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A TEST FOR ELECTRON TRANSFER IN THE INTERMETALLIC COMPOUND,

V_4Al_{23}

by

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A TEST FOR ELECTRON TRANSFER
IN THE INTERMETALLIC COMPOUND, V_4Al_{23} *

Alden Earl Ray and J. F. Smith

Abstract

Abnormally short interatomic distances are characteristic of aluminum-transition element compounds which occur at the aluminum-rich ends of the phase diagrams. A theory has been proposed which suggests that these short interatomic distances are due to a transfer of some of the outer electrons of the aluminum atoms to the unfilled 3d orbitals of the transition metal atoms. In the present investigation, x-ray diffraction techniques have been employed to test for spatial transfer of electrons in the intermetallic compound, V_4Al_{23} .

Three dimensional intensity data have been collected from a spherical crystal of V_4Al_{23} by the moving crystal-stationary counter technique. These data have been corrected for the effects of absorption, dispersion, secondary extinction, and anisotropic thermal motion of the atoms. It has been shown that reflections for which $\sin \theta/\lambda > 0.29A^{-1}$ should be insensitive and reflections for which $\sin \theta/\lambda < 0.29A^{-1}$ should be sensitive to the distribution of the outer electrons.

* This report is based on a Ph.D. thesis by Alden Earl Ray submitted August, 1959, to Iowa State University, Ames, Iowa. This work was done under contract with the U. S. Atomic Energy Commission.

The intensity data for which $\sin \theta/\lambda > 0.29\text{\AA}^{-1}$ were used in $(F_o - F_c)$ -syntheses to refine atomic coordinates and temperature factors and to place all the intensities on an absolute scale. An R value of 0.057 has been obtained for the structure refinement. After successive refinements of the structural parameters had minimized the $(F_o - F_c)$ -synthesis of the intensity data for which $\sin \theta/\lambda > 0.29\text{\AA}^{-1}$, a three dimensional $(F_o - F_c)$ -synthesis was computed with the intensity data for which $\sin \theta/\lambda < 0.29\text{\AA}^{-1}$. This synthesis revealed how the actual distribution of the outer electrons, given by the observed structure factors, differed from spherical distributions of outer electrons about atomic sites, represented by structure factors calculated with theoretical scattering factors for isolated atoms.

The final $(F_o - F_c)$ -synthesis did not indicate a spatial transfer of electrons from the aluminum atoms to the vanadium atoms to the extent implied by the theory noted above. However, strongly positive regions occurring in the $(F_o - F_c)$ -synthesis have been interpreted to indicate a directional character to the bonding interactions among small groups of atoms in the V_4Al_{23} structure. Further interpretation has been that all of the aluminum atoms and six of the eight vanadium atoms in the structure contribute approximately equal numbers of electrons to participate in the bonding, while the remaining two vanadium atoms contribute a smaller number of bonding electrons. Magnetic susceptibility measurements have shown that V_4Al_{23} is feebly

paramagnetic with little temperature dependence while in pure vanadium the paramagnetism is comparatively strong. 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} . However, the hybridization must be such that spatial localization of the bonding electrons around the vanadium atoms is not pronounced.

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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_2Al_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

*When an author is mentioned without an identifying date, only one publication by the author has been cited, and this publication has been previously identified.

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_2Al_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 naive 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_o , 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_o values on an absolute scale. A three dimensional $(F_o - F_c)$ - synthesis with only the F_o 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_o values to the F_c values in each of a series of ranges of $\sin \theta/\lambda$, including the range where the F_o values are sensitive to the outer electrons. The method of Robinson and Nicol required that the total count over the $(F_o - F_c)$ -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 V_4Al_{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 stoichiometric, 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

*Brown, P. J. Cambridge, England. The structure of V_4Al_{23} . Private communication. (1957).

on the F_o 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 $\sin \theta/\lambda = 0.25 \text{ \AA}^{-1}$ 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 $0 < \xi < 0.1 \text{ \AA}^{-1}$, where $\xi = \sin \theta/\lambda \cdot Z^{1/3}$, are sensitive to distributions of outer electrons having a deviation from spherical symmetry, and hence the region for which $\xi > 0.1 \text{ \AA}^{-1}$ should be insensitive to the outer electrons. For vanadium, $\xi = 0.1 \text{ \AA}^{-1}$ corresponds to $\sin \theta/\lambda = 0.29 \text{ \AA}^{-1}$. 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 $\sin \theta/\lambda > 0.29 \text{ \AA}^{-1}$ were used to obtain the final atomic coordinates, temperature factors, and scale factor. In contrast, those reflections for which $\sin \theta/\lambda < 0.29 \text{ \AA}^{-1}$ were used in the final $(F_o - F_c)$ -synthesis to test for electron transfer.

The F_o 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 $(F_o - F_c)$ -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).

PREPARATION OF A SPHERICAL CRYSTAL OF V_4Al_{23}

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 inch above the grinding surface. Sphere grinders modeled after those described by Whitmore and by Bond (1951) were both

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 inch above rather than tangent to the grinding surface at the base of the notch.)

found to produce elliptically shaped particles. The model shown in Figure 1 was much more successful in producing spherical 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_2O , 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 than 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 ± 0.002 millimeters for several random orientations of the particle. Individual measurements ranged from a maximum

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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,

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

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.

Cu $K\alpha$ 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 V_4Al_{23} 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 intensity 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 relative integrated intensity, I , was then given by

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

For each measurement, the crystal was rotated at a constant speed of one degree omega (ω) per minute through an angle of two degrees extending one degree ω on either side of the midpoint between the $K\alpha_1$ and $K\alpha_2$ diffraction maxima.

All reflections within range of the counter when Cu $K\alpha$ 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.

Figure 2. 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 about 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.)

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 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 μR for the spherical V_4Al_{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,

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

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

$$g = \frac{I_c - I_o}{2I_c I_o} , \quad (4)$$

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 of the intensity data and resulted in a 3 per cent decrease in the scale factor.

Cochran (1951) has described the use of the $(F_o - F_c)$ -synthesis, D , given by

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

for the refinement of crystal structures. The correct choices 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, ρ_c , at atomic centers from a corresponding F_c -synthesis. Approximations for the derivatives of ρ_c have been suggested by Cruickshank (1956). In this investigation, an analytical

expression of Shoemaker, et al. (1950), for ρ_c was employed to approximate the required derivatives. Near an atomic center, the shape of the electron density, ρ , is well represented by

$$\rho = \exp[a_0 + a_1 x^2 + a_2 y^2 + a_3 z^2 + a_4 x + a_5 y + a_6 z + a_7 yz + a_8 xz + a_9 xy]. \quad (6)$$

Seven blocks of 27 ρ -values, each containing the atomic center of an independent atom in the V_4Al_{23} structure, were obtained from an F_o -synthesis. Each block of ρ -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 ρ_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 $(F_o - F_c)$ -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 $(F_o - F_c)$ -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 V_4Al_{23} structure. An $(F_o - F_c)$ -synthesis of this plane contained all of 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 ρ -values required to compute the derivatives of ρ_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 $1/80$ th intervals along y and z and $1/40$ th intervals along x in orthorhombic coordinates. Two $(F_o - F_c)$ -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 coordinates 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 in 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 in 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 ($a=7.693\text{\AA}$. and $c=17.043\text{\AA}$).

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)	$x, 2x, 1/4$	.781	.7818	.7823	.0001	$1/4$	$1/4$	$1/4$	----
Al_1	12(k)	$x, 2x, z$	.213	.2116	.2112	.0002	.029	.0295	.0295	.0004
Al_2	12(k)	$x, 2x, z$	.124	.1255	.1261	.0002	.618	.6167	.6164	.0004
Al_3	12(k)	$x, 2x, z$	.455	.4583	.4583	.0003	.166	.1666	.1663	.0003
Al_4	6(h)	$x, 2x, 1/4$	.126	.1253	.1252	.0002	$1/4$	$1/4$	$1/4$	----
Al_5	4(f)	$1/3, 2/3, z$	$1/3$	$1/3$	$1/3$	----	.617	.6167	.6162	.0003

*{1} Previous results of Smith and Ray (1957).

{2} These data - least squares refinement.

{3} These data - $(F_o - F_c)$ -synthesis and differential synthesis refinements (identical results).

{4} Standard deviations in atomic coordinates given by the $(F_o - F_c)$ -synthesis refinement.

Table 2. Diagonal elements of anisotropic temperature factors in A₂ and their standard deviations for one specified atom of each independent symmetry type in V₄Al₂₃

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,1/4	0.49	0.04	0.56	0.04	0.67	0.03
Al ₁	12(k)	x,2x,z	1.41	0.07	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,1/4	0.68	0.07	0.74	0.07	0.82	0.05
Al ₅	4(f)	1/3,2/3,z	0.55	0.07	0.75	0.08	1.30	0.05

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	41.7	1.1
002	66.1	-71.8	053	76.7	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	41.3	8	248	31.3	29.8
006	5.7	-12.9	055	116.6	-119.0	13,17	41.3	-1.1	249	12.2	11.9
008	235.1	245.5	056	5.2	4.5	13,18	86.7	47.7	25,10	27.3	28.4
00,10	101.7	-102.8	057	19.6	2.5	14,0	52.0	52.4	25,11	15.8	-13.3
00,12	79.2	78.4	058	25.3	26.8	141	23.6	-21.6	25,12	6.7	7.3
00,14	219.8	-219.7	059	7.3	-7.4	142	26.6	26.6	25,13	4.4	-5.8
00,16	45.8	65.5	05,10	23.5	-23.5	143	55.3	55.2	25,14	18.8	19.3
00,18	6.0	7.7	05,11	45.7	46.2	144	2.9	-4.5	25,15	40.4	-37.6
00,20	15.0	15.0	05,12	14.9	20.4	145	4.3	3.9	25,16	27.2	24.3
010	26.9	25.3	05,13	6.6	6.0	146	14.0	13.7	250	35.4	-36.8
011	40.0	-40.2	05,14	8.0	-7.4	147	4.9	-6.1	251	26.4	26.0
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	-60.9	14,10	29.0	28.2	254	41.7	1.2
015	13.4	-12.6	061	47.4	-48.9	14,11	69.3	67.5	255	6.9	-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	26.3	-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	41.4	.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	50.2	-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	89.2	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	54.8	-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	6.0	-1.5
020	40.4	-43.6	073	5.1	-8.0	15,11	23.2	-21.5	268	29.6	29.8
021	34.1	-36.2	074	6.4	-12.0	15,12	45.7	44.3	269	5.9	5.6
022	41.8	6.3	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	-6.0
025	57.3	60.9	078	24.3	26.9	160	32.1	32.5	272	26.3	26.3
026	144.1	151.9	079	13.7	10.8	161	10.4	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	54.4	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	22.4	20.2	082	6.5	9.7	166	12.4	10.1	33,10	55.7	-58.3
02,12	64.7	64.7	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	71.6	085	29.0	30.8	169	41.4	1.5	33,16	53.5	52.5
02,15	43.2	41.6	110	21.8	15.3	16,10	12.5	-9.8	340	3.8	-4.8
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	50.1	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	6.1	344	40.8	42.3
02,20	1.8	2.5	11,10	51.9	50.3	172	5.6	4.6	345	25.2	25.5
030	139.7	-146.2	11,12	41.6	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	45.2
032	75.0	75.4	11,16	27.9	27.5	175	41.3	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	178.4	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	-29.6	127	11.2	-9.6	22,12	14.7	13.0	353	8.1	8.8
03,13	85.1	86.9	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	65.5	63.2
03,17	30.4	31.2	12,12	33.7	31.8	231	5.6	5.0	358	41.1	-41.8
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	-48.6	12,14	5.5	-3.5	233	50.7	52.0	35,10	12.1	15.1
040	9.0	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	-36.2	12,18	41.6	-54.4	237	147.0	144.2	362	35.5	37.5
044	67.2	60.5	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	8.5	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	42.8	59.4
04,18	14.5	-15.7	13,12	35.8	37.2	244	15.0	10.8	455	25.9	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									

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

RESULTS AND DISCUSSION

Each atom in the V_4Al_{23} 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).

$(F_o - F_c)$ -syntheses of the planes $(x, \bar{x}, z)$, $(x, y, 0)$, $(x, y, 9/80)$, and $(x, y, 1/4)$ are shown in Figures 4, 5, 6, and 7, respectively. The coefficients used in computing these $(F_o - F_c)$ -syntheses were taken from the fifty independent hexagonal reflections for which $\sin \theta / \lambda < 0.29 \text{Å}^{-1}$. The estimated standard deviation in the $(F_o - F_c)$ -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 $(x, \bar{x}, z)$ -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 $(F_o - F_c)$ -synthesis refinement. The most important features of this map is that each atomic site, except for the position of the V_1 atom, is centered in a strongly negative region, indicating that too much scattering power has been assumed in these regions.

Table 3. Interatomic distances in V_4Al_{23}

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

Figure 4. $(F_0 - P_0)$ -synthesis of the asymmetric unit of the plane $(x, \bar{x}, z)$, computed with reflections for which $\sin \theta/\lambda < 0.29\text{\AA}^{-1}$
 (Contours are drawn at intervals of $\sigma(D) = 0.13e.\text{\AA}^{-3}$ Positive regions greater than $\sigma(D)$ are shaded and zero contours are broken.)

Figure 5. $(F_0 - F_c)$ -synthesis of the plane $(x, y, 0)$, computed with reflections for which $\sin \theta / \lambda < 0.29 \text{ \AA}^{-1}$
 (Contours are drawn at intervals of $\sigma(D) = 0.13e \cdot \text{\AA}^{-3}$. 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. $(F_o - F_c)$ -synthesis of the plane $(x, y, 9/80)$, computed with reflections for which $\sin \theta / \lambda < 0.29 \text{ \AA}^{-1}$

(Contours are drawn at intervals of $\sigma(D) = 0.13 e \cdot \text{\AA}^{-3}$. Positive regions greater than $\sigma(D)$ are shaded and zero contours are broken.)

Figure 7. $(F_o - F_c)$ -synthesis of the plane $(x, y, 1/4)$, computed with reflections for which $\sin \theta/\lambda < 0.29 \text{ \AA}^{-1}$

(Contours are drawn at intervals of $\sigma(D) = 0.13 e \cdot \text{\AA}^{-3}$. Positive regions greater than $\sigma(D)$ are shaded and zero contours are broken.)

These same regions were essentially zero in the final $(F_o - F_c)$ -synthesis with reflections for which $\sin \theta/\lambda > 0.29\text{\AA}^{-1}$. 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 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 V_1 site (the Al_1 atoms are not in the $(x, y, 0)$ -plane, compare Figure 4). In addition, the negative region about the V_1 atom is extended in the direction of the Al_1 atoms and shortened in the direction of the 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 Al_1 and three Al_3 atoms. Figure 7 shows the $(F_o - F_c)$ -synthesis in the plane $(x, y, 1/4)$. The $\text{Al}_4\text{-V}_2$ distance is $2.521\text{\AA}$, 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 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 $(F_o - F_c)$ -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_4Al_{23} . The values of the magnetic susceptibilities, χ , obtained for these substances at 300°K were:

	$\chi \times 10^6 \text{ e.m.u. gm.}^{-1}$
Al	$+ 0.642 \pm 0.007$
V	$+ 5.85 \pm 0.02$
V_4Al_{23}	$+ 0.63 \pm 0.02$

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 $\sin \theta/\lambda > 0.29\text{\AA}^{-1}$. Hence, the $(F_o - F_c)$ -synthesis can only show how the actual electron distribution differs from the theoretical model in the region for which $\sin \theta/\lambda < 0.29\text{\AA}^{-1}$.

It is evident from the $(F_o - F_c)$ -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 $(F_o - F_c)$ -synthesis maps, and presumably the number of electrons participating in the bonding, could be obtained by computing structure factors with theoret-

ical scattering factors which account for the contributions of the core electrons only. An $(F_o - F_c)$ -synthesis with these F_c values and the F_o values from this investigation should then approximate the actual distribution of the outer electrons.

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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 ρ_o and ρ_c are the observed and calculated electron densities, the errors in D can be discussed in terms of errors involving ρ_o and those involving ρ_c . The standard deviation in ρ_o can be estimated by employing the formula of Cruickshank (1949) which is given by

$$\sigma(\rho_o) = \frac{1}{V} \left[\sum_3 m(\rho_o - \rho_c)^2 \right]^{1/2}, \quad (7)$$

where V is the unit cell volume, m is the structure factor multiplicity, and $\sum_3$ denotes a triple summation over all independent reflections within a limited region of reciprocal space. For those reflections for which $\sin \theta/\lambda < 0.29 \text{ \AA}^{-1}$, $\sigma(\rho_o)$ was found to be $0.13e \cdot \text{\AA}^{-3}$. The most important errors in ρ_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 $\sin \theta/\lambda < 0.29\text{\AA}^{-1}$ were negligible throughout the course of the $(F_o - F_c)$ -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_o values, it does not seem unduly optimistic to assume that $\sigma(D) = \sigma(F_o - F_c) \approx \sigma(F_o)$.

END