$ and ΣmF^2 for each of the low-order powder lines (m is the multiplicity and F the structure factor of the (hkl) reflexions). The intensities of powder lines can be derived from the values in the final column by making allowance for the Lorentz, polarization and absorption factors.

The density of crystals of $\alpha(\text{AlCrSi})$, determined by flotation methods, is $3.40_5 \pm 0.02 \text{ g.cm.}^{-3}$. This value, together with the lattice parameter quoted above and the chemical analysis shown in Table 1, gives an estimate of 83.7 ± 0.6 for the number of atoms per unit cell. With 84 atoms per unit cell the composition corresponds to 15.7 Cr atoms, 17.0₅ Si atoms and 51.2₅ Al atoms per cell, which is quite close to four 'molecules' of $\text{Cr}_4\text{Si}_4\text{Al}_{13}$ per cell.

Table 1. *Composition of $\alpha(\text{AlCrSi})$ samples*

(From Pratt & Raynor, 1951.)

Sample	Composition (atomic %)		
	Cr	Si	Al†
(1/6)	18.9	19.7	61.4
(1/8)	18.7	20.3	61.0
(1/10)	18.6	19.6	61.8
$\text{Cr}_4\text{Si}_4\text{Al}_{13}$	19.0 ₅	19.0 ₅	61.9

† Aluminium estimated by difference.

* Now at Physics Department, The University, Reading, England.

Table 2. *Low-order X-ray data for $\alpha(\text{AlCrSi})$*

(hkl)	$\sin \theta/\lambda = 1/2d(hkl)$ (\AA^{-1})	$ F_c $	$ F_o ^*$	ΣmF_o^2 $\times 10^{-4}$
111	0.0793	179	162	21
200	0.0916	96	101	6
220	0.1295	14	26	1
311	0.1519	117	128	39
222	0.1586	70	86	6
400	0.1832	3	33	1
331	0.1996	166	173	72
420	0.2048	112	125	37
422	0.2244	246	241	139
{ 333	0.2380	436	390	389
{ 511		340	333	
440	0.2591	436	412	204
531	0.2709	102	110	58
{ 600	0.2748	264	267	86
{ 442		120	134	
620	0.2897	53	59	8
533	0.3003	19	27	2
622	0.3038	99	104	26
444	0.3173	166	176	25
{ 711	0.3271	67	83	54
{ 551		109	125	
640	0.3303	115	133	42
642	0.3427	93	104	52
{ 731	0.3518	136	152	175
{ 553		142	163	
800	0.3664	239	243	35
733	0.3749	169	160	61
{ 644	0.3777	124	147	56
{ 820		34	41	
{ 660	0.3886	450	446	426
{ 822		288	280	
{ 555	0.3966	405	375	157
{ 751		80	96	
662	0.3993	107	115	32
840	0.4096	66	70	12

* Estimated from single-crystal photographs and scaled to $|F_c|$.

(ii) *Single-crystal photographs*

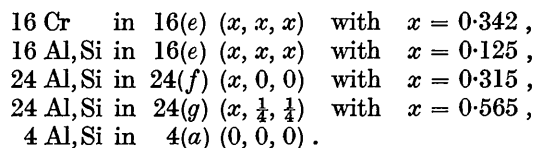
The Laue symmetry is $m\bar{3}m$ and there are no systematic absences beyond those caused by a face-centring of the unit cell. Of the three possible space groups only one, $T_d^2-F\bar{4}3m$, possesses sufficient special positions to accommodate separately all the Si and Cr atoms in the unit cell.

Intensities have been collected from oscillation photographs of a small (< 0.18 mm.) crystal of $\alpha(\text{AlCrSi})$ using filtered Mo $K\alpha$ radiation and banks of four films, with copper foil interleaved, mounted in a 6 cm. diameter camera. Oscillations of 10° were adequate, with an overlap of 3° to correlate successive oscillation ranges. Ten layer lines have been measured with the crystal oscillating about one of its cube axes. The intensities have been estimated visually by comparison with a standard intensity scale prepared from a very strong reflexion from the same crystal; they have been corrected for Lorentz and polarization factors, and also for the variation of absorbing power of the foils with angle of incidence. A further factor involving the angle of incidence on the films arises because the method of measurement does not yield an integrated intensity, but owing to the cubic sym-

metry it has been easy to compare the observed intensities of equivalent reflexions occurring on different layer lines. The final observed intensities have been taken as the average of the intensities of all the equivalent reflexions available.

4. Determination of the structure

The structure has been solved with the aid of Patterson syntheses. A Patterson projection down one of the cube axes did not suggest any satisfactory solution, so the full intensity data were used in a section of the three-dimensional $P(u, v, w)$ synthesis at $w = 0$. This section readily yielded a solution of the structure without distinguishing between the lighter silicon and aluminium atoms, viz.:



(Terminology as in *International Tables*, 1952.)

The chemical composition suggests that the silicon atoms occupy the 16-fold group of light-atom positions, and this has been confirmed by the later electron-density syntheses.

The successive stages of refinement of the structure may be followed with the aid of Table 3. Signs of

Table 3. *The x-parameters of $\alpha(\text{AlCrSi})$*

Atom	Position	A	B	C	D	E
Cr	(x, x, x)	0.342	0.341	0.3419	0.3417	0.3421
Si	(x, x, x)	0.125	0.126	0.1260	0.1260	0.1260
Al ₁	(x, 0, 0)	0.315	0.310	0.3092	0.3099	0.3103
Al ₂	(x, $\frac{1}{2}$, $\frac{1}{2}$)	0.565	0.560	0.5594	0.5599	0.5600
Al ₀	(0, 0, 0)					

A Parameters from Patterson, $P(u, v, 0)$.
 B Parameters from first $\rho(x, y)$ projection.
 C Parameters from second $\rho(x, y)$ projection.
 D Parameters from corrected second $\rho(x, y)$ projection.
 E Parameters from line syntheses $\rho(x, x, x)$, $\rho(x, 0, 0)$ and $\rho(x, \frac{1}{2}, \frac{1}{2})$.

$F(hk0)$ have been calculated on the basis of the parameters shown in column A of this table, and a projection of the electron density (ρ) down one of the cube axes, a_3 , synthesized at intervals of $a_0/60$. The parameters estimated from this $\rho(x, y)$ synthesis are shown in column B. Recalculation of $F(hk0)$ using these new parameters produces a change in the sign of six structure factors, and a second $\rho(x, y)$ synthesis, including these changes and computed at intervals of $a_0/120$, gives the parameters shown in column C. This second $\rho(x, y)$ synthesis is reproduced in Fig. 1.

It is to be noted that no artificial temperature factor has been incorporated in this synthesis. There is therefore a pronounced diffraction ring around the peak representing chromium atoms in spite of the fact that the synthesis contains 700 terms. Moreover, the

close proximity of the Si and Cr peaks in projection down a cube axis means that the estimated parameters may well be influenced by overlapping ripples from neighbouring peaks. Introduction of an artificial tem-

$\sin \theta/\lambda < 0.95 \text{ \AA}^{-1}$. Full tables comparing $|F_o|$ with $|F_c|$ are not included in this paper, but are available in a dissertation (Robinson, 1951).

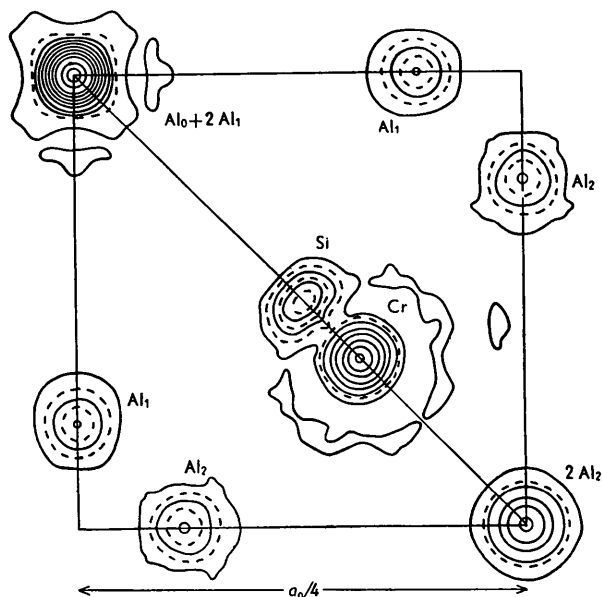


Fig. 1. Projection of electron density down a cube axis.

perature factor would reduce the diffraction ripples, but would also produce a broadening of the peaks, making it just as difficult to obtain a reliable estimate of the parameters of the Si and Cr atoms. In order to determine how much error may have been introduced as a result of the method of computation a $\rho(x, y)$ synthesis has been computed using as coefficients the calculated values of $F(hk0)$ based on the parameters shown in column *C*. The peaks of this synthesis show slight shifts from the assumed positions. These shifts are a measure of the errors introduced in computing the synthesis from the F 's, and may be used to correct the second $\rho(x, y)$ synthesis; these corrected parameters are shown in column *D* of Table 3.

A better method of obtaining parameters free from the effects of overlapping peaks involves the use of the three-dimensional intensity data. For this structure it is only necessary to calculate three line syntheses, $\rho(x, x, x)$, $\rho(x, 0, 0)$ and $\rho(x, \frac{1}{2}, \frac{1}{2})$, to determine all the unknown parameters from the three-dimensional data. The parameters found in this way are listed in the column *E* of Table 3 and give the best fit between observed and calculated structure factors; in computing the syntheses all values of $F(hkl)$ for reflexions having $\sin \theta/\lambda < 0.95 \text{ \AA}^{-1}$ have been included without the use of any artificial convergence factor. Some estimate of the accuracy of the structure may be obtained from the arbitrary factor $R_1 = \sum |F_o - F_c| \div \sum |F_o|$, which has a value of 0.12 when the summations are based on the parameters in column *E* of Table 3 and are made over all (hkl) reflexions having

5. Discussion

(i) General description of the structure

The structure of $\alpha(\text{AlCrSi})$ is based on an ideal formula $\text{Cr}_4\text{Si}_4\text{Al}_{13}$, and the main structural feature of the compound is to be found in the arrangement of silicon atoms. Each of these atoms is surrounded tetra-

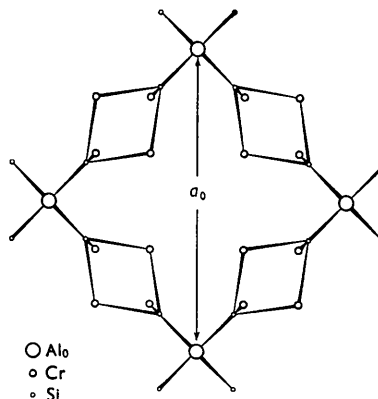


Fig. 2. Part of the tetrahedral framework of the $\alpha(\text{AlCrSi})$ structure shown in projection down a cube axis.

hedrally by three chromium atoms and one Al_0 atom. The tetrahedra are themselves linked together through the chromium and Al_0 atoms, for each of the former lies at the vertex of three tetrahedra and each of the latter at the vertex of four tetrahedra. Thus there is a continuous network of linked tetrahedra running throughout the structure (see Fig. 2).

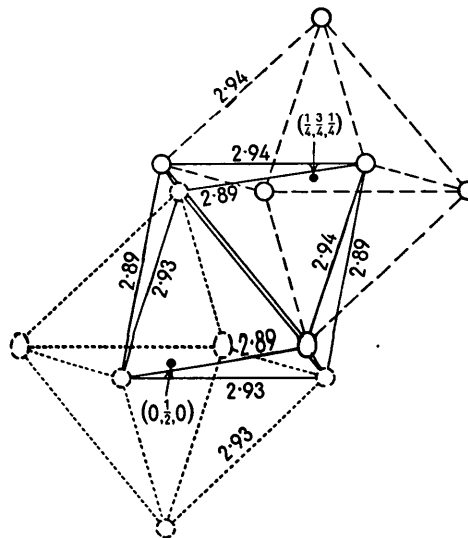


Fig. 3. Linkage of Al_1 octahedron surrounding the point $(0, \frac{1}{2}, 0)$ and the Al_2 octahedron surrounding the point $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ through a third, slightly distorted, octahedron (drawn in full lines). (Distances in Angstrom units.)

This network forms the framework of the structure and the remaining 48 aluminium atoms per unit cell fit around the framework by arranging themselves at the corners of regular octahedra. The octahedra of Al_1 atoms are centred on the lattice points $(0, 0, \frac{1}{2})$, $(\frac{1}{2}, 0, 0)$, $(0, \frac{1}{2}, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ whilst the Al_2 octahedra are centred on the points $(\frac{3}{4}, \frac{1}{4}, \frac{3}{4})$, $(\frac{3}{4}, \frac{1}{4}, \frac{1}{4})$, $(\frac{1}{4}, \frac{3}{4}, \frac{1}{4})$ and $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$. The relationship between Al_1 and Al_2 octahedra is such that a third, slightly distorted, octahedron is formed involving both Al_1 and Al_2 atoms (see Fig. 3). This distortion would be removed if the x -coordinate of the Al_1 and Al_2 atoms were 0.3125 and 0.5625, respectively, instead of the values listed in Table 3.

Each of the aluminium atoms in these octahedra is attached to the main framework through 'bonds' to two silicons and two chromiums.

(ii) Interatomic distances

The interatomic distances between close neighbours are shown in Table 4. Each Si atom is surrounded by four close neighbours—three Cr atoms at 2.41 Å and one Al_0 at 2.38 Å—and six more distant aluminium neighbours at about 2.80 Å. That the Si- Al_0 distance is shorter than the Si-Cr distance is rather unusual, but it may be explained by the fact that both Si and Al_0 are effectively in 4-coordination. Taking a value of 1.17 Å for the radius of a silicon atom in 4-coordination the radius of the Al_0 atoms would be 1.21 Å, corresponding to a 12-coordination radius of about 1.38 Å; this is somewhat smaller than the radii of atoms in metallic aluminium (1.43 Å). The occurrence of aluminium atoms in 4-coordination in a metallic structure is a most unusual feature of this structure.

Each chromium atom is surrounded by six close and

six more distant neighbours. Of the near neighbours three are silicons, as might be expected, but the other three are Al_1 atoms, which are themselves in 12-coordination. These Cr- Al_1 distances of length 2.46 Å are much shorter than would normally be expected, for the atomic diameters of Cr and Al atoms are both considerably larger than this, being *c.* 2.6 and 2.86 Å, respectively. It is significant that exactly the same kind of effect has been noted with regard to manganese atoms in Mn_3SiAl_9 (Robinson, 1952*a*) and in $MnAl_9$ (Nicol, 1953). In both these cases the shortened Mn-Al distances were to aluminium atoms showing a deficiency of electrons in electron-density maps. Of the more distant neighbours of the Cr atoms, three are Al_2 atoms at 2.77 Å and three are other Cr atoms at 2.84 Å, but it is unlikely that the latter represents a true contact distance.

The mean value of the distance between pairs of aluminium atoms is 2.91 ± 0.02 Å, which is somewhat greater than that usually encountered in structures of this type. This comparatively loose packing of the aluminium atoms in the octahedral groups strengthens the view that the tetrahedral network is the real framework of the structure and that, apart from the peculiar relationship of the Al_1 atoms to the Cr atoms, the aluminiums merely fill up the remainder of the space as best they can. The strength of the tetrahedral network may account for the high Brinell hardness number.

(iii) The first prominent Brillouin zone of the structure

It has already been shown (Raynor & Waldron, 1949; Robinson, 1952*a, b*) that a number of aluminium-rich intermetallic compounds appear at compositions which suggest that they are electron compounds with electron/atom ratios controlled by the form of the first prominent Brillouin zone. Like these other aluminium-rich compounds, $\alpha(AlCrSi)$ has a structure in which there is a marked layering of the atoms, and this very marked structural periodicity suggests that there must be associated Brillouin zones across whose faces there are very large energy discontinuities. The zone faces with the largest energy discontinuities may be taken to be those parallel to the planes in real space having the largest structure amplitudes, and if these faces are constructed in reciprocal space (i.e. $1/\lambda$ -space, where λ is the wavelength associated with an electron) they lie at a distance $1/2d(hkl)$ ($= p$) from the origin, where $d(hkl)$ is the interplanar spacing of the (hkl) plane. Observed and calculated structure factors of the low-order X-ray reflexions for $\alpha(AlCrSi)$ are shown in Table 2, and it may be noted that the largest values are for the {333}, {511}, {440}, {660}, {822} and {555} planes. Of these planes the first three fall into a group with p approximately 0.24 \AA^{-1} , and the last three into another group with p approximately 0.39 \AA^{-1} . There are therefore two possible prominent Brillouin zones, both of which are polyhedra, which closely

Table 4. Interatomic distances in the $\alpha(AlCrSi)$ structure

(Based on the parameters shown in column *E* of Table 3.)

Atom	Neighbour	No. of neighbours	Interatomic distance (Å)
Si	Al_0	1	2.38
	Cr	3	2.41
	Al_1	3	2.81
	Al_2	3	2.79
Cr	Si	3	2.41
	Al_1	3	2.46
	Al_2	3	2.77
	Cr	3	2.84
Al_0	Si	4	2.38
Al_1	Cr	2	2.46
	Si	2	2.81
	Al_1	4	2.93
	Al_2	4	2.89
Al_2	Cr	2	2.77
	Si	2	2.79
	Al_1	4	2.89
	Al_2	4	2.94

approach spherical shape since they have 44 faces almost equidistant from the origin of reciprocal space.

If V is the volume of the Fermi distribution of states in reciprocal space and v is the mean atomic volume, an electron compound would be expected to have an average of $2Vv$ free electrons per atom. Moreover, if the theory of Jones (1934) is applicable to complicated structures of this kind then the limit of the Fermi distribution would be expected to be close to the faces of a prominent Brillouin zone, and it is to be noted that an inscribed Fermi sphere would touch both prominent zones at 32 points. For the first prominent zone, shown in Fig. 4, the volume of the inscribed Fermi sphere (V) is $27\pi\sqrt{3}/2a_0^3 \text{ \AA}^{-3}$ and v is $a_0^3/84 \text{ \AA}^3$,

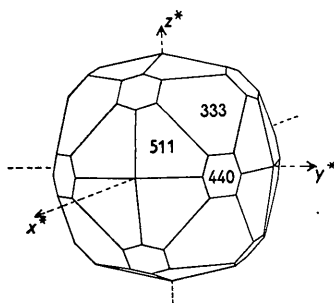


Fig. 4. The first prominent Brillouin zone of $\alpha(\text{AlCrSi})$.

so the inscribed Fermi distribution would correspond to 1.75 free electrons per atom. Similarly, the second prominent zone would correspond to 7.62 free electrons per atom.

If aluminium and silicon are given their normal 'valency' of +3 and +4 respectively, it is possible to calculate the 'effective valency' of chromium in this compound from the chemical composition on the assumption that the compound is an electron compound with an electron/atom ratio limited by a Fermi distribution touching one of the prominent zones. For the first zone and the composition of sample (1/8) (Table 1) the effective valency of Cr ($= x$) is given by

$$3 \times 61.0 + 4 \times 20.3 + 18.7x = 175, \\ \text{i.e. } x = -4.77.$$

For this zone the corresponding effective Cr valencies calculated from the compositions of samples (1/6) and (1/10) are -4.64 and -4.73 , respectively, whilst for the larger zone the values from all three samples would be impossibly large.

It is clear, therefore, that if $\alpha(\text{AlCrSi})$ is an electron compound its stability is controlled by the form of the first prominent Brillouin zone, and if this is so, each Cr atom prevents about 4.7 valency electrons of the other atoms from behaving as if they were free. This figure is in good agreement with Raynor's suggestion (1944) for the behaviour of transitional metal atoms in an electron-rich environment.

(iv) Electron counts

Attempts have been made to estimate from the electron-density syntheses the number of electrons associated with each type of atom in the structure, but it is difficult to get any reliable information as to whether the effective negative valency of the Cr atoms is due, as has been suggested by Raynor (1944), to the absorption of electrons into the vacancies in their 3d band. Counts made on the projection $\rho(x, y)$ are shown in Table 5(a). Although the estimate from the Cr peak

Table 5. Electron counts (scaled to Si = 14.0) from $\alpha(\text{AlCrSi})$ peaks (a) of the projection $\rho(x, y)$, and (b) of the line synthesis $\rho(x, x)$

(a)		(b)	
Peak	Electron count	Peak	Electron count
Cr	27.6	Cr	25.4
Si	14.0	Si	14.0
Al ₁	12.3	Al ₀	13.3
Al ₂	13.1		
2Al ₃	25.9		

is 3.6 electrons per atom greater than that expected from a normal Cr atom, this figure cannot be at all reliable in view of the proximity of the Si peak in this projection.

A more reliable estimate may be obtained from the count made on the line synthesis $\rho(x, x)$. This shows an excess of 1.4 electrons per Cr atom, and the estimate is not affected by any overlapping of peaks. It does depend, however, on the assumption that the atoms are spherically symmetrical. On the other hand there are two reasons why the value might well be an underestimate of the real state of affairs. First, the chemical composition for the sample (Table 1, (1/8)) shows that about 2% of the chromium positions (i.e. 0.3 sites per unit cell) cannot be occupied by Cr atoms, and must therefore be occupied by Si atoms or left vacant; in either case the expected electron count for a normal Cr atom would be slightly less than 24.0. Secondly, in calculating the phases for the terms in the $\rho(x, x)$ synthesis, it has been assumed that the Cr atoms have no excess electrons. This would be expected to minimize any excess estimated from the synthesis, since the structure has no centre of symmetry.

The Al₀ count of 13.3 electrons estimated from $\rho(x, x)$ suggests that the excess silicon in the sample examined (about one atom per unit cell) is to be found in the fourfold Al₀ positions, as might well be expected from the environment usually favoured by silicon atoms. According to whether the Cr sites contain 0.3 silicon atoms or 0.3 vacancies, the four Al₀ sites per cell would take 0.7 or 1.1 Si atoms.

A striking feature of the counts on $\rho(x, y)$ is the low count associated with Al₁ compared with that of Al₂. These counts are not affected by overlapping of peaks. It has been noted above that although in all other respects the environments of Al₁ and Al₂ atoms are

very similar, yet the Al_1 atoms approach unusually close to the Cr atoms, whilst the Al_2 atoms remain at a more normal distance. Similar relationships between electron deficiencies and shortened transition metal-aluminium interatomic distances have been noted in Mn_3SiAl_9 and in $MnAl_6$ and in both these cases it has been possible to give more reliable evidence for absorption of electrons into the vacancies in the $3d$ shells of the transitional metal atoms.

6. Conclusion

The structure of $\alpha(AlCrSi)$ is not very convenient for assessing directly whether or not electron absorption into the transitional metal atoms takes place, but electron counts suggest that there is some limited absorption by the Cr atoms. Moreover, the form of the first prominent Brillouin zone is consistent with the supposition that $\alpha(AlCrSi)$ is an electron compound, in which the transitional metal atoms prevent valency electrons of other atoms from behaving as if they were free electrons. The shortening of some interatomic distances, mentioned above, suggests that some form of bonding other than that normally encountered in metallic structures is taking place in isolated regions of structures of this type, i.e. some of the bonds appear to have an ionic character.

Acta Cryst. (1953). **6**, 859

Polarization Dichroism, Form Birefringence, and Molecular Orientation in Crystalline Haemoglobins

By M. F. PERUTZ

Medical Research Council Unit for the Study of the Molecular Structure of Biological Systems, Cavendish Laboratory and Molteno Institute, University of Cambridge, England

(Received 21 October 1952 and in revised form 8 July 1953)

The three principal absorption coefficients of the oxyhaemoglobin molecule were determined at $\lambda = 5800 \text{ \AA}$, using crystals of horse haemoglobin in which the molecules lie on lattice points. The coefficients are defined by an ellipsoid of revolution with an axial ratio of $2.6(\pm 0.1)$, the short axis of the ellipsoid enclosing an angle of $10^\circ(\pm 1^\circ)$ with the long axis of the molecule. This result was used to find the orientation of the molecules in two forms of human haemoglobin.

A comparative study of the molecular dichroism of different haemoglobin derivatives showed that oxy-, carboxy- and methaemoglobin and the addition compounds of methaemoglobin with azide and imidazole all have, within the limits of error, the same dichroic ratio of 2.6. Reduced haemoglobin alone has a dichroic ratio of 4.5. A similar difference was found between the dichroic ratios of reduced and metmyoglobin.

The birefringence of wet crystals of horse methaemoglobin changes with the refractive index of the suspension medium. The crystals were found to possess a strong negative intrinsic birefringence, which is compensated and masked by a positive form birefringence. n_α (intrinsic) is parallel to the direction of least absorption. n_γ (form) encloses a small angle with the long axis of the haemoglobin molecules.

Introduction

Bragg & Perutz (1952a) are developing a direct method of analysis of haemoglobin which depends on the plotting of the molecular Fourier transform in reci-

It is a pleasure to thank Prof. Sir Lawrence Bragg and Dr W. H. Taylor for the provision of facilities and for their interest in the progress of this work. For financial assistance I wish to thank the Ministry of Supply (Basic Properties of Metals Committee) and, later, the Royal Commissioners for the Exhibition of 1851.

References

- International Tables for X-ray Crystallography* (1952). Birmingham: Kynoch Press.
- JONES, H. (1934). *Proc. Roy. Soc. A*, **144**, 225.
- MONDOLFO, L. F. (1943). *Metallography of Aluminium Alloys*. Wiley: New York.
- NELSON, J. B. & RILEY, D. P. (1945). *Proc. Phys. Soc.* **57**, 160.
- NICOL, A. D. I. (1953). *Acta Cryst.* **6**, 285.
- PRATT, J. N. & RAYNOR, G. V. (1951). *J. Inst. Met.* **79**, 211.
- RAYNOR, G. V. (1944). *J. Inst. Met.* **70**, 531.
- RAYNOR, G. V. & WALDRON, M. B. (1949). *Phil. Mag.* (7), **40**, 198.
- ROBINSON, K. (1951). Ph.D. dissertation, University of Cambridge.
- ROBINSON, K. (1952a). *Acta Cryst.* **5**, 397.
- ROBINSON, K. (1952b). *Phil. Mag.* (7), **43**, 775.
- ROBINSON, K. (1953). *Acta Cryst.* **6**, 667.

procal space. By swelling and shrinkage of crystals of horse methaemoglobin the values of $|F|_{h0l}$ can be found at a large number of points along lines of constant h and the nodes and loops of the molecular