A test for electron transfer in the intermetallic compound, V4Al23

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A TEST FOR ELECTRON TRANSFER
IN THE INTERMETALLIC COMPOUND, V₄Al₂₃

by

Alden Earl Ray

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
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Major Subject: Metallurgy

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1959
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INTRODUCTION

This investigation was undertaken in order to test theories which have been proposed concerning electron transfer in some aluminum-rich intermetallic compounds of the transition elements. Many features of the structures of these compounds indicate that they may be of considerable importance in determining some of the factors which influence the formation of intermetallic compounds. Characteristic of all these structures are the abnormally short interatomic distances which occur between the transition metal atoms and some of the aluminum atoms. Raynor (1949) and Pauling (1951) have proposed apparently contradictory theories which suggest that these short contacts are due to rearrangement of electronic configurations in the compounds.

Raynor has proposed that the transition metal atoms absorb some of the outer electrons of neighboring aluminum atoms into their unfilled 3d orbitals. Pauling, on the other hand, has argued that for the compound Co$_2$Al$_9$ a transfer of electrons to the aluminum atoms would be expected, which is in the opposite direction to that suggested by Raynor's theory. By assuming the removal of one electron from each of the cobalt atoms in this structure, Pauling has been able to compute interatomic distances which are in essential agreement with the observed distances. It has been inferred that the basic arguments Pauling has used for predicting
interatomic distances in Co$_2$Al$_9$ are applicable to other aluminum-rich transition element compounds.

It is doubtful that electron transfer such as that proposed by Pauling could be detected in x-ray diffraction data. Pauling has suggested that a study of the magnetic properties would give additional experimental evidence concerning the electronic structures of these compounds. However, if electron transfer takes place to the extent proposed by Raynor, the transfer should be detectable by x-ray diffraction methods, especially so if three or more electrons are involved.

There have been several attempts by previous investigators (Douglas (1950); Robinson (1952), (1953); Nicol (1953)) to detect the electron transfer proposed by Raynor by x-ray diffraction techniques. Critical reviews of the results and of the methods employed in these investigations have been given by Taylor (1954) and by Black (1956). Although in each case the experimental evidence indicates a transfer in the direction of the transition element atoms, Taylor (1954, p. 694) concludes that in spite of the general similarity of the results obtained from quite different structures, it would certainly not be justified to assert that electron absorption (in its most naïve sense) by the transition metal atoms has been firmly established.

In his paper, Black (1956, p. 163) states, "It appears that the electron transfer effect must be smaller than the transfer required by Raynor's theory."
EXPERIMENTAL PROCEDURE

Black has suggested the essential requirements for detecting electron transfer involving two or more electrons in the aluminum-rich transition metal compounds, namely, (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 must 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 it would be reasonable to assume that the contributions of the core electrons to the intensities of the reflections were known.

There has been no attempt to obtain absolute intensity data by direct measurement in this investigation. Rather, the observed structure factors, $F_0$, were scaled to the calculated structure factors, $F_C$, in the range of $\sin \theta / \lambda$ where it was reasonable to assume that the contributions of the outer electrons of aluminum and vanadium were negligible. The single scale factor obtained in this manner was then used to place all $F_0$ values on an absolute scale. A three dimensional $(F_0 - F_C)$-synthesis with only the $F_0$ values considered sensitive to the outer electrons was then used to reveal how the actual electron distribution differed from the distribution based on the theoretical scattering factors for isolated atoms. The method of scaling used here differs from the method employed by Robinson (1952) and Nicol who scaled the $F_0$ values to the $F_C$ values.
in each of a series of ranges of \( \sin \theta/\lambda \), including the range where the \( F_0 \) values are sensitive to the outer electrons. The method of Robinson and Nicol required that the total count over the \((F_0-F_c)\)-synthesis be zero, while the method used in this investigation required that the total count be zero only in the range of \( \sin \theta/\lambda \) where the contributions of the outer electrons were negligible. The only assumptions about the theoretical atomic scattering factor curves required by the method of scaling used in this investigation were that the contributions of the core electrons to the theoretical scattering factors were correct and that the structural environment did not perturb the spherical distributions of the core electrons appreciably. In view of the inherent experimental difficulties involved in the direct measurement of integrated intensities on an absolute scale, such an arduous task did not seem justified until experimental techniques for making these measurements have been considerably improved.

The structure of the compound \( \text{V}_4\text{Al}_{23} \) has been determined by Smith and Ray (1957). This compound was chosen for the purposes of this investigation for several reasons, namely, (1) it has a large, fairly complex structure and therefore several observable reflections at relatively small diffraction angles; (2) there is little doubt as to the correctness of the structure since it has been determined independently by Brown\(^*\); (3) it is one of the few compounds of this type which appears

stoichometric, removing the need for assumptions concerning the total number of electrons in the unit cell; (4) techniques for growing relatively large crystals of the compound were known; (5) if the electron transfer actually takes place to the extent as that proposed by Raynor, it should be most easily detected in the aluminum-rich compounds of vanadium.

The effects of overlap of atomic positions in the electron density projections of the previous investigations have been serious. There are no planes in the \( V_4Al_{23} \) structure upon which the contents of the unit cell can be projected without a considerable degree of overlap of the individual electron density peaks. In order to resolve this difficulty, three dimensional intensity data were collected. In order to correct the three dimensional data for the effects of absorption without a prohibitive amount of labor, a spherical crystal of \( V_4Al_{23} \) was prepared.

Before it was possible to obtain a reliable scale factor for placing the intensity data on an absolute scale, it was first necessary to establish the range of \( \sin \theta/\lambda \) in which the outer electrons would be expected to have a significant effect on the \( F_0 \) values. The contribution of a 3s electron to the total scattering factor of an \( Al^{+2} \) ion is less than 0.5 per cent at \( \sin \theta/\lambda = 0.25 \text{ Å}^{-1} \) according to the results of Veenendaal, et al. (1959). The contributions of the outer electrons to the total scattering factor of vanadium were not available at the time of this investigation. However, Atoji (1957) has shown that for heavier atoms such as the elements in the first transition series, reflections for which \( 0 < \xi < 0.1 \text{Å}^{-1} \), where \( \xi = \sin \theta/\lambda z^{1/3} \), are sensitive to
distributions of outer electrons having a deviation from spherical symmetry, and hence the region for which $\xi > 0.1 \text{ A}^{-1}$ should be insensitive to the outer electrons. For vanadium, $\xi = 0.1 \text{ A}^{-1}$ corresponds to $\sin \theta / \lambda = 0.29 \text{ A}^{-1}$. The reflections which are most sensitive to the distribution of the outer electrons are not highly sensitive to changes in atomic coordinates and temperature factors; on the other hand, it is possible that a significant change in the distribution of the outer electrons could modify to some extent the final choice of atomic coordinates and temperature factors. Hence, only reflections for which $\sin \theta / \lambda > 0.29 \text{ A}^{-1}$ were used to obtain the final atomic coordinates, temperature factors, and scale factor. In contrast those reflections for which $\sin \theta / \lambda < 0.29 \text{ A}^{-1}$ were used in the final $(F_0 - F_C)$-synthesis to test for electron transfer.

The $F_0$ values have been corrected for the effects of absorption, secondary extinction, dispersion, and anisotropic thermal motion. No satisfactory attempts were made to account for these effects in the previous investigations. The final atomic coordinates were determined by use of $(F_0 - F_C)$-syntheses, and the anisotropic temperature factors were obtained by use of the differential synthesis. An initial refinement of the original structural parameters reported by Smith and Ray was made by the least squares method. Thus, during the structure refinement, a comparison of the atomic coordinates obtained by these three important techniques for the refinement of crystal structures was possible.

For the calculation of structure factors, the scattering factors of aluminum and vanadium were taken from the tables of Viervoll and Ögrim
(1949) and Qurashi (1954), respectively. The tables of Dauben and Templeton (1955) were employed to obtain corrections for dispersion by the K, L, and M electrons of vanadium. These dispersion corrections were applied in the manner outlined by Templeton (1955).
An arc-melted aluminum-vanadium alloy containing 6.0 weight per cent vanadium was heated to 710°C and held at temperature for six weeks in a beryllia crucible under a helium atmosphere. At the end of the heating period the sample was quenched to room temperature in an oil bath. Optical examination of the alloy revealed the presence of two phases, aluminum plus a compound. The aluminum matrix was removed electrolytically. The residue consisted of deep metallic blue crystals in the form of long hexagonal prisms. The crystals were identified as the intermetallic compound $V_4Al_{23}$ by x-ray analysis.

A crystal with a nearly regular hexagonal cross section was selected for grinding into a sphere. The length and breadth of this crystal were 2.5 and 1.0 millimeters, respectively. The crystal was cleaved normal to its hexagonal axis by imbedding it in a thin layer of clay and pressing on it sharply with a razor blade. A section approximately one millimeter in length was retained for further processing.

The instrument used for grinding this crystal into a sphere is shown in Figure 1. It is a slightly modified version of the sphere grinder described by Whitmore (1954). The original version had the air jet entering exactly tangent to the grinding surface. In the modified version, the air jet enters 0.010 inches above the grinding surface. Sphere grinders modeled after those described by Whitmore and by Bond (1951) were both found to produce elliptically shaped particles. The model shown in Figure 1 was much more successful in producing spherical...
Figure 1. Model of the sphere grinder employed for preparing a spherical crystal of $V_4Al_{23}$

(This model differs from the sphere grinder described by Whitmore (1954) in that the air jet enters 0.010 inches above rather than tangent to the grinding surface at the base of the notch).
SECTION "A-A"

8-32 MACH. SCREWS

70 WIRE SIEVE

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particles, possibly due to an additional tumbling given the particles by the nontangential air jet.

The grinding surface of the sphere grinder was coated with a thin layer of 400 grit silicon carbide suspended in a Duco-acetone solution. A thin layer of the abrasive mixture was applied with a small camel's hair brush and allowed to dry four hours before grinding was commenced. A pressure of ten pounds per square inch was maintained at the orifice entrance during the grinding period. The total grinding time was approximately two hours. However, it was necessary to reapply the abrasive coating after twenty to thirty minutes of continuous grinding. When the crystal appeared spherical to the naked eye, it was removed from the grinder and placed in a solution of 100 parts H$_2$O, 5 parts concentrated HCl, 2 parts concentrated HNO$_3$, and 1 part 40 per cent HF. This solution reacted with the surface of the crystal non-preferentially. Diffraction patterns indicated that ten minutes in the etchant satisfactorily removed the worked surface from the crystal. The crystal was rinsed first in water then in alcohol and allowed to dry in air.

The crystal was measured with the aid of a microscope equipped with a Filar eyepiece. The average radius was found to be $0.125 \pm 0.002$ millimeters for several random orientations of the particle. Individual measurements ranged from a maximum of 0.127 to a minimum of 0.123 millimeters. The reproducibility of a single measurement was about one per cent.
COLLECTION OF THE INTENSITY DATA

In general, the procedures outlined by Furnas (1957) for the moving crystal-stationary counter technique were employed for the collection of the intensity data. The intensity measurements were taken with a proportional counter positioned in the film holder track of a Weissenberg camera. The intensity of each reflection was accumulated on a decimal scaler, while the peak shape was simultaneously plotted by 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 certain that the counter was properly positioned to receive the entire diffracted beam. A set of circular apertures, ranging in diameter from 0.50 to 1.50 degrees two theta (2θ) in intervals of 0.05 degrees, were employed to ensure maximum peak to background ratios. Equation 1 was used to determine the proper aperture diameter, T, for a given reflection,

\[ T = 1.1(2C \cos \theta + S + 2\Delta \theta) \]  

where C is the diameter of the crystal, \( \theta \) 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.

Cu Kα radiation was employed since this was the shortest wavelength which brought all of the low angle reflections within range of the counting apparatus (from 8 to 147 degrees 2θ). Since balanced filters were
not available, an attempt was made to correct for the contribution of
the spectral streaks to the intensities of the diffraction peaks. An
examination of the spectral streaks from the V₄Al₂₃ crystal revealed
that, within the experimental errors of the measurements, the intensities
of the streaks were a linear function 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, an estimate of its contribution to the integrated in­
tensity could be obtained. A total of eight measurements were taken to
determine the integrated intensity of a given diffraction peak. Figure
2 shows the various counter positions for the measurements. The rela­
tive integrated intensity, I, was then given by

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

(2)

For each measurement, the crystal was rotated at a constant speed of
one degree omega (ω) per minute through an angle of two degrees extend­
ing one degree ω on either side of the midpoint between the Kα₁ and Kα₂
diffraction maxima.

All reflections within range of the counter when Cu Kα radiation
was employed were measured by the procedures outlined above. With few
exceptions, equivalent reflections were found to agree within the limits
of the statistical counting errors. In order to detect drifts in the
intensity of the x-ray source, a standard peak was chosen and monitored
every four hours. The measured intensity of this peak did not fluctuate
Figure 2. Relative $\theta$ and $\omega$ 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 about $\omega$ 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).
SPECTRAL STREAK

$\omega = 2\theta$
$1^\circ = 2\text{mm.}$
more than 1.5 per cent during the period the intensity data were being collected.

The intensity data were corrected for absorption by use of the tables of Evans and Ekstein (1952). The value of \( \mu R \) for the spherical \( \text{V}_4\text{Al}_{23} \) crystal was 3.62±0.07. Corrections for the Lorentz-polarization and velocity factors were made by employing the Incor I program for the IBM-650 computer. The Incor I program has been described elsewhere by Fitzwater (1957) and was written by A. Zalkin and R. E. Jones.
REFINEMENT OF ATOMIC COORDINATES, TEMPERATURE FACTORS, AND SCALE FACTOR

The method of least squares was used for the initial refinement of the original structural parameters of $V_4Al_{23}$ primarily because of the speed and flexibility of the LSII-M program for the IBM-650 which utilizes this technique. This program has been described by Fitzwater (1958). After four least squares refinement cycles no further significant shifts in atomic coordinates or individual isotropic temperature factors were indicated. The value of the reliability index,

$$R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|},$$

was 0.093 at this point in the structure refinement.

The value of $R$ was reduced to 0.077 after a correction was made for secondary extinction. 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. Secondary extinction coefficients, $g$, computed for each of these eight reflections from

$$g = \frac{I_c - I_o}{2I_c I_o},$$

where $I_c$ is the calculated and $I_o$ is the observed integrated intensity,
were found to have very little scatter about an average value of 
\( g = 1.1 \times 10^{-6} \). This method for computing secondary extinction coefficients 
has been suggested by James (1954). Since there is no satisfactory 
method to correct for the simultaneous occurrence of both primary and secondary extinction and since a correction for secondary extinction 
alone effectively removed the forementioned systematic discrepancy, 
primary extinction effects were assumed to be negligible. The secondary 
extinction coefficient, \( g = 1.1 \times 10^{-6} \), was applied to all the intensity 
data and resulted in a 3 per cent decrease in the scale factor.

Cochran (1951) has described the use of the \((F_0-F_C)\)-synthesis, \( D \), 
given by

\[
D = \frac{1}{V} \sum_{h} \sum_{k} \sum_{l} (F_0 - F_C) \cos 2\pi(hx+ky+lz),
\]

for the refinement of crystal structures. 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 \( \partial^2 D / \partial x_i \partial x_j = 0 \), respectively, at each atomic 
center. In the isotropic approximation, \( \partial^2 D / \partial x_i \partial x_j \) becomes \( \partial^2 D / \partial r^2 \).

In order to compute the shifts in the structural parameters which minimize 
\( D \) and its derivatives at atomic centers, it is necessary to obtain second 
and fourth derivatives of the calculated electron density, \( \rho_C \), at atomic 
centers from a corresponding \( F_C \)-synthesis. Approximations for the deriva-
tives of \( \rho_C \) have been suggested by Cruickshank (1956). In this 
investigation, an analytical expression due to Shoemaker, et al. (1950), 
for \( \rho_C \) was employed to approximate the required derivatives. Near an 
atomic center, the shape of the electron density, \( \rho \), is well represented
by
\[ \rho = \exp \left[ a_0 + a_1 x^2 + a_2 y^2 + a_3 z^2 + a_4 x + a_5 y + a_6 z + a_7 yz + a_8 xz + a_9 xy \right]. \] (6)

Seven blocks of 27 \( \rho \)-values, each containing the atomic center of an independent atom in the \( \text{V}_4\text{Al}_{23} \) structure, were obtained from an \( F_c \)-synthesis. Each block of \( \rho \)-values was fitted to Equation 6 by the method of least squares. The sets of coefficients thus obtained were then used to compute the derivatives of \( \rho_c \) directly. For the isotropic refinement of the temperature factors, \( \partial^4 \rho_c / \partial z^4 \) was substituted for \( \partial^4 \rho_c / \partial r^4 \) since it was apparent from the first \( (F_0-F_c) \)-synthesis that a correction for anisotropic thermal motion would be necessary. In the anisotropic case the element of the anisotropic temperature factor, \( B_{33} \), is related to the curvature of the electron density in the \( z \) direction and is the only anisotropic temperature factor not affected by symmetry within a set of structurally related atoms.

The amount of computation necessary for an \( (F_0-F_c) \)-synthesis refinement cycle was significantly reduced by transforming from hexagonal to orthorhombic coordinates and indices. The \((0,y,z)\)-plane in the orthorhombic unit cell selected for reference contains the atomic center of at least one atom of each crystallographically independent type in the \( \text{V}_4\text{Al}_{23} \) structure. An \( (F_0-F_c) \)-synthesis of this plane contained all the information necessary to determine the derivatives of \( D \) in directions not restricted by symmetry. Moreover, the \((0,y,z)\)-plane is a mirror plane. Therefore, to obtain the sets of \( \rho \)-values required to compute the derivatives of \( \rho_c \), it was necessary to compute an \( F_c \)-synthesis for the \((0,y,z)\)-plane and for only one plane adjacent to it. Thus only three
Fourier sections were required for a complete three dimensional isotropic refinement cycle. The TDF-2 program for the IBM-650, written by Fitzwater and Williams (1958), was employed to compute the three dimensional Fourier series. The Fourier sections were evaluated at 1/80th intervals along y and z and 1/40th intervals along x in orthorhombic coordinates. Two (F_D - F_C)-synthesis refinement cycles were required to minimize the slope of D in the y and z directions and the curvature of D in the z direction. The value of R at this point was 0.063.

After the isotropic refinement, the curvature of D was essentially zero in the z direction at the atomic centers. However, the curvatures of D in the x and y directions were still appreciable, indicating that it would be necessary to correct for the anisotropic thermal motion of the atoms. Anisotropic temperature factors were computed with the aid of IBM-650 programs written for this purpose. The theory and application of these programs have been described by Shiono (1959). Only the diagonal elements of the anisotropic temperature factors, B_{11}, B_{22}, and B_{33}, were used to compute the final structure factors since the non-diagonal elements, B_{12}, B_{13}, and B_{23}, were small and of the same order of magnitude as their standard deviations. It was necessary to compute anisotropic temperature factors for the independent atoms only, since Trueblood (1956) has given the transformations necessary for evaluating temperature factors of structurally related atoms.

An intermediate step in the calculation of anisotropic temperature factors gave the results of a third important technique used for the refinement of crystal structures, the differential synthesis method which
has been described by Booth (1946). The atomic coordinates given by the
differential synthesis method were identical to the final atomic co­
ordinates given by the \((F_o-F_c)\)-synthesis method. A comparison of atomic
coordinates at various stages of the structure refinement, i.e.,
original coordinates, least squares, \((F_o-F_c)\)-synthesis, and differential
synthesis, is given by Table 1. Table 2 lists the diagonal elements of
the anisotropic temperature factors for one specified atom of each
structurally independent type. The standard deviations in the atomic
coordinates and anisotropic temperature factors were computed with the
aid of programs for the IBM-650 written by Shiono (1959). Programs
written by Shiono (1957, 1959) were also employed to calculate the final
structure factors with anisotropic temperature factors. A comparison of
the final \(F_o\) and \(F_c\) values for each independent hexagonal reflection is
given by Figure 3. The final value of R for all data was 0.057.
Table 1. Comparison of atomic coordinates at various stages of the structure refinement of $V_4Al_{23}$. The coordinates are given in fractions of the hexagonal unit cell edges ($a=7.693\text{Å}$ and $c=17.043\text{Å}$).

<table>
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<tr>
<th>Atom type</th>
<th>Wyckoff notation</th>
<th>Position in P6$_3$/mmc</th>
<th>$x/a^*$</th>
<th>z/c*</th>
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<tr>
<td>$V_1$</td>
<td>2(a)</td>
<td>0,0,0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>$V_2$</td>
<td>6(h)</td>
<td>x,2x,1/4</td>
<td>.781</td>
<td>.7823</td>
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<tr>
<td>$Al_1$</td>
<td>12(k)</td>
<td>x,2x,z</td>
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<td>.2112</td>
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<td>$Al_2$</td>
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<td>x,2x,z</td>
<td>.124</td>
<td>.1261</td>
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<td>$Al_3$</td>
<td>12(k)</td>
<td>x,2x,z</td>
<td>.455</td>
<td>.4583</td>
</tr>
<tr>
<td>$Al_4$</td>
<td>6(h)</td>
<td>x,2x,1/4</td>
<td>.126</td>
<td>.1252</td>
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<tr>
<td>$Al_5$</td>
<td>4(f)</td>
<td>1/3,2/3,z</td>
<td>1/3</td>
<td>1/3</td>
</tr>
</tbody>
</table>

*(1) Previous results of Smith and Ray (1957).
(2) These data - least squares refinement.
(3) These data - (F$_0$-F$_C$)-synthesis and differential synthesis refinements (identical results).
(4) Standard deviations in atomic coordinates given by the (F$_0$-F$_C$)-synthesis refinement.
Table 2. Diagonal elements of anisotropic temperature factors in Å\(^2\) and their standard deviations for one specified atom of each independent symmetry type in V\(_4\)Al\(_{23}\)

<table>
<thead>
<tr>
<th>Atom type</th>
<th>Wyckoff notation</th>
<th>Position in P6(_3)/mmc</th>
<th>(B_{11})</th>
<th>(\sigma(B_{11}))</th>
<th>(B_{22})</th>
<th>(\sigma(B_{22}))</th>
<th>(B_{33})</th>
<th>(\sigma(B_{33}))</th>
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<td>V(_1)</td>
<td>2(a)</td>
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<td>0.04</td>
<td>0.53</td>
<td>0.04</td>
<td>0.36</td>
<td>0.03</td>
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<tr>
<td>V(_2)</td>
<td>6(h)</td>
<td>x,2x,1/4</td>
<td>0.49</td>
<td>0.04</td>
<td>0.56</td>
<td>0.04</td>
<td>0.67</td>
<td>0.03</td>
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<td>Al(_1)</td>
<td>12(k)</td>
<td>x,2x,z</td>
<td>1.41</td>
<td>0.07</td>
<td>0.92</td>
<td>0.07</td>
<td>1.13</td>
<td>0.06</td>
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<td>Al(_2)</td>
<td>12(k)</td>
<td>x,2x,z</td>
<td>0.71</td>
<td>0.07</td>
<td>0.84</td>
<td>0.07</td>
<td>0.94</td>
<td>0.05</td>
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<td>Al(_3)</td>
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<td>Al(_4)</td>
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<td>0.68</td>
<td>0.07</td>
<td>0.74</td>
<td>0.07</td>
<td>0.82</td>
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<td>Al(_5)</td>
<td>4(f)</td>
<td>1/3,2/3,z</td>
<td>0.55</td>
<td>0.07</td>
<td>0.75</td>
<td>0.08</td>
<td>1.30</td>
<td>0.05</td>
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Figure 3. Comparison of the observed structure factors, $F_0$, with the final calculated structure factors, $F_c$
RESULTS AND DISCUSSION

Each atom in the V₄Al₂₃ structure has twelve neighboring atoms within 3.0Å. The interatomic distances between all atoms considered to be in contact, i.e., distances less than 3.0Å, are listed in Table 3. The standard deviations in the interatomic distances were estimated by the methods suggested by Lipson and Cochran (1953).

\((F_0-F_c)\)-syntheses of the planes \((x,x,z)\), \((x,y,0)\), \((x,y,9/80)\), and \((x,y,1/4)\) are shown in Figures 4, 5, 6, and 7, respectively. The coefficients used in computing these \((F_0-F_c)\)-syntheses were taken from the fifty independent hexagonal reflections for which \(\sin \theta/\lambda < 0.29\)Å⁻¹.

The estimated standard deviation in the \((F_0-F_c)\)-syntheses, \(\sigma(D)\), is 0.13 electrons per cubic Angstrom (e.Å⁻³) [see Appendix]. The contours are drawn at intervals of \(\sigma(D)\). Positive regions greater than \(\sigma(D)\) are shaded and zero contours are broken. These particular Fourier sections were chosen because they illustrate most clearly the areas about the atoms involved in the abnormally short contacts.

The \((x,x,z)\)-plane shown in Figure 4 passes through the atomic center of each type of independent atom in the structure. This is the \((0,y,z)\)-plane in the orthorhombic unit cell which was used in determining the derivatives of \(D\) during the \((F_0-F_c)\)-synthesis refinement. The most important feature of this map is that each atomic site, except for the position of the \(V_I\) atom, is centered in a strongly negative region, indicating that too much scattering power has been assumed in these regions. These same regions were essentially zero in the final
Table 3. Interatomic distances in V₄Al₂₃

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<th>Atom</th>
<th>Neighbor</th>
<th>No. of neighbors</th>
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<th>Standard deviation (Å)</th>
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<tr>
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<td>2.905</td>
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Figure 4. $(F_C - F_C')$-synthesis of the asymmetric unit of the plane $(x,x,z)$, computed with reflections for which $\sin \theta/\lambda < 0.29\text{Å}^{-1}$

(Contours are drawn at intervals of $\sigma(D) = 0.13\text{Å}^{-3}$ Positive regions greater than $\sigma(D)$ are shaded and zero contours are broken).
Figure 5. \((F_O - F_C)\)-synthesis of the plane \((x,y,0)\), computed with reflections for which \(\sin \theta/\lambda < 0.29\) Å\(^{-1}\).

(Contours are drawn at intervals of \(\sigma(D) = 0.13\) e Å\(^3\). Positive regions greater than \(\sigma(D)\) are shaded and zero contours are broken. Plus and minus signs designate \(A_1\) and below the \((x,y,0)\) plane, respectively.)
Figure 6. \((F_0 - F_c)\)-synthesis of the plane \((x, y, 9/80)\), computed with reflections for which \(\sin \theta / \lambda < 0.29 \text{Å}^{-1}\)

(Contours are drawn at intervals of \(\sigma^* (D) = 0.13 \text{e.Å}^{-3}\). Positive regions greater than \(\sigma^* (D)\) are shaded and zero contours are broken).
Figure 7. \((F_0 - F_c)\)-synthesis of the plane \((x, y, 1/4)\), computed with reflections for which \(\sin \theta/\lambda < 0.29\AA^{-1}\)

(Contours are drawn at intervals of \(\sigma(D) = 0.13\text{e}\AA^{-3}\). Positive regions greater than \(\sigma(D)\) are shaded and zero contours are broken).
(F_0 - F_c)-synthesis with reflections for which \(\sin \theta/\lambda > 0.29\text{Å}^{-1}\). The overall background is generally positive and the positive regions within the first contours are more diffuse than the negative regions. The \(\text{Al}_2-\text{V}_1\) and \(\text{Al}_2-\text{V}_2\) distances are both significantly shorter than would be predicted on the basis of the apparent atomic radii in the pure metals. There are no positive areas directly between either of these short bonds which might indicate a direct transfer of electrons to either the aluminum or vanadium atoms.

The \((x,y,0)\)-section, Figure 5, illustrates the region about the \(\text{V}_1\) atom. The negative region about this atom differs from that about the other atomic sites in that there is no deep minimum at the \(\text{V}_1\) site (the \(\text{Al}_1\) atoms are not in the \((x,y,0)\)-plane, compare Figure 4). In addition, the negative region about the \(\text{V}_1\) atom is extended in the direction of the \(\text{Al}_1\) atoms and shortened in the direction of the \(\text{Al}_2\) atoms.

There is a definite positive region centered on the \(6_3\) axis in the plane \((x,y,9/80)\), Figure 6. The other appreciable positive region in Figure 6 is centered on a 3-fold axis in a large interstice which occurs in the structure between a group of three \(\text{Al}_1\) and three \(\text{Al}_3\) atoms.

Figure 7 shows the \((F_0 - F_c)\)-synthesis in the plane \((x,y,1/4)\). The \(\text{Al}_4-\text{V}_2\) distance is 2.521Å, which is the shortest bond in the structure. Again, there is no positive region centered directly between the centers of these atoms. Rather, there is a positive region located in another large interstice which is centered at the \(1/2,1/2,1/4\) position. Two \(\text{Al}_3\) atoms related by the mirror in the \((x,y,1/4)\)-plane are located almost directly above and below this positive area.
There appears to be a tendency for the positive regions to be associated with some of the larger interstices in the structure. If the valence electrons were uniformly distributed throughout the structure, corresponding to a free electron approximation and, as in the present case, the theoretical model is based on a spherical distribution of electrons about atomic centers, one would expect positive regions in the \((F_0 - F_c)\)-synthesis to occur where the least scattering power has been assumed, i.e., in the large interstices. However, no significant positive area occurs at the 1/3, 2/3, 1/4 position, which is the largest interstice in the structure. The fact that some of the larger interstices have appreciable positive regions associated with them while others do not leads to the speculation that the preferential distribution of positive regions may be indicative of directionality in the bonding interaction among small groups of atoms. The extension of the negative region about the \(V_1\) atoms in the \((x,y,0)\)-plane may be indicative of delocalization of the outer electrons of the \(V_1\) atoms toward the \(Al_1\) atoms.

Supplementary information concerning the bonding is obtainable from magnetic susceptibility data. Greiner (1959) has measured the magnetic susceptibilities of aluminum, vanadium, and the compound \(V_4 Al_{23}\). The values of the magnetic susceptibilities, \(\chi\), obtained for these substances at 300°K were:
The temperature dependence of the magnetic susceptibility of $V_{4Al_{23}}$ was negligible. These measurements indicate that electrons which are unpaired in pure vanadium are paired in $V_{4Al_{23}}$ and suggest that levels arising from atomic d-states in vanadium participate in the bonding in $V_{4Al_{23}}$.

It appears that all of the aluminum atoms and the six $V_2$ atoms contribute approximately equal numbers of bonding electrons, while the two $V_1$ atoms contribute a smaller number. However, the hybridization must be such that spatial localization of the bonding electrons about the vanadium atoms is not pronounced. In any case, there is no indication of a spatial transfer of electrons from the aluminum atoms to the vanadium atoms to the extent implied by Raynor's theory.
SUMMARY

The theoretical model assumed in this investigation was that of spherical distributions of electrons centered about atomic sites in the \( V_4Al_{23} \) structure, represented by the theoretical scattering factors for the isolated atoms. It was further assumed that the actual electron distribution is well represented by the theoretical model in the region of reciprocal space for which \( \sin \frac{\theta}{\lambda} > 0.29 \text{Å}^{-1} \). Hence, the \((F_0-F_C)\)-synthesis can only show how the actual electron distribution differs from the theoretical model in the region for which \( \sin \frac{\theta}{\lambda} < 0.29 \text{Å}^{-1} \).

It is evident from the \((F_0-F_C)\)-synthesis maps that too much scattering power has been assumed in the immediate vicinity of each atomic site since the negative regions associated with these sites represent electron density differences which are generally two to three times greater than the estimated experimental errors. This is not surprising since outer electrons would be expected to be delocalized from the centers of atomic sites in order to participate in the bonding. While there is a definite indication of directed bonding, there is no indication of a spatial transfer of electrons from the aluminum atoms to the vanadium atoms to the extent implied by Raynor's theory.

An estimate of the number of electrons associated with the positive regions in the \((F_0-F_C)\)-synthesis maps, and presumably the number of electrons participating in the bonding, could be obtained by computing structure factors with theoretical scattering factors which account for the contributions of the core electrons only. An \((F_0-F_C)\)-synthesis
with these $F_C$ values and the $F_O$ values from this investigation should then approximate the actual distribution of the outer electrons.
REFERENCES


Raynor, G. V. (1949). Progr. in Metal Phys. 1, 1.
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APPENDIX

In order that conclusions would not be drawn from results which were not significantly outside the range of experimental errors, an estimate was made of the standard deviations in the difference maps shown in Figures 4, 5, 6, and 7. Since \( D = \rho_o - \rho_c \), where \( \rho_o \) and \( \rho_c \) are the observed and calculated electron densities, the errors in \( D \) can be discussed in terms of errors involving \( \rho_o \) and those involving \( \rho_c \). The standard deviation in \( \rho_o \) can be estimated by employing the formula of Cruickshank (1949) which is given by

\[
\sigma(\rho_o) = \frac{1}{V} \left[ \frac{\sum}{3} m(F_o - F_c)^2 \right]^{1/2},
\]

where \( V \) is the unit cell volume, \( m \) is the structure factor multiplicity, and \( \sum \) denotes a triple summation over all independent reflections within a limited region of reciprocal space. For those reflections for which \( \sin \theta/\lambda < 0.29 \text{Å}^{-1} \), \( \sigma(\rho_o) \) was found to be 0.13e.Å^{-3}. The most important errors in \( \rho_c \) arise from (1) rounding errors in the calculation of the structure factors, (2) linear interpolation between fixed points in the scattering factor tables, and (3) incorrect atomic coordinates and temperature factors. Shiono (1959) reports that his structure factor programs, which were employed in this investigation, maintain five figure accuracy throughout. Comparison of structure factors computed for orthorhombic reflections, which were equivalent because of the hexagonal symmetry, supports this conclusion. The scattering factor tables in the structure factor programs of Shiono are set up so that the
scattering factor curves are divided into 47 equal intervals of \( \sin \theta \) between \( \sin \theta = 0 \) and \( \sin \theta = 1 \). Inspection of the differences between scattering factors obtained by linear interpolation from these tables and those obtained directly from the scattering factor curves revealed that these differences were less than the estimated errors involved in the construction of the curves, i.e., approximately one per cent of the total scattering factors. There seems no reason to believe the standard deviations in the atomic coordinates and anisotropic temperature factors have been greatly underestimated since they are based on well established practice. The changes in the calculated structure factors for reflections with \( \sin \theta / \lambda < 0.29 \text{Å}^{-1} \) were negligible throughout the course of the \((F_0 - F_c)\)-synthesis refinement and the isotropic to anisotropic temperature factor refinement cycle. Accordingly, since the errors in the \( F_c \) values are very small compared to the errors involved in measuring the \( F_0 \) values, it does not seem unduly optimistic to assume that

\[
\sigma(D) = \sigma(F_0 - F_c) \approx \sigma(F_0).
\]