

A Test for Electron Transfer in V_4Al_{23} *

BY A. E. RAY† AND J. F. SMITH

Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa, U.S.A.

(Received 16 September 1959 and in revised form 23 November 1959)

Three-dimensional intensity data have been collected from a spherical crystal of V_4Al_{23} by the moving crystal-stationary counter technique. Corrections were made for the effects of absorption, dispersion, extinction, and anisotropic thermal motion of the atoms. The crystal structure was refined by the method of least squares and by difference syntheses to a reliability index of 0.057. The intensity data were placed on an absolute scale using only those reflections for which $(\sin \theta)/\lambda > 0.29 \text{ \AA}^{-1}$ and which are relatively insensitive to the distribution of the outer electrons. Difference syntheses were then computed for the reflections, $(\sin \theta)/\lambda < 0.29 \text{ \AA}^{-1}$, which are most sensitive to the distribution of the outer electrons. These difference syntheses are a measure of the difference between the equilibrium electron distribution in the crystal and that in the isolated free atoms. The results do not indicate a significantly increased electron concentration in the vanadium d levels as proposed by Raynor.

Introduction

A considerable number of compounds occurring between aluminum and transition metals have been examined, and the structures of the aluminum-rich compounds exhibit several characteristic features (Taylor, 1954). One of the most interesting of these features is the occurrence of abnormally short contacts between the transition metal atoms and some of the aluminum atoms. It has been suggested that these abnormally short contacts may be associated with localized electron transfer between the atoms concerned. However, the direction and degree of such transfer is open to question. Raynor (1949) has suggested that the unfilled $3d$ orbitals of the transition metals absorb some of the outer electrons from the neighboring aluminum atoms, and thus the electron transfer should be toward the transition metal atoms. Pauling (1951), on the other hand, has discussed the case of Co_2Al_9 and has used arguments based upon valence-bond strength, atomic electron configuration, and electronegativity which would indicate that the electron transfer should be toward the aluminum atoms. Pauling's view with respect to the atomic electron configuration is not supported by the magnetic susceptibility measurements of Föex & Wucher (1954).

Attempts have been made by Douglas (1950), Robinson (1952, 1953), and Nicol (1953) to detect electron transfer by X-ray diffraction techniques. In each case the experimental evidence has shown some indication of electron transfer toward the transition metal atoms. However, critical reviews of the results by Taylor (1954) and by Black (1955) point out that

the evidence for electron transfer is not conclusive and indeed if transfer occurs it must be considerably smaller than required by Raynor's theory.

The essential requirements for detecting electron transfer involving two or more electrons in the aluminum-rich transition metal compounds have been delineated by Black (1955): (1) the compound under investigation must have several observable reflections in the limited region of reciprocal space where the outer electrons contribute to the integrated intensities of the diffraction peaks; (2) the integrated intensities of the reflections should be placed on an absolute scale by experiment so that there would be no need for any assumptions about the atomic scattering factor curves; (3) accurate atomic coordinates must be obtained so that errors in adjustable parameters would not lead to erroneous results. In the present investigation the compound V_4Al_{23} was chosen as the material to be examined, and it quite adequately fulfills the first and third requirements since the unit cell is sufficiently large that a significant number of reflections occur in the front reflection region and since two independent determinations of the structure by Smith & Ray (1957) and by Brown (1957) are in good agreement. In addition, there is no evidence of deviation from stoichiometry. Finally, vanadium has a large number of vacant d states so that electron transfer to the extent predicted by Raynor should be more easily detectable than in the case of transition elements of higher atomic number.

With regard to Black's second requirement, the intensities were not placed on an absolute scale by direct experiment. Rather the reflections from the diffraction region, $(\sin \theta)/\lambda > 0.29 \text{ \AA}^{-1}$, were used after structure refinement to place the observed intensities on an absolute scale. While this method does involve the assumption that the scattering factor curves are not seriously in error when $(\sin \theta)/\lambda > 0.29 \text{ \AA}^{-1}$, this

* Contribution No. 804. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

† Present address: Monsanto Chemical Co., Research Dept., Dayton 7, Ohio.

assumption is likely to cause less uncertainty than would result from the inherent experimental difficulties involved in a direct determination of the integrated intensities on an absolute scale because of the limitations of available techniques. The insensitivity of the scattering factor curves to the outer electron distribution is shown by the results of Veenendaal *et al.* (1959) who found that the contribution of a $3s$ electron to the total scattering power of an Al^{+2} ion is less than 0.5% at $(\sin \theta)/\lambda > 0.25 \text{ \AA}^{-1}$. Though the contributions of the outer electrons to the total scattering factor of vanadium were not available at the time of this investigation, the results of Atoji (1957) have shown that for heavier atoms, such as the elements in the first transition series, reflections for which $0 < \xi < 0.1 \text{ \AA}^{-1}$ are sensitive to the distribution of outer electrons. In this case $\xi = Z^{-\frac{1}{2}} (\sin \theta)/\lambda$ where Z is the atomic number, and the insensitive region, $\xi > 0.1 \text{ \AA}^{-1}$, corresponds to $(\sin \theta)/\lambda > 0.29 \text{ \AA}^{-1}$ for vanadium.

In outline, the procedure which was followed consisted of the collection of three-dimensional intensity data with a proportional counter. These data were then corrected for absorption, dispersion, and extinction in addition to the more common corrections for Lorentz-polarization and velocity factors. Reflections for which $(\sin \theta)/\lambda > 0.29 \text{ \AA}^{-1}$ were used to refine the structure since these reflections were most sensitive to atomic coordinates and to thermal motion and relatively insensitive to the outer electron distributions. Initial refinement was by the method of least squares with subsequent refinement by difference syntheses. Corrections for anisotropic thermal motion of the atoms were made, and the intensity data were placed on an absolute scale. The reflections for which $(\sin \theta)/\lambda < 0.29 \text{ \AA}^{-1}$ were then utilized in $(F_o - F_c)$ -syntheses to obtain a measure of the delocalization of the valence electrons of the isolated atoms to the bonding configuration in the solid. The calculated structure factors, F_c , were based upon the scattering factor tables of Viervoll & Øgrim (1949) for aluminum and of Qurashi (1954) for vanadium. The calculated structure factors thus presuppose a spherical distribution of the valence electrons about the atoms while the observed structure factors, F_o , are a measure of the actual distribution. Hence, positive regions in the difference sections should represent regions where the valence electron density in the compound is greater than the valence electron density in the isolated atoms, and the negative regions represent the inverse.

Experimental details and results

The compound V_4Al_{23} crystallizes with hexagonal symmetry in the space group $D_{6h}^4 - P6_3/mmc$ with lattice parameters, $a = 7.692_8$ and $c = 17.04_0 \text{ \AA}$ and with two formula weights/unit cell. The crystal used in this investigation was originally in the form of a long hexagonal prism. This crystal was cleaved normal to

the hexagonal axis so that the length and breadth were both approximately equal to 1 mm. The crystal was then ground into spherical shape in a sphere grinder of the type described by Whitmore (1954). A minor, but important, modification was made in the design of the sphere grinder in that the entry of the air jet was placed about 0.010 inches above the grinding surface rather than tangent thereto. This placement of the air jet increased the tumbling action and eliminated the formation of elliptically shaped crystals. The worked surface of the spherical crystal was removed by etching with a mixture of mineral acids. The crystal radius was determined with the aid of a microscope equipped with a Filar eyepiece. The average radius determined from several random orientations of the crystal was found to be 0.125 ± 0.002 mm.

In general, the procedures outlined by Furnas (1957) for the moving crystal-stationary counter technique were employed for the collection of intensity data. The intensity data were taken with a proportional counter which replaced the film holder on a Weissenberg camera. Copper $K\alpha$ radiation was employed. The intensity of each reflection was accumulated on a decimal scaler while the peak shape was simultaneously plotted on a strip chart recorder. The strip chart recorder was used primarily as a monitoring device to detect extraneous pulses from the X-ray source and to make sure that the counter was properly positioned to receive the entire diffraction peak. A set of circular apertures, ranging in diameter from 0.50 to 1.50 degrees 2θ in intervals of 0.05 degrees, was used to ensure maximum peak to background ratios. Furnas' equation was used to determine the proper aperture diameter, T , for a given reflection,

$$T = 1.1(2\Delta\theta + S + 2C \cos \theta), \quad (1)$$

where C is the diameter of the crystal, θ is the Bragg angle, S is the diameter of the source, and $2\Delta\theta$ is the sum of the full breadths of the $K\alpha_1$ and $K\alpha_2$ peaks plus their separation. The factor 1.1 was inserted to allow for small orientation errors.

Since balanced filters were not available, correction for the contributions of the spectral streaks to the diffraction peaks were made in the following way. It was observed that within experimental precision the spectral streaks from the V_4Al_{23} crystal were linear functions of 2θ for a distance extending approximately four degrees 2θ on either side of the diffraction peaks. By measuring the intensity of the spectral streak above and below a diffraction peak and by correcting for the background obtained from either side of the streak, a correction for the streak contribution to the integrated intensity could be obtained. Thus a total of eight measurements were taken to determine the integrated intensity of a given diffraction peak. Fig. 1 shows the various counter positions for the measurements, and the integrated intensity of the peak, I , is given by

$$I = \frac{1}{2}[2A - (B+C) - (D-E) - (F-G)], \quad (2)$$

where $A, B, C, D, E, F,$ and $G,$ are the measured intensities at the positions illustrated in Fig. 1.

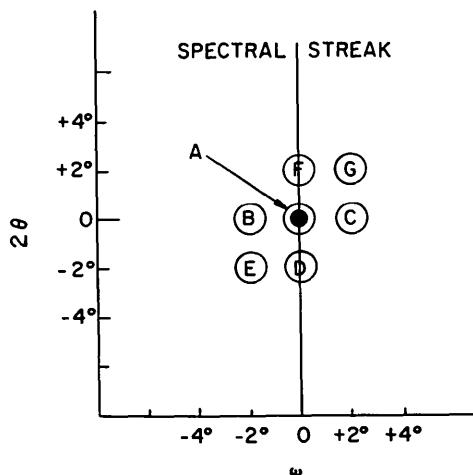


Fig. 1. Relative 2θ and ω positions of the proportional counter aperture for measuring the integrated intensity, I , of a zero level diffraction peak. The intensity of the diffraction peak, A , was measured as the crystal was rotated, ω , in both the forward and reverse directions. Background measurements were taken at B and C . A correction was made for the contribution of the spectral streak to I by measuring the spectral streak at D and F and the background at E and G .

All reflections within the range, $8 < 2\theta < 147$ degrees, were measured with this procedure. With a very few exceptions, equivalent reflections were found to agree within the limits of the statistical counting errors. On a relative scale the range of measured intensities was from 1 to 20,000. In order to detect drifts in the intensity of the X-ray source, a standard peak, (017), was chosen and monitored every four hours. The measured intensity of this peak did not fluctuate more than 1.5% during the period when the intensity data were being collected. The intensity data were corrected for absorption by use of the tables of Evans & Ekstein (1952). The value of the absorption coefficient, μR , for the spherical V_4Al_{23} crystal was 3.62 ± 0.07 . Standard corrections for the Lorentz-polarization and velocity factors were made. The tables of Dauben & Templeton (1955) were employed

to obtain dispersion corrections which were applied in the manner outlined by Templeton (1955).

Initial refinement of the original structural parameters of V_4Al_{23} was done by the method of least squares. After four cycles no further significant shifts in atomic coordinates or individual isotropic temperature factors were indicated. The value of the reliability index,

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad (3)$$

at this point was 0.093. Inspection of the structure factors for the eight most intense reflections revealed that, without exception, the observed structure factors were smaller in absolute magnitude than the corresponding calculated values. This systematic discrepancy was attributed to extinction effects. Since no adequate technique exists for the simultaneous correction of both primary and secondary extinction, the method suggested by James (1954) was used to correct for secondary extinction. In this method, secondary extinction coefficients, g , were computed for each of the eight intense reflections from

$$g = (I_c - I_o) / 2I_c I_o, \quad (4)$$

where I_c is the calculated and I_o is the observed integrated intensity, and an average value of $g = (1.1 \pm 0.3) \times 10^{-6}$ was obtained. Application of this extinction factor to all of the intensity data resulted in a reduction of the reliability index to a value of 0.077. Since the application of the secondary extinction correction effectively removed the forementioned systematic discrepancy between calculated and observed intensities, the effects of primary extinction were assumed to be negligible. It should be noted that the extinction correction is small, and any residual errors due to extinction should not significantly affect the front reflection peaks.

Subsequent refinement of the structure was done by $(F_o - F_c)$ -synthesis,

$$D = \frac{1}{V} \sum_h \sum_k \sum_l (F_o - F_c) \cos 2\pi(hx + ky + lz), \quad (5)$$

the use of which has been described by Cochran (1951). The correct choice of scale factor, atomic coordinates, and temperature factors are those which result in $D=0$, $\partial D/\partial x_i=0$, and $\partial^2 D/\partial x_i \partial x_j=0$, respec.

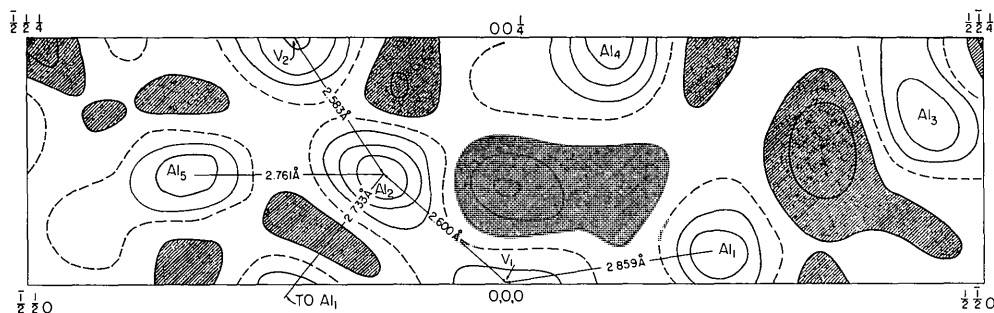


Fig. 2. $(F_o - F_c)$ -synthesis of the asymmetric unit of the plane (x, \bar{x}, z) computed with reflections for which $(\sin \theta)/\lambda < 0.29 \text{ \AA}^{-1}$.

Table 1. Comparison of atomic coordinates at various stages of the structure refinement

Atom type	Wyckoff notation	Position in $P6_3/mmc$	x/a^*				z/c^*			
			(1)	(2)	(3)	(4)	(1)	(2)	(3)	(4)
V_1	2(a)	0, 0, 0	0	0	0	—	0	0	0	—
V_2	6(h)	$x, 2x, \frac{1}{2}$	0.781	0.7818	0.7823	0.0001	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	—
Al_1	12(k)	$x, 2x, z$	0.213	0.2116	0.2112	0.0002	0.029	0.0295	0.0295	0.0004
Al_2	12(k)	$x, 2x, z$	0.124	0.1255	0.1261	0.0002	0.618	0.6167	0.6164	0.0004
Al_3	12(k)	$x, 2x, z$	0.455	0.4583	0.4583	0.0003	0.166	0.1666	0.1663	0.0003
Al_4	6(h)	$x, 2x, \frac{1}{2}$	0.126	0.1253	0.1252	0.0002	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	—
Al_5	4(f)	$\frac{1}{3}, \frac{2}{3}, z$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	—	0.617	0.6167	0.6162	0.0003

* (1) Previous results of Smith & Ray (1957).

(2) These data—least-squares refinement.

(3) These data—refinement by difference synthesis.

(4) Standard deviations in atomic coordinates given by the difference synthesis refinement.

Table 2. Anisotropic temperature factors in \AA^2 and their standard deviations for one specified atom of each independent symmetry type in V_4Al_{23} ; B_{11} , B_{22} , and B_{33} are associated with the hexagonal directions, [110], $[1\bar{1}0]$, and [001], respectively

Atom type	Wyckoff notation	Position in $P6_3/mmc$	B_{11}	$\sigma(B_{11})$	B_{22}	$\sigma(B_{22})$	B_{33}	$\sigma(B_{33})$
V_1	2(a)	0, 0, 0	0.61	0.04	0.53	0.04	0.36	0.03
V_2	6(h)	$x, 2x, \frac{1}{2}$	0.49	0.04	0.56	0.04	0.67	0.03
Al_1	12(k)	$x, 2x, z$	1.41	0.08	0.92	0.07	1.13	0.06
Al_2	12(k)	$x, 2x, z$	0.71	0.07	0.84	0.07	0.94	0.05
Al_3	12(k)	$x, 2x, z$	0.82	0.07	0.79	0.07	1.03	0.05
Al_4	6(h)	$x, 2x, \frac{1}{2}$	0.68	0.07	0.74	0.07	0.82	0.05
Al_5	4(f)	$\frac{1}{3}, \frac{2}{3}, z$	0.55	0.07	0.75	0.08	1.30	0.05

tively, at each atomic site. Initial refinement by difference synthesis was done with the approximation of isotropic temperature factors. The initial refinement led to a minimization of the slopes of D and of the curvature of D in the z direction and resulted in a value of $R=0.063$. After isotropic refinement, the curvatures of D in the x and y directions were still appreciable and indicated the necessity of incorporating anisotropic temperature factors. These anisotropic temperature factors were computed with the aid of the IBM-650 programs written by Shiono (1959), and because of the nature of the programs the refinement was most easily done in an orthorhombic representation of the hexagonal structure (*International Tables* O_2 representation). Only the diagonal elements of the anisotropic temperature factors, B_{11} , B_{22} , and B_{33} were found to be significant since the non-diagonal elements, B_{12} , B_{13} , and B_{23} were of the same order of magnitude as their standard deviations.

It should be emphasized that throughout the structure refinement the adjustable parameters were derived from reflections in the range, $(\sin \theta)/\lambda > 0.29 \text{ \AA}^{-1}$, since the refinement programs were modified to substitute F_c for F_o in the case of reflections with $(\sin \theta)/\lambda < 0.29 \text{ \AA}^{-1}$. However, the reliability indices were computed with all reflections. The final reliability index after structure refinement with anisotropic temperature factors was 0.057. In Table 1 is shown a comparison of the final values for the atomic coordinates with those obtained from the least-squares refinement and those obtained in the original structure

determination. In Table 2 are shown the values obtained for the anisotropic temperature factors; B_{11} , B_{22} , and B_{33} are associated with the hexagonal directions, [100], $[1\bar{1}0]$, and [001], respectively. The transformations necessary for evaluating temperature factors of structurally related atoms are given by Trueblood (1956). A comparison of the final calculated structure factors and the observed structure factors for the 376 independent reflections in the accessible sphere of reflection is shown in Table 3. Atomic coordination and bond distances are shown in Table 4. It is of interest to note that the average bond distances computed from the method and tabulation of Pauling (1956) generally agree within 0.03 \AA with the average observed distances; however, the variation in the individual bond distances about a given atom is considerably greater than this amount.

The fifty independent reflections for which $(\sin \theta)/\lambda < 0.29 \text{ \AA}^{-1}$ were used to compute $(F_o - F_c)$ -syntheses for the planes (x, \bar{x}, z) , $(x, y, 0)$, $(x, y, 9/80)$, and $(x, y, 1/4)$. These sections are shown in Figs. 2, 3, 4, and 5, respectively. The estimated standard deviation in the $(F_o - F_c)$ -syntheses, $\sigma(D)$, is 0.13 e.\AA^{-3} , and the contours are drawn at intervals of $\sigma(D)$. Positive regions greater than $\sigma(D)$ are shaded and zero contours are broken. These four sections were chosen because they illustrate most clearly the regions about the atoms involved in the abnormally short contacts, and the (x, \bar{x}, z) -plane shown in Fig. 2 passes through the atomic center of each type of independent atom in the structure.

Discussion

This investigation was an attempt to push the method of approach to the limits of resolution. The precision of the difference densities has been stated, but because of the complexity of the problem an assessment of the true accuracy is virtually impossible. In particular, quantitative assessment of the degree of validity of the scaling procedure, the intensity corrections, and the reliability of the theoretical scattering factors for the free atoms is not tractable on an item by item basis. However, a significant test which may be applied to the composite data is the summation of the

difference densities over the entire unit cell. In principle, such a summation should be identically zero since there should be identical totals of electrons in the calculated and in the observed electron distributions. The numerical result of a summation of the difference densities for the fifty reflections with $\sin \theta/\lambda < 0.29 \text{ \AA}^{-1}$ was -4.7 electrons per orthorhombic cell. This small residue is equivalent to 0.3% of the total number of electrons and amounts to an average of only 0.04 electron per atom. On the basis of the close proximity of the summation to zero, it is believed that the scaling and extinction corrections have a high probability of being reliable. If this is

Table 3. Comparison of the observed structure factors, F_o , with the final calculated structure factors, F_c

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
000		782.0	052	63.1	62.4	13,14	46.9	46.8	246	<1.7	1.1
002	66.1	-71.8	053	96.7	99.2	13,15	17.6	14.7	247	78.2	-80.8
004	76.4	78.5	054	149.9	153.4	13,16	<1.3	.8	248	31.3	29.8
006	9.7	-12.9	055	116.6	-119.0	13,17	<1.3	-1.1	249	12.2	11.9
008	235.1	245.5	056	5.2	4.9	13,18	46.7	47.7	24,10	27.3	28.4
00,10	101.7	-102.8	057	10.6	8.5	140	52.0	52.4	24,11	15.8	-13.3
00,12	79.2	78.4	058	25.3	26.8	141	23.6	-21.6	24,12	6.7	7.3
00,14	219.8	-219.7	059	7.3	-7.4	142	24.6	26.6	24,13	4.4	-5.8
00,16	65.8	65.5	05,10	23.9	-23.5	143	55.3	55.2	24,14	18.8	19.3
00,18	6.0	7.7	05,11	45.7	46.2	144	2.9	-4.5	24,15	40.4	-37.6
00,20	13.0	15.0	05,12	14.9	20.4	145	4.3	3.9	24,16	27.2	24.3
010	24.9	25.3	05,13	6.6	6.0	146	14.0	13.7	250	35.4	-34.8
011	40.0	-40.2	05,14	8.0	-7.4	147	4.9	-6.1	251	24.4	24.0
012	41.1	39.1	05,15	28.0	-25.5	148	43.0	40.9	252	30.3	28.9
013	39.6	38.7	05,16	12.7	-13.5	149	5.7	5.7	253	53.4	-53.6
014	19.5	20.6	060	62.3	-60.0	14,10	29.0	28.2	254	<1.7	1.2
015	13.4	-12.6	061	67.4	-68.9	14,11	69.3	67.5	255	8.9	-3.6
016	29.1	-31.5	062	42.1	44.2	14,12	4.0	4.9	256	9.0	8.7
017	147.5	156.3	063	117.5	119.0	14,13	21.6	-21.7	257	9.5	8.1
018	76.3	78.3	064	24.3	-27.3	14,14	4.6	4.8	258	8.5	8.9
019	6.8	-7.0	065	20.5	-20.7	14,15	<1.4	.9	259	3.1	-3.5
01,10	51.1	49.1	066	25.0	23.6	14,16	24.6	23.5	25,10	40.2	40.5
01,11	8.8	10.2	067	33.0	32.4	150	30.2	-27.4	25,11	73.6	-68.7
01,12	12.2	-10.0	068	10.9	-7.0	151	14.1	13.6	25,12	6.4	-5.6
01,13	18.7	19.2	069	15.0	-18.0	152	13.8	14.1	25,13	25.3	24.8
01,14	19.8	20.6	06,10	59.3	61.4	153	19.1	-21.0	260	29.7	29.3
01,15	64.2	59.8	06,11	150.2	136.6	154	13.3	-12.2	261	38.8	-37.5
01,16	54.0	52.6	06,12	17.0	-19.6	155	13.2	-17.0	262	29.7	29.1
01,17	34.1	-33.8	06,13	58.5	-57.5	156	85.2	87.2	263	54.7	-53.3
01,18	7.1	13.8	06,14	60.2	57.4	157	54.8	-53.7	264	103.9	95.3
01,19	6.7	8.7	070	8.4	11.6	158	56.8	-54.5	265	65.5	64.6
01,20	21.1	21.5	071	25.6	22.6	159	13.5	-13.8	266	5.2	-6.1
01,21	36.4	-33.5	072	11.5	14.2	15,10	20.9	18.1	267	4.0	-1.5
020	40.6	-43.6	073	9.1	-8.0	15,11	23.2	-21.5	268	29.6	29.8
021	34.1	-36.2	074	8.4	-12.0	15,12	45.7	44.3	269	5.9	5.6
022	<1.8	0.3	075	5.2	-4.9	15,13	2.4	-2.1	26,10	18.5	-18.1
023	14.4	13.8	076	5.9	8.9	15,14	53.1	51.3	270	18.6	-17.2
024	41.5	-40.9	077	32.2	26.9	15,15	27.4	-25.7	271	4.3	-4.0
025	57.3	60.9	078	26.3	26.9	160	32.1	32.5	272	26.3	24.3
026	144.1	151.9	079	13.7	10.8	161	10.6	12.0	330	313.7	308.4
027	88.5	93.3	07,10	31.5	30.6	162	4.0	4.3	332	33.1	-34.6
028	91.6	-96.0	07,11	24.9	-21.3	163	24.1	24.0	334	45.4	46.7
029	29.7	31.2	080	15.8	16.1	164	54.6	53.3	336	12.3	-13.3
02,10	21.5	23.1	081	6.9	8.2	165	11.7	-12.9	338	131.9	139.2
02,11	22.6	20.2	082	6.5	9.7	166	12.4	10.1	33,10	55.7	-58.3
02,12	84.7	84.7	083	36.5	-35.7	167	3.1	5.4	33,12	49.7	54.4
02,13	20.1	20.2	084	17.2	-15.2	168	18.0	19.7	33,14	136.5	-127.1
02,14	74.3	71.5	085	29.0	30.8	169	<1.4	1.5	33,16	53.5	52.5
02,15	43.2	41.6	110	21.0	15.3	16,10	12.5	-9.8	340	3.8	-6.8
02,16	31.8	-30.2	112	47.1	47.1	16,11	20.8	18.5	341	45.4	-46.9
02,17	5.0	-6.1	114	10.3	-4.0	16,12	41.0	38.1	342	38.9	36.0
02,18	75.2	72.2	116	16.6	17.2	170	115.4	110.1	343	13.9	-16.0
02,19	24.2	-22.2	118	37.6	37.7	171	6.1	8.1	344	40.8	42.5
02,20	3.8	2.5	11,10	51.9	50.3	172	5.6	4.6	345	25.2	25.5

Table 3 (cont.)

hkl	F _O	F _C	hkl	F _O	F _C	hkl	F _O	F _C	hkl	F _O	F _C
030	139.7	-146.2	11, 12	<1.6	1.1	173	17.2	-15.2	346	12.3	12.7
031	111.8	118.7	11, 14	27.8	28.6	174	5.4	-6.8	347	43.0	48.2
032	75.0	75.6	11, 16	27.9	27.5	175	<1.3	0.3	348	11.3	12.4
033	199.5	-217.3	11, 18	23.2	27.8	176	12.8	11.0	349	9.0	-12.2
034	32.5	-33.8	11, 20	10.8	12.9	177	4.8	-4.3	34, 10	16.1	16.9
035	23.8	21.6	120	51.9	52.5	178	54.8	53.7	34, 11	5.0	-7.3
036	31.8	30.8	121	65.1	-71.2	220	178.8	173.2	34, 12	2.3	4.4
037	44.7	-44.4	122	55.0	56.9	222	16.9	16.7	34, 13	9.3	-9.6
038	26.6	-25.5	123	94.4	-101.7	224	8.9	-12.1	34, 14	21.2	22.9
039	14.2	14.9	124	160.0	166.0	226	23.4	20.9	350	19.9	-22.0
03, 10	89.7	94.6	125	100.8	106.4	228	81.4	81.8	351	18.2	-21.5
03, 11	226.3	-234.9	126	9.6	12.5	22, 10	9.3	11.5	352	6.2	9.2
03, 12	29.0	-29.8	127	11.2	-9.8	22, 12	14.7	13.0	353	8.1	8.8
03, 13	85.1	86.0	128	31.6	31.5	22, 14	49.1	-44.6	354	19.8	-21.3
03, 14	99.1	98.0	129	3.7	1.6	22, 16	29.6	31.2	355	34.6	32.5
03, 15	34.0	-35.8	12, 10	24.4	-25.8	22, 18	32.1	31.1	356	91.6	89.5
03, 16	11.0	11.4	12, 11	48.4	-49.7	230	28.0	27.9	357	63.5	63.2
03, 17	30.4	31.2	12, 12	33.7	31.8	231	5.6	8.0	358	61.1	-61.8
03, 18	41.6	41.7	12, 13	7.0	-6.8	232	8.4	8.9	359	17.7	15.6
03, 19	48.3	-44.6	12, 14	5.5	-3.5	233	50.7	52.0	35, 10	12.1	15.1
040	39.0	35.1	12, 15	24.5	22.5	234	19.3	-18.7	35, 11	14.7	13.1
041	30.5	-28.7	12, 16	10.0	-11.1	235	39.0	-37.1	360	41.0	-38.2
042	12.5	12.9	12, 17	44.4	42.5	236	45.6	-48.0	361	43.0	46.0
043	39.7	-38.2	12, 18	61.6	-54.4	237	147.0	144.2	362	35.5	37.5
044	87.2	90.5	12, 19	66.2	-59.7	238	81.0	84.2	363	69.8	-69.8
045	25.1	26.7	12, 20	25.5	26.1	239	6.4	8.2	364	17.3	-16.5
046	40.3	40.6	130	18.8	-17.8	23, 10	49.0	48.2	365	20.8	20.0
047	24.1	-26.7	131	27.9	-25.5	23, 11	14.6	15.6	440	31.9	-32.5
048	8.1	-10.0	132	19.3	16.4	23, 12	14.7	-13.7	442	23.7	27.5
049	13.7	-11.2	133	22.0	21.1	23, 13	23.6	26.4	444	5.2	-5.4
04, 10	23.5	-22.6	134	18.6	-20.6	23, 14	12.2	13.3	446	7.5	10.1
04, 11	21.7	-19.4	135	13.8	17.3	23, 15	52.9	51.0	448	4.7	6.9
04, 12	58.2	56.6	136	63.4	65.8	23, 16	67.8	64.4	44, 10	33.6	39.7
04, 13	14.4	-13.2	137	19.1	19.4	23, 17	52.6	-47.8	450	33.5	36.0
04, 14	9.0	10.0	138	24.8	-24.7	240	14.3	9.5	451	13.0	-15.6
04, 15	4.1	1.9	139	3.4	6.0	241	24.0	23.4	452	9.4	9.9
04, 16	8.4	-9.2	13, 10	33.1	33.2	242	18.3	18.9	453	30.8	-31.8
04, 17	18.0	18.3	13, 11	31.5	28.8	243	29.2	-26.8	454	62.8	59.4
04, 18	16.5	-15.7	13, 12	35.8	37.2	244	15.0	10.8	455	26.9	31.6
050	32.0	30.4	13, 13	7.8	-9.2	245	19.3	18.5	456	12.8	-11.5
051	71.9	73.1									

Table 4. Atomic coordination and bond distances in V₄Al₂₃

Atom	Neighbor	No. of neighbors	Distance	Standard deviation	Atom	Neighbor	No. of neighbors	Distance	Standard deviation
V ₁	Al ₁	6	2.859 Å	0.007 Å	Al ₃	Al ₃	2	2.896 Å	0.010 Å
	Al ₂	6	2.600	0.007		Al ₄	2	2.826	0.007
V ₂	V ₂	2	2.669	0.003		Al ₅	1	2.761	0.008
	Al ₂	2	2.583	0.007	Al ₄	V ₂	2	2.800	0.007
	Al ₃	4	2.800	0.007		Al ₁	2	2.854	0.010
	Al ₄	2	2.521	0.003		Al ₂	2	2.896	0.010
	Al ₅	2	2.752	0.005		Al ₃	2	2.884	0.007
Al ₁	V ₁	1	2.859	0.007		Al ₃	1	2.853	0.011
	Al ₁	2	2.819	0.006	Al ₄	2	2.807	0.007	
	Al ₁	2	2.988	0.006	Al ₅	1	2.905	0.008	
	Al ₂	2	2.733	0.010	Al ₅	V ₂	2	2.521	0.003
	Al ₂	2	2.865	0.010		Al ₂	4	2.826	0.007
	Al ₃	2	2.854	0.010		Al ₃	4	2.807	0.007
	Al ₅	1	2.969	0.009		Al ₄	2	2.889	0.006
	Al ₂	V ₁	1	2.600	0.007	Al ₅	V ₂	3	2.752
V ₂		1	2.583	0.007	Al ₁		3	2.969	0.009
Al ₁		1	2.733	0.010	Al ₂		3	2.761	0.008
Al ₁		2	2.865	0.010	Al ₃		3	2.905	0.008
Al ₂		2	2.910	0.005					

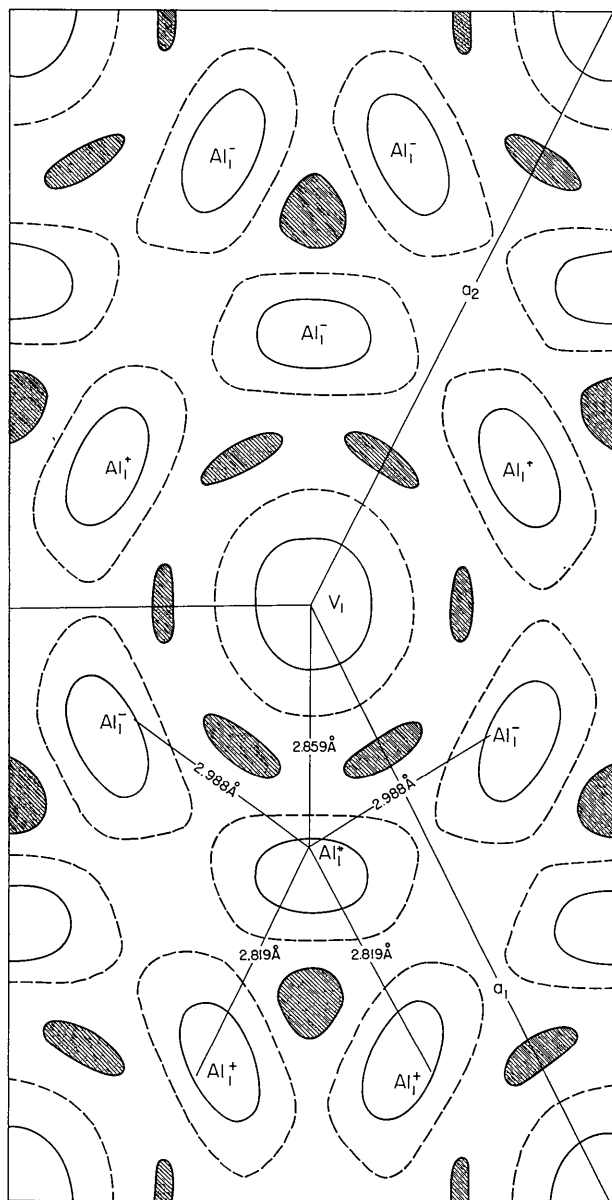


Fig. 3. $(F_o - F_c)$ -synthesis of the plane $(x, y, 0)$ computed with reflections for which $(\sin \theta)/\lambda < 0.29 \text{ \AA}^{-1}$. Plus and minus signs designate Al_1 atoms above and below the $(x, y, 0)$ plane.

true, the two remaining factors which are most likely to introduce erroneous detail in the difference sections are possible inaccuracies in the theoretical scattering factors and in the corrections for thermal motion. Since the spherical symmetry of the theoretical scattering factors is valid and since the vibrational amplitudes are centered at the atomic coordinates, it seems unlikely that inaccuracies in either of these two factors would alter the basic symmetry of the difference sections but rather would alter the contour details. Hence, interpretations based on the symmetry of

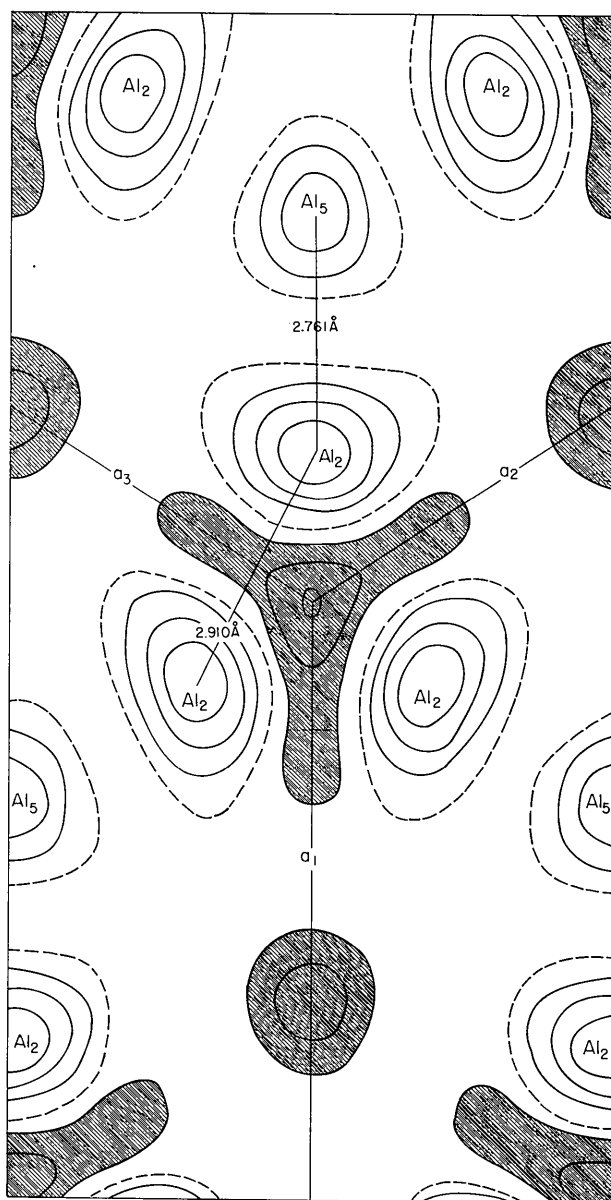


Fig. 4. $(F_o - F_c)$ -synthesis of the plane $(x, y, 9/80)$ computed with reflections for which $(\sin \theta)/\lambda < 0.29 \text{ \AA}^{-1}$.

the difference sections seem warranted but interpretations based upon the finer details of the difference contours should be made skeptically and should be critically evaluated.

The difference sections show that, without exception, the atomic centers are located at minima. On the basis of the arguments advanced in the preceding paragraph, the depths of these minima may not be highly significant but the occurrence of the minima is not likely to be spurious. Indeed a consideration of the difference in state represented by the observed scattering factors as contrasted with the calculated scattering factors makes the occurrence of minima seem

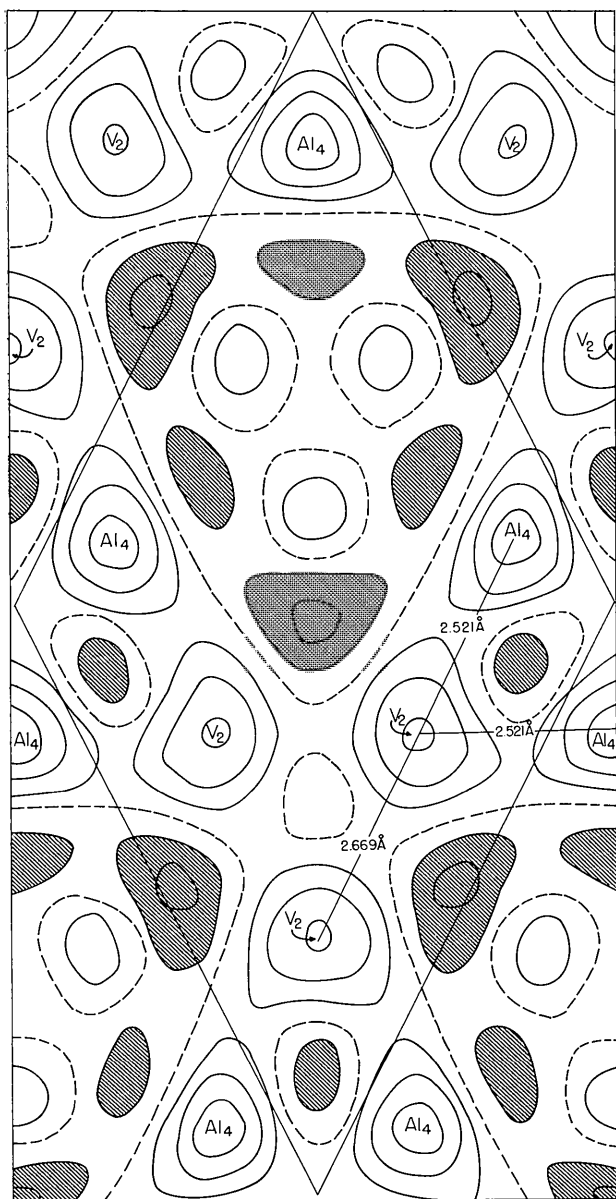


Fig. 5. $(F_o - F_c)$ -synthesis of the plane $(x, x, \frac{1}{2})$ computed with reflections for which $(\sin \theta)/\lambda < 0.29 \text{ \AA}^{-1}$.

quite reasonable. Brooks (1956) has surveyed the problem of bonding in metals and has pointed out that the binding energy results from an alteration of the valence electron wave functions in the solid as compared with the isolated atoms. This alteration in wave function represents a delocalization of the valence electrons from the immediate vicinity of the atoms to the crystal orbitals. In accord with the uncertainty principle, the spatial delocalization allows a reduction in electronic momentum with an attendant reduction in kinetic energy. This decrease in kinetic energy represents an appreciable fraction of the cohesive energy of the solid. Normalization of the crystalline

wave functions might reasonably be expected to lead to a lower probability density about the core in the crystal than about the free atom core since the valence electrons in the crystal have a higher probability of being in the interatomic regions. That this result of normalization may be expected can easily be shown by constructing the normalized bonding orbital for the hydrogen molecule as a linear combination of atomic orbitals. Hence, it seems that the nature of the bonding should give rise to some depletion of the difference densities at the atomic sites.

Brown (1959) has recently completed a determination of the structure of V_7Al_{45} and on the basis of bond angles and distances in the three aluminum-rich vanadium compounds has postulated that the nearly linear V-Al-V configuration has more directional character than the normal metallic bond. Hybridization of d states to form directional bonds has also been suggested by Robins (1958) in connection with the bonding of transition metals in carbides, borides, and silicides. In the case of V_4Al_{23} , the recent measurements of magnetic susceptibility and electrical resistivity, made in conjunction with the present investigation by Greiner (1959), are consistent with the view that the atomic d states are significantly modified in the crystal and have probably become hybridized to form a part of the valence band. The magnetic susceptibility values obtained by Greiner at 298 °K. were in units of 10^{-6} e.m.u./g.: aluminum, $+0.642 \pm 0.007$; vanadium, $+5.85 \pm 0.02$; and V_4Al_{23} , $+0.63 \pm 0.02$. These measurements were made on samples of the same aluminum and crystal bar vanadium which were used to prepare the V_4Al_{23} crystal used in the present investigation. The weak and temperature independent paramagnetism of V_4Al_{23} implies that any non-bonding electrons must be paired and indicates a low density of states at the top of the filled portion of the valence band. Greiner has also measured the resistivity of V_4Al_{23} parallel to the c -axis and obtained a room-temperature value of $45 \mu\Omega$ cm. with a positive temperature coefficient of $3.01 \times 10^{-3} \text{ }^\circ\text{C}^{-1}$. This is about double the resistivity of vanadium and more than fifteen times the resistivity of aluminum. Such a high resistivity indicates a reduction in the number and/or mobility of the charge carriers in the compound as compared to the elements. Since the mobility of the charge carriers is related inversely to the density of states through the scattering probability and since the magnetic susceptibility indicates a low density of states, it seems most likely that the high resistivity is due to a reduced number of charge carriers. Such a reduction could occur if the d orbitals of vanadium had become hybridized to form directed valence bonds. Some corroboration for directionality of interactions is furnished by the anisotropic temperature factors obtained from the present data. These indicate appreciably greater restrictions in vibrational amplitude along some directions than others; in particular, the V_2 atom has minimal vibrational

amplitude along the c -axis which is the resultant direction of the nearly linear V-Al-V coordinations mentioned by Brown. As a matter of interest it may also be noted that if the bonding electrons in the crystal were arranged in a non-directional and homogeneous free electron distribution, then maxima in the difference densities should occur at the interstices of the structure with an intensity directly dependent upon the size of the interstice. Examination of the difference sections shows that the largest interstice in the structure at the position $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$ has no maximum and this result is at least in qualitative accord with the existence of preferential electron distributions which must accompany directional bonding. It would have been interesting to determine whether a computation of the difference densities, with all observed reflections and based upon calculated structure factors which included only core contributions, would show any indication of concentration of electron densities along interatomic vectors. Unfortunately, a scattering factor curve for the V^{+5} ion was not available.

Since the purpose of the investigation was to test for electron transfer, it may be noted that the transfer of two or more electrons to vanadium atoms as required by Raynor's theory would increase the scattering power of the vanadium atoms by the order of 9% or more in the front reflection region. On this basis it would be expected that the vanadium atoms would be coincident with the positions of maxima in the difference sections. Such is not the case. Even if the summation of the difference densities is not accepted as a criterium for the validity of the scaling and the absence of vanadium maxima were rationalized as scaling error, the existence of scaling error should affect the entire distribution and the vanadium positions should still show as appreciably more positive than the aluminum positions. The difference sections show the aluminum and vanadium difference densities to be approximately equal; this observation indicates that extensive electron transfer to vanadium atoms is highly improbable.

The authors wish to express their appreciation to Dr D. R. Fitzwater and Mr D. E. Williams for discussions and assistance with regard to the computational procedure, to Mr R. Shiono for the generous loan of his programs for the IBM-650 computer, and

to Miss M. Moeller for her assistance in the accumulation of the intensity data. The authors are also indebted to Dr R. E. Rundle for pertinent discussions.

References

- ATOJI, M. (1957). U.S. Atomic Energy Commission Report No. ISC-263.
- BLACK, P. J. (1955). *Phil. Mag.* **46**, 155.
- BROOKS, H. (1956). *Theory of Alloy Phases*, p. 199. Cleveland: Amer. Soc. Metals.
- BROWN, P. J. (1957). Dissertation for Ph.D. degree, University of Cambridge, England.
- BROWN, P. J. (1959). *Acta Cryst.* **12**, 995.
- COCHRAN, W. (1951). *Acta Cryst.* **4**, 408.
- DAUBEN, C. H. & TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 841.
- DOUGLAS, A. M. B. (1950). *Acta Cryst.* **3**, 19.
- EVANS, H. R. & EKSTEIN, M. J. (1952). *Acta Cryst.* **5**, 540.
- FÖEX, G. & WUCHER, J. (1954). *C. R. Acad. Sci., Paris*, **238**, 1281.
- FURNAS, T. C. (1957). *Single Crystal Orienter Instruction Manual*. Milwaukee, Wisconsin: General Electric Company, X-ray Department.
- GREINER, J. D. (1959). Iowa State University, unpublished research.
- JAMES, R. W. (1954). *The Crystalline State*, Vol. 2, 2nd ed. London: Bell.
- NICOL, A. D. I. (1953). *Acta Cryst.* **6**, 285.
- PAULING, L. (1951). *Acta Cryst.* **4**, 138.
- PAULING, L. (1956). *Theory of Alloy Phases*, p. 220. Cleveland: Amer. Soc. Metals.
- QURASHI, M. M. (1954). *Acta Cryst.* **7**, 310.
- RAYNOR, G. V. (1949). *Progress in Metal Physics* **1**, 1.
- ROBINS, D. A. (1958). *Powder Metallurgy* No. 1/2, 172.
- ROBINSON, K. (1952). *Acta Cryst.* **5**, 397.
- ROBINSON, K. (1953). *Acta Cryst.* **6**, 854.
- SHIONO, R. (1959). IBM-650 Programs for Crystallographic Computing, University of Pittsburgh, Computation and Data Processing Center, Technical Report No. 9.
- SMITH, J. F. & RAY, A. E. (1957). *Acta Cryst.* **10**, 169.
- TAYLOR, W. H. (1954). *Acta Metallurg.* **2**, 684.
- TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 842.
- TRUEBLOOD, K. N. (1956). *Acta Cryst.* **9**, 359.
- VEENENDAAL, A. L., MACGILLAVRY, C. H., STAM, B., POTTERS, M. L. & ROMGENS, M. J. H. (1959). *Acta Cryst.* **12**, 242.
- VIERVOLL, H. & ØGRIM, O. (1949). *Acta Cryst.* **2**, 277.
- WHITMORE, R. L. (1954). *J. Sci. Instrum.* **31**, 223.