TECHNICAL REPORT

TECHNICAL REPORT

68-15c

OCTOBER 1968

RADIATION DAMAGE OF ORDERED V_6C_5 BY ELECTRON MICROSCOPE BEAM BOMBARDMENT

By

J. D. Venables

and R. G. Lye

NASA CONTRACT NASw-1290
EIGHTH TECHNICAL REPORT TO NASA

RADIATION DAMAGE OF ORDERED V_6C_5 BY ELECTRON MICROSCOPE BEAM BOMBARDMENT

Eighth Technical Report to NASA

by

J. D. Venables and R. G. Lye

National Aeronautics and Space Administration

Contract NASw-1290

October 1968

Research Institute for Advanced Studies
(RIAS)
Martin Marietta Corporation
1450 South Rolling Road
Baltimore, Maryland 21227

Radiation Damage of Ordered V_6C_5 by Electron Microscope Beam Bombardment

By

John D. Venables† and R. G. Lye

Research Institute for Advanced Studies
(Martin Marietta Corp.) Baltimore, Maryland USA 21227

ABSTRACT

The superlattice and domain structures exhibited by the ordered compound V_6C_5 are disrupted by electron microscope beam bombardment. The effect is attributed to the disordering of the carbon sublattice that results from displacement of the carbon atoms by the impinging electrons. Studies have been made of the disordering rate under electron bombardment at energies from 33 keV to 100 keV, using a Faraday cup to measure superlattice spot intensities. The results are compared with the predictions of a simple theory for the damage process, from which it is concluded that the displacement energy of carbon atoms in V_6C_5 has the surprisingly low value of 5.4 eV.

---

† Current address: School of Physics, University of Warwick, Coventry.

To be published in the Philosophical Magazine.

§1. INTRODUCTION

Two ordered compounds of vanadium carbide occur within the nominally cubic (rocksalt) phase field of the vanadium-carbon phase diagram. de Novion et al. (1966) have reported that material prepared with a composition close to V_8C_7 forms in a cubic structure with a lattice parameter twice that of the parent rocksalt unit cell dimension, whereas Venables et al. (1968) have presented evidence that an hexagonal (trigonal) structure is formed when the carbon-to-metal ratio is close to the integral composition V_6C_5.

These structures are based on two interpenetrating fcc lattices, one of which is completely occupied by the metal atoms, whereas the other is occupied only partially by the carbon atoms. The carbon atoms (and vacancies) are distributed in an ordered manner on their sublattice in two different periodic arrangements according to the carbon concentration. As a consequence of this ordering, the X-ray and electron diffraction patterns of these compounds exhibit supplementary spots which reflect the symmetry of the superlattice. Furthermore, V_6C_5 exhibits a domain structure which arises because the c-axis of the hexagonal (trigonal) carbon superlattice can be oriented parallel to any one of four equivalent <111> directions in the vanadium lattice (Venables et al. 1968).

When a sample of the ordered compound V_6C_5 is examined for extended periods of time in a 100 kV electron microscope, both the superlattice diffraction spots and the domain structure diminish in intensity, disappearing entirely after approximately 1/2 hour. This effect is interpreted to arise because the carbon atoms are displaced by the incident electrons.

However, the conclusion that a material as refractory as vanadium carbide can be damaged by relatively low energy electrons is somewhat surprising and has important implications, not only for the general problem of radiation damage in solids, but also for the stability of various refractory materials employed in nuclear reactor technology (e.g. actinide series carbides and nitrides). Accordingly, this disordering phenomenon has been subjected to a detailed analysis in order to obtain a quantitative value for the energy required to displace a carbon atom in V_6C_5. In §2, a description is given of the techniques employed to obtain quantitative measurements of the disordering rate from studies of the superlattice electron diffraction spot intensities. Several alternative explanations of the observed effect are considered and dismissed on the basis of arguments presented in §3. In §4, a relationship describing the variation in the intensity of V_6C_5 superlattice diffraction spots under electron bombardment is derived on the basis of a simple model for the radiation damage process. This relation is used in §5 to interpret the experimental observations of electron bombardment disordering and thus to obtain a value for the carbon atom displacement energy, E_d. Finally, in §6, the measured value of E_d is discussed in terms of the limitations of the model, and some implications are drawn regarding the bonding in V_6C_5 and the susceptibility to radiation damage of other similar materials.

§2. EXPERIMENTAL

2.1. Sample Preparation

The vanadium carbide single crystal samples employed in this study were grown by conventional floating zone techniques as described by Frecht and Hollox (1968). The carbon-to-metal ratio was close to the integral composition V_6C_5; the material being identical in every respect to the ordered compound discussed in a previous paper (Venables et al. 1968).

For the in situ radiation damage experiments, thin foils suitable for transmission electron microscopy were prepared by jet dimpling 3mm disks with a 20% sulphuric acid - 80% methanol solution at 7 volts, followed by electrolytic polishing in the same solution. The hole produced during polishing was kept as small as possible by switching off the current supply at the instant of breakthrough. Because of their inherent rigidity, samples prepared in the above manner are preferred over those produced by the "window" (Nicholson et al. 1958) or "figure-of-eight" (Brandon and Nutting 1959) techniques.

2.2. Measurement of Beam Flux and Superlattice Diffraction Spot Intensity

Both the incident electron flux and the intensity of the superlattice diffraction spots were measured with a Faraday cup positioned in the lower part of the microscope column, fig. 1. The cup itself was housed in a grounded shield to prevent interference by stray electrons. A phosphor coating applied to the top of the shield aided in aligning the beam or the

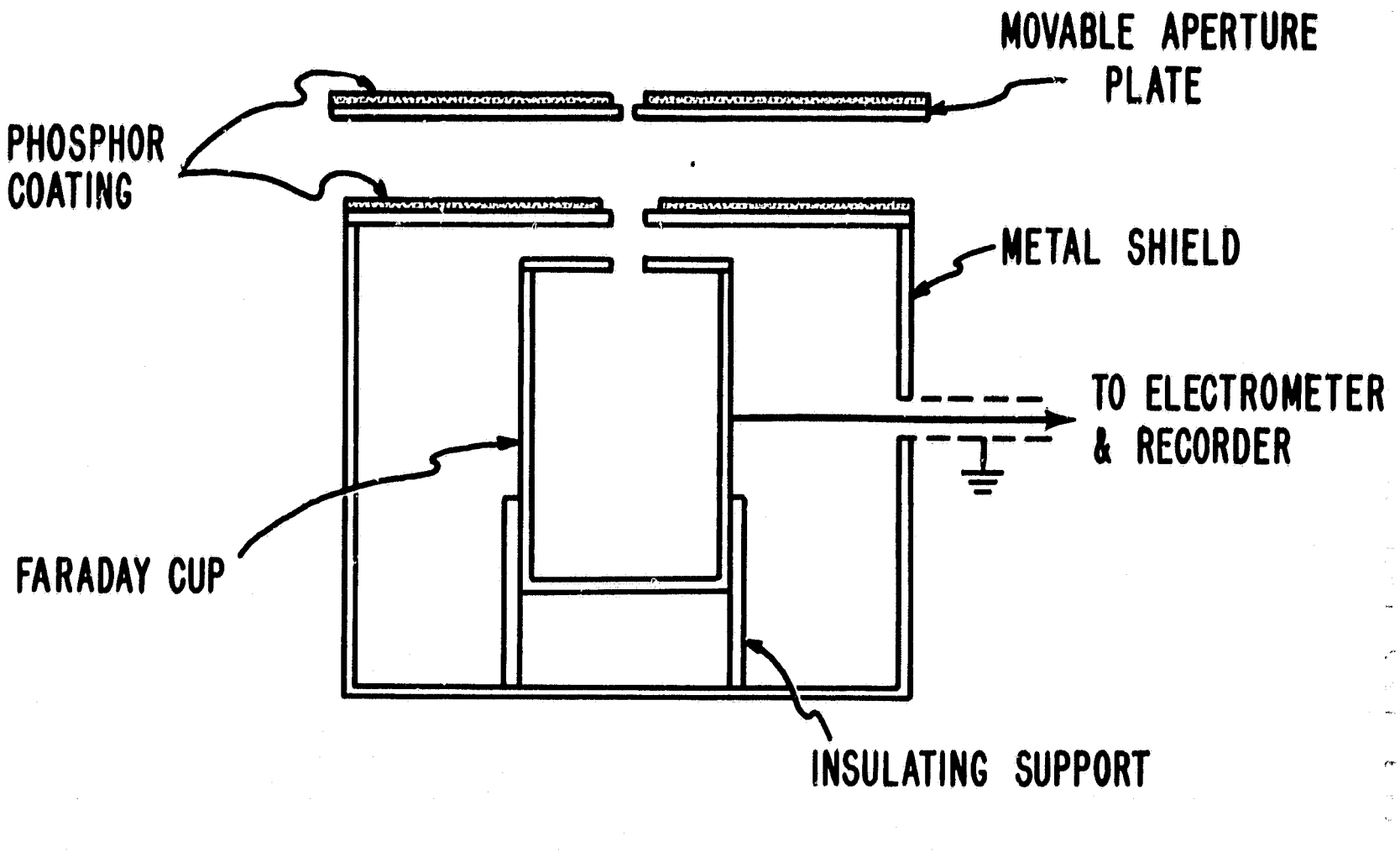


Fig. 1. Design of the Faraday cup used to measure electron microscope beam flux and to monitor V_6C_5 superlattice spot intensities during electron bombardment. The cup is positioned centrally in the lower part of the microscope column where phosphor screens, used as aids in aligning beam with aperture or hole in cup, may be observed through normal viewing ports. The metal shield protects the cup from stray electrons, whereas the aperture plate serves to reduce background intensity around superlattice spot.

diffraction spot with the hole in the cup. The electron current flow through the cup was measured with a General Radio 1230-A electrometer that is capable of measuring currents as small as 10^{-13} amp.

Two relatively independent methods were employed to measure the incident flux. In the first of these, the central portion of the electron beam was aligned over the hole in the shield. To prevent undesirable focussing effects due to charging of the phosphor coating, the selected area diffraction blades were positioned to block all radiation except that passing into the Faraday cup. With the sample removed and the aperture plate swung out of the way, measurements were made of the electron flow through the cup. Using the appropriate magnification factor, which was determined with a grating replica, the area of the hole could be translated into a corresponding area at the sample plane. From these measurements the electron current density at the sample plane could be determined.

In the second method, the selected area diffraction blades were used to select only the region of the beam that was determined to be of uniform intensity. (The Faraday cup was utilized as a probe to measure the intensity distribution across the diameter of the beam.) After the area delineated by the blades was measured by means of reference marks inscribed on the phosphor, the microscope was switched into the diffraction mode and current measurements were obtained for the sharply focussed electron beam. The effective area in the sample plane contributing to the

measured beam intensity was calculated, using the magnification factor established above, and the electron flux was determined from the ratio of the current to the area.

Although consistent values of the flux were obtained from the two methods (within 1-2%), both results would be in error if a significant fraction of the electrons were lost from the beam after leaving the sample plane. To determine the "efficiency" of the microscope lens system a second Faraday cup was placed immediately above the sample plane. The total beam current entering the sample plane was then measured and found to be identical to the total beam current measured in the lower column, indicating that the "efficiency" is close to 100%.

Measurements of the superlattice diffraction spot intensity were made in a manner similar to the second method described for measuring the beam flux. The selected area diffraction blades were positioned to ensure that only the uniformly irradiated portion of the sample within the central area of the beam would contribute to the diffracted intensity. In addition, the movable aperture shown in fig. 1 was positioned over the Faraday cup to reduce the background intensity as much as possible. A strip chart recorder, connected to the output of the electrometer, as indicated in fig. 1, was used to record the superlattice diffraction spot intensity during the bombardment.

In order to determine accurately the changes in intensity that result from disordering by radiation damage, it was necessary to eliminate spurious changes caused by distortion of the sample during bombardment. To accomplish

this, Kikuchi lines associated with the primary diffracting planes were constantly monitored on the phosphor coating covering the aperture plate. Any change in the position of the Kikuchi pattern could be corrected by adjusting the goniometer tilt stage.

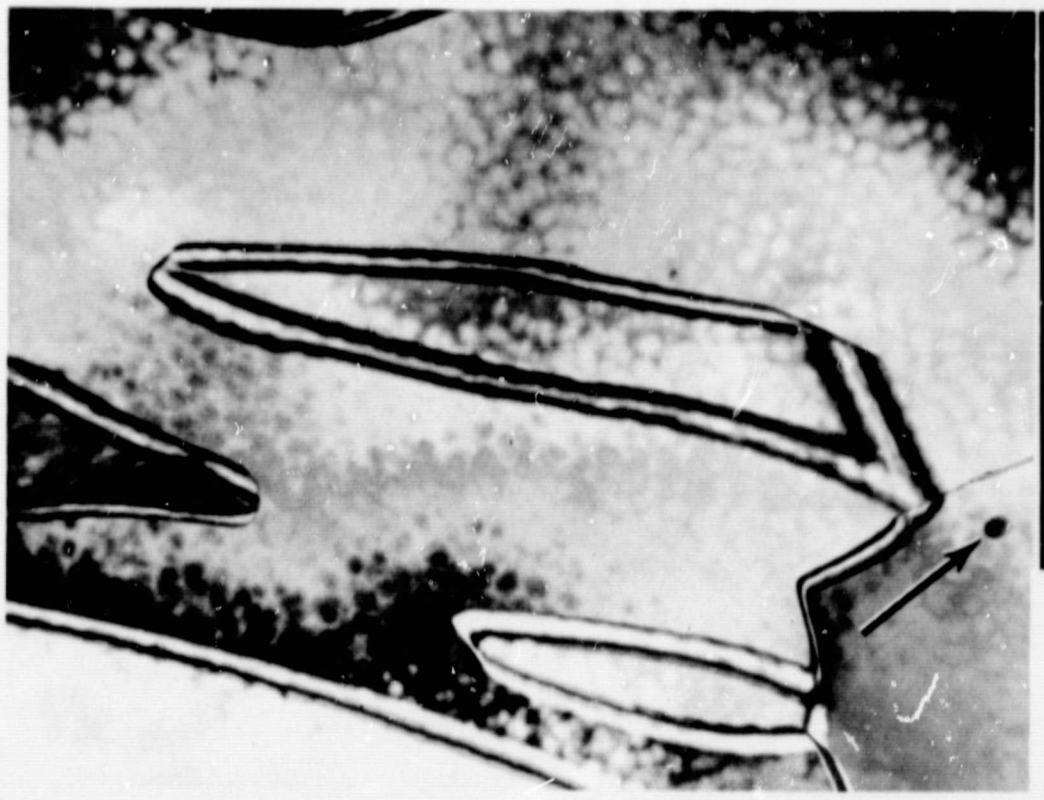
Radiation damage experiments were performed at four different values of the accelerating potential. Three of these values, nominally 50, 80, and 100 kV, are available on the JEM-7 microscope used for these experiments. The other potential, 33 kV, was obtained by removing two high voltage oscillator tubes (at the suggestion of the manufacturer) and adjusting the span of the intermediate lens current supply to permit focussing the diffraction pattern. Precise values of voltages, i.e. 33.0, 47.3, 79.9, and 100 kV, were measured by means of high resolution diffraction patterns obtained from a gold foil.

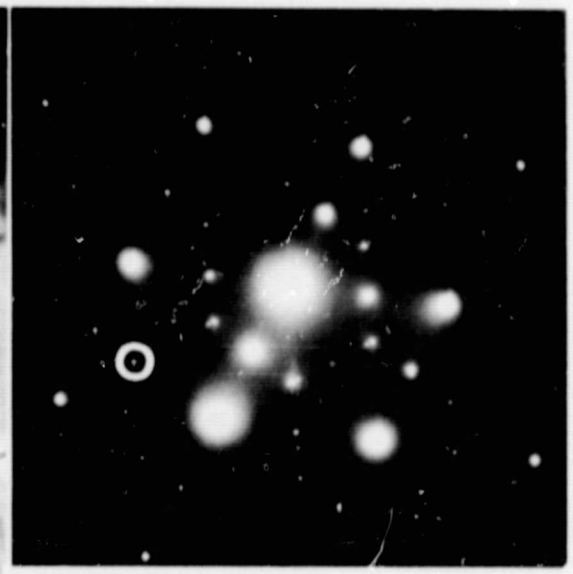
§3. OBSERVATIONS

The marked influence of electron bombardment on the structure of the ordered compound V_6C_5 is readily apparent from fig. 2. During the initial stages of bombardment, fig. 2(a), the domain structure and superlattice spot pattern remain visible. After a 10-20 min. exposure to the 100 keV electron beam, however, the domains and supplemental spots disappear entirely, fig. 2(b), although the intensity of the primary pattern increases slightly †. Similar effects are observed at the other accelerating potentials, and in particular, even at the lowest potential employed in this study, 33 kV.

† The increased intensity of the primary pattern is not clearly depicted in fig. 2(b) because of photographic reproduction difficulties, but it is quite apparent on the microscope viewing screen. This increase results from redistribution of the diffracted electrons into the primary spot pattern as the supplemental pattern decreases in intensity.

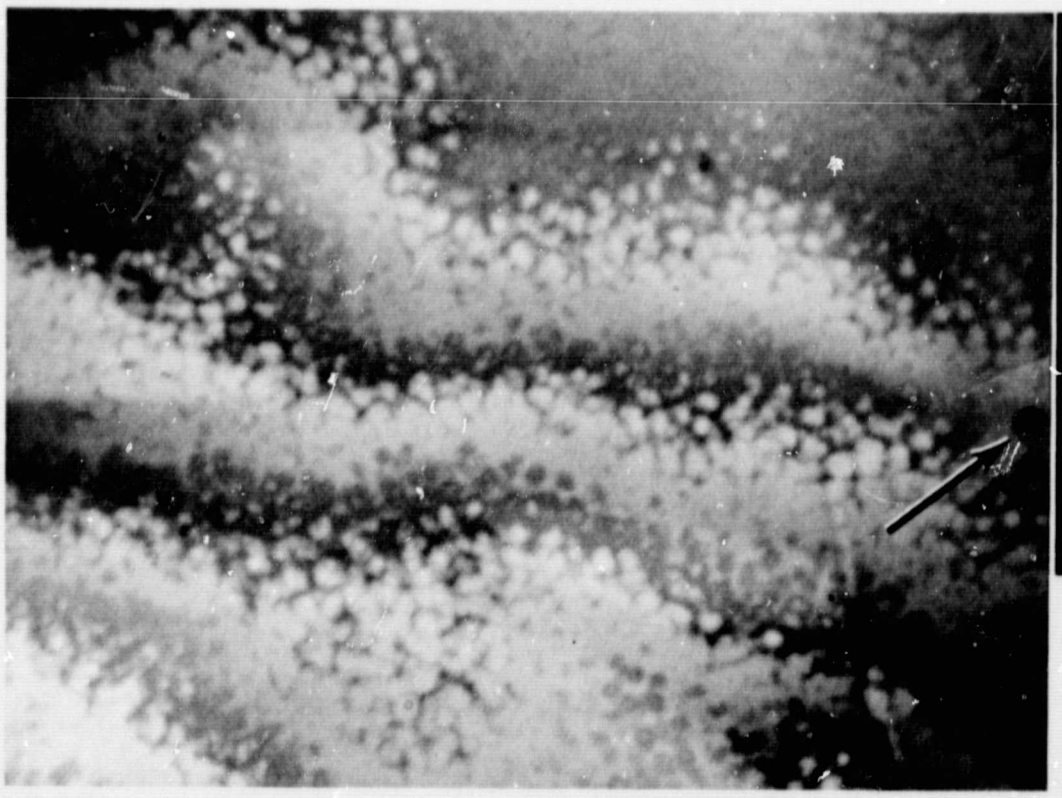
Fig. 2. Transmission electron micrographs and selected area diffraction patterns from a (110) foil (indices referred to cube axes) of V_6C_5, (a) before extensive irradiation with electron beam and (b) after 1/2 hour exposure to 100 keV electrons. (The fiducial mark indicated by arrows shows that the two micrographs were taken from the same region.) The domain structure and superlattice spots have disappeared in (b) due to radiation damage by the incident electron beam. Quantitative measurements of the rate of disordering were obtained by monitoring the intensity of diffraction spots derived from superlattice planes of the form $\{20\bar{2}\}$. A typical spot of this type is circled in (a) above.





BEFORE
IRRADIATION

a



AFTER
IRRADIATION

b

This disordering phenomenon is attributed to the displacement of carbon atoms by impinging electrons, and the hypothesis will be subjected to a detailed analysis in subsequent sections. That the effect is due to radiation damage caused by electron bombardment was not obvious immediately, however, and several alternative explanations were explored and dismissed on the basis of the following arguments:

1. The effect can not be due to the formation of a surface contimination film, because it is observed that the primary spots <u>increase</u> in intensity as the intensity of the superlattice spots decrease. The formation of a contamination film would cause a uniform decrease in the intensity of all the spots. Furthermore, all the present experiments were performed with a highly efficient cold finger positioned close to the sample area, and no evidence for a contamination film was noted at any time.

2. The effect is not due to ion bombardment. Pashley and Presland (1961) have reported that defect clusters form in gold foils while under observation in the electron microscope. Because gold atoms are too heavy to be displaced by 100 keV electrons, they proposed that (oxygen) ion bombardment was responsible, and performed a critical experiment that supported their proposal. Using magnetic deflection, they separated the electrons from the much heavier ions, and observed that the defect clusters were formed at the point of impact of the ions. The opposite result was obtained, however, when this technique was employed in the present work on

V_6C_5. The damaged region in V_6C_5 was always associated with the electron beam, which is consistent with the proposal that the effect is, principally, due to electron bombardment.

3. The effect is not due to thermal disordering. Watanabe et al. (1962) have demonstrated that the temperature of a metallic foil increased by less than 100°C when it was bombarded with a beam of 100 keV electrons focussed to a 5μ spot at a current density of 2 amp/cm^2. The present experiments on vanadium carbide, which also exhibits metallic thermal conductivity, were performed at current densities between 0.5 amp/cm^2 and 1.4 amp/cm^2. Thus, the sample temperature should have been far below the order-disorder transformation temperature of 1250°C reported for this material by Hollox and Venables (1967).

4. The effect is not due to injection of carbon vacancies. Dobson et al. (1968) have observed that, under appropriate conditions, vacancies can be injected into specimens of aluminum alloys while they are under observation in the microscope. Thus, it might be argued that, if a specimen of V_6C_5 attained a sufficiently high temperature during bombardment, carbon atoms could unite with residual oxygen at the surface to form CO gas, possibly leaving behind a supply of vacancies sufficient to destroy the vacancy ordering in the lattice. It is observed, however, that when a previously disordered region of the sample is beam-heated in the microscope (by shutting off the second condenser lens, removing the condenser aperture and increasing the beam intensity), it re-orders at an extremely

rapid rate. This rapid (less than 1 sec.) disorder-to-order transformation† is inconsistent with the long range diffusion that would be required to eliminate injected vacancies. For example, calculations utilizing the self-diffusion coefficients reported by Torkar et al. (1966) for carbon in vanadium carbide indicate that 10 min. would be required for carbon atoms to diffuse into the 2μ diameter disordered region from the surrounding sample volume at 1250°C, the order-disorder temperature.

It is concluded, therefore, that the phenomenon illustrated in fig. 2 arises primarily because of the displacement of carbon atoms by the incident electrons, and a model for this disordering mechanism will be developed in the following section.

§4. A SIMPLE MODEL FOR THE DISORDERING

4.1. The Displacement Process

The structures of the ordered compounds V_6C_5 and V_8C_7 can be represented in a useful approximation as two interpenetrating fcc sub-lattices, one of which (the V-sublattice) is completely occupied by the vanadium atoms, whereas the other (the C-sublattice) is only partially occupied by the carbon atoms. In the C-sublattice, there are N sites per unit volume, of which the fraction r is occupied in the ordered compound

---

†This disorder-to-order transformation occurs at a temperature slightly below the order-disorder temperature, as is indicated by the fact that a slight additional increase in beam intensity, beyond the point at which the damaged region becomes ordered, causes the heated area to become disordered again. This temperature difference represents the degree to which the radiation damaged area is supercooled. Unfortunately, it was not possible to measure this temperature differential, because of the method used to heat the sample.

During these experiments it was demonstrated that the order-disorder transformation also is extremely rapid. Attempts to quench in the disordered state by rapidly deflecting the beam away from the heated area usually were unsuccessful.

and the fraction (1-r) is vacant (r = 5/6 for V_6C_5 and 7/8 for V_8C_7). Following a common convention, the sites that are occupied in the perfectly ordered compound will be designated the α sites, and the vacant sites will be designated β sites.

If the ordered compound has its stoichiometric composition, there will be rN carbon atoms per unit volume and (1-r)N vacant sites per unit volume in the C-sublattice. In the perfectly ordered state, all of the rN carbon atoms will be on the rN α sites, and all of the (1-r)N β sites will be vacant. Otherwise, there will be a smaller number, n_a, of carbon atoms per unit volume on the α sites, and the remainder, $n_b = rN-n_a$, will be distributed over the β sites.

When crystals of these materials are subjected to bombardment by energetic particles, some atoms may be displaced from their normal positions. To effect such displacements, however, the incident particles must deliver to the atoms an energy greater than some more or less well-defined threshold energy, E_d. The threshold energy is expected to have a value near 25 eV (Seitz and Koehler 1956), but in fact it varies from $\simeq$ 10 eV to $\simeq$ 30 eV in different materials (Dienes and Vineyard 1957). For example, Corbett et al. (1957) determined the value 22 $\pm$ 3 eV for copper, and Denney (1953) found a threshold energy of 27 eV for displacing Fe atoms in a Cu-Fe alloy. Thus, the threshold energy for displacing vanadium atoms in vanadium carbide is expected to be approximately 25 eV also. Consequently, if the bombarding particles are electrons, they must have energies in excess of 580 keV in

order to displace the vanadium atoms by direct collisions. At this incident energy, however, the relatively low mass of the carbon atoms allows some of them to receive as much as 110 eV from the electrons, and these carbon atoms in turn can transmit up to 65 eV to vanadium atoms in secondary collisions. Thus, the radiation damage caused by high energy electrons is expected to be a complex superposition of primary and secondary effects involving both kinds of atoms.

The problem is much simpler when the incident electrons have energies less than 220 keV, for then the vanadium atoms would not be displaced either by the incident electrons or by the most energetic primary displaced carbon atoms. It follows that only the C-sublattice will be disrupted by electrons having energies in the range employed in the present investigation (33 keV to 100 keV). Of course, the V-sublattice will absorb energy from the electron beam and thereby increase the temperature of the specimen, but otherwise it will remain unaffected. The vanadium atoms, however, will scatter the displaced carbon atoms, modifying their kinetic energies and terminal displacements.

If the threshold energy for displacing carbon atoms in vanadium carbide were also 25 eV, bombardment by electrons would be expected to cause little rearrangement of the atoms unless the incident energy were greater than 122 keV. However, the observations reported above indicate that the spots in the diffraction pattern that are associated with ordering in the C-sublattice become degraded at a significant rate during electron

bombardment at energies as low as 33 keV, which implies that the threshold energy for displacing carbon atoms must be less than 6.22 eV. To obtain a more quantitative estimate for the displacement energy, the experimental results have been analyzed according to the following simple model:

1. The elastic collisions between the incident electrons and the carbon atoms satisfy the relativistic Rutherford scattering relations to a good approximation (Seitz and Koehler 1956). Thus, the probability that a carbon atom receives an energy in the interval dE at E is proportional to E^{-2} for $E \leq E_m$, where

$$E_m = (4m_e/M_c)(1 + E_e/2m_e c^2)E_e, \quad \ldots\ldots\ldots \quad (1)$$

in which m_e and M_c are the masses of the electron and the carbon atom, respectively, and E_e is the energy of the incident electrons. The conditions employed in the electron microscope ensure that the energy of the bombarding electrons decreases by an insignificant fraction during their passage through the specimen. (For example, 51 keV electrons lose approximately 310 eV by electron-electron collisions in traversing a foil of V_6C_5 1000 Å in thickness.) Consequently, the distribution in initial energies of the carbon atoms also remains uniform throughout the foil.

2. The carbon atoms are assumed to lie in spherically symmetric potential wells of uniform depth, E_d, the same for both the α and the β sites. Thus, no carbon atom can be displaced unless it receives an energy greater than E_d from the incident electrons.

3. Those carbon atoms that receive energies $E_1 > E_d$ are displaced initially from their equilibrium positions into the forward cone bounded by the half angle $\psi = \pi/2 - \theta_m/2$, where $\sin^2(\theta_m/2) = E_d/E_m$. As will become evident later, the cone is somewhat restricted, ψ varying from approximately 59° for 100 keV electrons to 22° for 33 keV electrons. If only the portion $(E_1 - E_d)$ of the energy received by the carbon atoms from the incident electrons is available as kinetic energy of motion of the displaced atoms, their mean initial kinetic energy is $(\langle E_1 \rangle - E_d)$ where $\langle E_1 \rangle$ is given by

$$\langle E_1 \rangle / E_d = (1 + x_m) x_m^{-1} \ell n(1 + x_m), \quad \ldots\ldots\ldots \quad (2)$$

in which $x_m = (E_m - E_d)/E_d$. Because the energy of the bombarding electrons is rather small, $(\langle E_1 \rangle - E_d)/E_d < 1$ throughout the range of the present study. Moreover, the fraction of the displaced carbon atoms that receive kinetic energies greater than E_d also is small:

$$\left.\begin{aligned} n(E_1 > 2E_d)/n(E_1 > E_d) &= (x_m - 1)/2x_m, \quad x_m \geq 1, \\ &= 0 \qquad\qquad , \quad x_m < 1. \end{aligned}\right\} \quad \ldots \quad (3)$$

Thus, significant multiplication of the displaced carbon atoms by secondary collisions is expected to occur only near the upper limit of bombarding energies employed in this study. According to the analysis of Seitz and Koehler (1956), the multiplication factor, $\bar{\nu}$, obtained by averaging over

the initial energy distribution, has the value unity when the maximum energy received by the displaced atoms lies between E_d and twice this threshold energy. It increases slowly at higher energies, and attains a value near 1.15 at $x_m = 2.72$, which corresponds to bombardment by 100 keV electrons if the energy lost in collisions with the vanadium atoms is neglected.

4. The displaced carbon atoms undergo hard-sphere collisions with the neighboring atoms in their line of flight (Seitz and Koehler 1956). If the cone of initial displacements is sufficiently broad, the atoms will be scattered isotropically, losing on the average 0.31 of their energy in each collision with a vanadium atom and 0.5 of their energy in each collision with a carbon atom. The mean energy lost in the first of such collisions, $\langle \delta E_{1j} \rangle$, when averaged over the distribution of initial energies, is given by

$$(\langle \delta E_{1j} \rangle / E_d) = (C_j/2)[(1+x_m)x_m^{-1} \ell n(1+x_m) - (1+x_m)^{-1}], \quad \ldots\ldots (4)$$

where

$$C_j = C_c \equiv 1 \qquad \text{for collisions with C atoms,}$$

and

$$C_j = C_v \equiv 4\, M_c M_v (M_c + M_v)^{-2} = 0.618 \qquad \text{for collisions with V atoms,}$$

in which M_c and M_v are the masses of the carbon and vanadium atoms respectively. When the first collisions are with vanadium atoms, the mean energy loss is less than the excess over E_d of the initial mean energy, i.e.,

$$\frac{\langle \delta E_{1v} \rangle}{\langle E_1 \rangle - E_d} = \frac{(C_v/2)[(1+x_m)x_m^{-1} \ell n(1+x_m) - (1+x_m)^{-1}]}{[(1+x_m)x_m^{-1} \ell n(1+x_m) - 1]} < 1. \quad \ldots\ldots (5)$$

Thus, on the average, a primary displaced carbon atom can make at least one collision with a vanadium atom in the nearest neighbor shell before its energy falls below E_d. Most of the displaced carbon atoms, therefore, can penetrate beyond the nearest neighbor shell of vanadium atoms, and the resultant scattering will broaden the distribution of velocity vectors to encompass a greater fraction of the sites in the nearest neighbor shell of the C-sublattice than was accessible in the initial cone. This scattering will also change the distribution in energy of the displaced atoms as they approach the nearest neighbor shell of the C-sublattice, and the reduction in the mean energy will, in turn, decrease the probability of multiplication by subsequent collisions with carbon atoms.

The energy loss ratio for collisions with carbon atoms, $\langle \delta E_{1c} \rangle / (\langle E_1 \rangle - E_d)$, remains greater than unity throughout most of the range of energies employed in these studies, becoming less than unity only for $x_m \gtrsim 2.15$ ($E_e \gtrsim 85$ keV). The ratio decreases very slowly at higher energies, however, and only attains a value near 0.96 for $x_m = 2.72$, which corresponds to an incident electron energy of 100 keV if changes in the energy distribution caused by prior scattering from vanadium atoms are neglected. Accordingly, the displaced atoms are scattered strongly by the nearest neighbor shell of carbon atoms, and subsequent scattering by the second shell of vanadium atoms ensures that few of the displaced atoms reach the second shell of the C-sublattice. It follows, therefore, that the carbon atoms have a high probability of being permanently displaced only if a vacant site is accessible in the nearest neighbor shell of the C-sublattice.

5. The displaced carbon atoms are trapped at vacant sites within the C-sublattice, not at the tetrahedral interstitial positions within the metal sublattice. The latter possibility was investigated experimentally by comparing the intensities of the 111 and 222 sets of primary lattice spots, which are sensitive to the fraction of carbon atoms in the tetrahedral sites. It can be shown that the ratio of the intensity of the 111 spot to that of the 222 spot would increase if carbon atoms were transferred from octahedral to tetrahedral sites. In particular, this ratio would increase by the factor 1.59 if 1/4 of the carbon atoms were transferred, whereas no change would be expected from a simple redistribution within the octahedral sites. During the bombardment, the intensities of both 111 and 222 spots were found to increase significantly, as expected, but the ratio of their intensities remained constant within approximately 15%. It can be concluded, therefore, that at most a small fraction ($< 10\%$) of the displaced atoms are trapped at tetrahedral sites under the experimental conditions employed here. Studies have not yet been made to examine the stability of the tetrahedral sites under bombardment at low temperatures.

6. It is assumed that when a low-energy displaced atom approaches a vacant site in the C-sublattice it will be captured with equal likelihood whether the site belongs to the α- or the β- sublattice. Thus, a displaced atom has probabilities of being captured by α- and β- sites that depend only on the concentrations of the two kinds of sites accessible to it from

its initial position in the lattice. Two kinds of α sites can be distinguished in V_6C_5 according to the concentrations of β sites in the nearest neighbor shell of the C-sublattice: 3/5 of the α sites have 2 β sites among the 12 positions in this shell; the remaining 2/5 have 3 β sites. Thus, the fraction of β sites surrounding an α site has the average value $f_{\beta/\alpha} = 1/5$. Only one kind of β site can be distinguished on this basis, and it has only α sites in its nearest neighbor shell, i.e., $f_{\alpha/\beta} = 1$. (The corresponding fractions in V_8C_7 are $f_{\beta/\alpha} = 1/7$ and $f_{\alpha/\beta} = 1$.)

It will be assumed that these fractions represent the concentrations of α or β sites available to a displaced atom from the other kind of site regardless of the energy of the impinging electron beam or of its orientation relative to the crystallographic axes. At energies somewhat greater than those employed here, it appears probable that the range of the primary displaced carbon atoms will become sufficiently great that their probabilities of being captured by α and β sites will approach the average concentrations of the two kinds of sites in the carbon sublattice, i.e. $f_{\beta/\alpha} \rightarrow 1/6$ and $f_{\alpha/\beta} \rightarrow 5/6$ in V_6C_5; $f_{\beta/\alpha} \rightarrow 1/8$ and $f_{\alpha/\beta} \rightarrow 7/8$ in V_8C_7, under high energy electron bombardment. The behavior of the carbon atoms is more difficult to describe when they are displaced by low-energy bombarding electrons having energies near the threshold. It seems likely that under these circumstances the orientation of the beam may influence not only the distribution of α and β sites accessible to the displaced atom, but also the effective value of the energy required for displacement (Brown and Augustyniak 1959, Walker 1962). These complexities will not be considered

here. Instead, it will be assumed for simplicity that all of the sites in the nearest neighbor shell are equally accessible throughout the range of energies investigated, and that the displaced atoms reach the second shell of the C-sublattice in such small numbers that they have little effect on the fractions $f_{\alpha/\beta}$ and $f_{\beta/\alpha}$.

4.2. The Rate of Disordering

According to the above description, the rate of change of the number of carbon atoms on α sites is the difference between the rate of displacement from α to β sites that results from electron bombardment and the rate of the reverse displacements that occur when some of the β sites are occupied:

$$dn_a/dt = J\sigma_d\bar{\nu}[-f_1 n_a + f_2 n_b], \quad \ldots\ldots\ldots \quad (6)$$

where J is the incident electron flux (electrons/cm^2sec.);

σ_d is the cross-section for displacement of a carbon atom by the incident electrons, assumed to be the same for both α and β sites in both V_6C_5 and V_8C_7;

f_1 is the fraction of displacement collisions with atoms on α sites that result in transfer to β sites, $f_1 = f_{\beta/\alpha}(1-n_b/N_b)$;

f_2 is the fraction of displacement collisions with atoms on β sites that result in transfer to α sites, $f_2 = f_{\alpha/\beta}(1-n_a/N_a)$;

and $\bar{\nu}$ is the factor required to account for the multiplication that may occur if the primary displaced atom has an energy sufficient to effect a secondary displacement.

Equation (6) can be integrated directly to yield

$$p = n_a/rN = r + (1-r)\exp-(aJ\sigma_d\bar{\nu})t, \quad \ldots\ldots\ldots \quad (7)$$

if it is assumed that the crystal is perfectly ordered at t = 0. The coefficient a in the exponential has the value 6/5 for V_6C_5 and 8/7 for V_8C_7 if the displaced atoms have access only to the nearest neighbor shell of the C-sublattice, the limitation that is expected to prevail in the present study. At somewhat higher bombarding energies, a is expected to decrease gradually toward unity as the range of the primary displaced atoms approaches the radius of the second shell in the C-sublattice.

This result may be used to interpret the experimental observations of electron bombardment disordering, because the probability that an α site is occupied by a carbon atom, $p = n_a/rN$, is related in a simple manner to the measured intensity of a superlattice diffraction spot. According to the present model, the Bragg-Williams (1935) long-range order parameter, S, defined by the relation

$$S \equiv (p-r)/(1-r), \quad \ldots\ldots\ldots\ldots\ldots \quad (8)$$

assumes the simple form

$$S = \exp - (aJ\sigma_d\bar{\nu})t. \quad \ldots\ldots\ldots\ldots \quad (9)$$

On the other hand, the intensity, I, of a diffraction spot is proportional to the square of its structure factor, $|F(h,k,\ell)|^2$, and it can be shown quite readily that the structure factor of a superlattice diffraction spot from V_6C_5 or V_8C_7 is proportional to S:

$$|F(h,k,\ell)|_{S.L.} = Sf_c[A_\alpha^2 + B_\alpha^2]^{1/2}, \quad \ldots\ldots\ldots \quad (10)$$

where f_c is the atomic scattering factor for carbon,

$$\left.\begin{aligned} A_\alpha &= \Sigma \cos 2\pi(hx + ky + \ell z), \\ B_\alpha &= \Sigma \sin 2\pi(hx + ky + \ell z), \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (11)$$

and the summations extend over only the α sites of the C-sublattice. Thus, the variation in the intensity of one of these superlattice diffraction spots under electron bombardment is described by the relation

$$d\ell nI/dt = - 2aJ\sigma_d\bar{\nu}. \quad \ldots\ldots\ldots\ldots \quad (12)$$

The cross-section, σ_d, for displacing carbon atoms has been determined on this basis for several energies of the incident electrons, and the results are presented in the following section.

§5. RESULTS

The measured rates of decay in the intensity of a superlattice spot were employed in the relation (12) derived above to determine the cross-sections for displacement of carbon atoms in V_6C_5 at several energies of

the incident electrons. Figure 3 illustrates a typical result for 79.9 keV electrons. The plotted intensity is given in terms of the electron current diffracted from superlattice planes belonging to the form $(20\bar{2}0)$†, fig. 2. Corrections have been made for the background intensity, contributed by inelastically scattered electrons, by subtracting the residual current that remained after the supplemental spots had disappeared. The absolute value of the intensity at t = 0 is not particularly meaningful, because it depends on the thickness of the foil and on its precise orientation relative to the electron beam. The linearity of this plot is typical of results obtained throughout the study. Moreover, the slopes of similar plots were found to be accurately proportional to the electron flux, as predicted by (12).

By substituting the measured values for the slope, $d\ell nI/dt = 3.15 \times 10^{-3} sec^{-1}$, and flux, $J = 6.15 \times 10^{18}$ electrons/cm^2sec, and the calculated value of $\bar{\nu} = 1.05$ into (12), a displacement cross-section $\sigma_d = 203$ barns, was obtained from the data shown in fig. 3. This value of σ_d is plotted in fig. 4 with the other experimental values of the cross-section obtained from measurements at $E_e = 33.0$, 47.3, 79.9, and 100 keV. The experimental points are compared with theoretically derived curves of

---

†All quantitative measurements of the rate of disordering were obtained from superlattice spots of this type because the spots are well isolated from the primary pattern in the (110) foils (indices referred to cube axes) used for these experiments. The $20\bar{2}0$ spots are associated with domains having a $<11\bar{2}8>$ direction normal to the foil plane, thus the bombardment direction is $<11\bar{2}8>$ referred to the superlattice axes, or <110> referred to the cube axes.

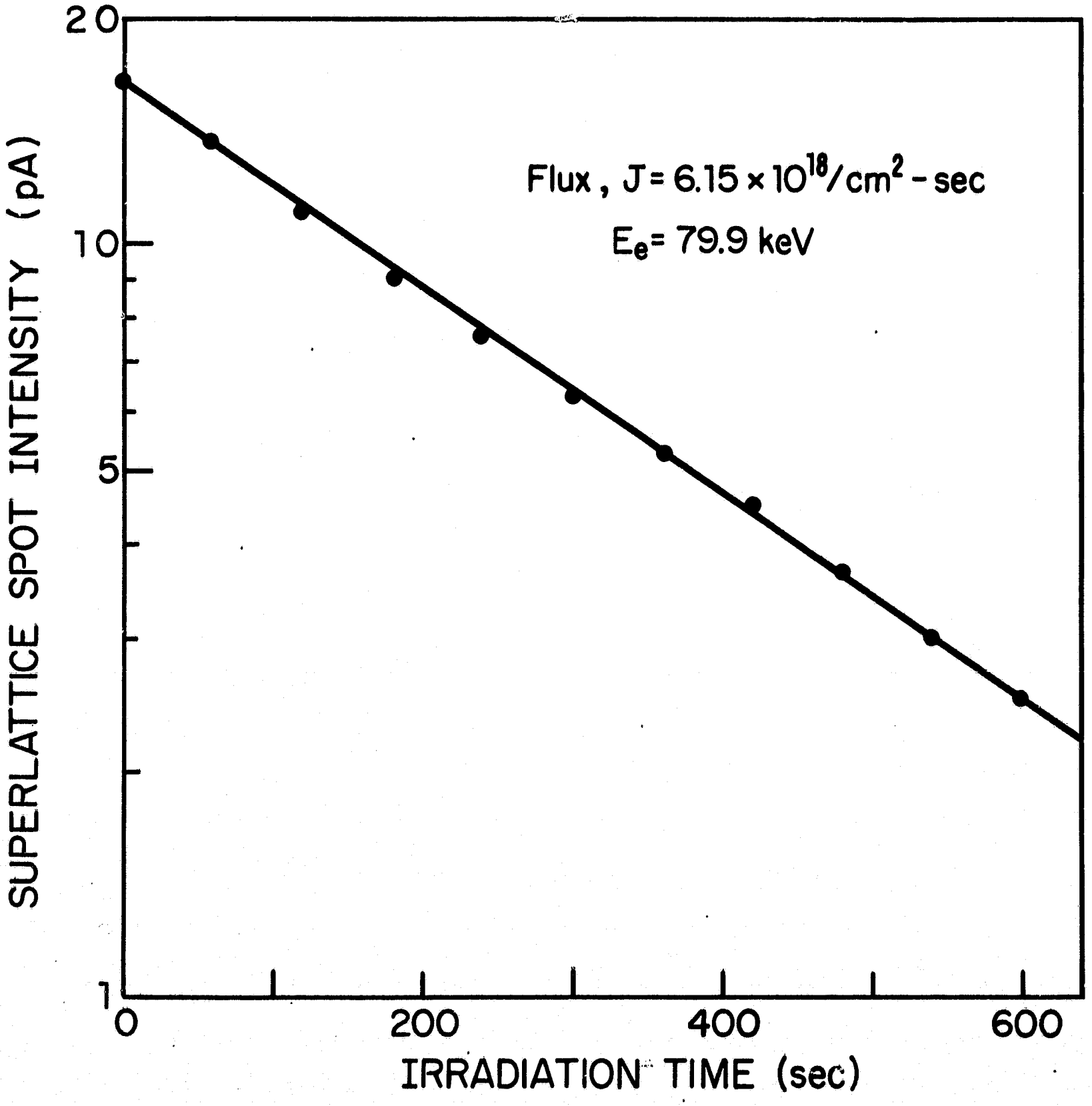
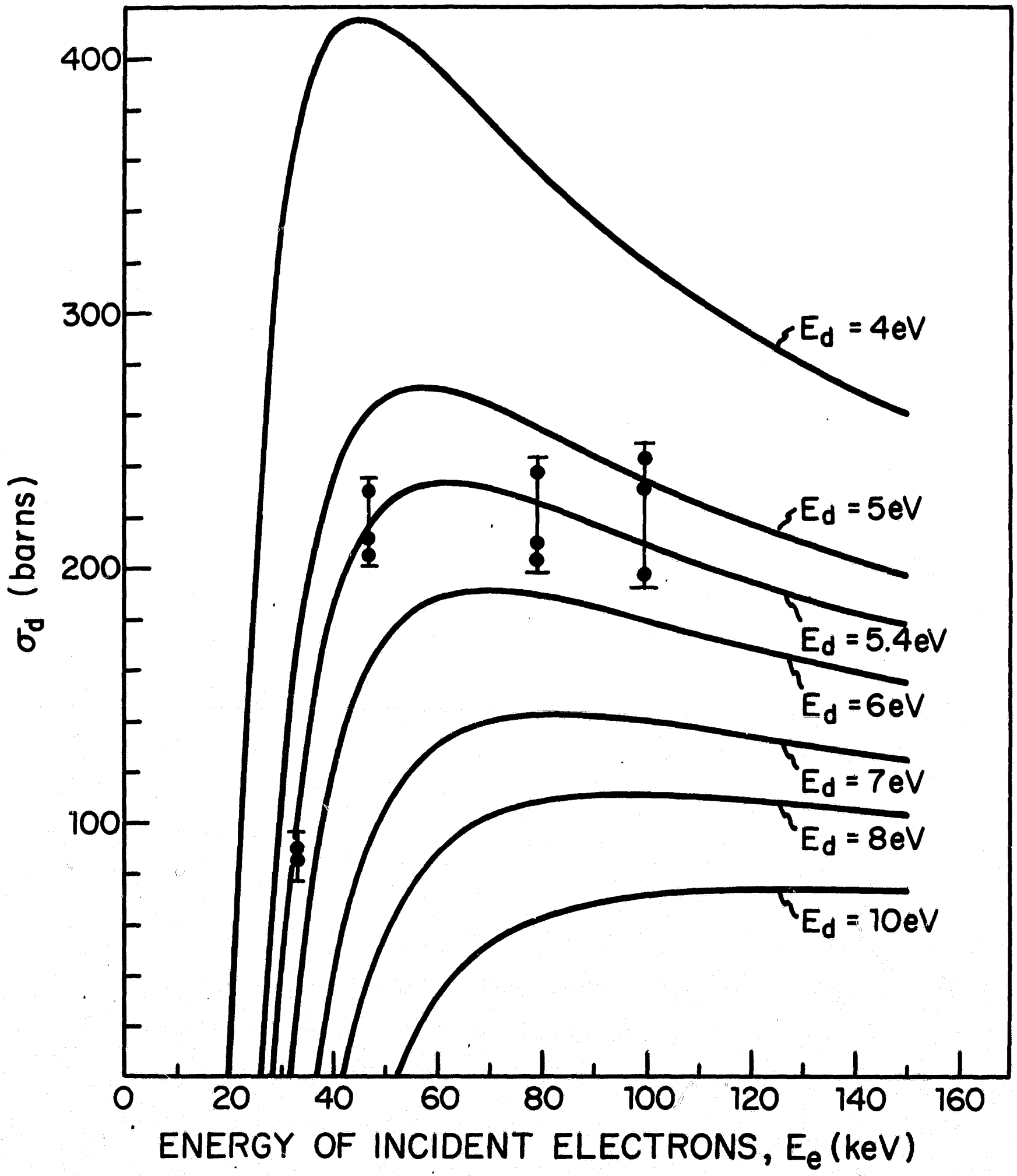


Fig. 3. Decay in intensity of a superlattice spot as a function of electron bombardment time. The intensity is given in terms of the current of electrons diffracted from superlattice planes belonging to the form $\{20\bar{2}0\}$. A displacement cross-section σ_d = 203 barns was calculated from this data as described in text.

Fig. 4. Theoretical curves of the displacement cross-section, σ_d, vs. incident electron energy, E_e, for several values of the parameter E_d. The data points are displacement cross-sections measured for V_6C_5 by means of radiation damage experiments in the electron microscope. The parameter of the curve providing the closest fit to the experimental points indicates that the energy required to displace a carbon atom in V_6C_5 is approximately 5.4 eV.


400
300
200
100
σ_d (barns)
E_d = 4eV
E_d = 5eV
E_d = 5.4eV
E_d = 6eV
E_d = 7eV
E_d = 8eV
E_d = 10eV
0
20
40
60
80
100
120
140
160
ENERGY OF INCIDENT ELECTRONS, E_e (keV)

σ_d *vs* E_e that were calculated for several values of the displacement energy parameter, E_d, from the formulae presented in a review article by Seitz and Koehler (1956). (The formulae were derived on the basis of a sharp cut-off model for atomic displacements, and include relativistic corrections to the classical Rutherford scattering.) The parameter of the curve providing the best fit to the experimental points indicates that, within the approximations discussed in §4, the energy required to displace a carbon atom in V_6C_5 is close to 5.4 eV.

§6. DISCUSSION

Rather good agreement is observed in fig. 4 between the shape of the theoretical curve for E_d = 5.4 eV and that defined by the measured values of σ_d. Two factors, however, may influence the result. i) If the threshold energy for displacing carbon atoms exhibits a pronounced angular dependence, which has been neglected here, it may modify the energy-dependence of the cross-section and change the effective value of the threshold for different bombarding energies. Such an effect may account for the small positive deviation from the calculated curve of the experimental points at 100 keV. If so, it suggests that a somewhat smaller value of E_d would be determined from comparable measurements made with the incident beam oriented along crystallographic directions other than the <110> employed here. (ii) The arguments presented above suggest that most of the displaced carbon atoms move to vacant sites in the nearest neighbor shell of the carbon sublattice, or return to their original sites.

Thus, the probabilities that the displaced atoms move to α or β sites are proportional to the relative numbers of the two kinds of sites in the nearest neighbor shell surrounding the original positions of the atoms. When the mean range of the displaced atoms exceeds the radius of this shell, however, or when the fraction of secondary displaced atoms becomes large, the probabilities become more nearly proportional to the average concentration of the two sites throughout the lattice. Whenever the latter circumstances apply, the values of σ_d obtained by the present analysis would be approximately 20% smaller than the correct values.

It should be noted that these two uncertainties in the values of σ_d have a rather small influence on the value of E_d inferred from the data, and they both suggest that the present estimate, E_d = 5.4 eV, is an upper limit to the threshold energy. Even so, this value is unexpectedly low in comparison with the values that have been reported in the literature for most other materials. Nevertheless, the result appears to be qualitatively consistent with current understanding of the refractory hard-metals. The principal components of the bonding in these materials appear to arise from interactions between occupied orbitals associated with the metal atoms (Lye and Logothetis 1966, Lye et al. 1968). These bonds are strengthened significantly by the potential of the carbon atoms in the region of overlap between the metal atom orbitals (Costa and Conte 1964). Conversely, the carbon-carbon and carbon-metal bonding associated with 2p-orbital interactions are weakened, because electrons are transferred from the 2p-state of the carbon atom to crystalline states derived from the d-orbitals of the transition metal atom.

According to this point of view, the energy required to displace a carbon atom is expected to be smaller in vanadium carbide than it is in graphite, whereas the energy required to displace a vanadium atom in the carbide is expected to be greater than it is in the metal. Support for this argument is provided by comparing the small value obtained for E_d in this study of V_6C_5 (5.4 eV) with the values reported for graphite: 25 eV, according to Eggen (c.f. tabulation given by Billington and Crawford (1961)), or 60 eV, according to Lucas and Mitchell (1964). Unfortunately, experimental data are not yet available to permit comparing the displacement energies for vanadium atoms, but indirect evidence is available from the partial molar heats of vaporization of the related carbides ZrC and NbC (Storms 1968). The heats of vaporization for the metal atoms in these compounds increase to values well above those for the pure metals as the carbon content is increased toward the stoichiometric concentration. The approximate proportionality between the heat of vaporization and the displacement energy obtained from elementary considerations (Seitz and Koehler 1956) suggests, therefore, that the displacement energy for the metal atom in these compounds is much greater than it is in the parent metals. Quantitative measurements of the displacement energy for the metal atoms in these compounds would appear to have considerable value for clarifying the nature of their bonding.

Finally, it seems reasonable to expect that the displacement energies for carbon and nitrogen in the actinide series compounds will have values comparable with that found here for V_6C_5. Thus, these compounds may

be rather more susceptible to radiation damage than had been anticipated previously, which suggests that quantitative investigations of the non-metal displacement energies in the actinide compounds also may have considerable value.

ACKNOWLEDGEMENTS

It is a pleasure to acknowledge the assistance provided by Dr. D. Kahn, who performed computer calculations for the relativistic Rutherford displacement cross-sections and for the electron diffraction structure factors. The electron microscope foils were prepared by Mr. M. Meyerhoff, who also provided capable assistance on other aspects of the work. The single-crystals employed in this study were grown by Mr. W. Precht. Thanks are due to Dr. J. P. Martin for various helpful comments, and to Dr. A.R.C. Westwood for his criticism and encouragement during the course of this work. Finally, the authors are grateful for financial support provided by NASA Research Division, Code RRM, Materials Research Branch, under Contract NASw-1290.

REFERENCES

BILLINGTON, D. S. and CRAWFORD, J. H., 1961, Radiation Damage in Solids (New Jersey: Princeton Univ. Press), p. 25.

BRAGG, W. L. and WILLIAMS, E. J., 1935, Proc. R. Soc. A, 151, 540.

BRANDON, D. G. and NUTTING, J., 1959, Acta metall., 7, 101.

BROWN, W. L. and AUGUSTYNIAK, W. M., 1959, J. appl. Phys., 30, 1300.

CORBETT, J. W., DENNEY, J. M., FISKE, M. D., and WALKER, R. M., 1957, Phys. Rev., 108, 954.

COSTA, P. and CONTE, R. R., 1964, in Nuclear Metallurgy Symposium, Vol. 10 (New York: Metallurgical Society of AIME), p. 3.

DENNEY, J. M., 1953, Phys. Rev., 92, 531.

De NOVION, C. H., LORENZELLI, R. and COSTA, P., 1966. C.r. hebd. Séanc. Acad. Sci., Paris, 263, 775.

DIENES, G. J. and VINEYARD, G. H., 1957, Radiation Effects in Solids (London: Interscience Publishers), p. 61.

DOBSON, P. S., KRITZINGER, S., and SMALLMAN, R. E., 1968, Phil. Mag., 17, 769.

HOLLOX, G. E. and VENABLES, J. D., 1967, Proc. Intl. Conf. on Strength of Metals and Alloys, Tokyo, in press.

LUCAS, M. W. and MITCHELL, E.W.J., 1964, Carbon 1, 345.

LYE, R. G., HOLLOX, G. E., and VENABLES, J. D., 1968, in Anisotropy in Single-Crystal Refractory Compounds, ed. Vahldiek, F. W. and Mersol S. A., Vol. 2, (New York: Plenum Press) p. 445.

LYE, R. G., and LOGOTHETIS, E. M., 1966, Phys. Rev., 147, 622.

NICHOLSON, R. B., THOMAS, G., and NUTTING, J., 1958, Brit. J. appl. Phys., 9, 25.

PASHLEY, D. W. and PRESLAND, A.E.B., 1961, Phil. Mag., 6, 1003.

PRECHT, W. P. and HOLLOX, G. E., 1968, J. Crystal Growth, to be published.

SEITZ, F. and KOEHLER, J. S., 1956, in Solid State Physics, ed. Seitz, F. and Turnbull, D., Vol. 2 (New York: Academic Press) p. 307ff.

STORMS, E. K., 1968, in Fundamentals of Refractory Compounds, ed. Hausner, H.H. and Bowman, M. G., (New York: Plenum Press) p. 90, and private communication.

TORKAR, K., OEL, H., and ILLIGEN, A., 1966, Berichte der Deutchen Keramischen Gesellshaft, 43, 162.

VENABLES, J. D., KAHN, D., and LYE, R. G., 1968, Phil. Mag., 18, 177.

WALKER, R. M., 1962 in Radiation Damage in Solids (New York: Academic Press) p. 594ff.

WATANABE, M., SOMEYA, T., and NAGAHAMA, Y., 1962, Fifth International Congress for Electron Microscopy. Paper A-8, 1 (New York: Academic Press).