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The Structure of Co_2Al_9

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The structure of an alloy of composition Co_2Al_9 has been determined. A discussion is given of the experimental data, and of the derivation and accuracy of atomic co-ordinates and electron counts. The structure is described and discussed. It is concluded that the results of the electron counts, and also the forms of the first prominent Brillouin zones for both Co_2Al_9 and Co_2Al_5, are in agreement with the hypothesis, suggested by Raynor, that in electron-rich phases transition elements absorb electrons from the structure as a whole.

1. Introduction

The constitution of binary and ternary alloys of aluminium with the transition metals of the first long period has been studied by Bradley (Bradley, Bragg & Sykes, 1940), Hume-Rothery, Raynor, and their collaborators (see, for example, Raynor & Waldron (1948)). The aluminium-rich portions of these systems contain a considerable number of phases with complex structures, of which the greater proportion have not yet been analysed.

The recent work of Raynor and his collaborators in Birmingham has shown that these phases are of considerable theoretical interest. Raynor & Waldron (1949) have suggested that in such aluminium-rich phases the transition metals absorb, from the structure as a whole, electrons which then occupy the vacancies postulated by Pauling (1938, 1949) in the so-called non-bonding or atomic orbitals in the 3-*d* level. If this suggestion is accepted, then it is found that many analogous phases in different systems have identical electron/atom ratios. Investigation of the structures of these phases, and of the relationships between them, may be expected to provide further experimental evidence with which to test the correctness of these theories of the electronic configuration and behaviour of the transition metals in alloy phases.

Preliminary accounts of the results of the investigation of the structure of Co_2Al_9 have been published (Parker, 1945; Douglas, 1948*a*) and full details of both experimental procedure and results are available in a dissertation (Douglas, 1948*b*). The present paper contains an outline account of the methods used in analysing the structure, and of the tests employed in assessing the probable accuracy attained (§§ 3 and 4), and a discussion of the important features of the structure (§ 5).

2. The aluminium–cobalt equilibrium diagram

The phase diagram determined by X-ray methods (Bradley & Seager, 1939) is shown in Fig. 1. The structures of two of the phases are known, those of Co_2Al_5 (Bradley & Cheng, 1938) and of CoAl (Bradley & Seager, 1939). The two phases Co_4Al_{13} and $CoAl_3$ were not detected by earlier workers. The remaining phase, now described as Co_2Al_9, was previously thought to be Co_3Al_{13} (Brunck, 1901). Bradley & Seager (1939) were unable to decide between the two possible formulae, and chemical analysis by Raynor (1947) showed a constant composition midway between these two formulae. The present research has shown that the ideal formula is Co_2Al_9.

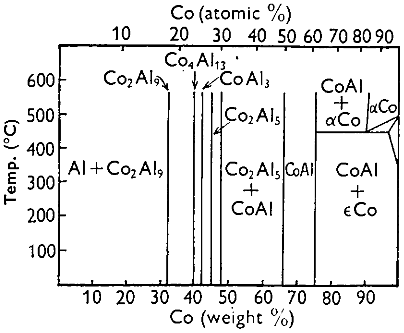

Fig. 1. The Co–Al phase diagram as determined by X-ray methods (cf. Bradley & Seager, 1939).

3. Experimental

(i) *Preparation of material*

A small ingot of composition Co_2Al_9 was made by melting together electrolytic cobalt (99·8 % pure) and aluminium (99·992 % pure). After annealing for 48 hr. at 900° C., the material was very brittle, and X-ray powder photographs showed that it was homogeneous and free from strain; comparison with photographs published by Bradley & Taylor (1940) showed that it was identical with the Co_2Al_9 phase found by Bradley & Seager (1939).

Attempts to analyse the powder pattern by methods described by Lipson (1949) were unsuccessful; it was therefore necessary to obtain single crystals. The crushed powder contained a small proportion of regularly shaped fragments approximately $0{\cdot}2 \times 0{\cdot}1 \times 0{\cdot}05$ mm. which proved to be single crystals. These could be shattered by pressure from a razor-blade, and approximately cubic fragments were selected for examination by X-rays.

(ii) *X-ray data*

The structure was found to be monoclinic with space group $P2_1/a$. Accurate cell dimensions could not be determined from the complex powder pattern, so a modification of the method due to Farquhar & Lipson (1946) was adopted, in which a single crystal was mounted in a 9 cm. camera. The accurate values of a, c and β found by this method, together with the value of b found by interpretation of the powder pattern up to $\theta \sim 50°$, are

$$a = 8\cdot5565 \pm 0\cdot0005, \qquad b = 6\cdot290 \pm 0\cdot005,$$
$$c = 6\cdot2130 \pm 0\cdot0005\,\text{A.}, \quad \beta = 94\cdot760° \pm 0\cdot005°.$$

Equatorial Weissenberg photographs, and oscillation photographs using the multiple-film technique, were used for intensity estimations. The absorption effect was reduced by the use of Mo $K\alpha$ radiation and a very small, approximately cubic, single crystal. Intensity estimations were made by comparison with a standard intensity scale made with the same specimen, and the usual corrections for the Lorentz and polarization factors were applied; a correction for variation with ζ was made by the method described by Clews & Cochran (1949), who show that after these corrections are made the observational data can be expressed in the form

$$I_{hkl} = F^2{}_{hkl}[s(\sin\theta)]^2,$$

where F_{hkl} is the structure amplitude, and $s(\sin\theta)$ is a function of $\sin\theta$ so far undetermined (see also §4 (ii)).

(iii) *The ideal formula*

The density, determined by displacement, was found to be $3\cdot60 \pm 0\cdot02$ g.cm.$^{-3}$. The density calculated on the basis of four cobalt and eighteen aluminium atoms per unit cell, which numbers are in agreement with space-group requirements, is $3\cdot60 \pm 0\cdot005$ g.cm.$^{-3}$. Thus both space-group and density determinations indicate that the ideal formula is Co_2Al_9. The results of chemical analysis (Raynor, 1947) indicate a slight excess of 0·075 cobalt atom per unit cell which would result in a calculated density of $3\cdot62 \pm 0\cdot005$ g.cm.$^{-3}$, a value not excluded by the accuracy of the experimental determination.

4. Determination of the structure

(i) *Procedure*

The values of I_{hkl} obtained as above were used to evaluate two-dimensional Patterson projections along the c and b axes, and also a Patterson–Harker three-dimensional section at $y = \frac{1}{2}$. From the two latter it proved possible to determine approximate values of the x and z co-ordinates of all the atoms in the unit cell. These parameters were then refined by successive electron-density projections along the b axis.

The Patterson projection along the c axis was too complex for direct interpretation. Probable approximate values of the y co-ordinates were therefore found by packing the atoms together in conformity with the interatomic distances found by Bradley & Cheng (1938) in the analysis of Co_2Al_5. These co-ordinates were confirmed and refined by electron-density projections along the c axis.

Despite the use of the large number of reflexions observable with Mo $K\alpha$ radiation, the two final electron-density projections showed considerable diffraction effects. An artificial temperature factor, $\exp[-2\sin^2\theta]$, was therefore introduced, and the resultant projections are shown in Fig. 2 (a and b).

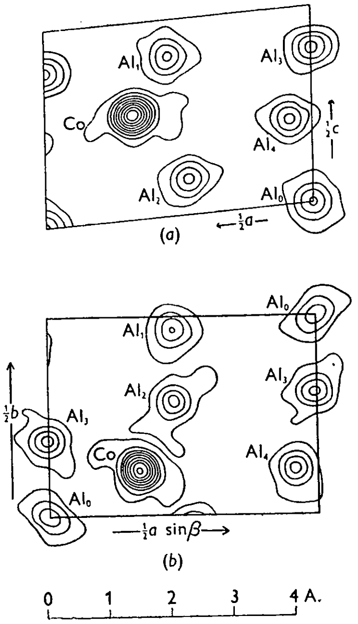

Fig. 2. (a) Electron-density projection along the b axis, or ($h0l$) projection. (b) Electron-density projection along the c axis, or ($hk0$) projection.

An artificial temperature factor has been introduced into both Fourier series, and the contours are plotted in arbitrary units.

(ii) *Accuracy of the atomic co-ordinates*

The interest of the structure arises partly from the discussion of interatomic distances, and partly from the counting of electrons in the atomic peaks. In view of the importance of a correct assessment of the accuracy achieved, the following discussion is given in some detail.

In the process of refining the atomic parameters, the factor $R = \frac{\Sigma||F_o|-|F_c||}{\Sigma|F_o|}$, where F_o is the observed and F_c the calculated structure amplitude, was used to estimate whether or not the accuracy was increasing. In order to obtain F_o the approximate value of the function $s(\sin\theta)$ had to be determined; this was done by calculating $\Sigma\{(\sqrt{I_{hkl}})/F_c\}$ for $\sin\theta = 0\cdot1$–$0\cdot2$, $0\cdot2$–$0\cdot3$, etc. The value of R decreased steadily to 0·15 for the projections along b, and to 0·18 for the projections along c.

Errors in determining the atomic positions may arise from:

(1) Experimental errors in I_{hkl}.

(2) Termination of the Fourier series at a point where the coefficients are still appreciable.

(3) An inaccurate method of locating peak positions.

(4) Overlapping of the peaks in projection.

(5) Computational errors due to rounding-off of sine and cosine terms to two figures.

Cox & Cruickshank (1948) have shown that the effect of (5) is very small, and inspection of the cross-section of the peaks in Fig. 2 shows that (4) can be neglected in this case. The atomic position was taken to be that at which $\partial\rho/\partial x$, etc., become zero, and the method first used to locate these peak positions was to fit a paraboloid to nine points about the peak position. However, it was found that, when the electron density was only evaluated at intervals of $\frac{1}{60}$th of the unit-cell sides, the error arising from the paraboloid method was of the same order of magnitude as that due to experimental errors ((1), above). Thereafter the peak positions were determined by a differential-synthesis method (Booth, 1946*a*, *b*).

The error due to termination of series ((2), above) was allowed for in two different ways: (*a*) by the use of an artificial temperature factor (§4(i)), (*b*) by the use of the F_c-synthesis method (Booth, 1946*c*). The corrections given by the two methods for the $(h0l)$ projection are shown in Table 1. It will be seen that, while all the signs of the shifts agree, the magnitude of those given by method (*b*) is, with one exception, always the greater, indicating that method (*a*) had not completely eliminated the error.

Table 1. *Comparison of the results of two methods of correcting for termination errors for the* $(h0l)$ *projection*

		Application of an artificial temperature factor	Use of F_c synthesis
Co	x	0·0007	0·0008
	z	0·0000	0·0003
Al_1	x	0·0002	0·0002
	z	−0·0003	−0·0005
Al_2	x	0·0003	0·0008
	z	0·0002	0·0016
Al_3	x	−0·0005	−0·0006
	z	−0·0018	0·0013
Al_4	x	−0·0005	−0·0008
	z	−0·0015	−0·0026

The magnitude of the effect of experimental errors in I_{hkl} was estimated by a method due to Cruickshank (1949) which depends on a determination of

$$\Delta F = (F_c - F_o).$$

This method does not give the magnitude of the finite-summation errors, if these have not already been corrected, so that a modification of the method was adopted in order to estimate the total error. The standard deviation in the x-parameter can be expressed as $\sigma(x) = \dfrac{\sigma(\partial\rho/\partial x)}{\partial^2\rho/\partial x^2}$, where ρ is the electron density and $\sigma\left(\dfrac{\partial\rho}{\partial x}\right) = \left\{\int_A \left(\dfrac{\partial\rho_0}{\partial x} - \dfrac{\partial\rho_t}{\partial x}\right)^2 \dfrac{dA}{a}\right\}^{\frac{1}{2}}$, where ρ_t is the true electron density.

If the function $\left\{\Sigma\left(\dfrac{\partial\rho_0}{\partial x}\right)^2\right\}^{\frac{1}{2}}$ is estimated over a considerable area between the peaks, where $\partial\rho_t/\partial x$ is zero, then a measure of the total error in peak position can be obtained. The estimated experimental and total errors in the x parameters are shown in Table 2. The first column shows the difference between the parameters obtained from the two projections, and corrected for termination errors by the F_c method. The second column shows the total error, and the third the experimental error, in the projection to which an artificial temperature factor has been applied, and the difference between them confirms that not all the termination error has been removed by the use of the artificial temperature factor. The fourth column shows the residual error after correction by the F_c synthesis, and the fifth column shows the total error in the projection before the artificial temperature factor was applied.

Table 2. *Errors in x parameters*

	1	2	3	4	5
Co	0·0009	0·0007	0·0005	0·0006	0·0014
Al_1	0·0000	0·0018	0·0014	0·0010	0·0027
Al_2	0·0015	0·0018	0·0014	0·0013	0·0033
Al_3	0·0012	0·0017	0·0013	0·0016	0·0040
Al_4	0·0008	0·0017	0·0013	0·0015	0·0038

1. Difference between x parameters obtained from $(h0l)$ and $(hk0)$ syntheses after application of artificial temperature factor.
2. Total error for $(h0l)$ synthesis with temperature factor estimated by averaging slope of background over 200 observations.
3. Experimental error for $(h0l)$ synthesis with temperature factor, estimated by Cruickshank's formula.
4. Total error estimated by Cruickshank's formula for $(h0l)$ synthesis without temperature factor, after correction by F_c synthesis.
5. Total error for $(h0l)$ synthesis without temperature factor, estimated by averaging slope of background over 200 observations.

The atomic parameters and their standard deviations are shown in Table 3. The most important residual error is the experimental error, and this can be reduced by use of three-dimensional synthesis. Such a synthesis is at present being carried out, using values of $\sqrt{I_{hkl}}$ to which an artificial temperature factor of $\exp[-4\sin^2\theta]$ has been applied.

Table 3. *Atomic parameters and standard deviations*

	x	σ_x	y	σ_y	z	σ_z	σ_r (A.)
Co	0·3335	0·0006	0·6149	0·0011	0·2646	0·0007	0·0096
Al_1	0·2682	0·0011	0·9619	0·0027	0·4044	0·0016	0·0218
Al_2	0·2309	0·0011	0·2899	0·0027	0·0889	0·0021	0·0234
Al_3	−0·0014	0·0013	0·1931	0·0026	0·3891	0·0016	0·0222
Al_4	0·0417	0·0013	0·6148	0·0025	0·2159	0·0021	0·0232

σ for Co–Al interatomic distances = 0·027 A.
σ for Al–Al interatomic distances = 0·034 A.

(iii) *Electron counts*

The electron-density peaks in the two projections shown in Fig. 2 (*a* and *b*) were sufficiently well resolved for estimates of the total number of electrons under each peak to be made. These electron counts were on an arbitrary scale, since the influence of the factors represented by $s(\sin\theta)$ was uncertain, and, in order to obtain absolute values, it was necessary to assume that the electron density was zero in the areas between the peaks. The results thus obtained are shown in Table 4. The accuracy of the electron count was estimated in three different ways:

(*a*) Assuming that the numbers of electrons under each Al peak should be identical, the standard deviation of the ten counts, 0·48, gives an estimate of the error.

(*b*) The standard deviation of the total electron count over the unit cell can be found in terms of

$$\Delta\sqrt{I} = |\sqrt{I_c} - \sqrt{I_o}|.$$

It can be shown that for the $(h0l)$ projection

$$\sigma_N = \frac{g(\sqrt{2})\,ac}{8\pi^2}\left\{\Sigma\Sigma\frac{(\Delta\sqrt{I})^2}{h^2l^2}\right\}^{\frac{1}{2}},$$

where g is the constant used to convert arbitrary to absolute electron densities. The value of σ_N was found to be 0·48.

(*c*) The number of electrons in four background areas, each of size comparable with an atomic peak, was estimated and the standard deviation was calculated from

$$\sigma'_N = \left\{\frac{\Sigma(N_o)^2}{n}\right\}^{\frac{1}{2}},$$

where N_o is the number of electrons observed, and n the number of observations. This method gave a standard deviation of 0·45 for both cobalt and aluminium peaks, since these have approximately the same area in projection.

Table 4. *Number of electrons associated with the atomic peaks*

Atom	$(h0l)$ projection	$(hk0)$ projection
Co	29·2	28·9
Al_0	12·4	11·6
Al_1	12·7	12·3
Al_2	12·5	12·8
Al_3	11·6	12·9
Al_4	11·8	12·7

The unit cell contains 4Co, $2Al_0$ and 4 each of Al_1, Al_2, Al_3, Al_4; the total number of electrons in the unit cell is therefore 342. As deduced from the counts for the individual atoms it is 336 for the $(h0l)$ projection, 342 for the $(hk0)$ projection.

5. Discussion

(i) *Description of the structure and discussion of the interatomic distances*

The characteristic feature of the structure is that the aluminium atoms lie approximately in layers parallel to (100) at heights $x=0$ and $\frac{1}{4}$. The cobalt atoms are situated between the layers in such a manner that each has nine neighbouring aluminium atoms, as can be seen in Fig. 3.

The interatomic distances are given in Table 5 and the reduction in length of the Co–Al_0 bond, in comparison with the other Co–Al distances (where Al_0 lies on a centre of symmetry), seems to be statistically significant. Electron counts do not show any significant

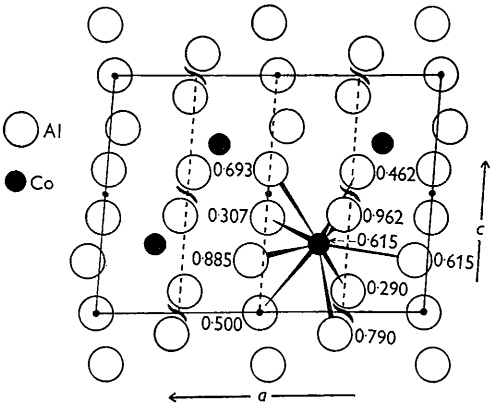

Fig. 3. Projection of the Co_2Al_9 structure along the *b* axis, showing the arrangement of aluminium atoms in planes parallel to (100), and the nine aluminium atoms surrounding one cobalt atom. The *y* co-ordinates of these ten atoms are given in fractions of *b*.

Table 5. *Interatomic distances* (A.)

From Co′		From Al'_0		From Al'_1	
Al_1	$2{\cdot}43_0$	Co′	$2{\cdot}37_5$	Co′	$2{\cdot}49_0$
Al'_1	$2{\cdot}49_0$	Co″	$2{\cdot}37_5$	Co	$2{\cdot}43_0$
Al_2	$2{\cdot}44_5$				
Al'_2	$2{\cdot}48_0$	Al'_3	$2{\cdot}70_5$	Al'_2	$2{\cdot}84_5$
		Al_3	$2{\cdot}70_5$		
Al_3	$2{\cdot}53_5$	Al''_4	$2{\cdot}78_0$	Al_3	$2{\cdot}72_0$
Al'_3	$2{\cdot}48_5$	Al'''_4	$2{\cdot}78_0$	Al'_3	$2{\cdot}88_0$
Al_4	$2{\cdot}49_0$			$(Al'''_4$	$3{\cdot}08_5)$
Al'_0	$2{\cdot}37_5$	Al'_2	$2{\cdot}71_0$		
		Al'''_2	$2{\cdot}75_0$	Al''_3	$2{\cdot}84_0$
Al''_4	$2{\cdot}50_0$			Al'''_3	$2{\cdot}94_0$
		Al_2	$2{\cdot}75_0$	Al'_4	$2{\cdot}74_5$
		Al''_2	$2{\cdot}71_0$	Al_4	$2{\cdot}91_5$

From Al_2		From Al'_3		From Al''_4	
Co′	$2{\cdot}44_5$	Co″	$2{\cdot}53_5$	Co′	$2{\cdot}50_0$
Co	$2{\cdot}48_0$	Co′	$2{\cdot}48_5$	Co‴	$2{\cdot}49_0$
Al_1	$2{\cdot}84_5$	Al_3	$2{\cdot}79_0$	Al_3	$2{\cdot}78_0$
		Al''_4	$2{\cdot}82_5$	Al'_3	$2{\cdot}82_5$
Al_0	$2{\cdot}71_0$	Al'''_4	$2{\cdot}78_0$	Al'_0	$2{\cdot}78_0$
Al_4	$2{\cdot}76_5$	Al'_0	$2{\cdot}70_5$		
Al''_3	$2{\cdot}90_0$			Al_1	$2{\cdot}74_5$
Al'_4	$2{\cdot}94_0$	Al_1	$2{\cdot}94_0$	Al'_2	$2{\cdot}94_0$
		Al_2	$2{\cdot}83_5$		
Al'_0	$2{\cdot}75_0$	Al'_1	$2{\cdot}88_0$	Al''_1	$2{\cdot}91_5$
Al'_3	$2{\cdot}83_5$			Al''_2	$2{\cdot}76_5$
$(Al'''_4$	$3{\cdot}03_0)$	Al''_1	$2{\cdot}84_0$	$(Al'''_1$	$3{\cdot}08_5)$
		Al'''_1	$2{\cdot}72_0$	$(Al'''_2$	$3{\cdot}03_0)$
		Al''_2	$2{\cdot}90_0$		

Average Co–Al distance $= 2{\cdot}47_0$ A.
Average Al–Al distance $= 2{\cdot}84_0$ A.
Standard deviation of Co–Al (neglecting Al_3 and Al'_0) $= 0{\cdot}02_5$ A.

The Al atoms surrounding any one Al atom are arranged in three groups, the first consisting of atoms in the same layer and the other two of atoms in the layers on either side of the particular atom considered.

difference between Al_0 and the other aluminium atoms (see § 4 (iii)). The mean value of 2·47 A. for the Co–Al distance is identical with the mean value found in Co_2Al_5 and also in CoAl, but is certainly appreciably shorter than would be predicted from the distance of closest approach between atoms in pure cobalt (2·51 A.) and in pure aluminium (2·86 A.), namely, 2·68 A.

This apparent reduction of interatomic distance between cobalt and aluminium may be due to one or more of several factors, the variations of which have been found to affect the apparent radius of an atom. The first factor is the variation of co-ordination number. Aluminium and cobalt are both 12-co-ordinated in the elements, whereas in Co_2Al_9 the cobalt atoms are 9-co-ordinated, three aluminium atoms are 9-co-ordinated, one is 10- and one is 12-co-ordinated. Corrections applied to the interatomic radii derived from the pure metals by Pauling's method (1947) predict an average Co–Al distance of $2{\cdot}61_5$ A., which, though nearer the observed value of $2{\cdot}47_0$ A., is still rather high.

Another factor may affect the atomic radius of aluminium, namely, the overlap of electrons across the first Brillouin zone. Matyas (1948) has shown that this occurs across the (111) planes in pure aluminium, while it will be shown below that it is probable that no overlap occurs across the first prominent Brillouin zone in Co_2Al_9. Such an overlap causes an expansion of the lattice, and hence an increase of the apparent atomic radius of aluminium in the pure metal. An estimate of the necessary correction is given by the work of Axon & Hume-Rothery (1948) on the 'apparent atomic diameter' of aluminium in dilute solution in copper, gold and silver. From this these authors conclude that the best value to take for the atomic diameter corrected for Brillouin zone overlap is 2·71 A., and that this is likely to be still somewhat high. Since the number of valency electrons is not known, no such correction can be made for the cobalt atom; the predicted value for the Co–Al distance now becomes 2·53 A. The difference between this and the observed value of 2·47 A. probably exceeds the experimental error (cf. Table 3).

It is interesting to note that there is no apparent connexion between these shortened interatomic distances and the electron absorption effect, since the observed Co–Al distance is the same in Co_2Al_9 as in CoAl, where electron absorption is unlikely to occur. Such absorption might be expected to lead to an increase rather than to a decrease in these interatomic distances. The predicted average Al–Al distance, taking into account the two factors which may be supposed to affect the Co–Al distance, is now 2·65 A., which is considerably less than the average observed value of 2·84 A., and below even the minimum value of $2{\cdot}70_5$ A.

(ii) *Electron counts*

The data collected in Table 4 and discussed in § 4 (iii) show that the difference between the numbers of electrons associated with the cobalt peak and the atomic number of cobalt (27) is ~ 2, which, on the estimate of standard deviation of the electron counts, is statistically significant. This is in agreement with Raynor's assumption of electron absorption by the transition metals, which would predict an average absorption of 1·71 electrons per cobalt atom. It should be emphasized that this electron count is dependent upon the assumption that the electron density falls to zero between the atoms. If this assumption is not justified, the above conclusions must be modified. Thus, if there is in fact a distribution of electrons throughout the unit cell, such as was found in the case of magnesium by Grimm, Brill, Hermann & Peters (1938), then the number of electrons per cobalt peak is reduced. A uniform distribution throughout the unit cell of 2·5 electrons per atom, which is the number expected if the aluminium atoms contribute three and the cobalt atoms contribute no electrons to this general distribution, would reduce the number of electrons per cobalt peak from 29·0 to 27·0.

In order to decide the exact distribution of the electrons it will be necessary to obtain, experimentally, very accurate absolute measurements of the structure amplitude F_0, and hence derive absolute values of electron density from a three-dimensional synthesis.

(iii) *The relation between the electron/atom ratio and the first prominent Brillouin zone in* Co_2Al_9 *and in* Co_2Al_5

From the data obtained from the single-crystal photographs of Co_2Al_9 it can be shown that the first prominent Brillouin zone, consisting of planes in *k* space corresponding to crystal planes having high structure amplitudes, comprises (401), ($\bar{4}11$), (013), (321), ($\bar{1}31$), ($\bar{1}13$) and (031). Values of I_{hkl} for these planes are shown in Table 6. Raynor & Waldron (1949) have shown that these planes form a zone which approximates remarkably closely to a sphere. (The plane (031) was omitted from Raynor & Waldron's calculations.) It can be shown that a sphere in *k* space which touches a plane of spacing corresponding to the average interplanar spacing of 1·960 A. contains 2·120 electrons per atom. It is usual for the structure of an 'electron compound' to be such that the electron/atom ratio is equal to, or slightly greater than, the number of electrons per atom contained in such an inscribed sphere. The fact that the number of electrons per atom calculated for the composition of Co_2Al_9 on the assumption of electron

Table 6. *The planes forming the first Brillouin zone for* Co_2Al_9

hkl	I_{hkl} from single crystal data	*d*, from powder lines
031	507	1·990 A.
401	359	1·960 A.
$\bar{4}11$	138	
013	491	
321	488	
$\bar{1}31$	531	1·940 A.
$\bar{1}13$	406	

absorption (see §5(ii)), namely, 2·144, is in good agreement with that contained by the inscribed sphere is, therefore, evidence in support of Raynor's hypothesis.

It can also be shown that similar evidence in favour of Raynor's hypothesis is provided by Co_2Al_5. According to Bradley & Cheng (1938), the planes with high structure amplitudes are $(30\bar{3}1)$, $(21\bar{3}2)$, $(20\bar{2}3)$, $(22\bar{4}0)$ and (0004), and the zone which these form in k space is shown in Fig. 4. An average inscribed sphere, corresponding to an interplanar spacing of 2·033 A., contains 1·718 electrons per atom, and the electron/atom ratio calculated for the electron-rich phase boundary of Co_2Al_5 (at 27 atomic % Co), on the assumption of electron absorption, is 1·728.

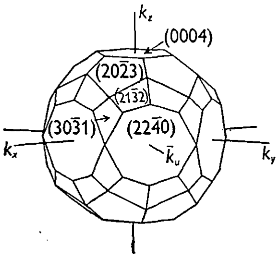

Fig. 4. The first prominent Brillouin zone for Co_2Al_5.

6. Conclusion

The preliminary results of counts of the number of electrons associated with the cobalt atoms in Co_2Al_9 is in accord with the suggestion that transition metals absorb non-valency electrons into their d orbitals in electron-rich alloys, but further experimental work is required to confirm this point. The forms of the first prominent Brillouin zones for both Co_2Al_9 and Co_2Al_5 provide additional evidence in favour of this theory of electron absorption, if it is assumed that the two phases behave as 'electron compounds'.

It is clear that the details of the structure of Co_2Al_9, such as the interatomic distances, cannot yet be satisfactorily interpreted. It is hoped that further work on other complex aluminium-rich alloys, such as those containing manganese, will contribute to the elucidation of this problem.

I am greatly indebted to Prof. Sir Lawrence Bragg for his continued interest and support, and to Dr W. H. Taylor and Dr W. Cochran for many valuable discussions. My thanks are also due to Mrs Musgrave and Mrs Cosslett who helped with the calculations. I am indebted to the British Iron and Steel Research Association for the financial support of this work. Dr G. V. Raynor has kindly supplied a number of crystals of Co_2Al_9 and other aluminium-rich alloys. This investigation, and related researches at present in progress in this laboratory, are carried out in close collaboration with him.

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