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Effect of High Pressure on Self-Diffusion in Beta-Titanium† *

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Diffusion of Ti^{44} into β-titanium has been measured as a function of pressure at approximately 1000 °C using standard lathe-sectioning techniques. The diffusion coefficient is found to decrease with pressure, indicating a positive activation volume. This result contradicts earlier reports of negative activation volumes for diffusion of Fe in β-Ti and U in γ-U. The value obtained for the activation volume for self-diffusion in β-Ti is approximately 3.6 ± 1.0 cm^3/mole, corresponding to $\Delta V/V_M = 0.33 \pm 0.1$, where V_M is the molar volume. Comparison is made with atomic models and various proposed mechanisms for diffusion in the anomalous body-centered cubic (bcc) metals. The magnitude of ΔV appears to be too large to be consistent with the "extrinsic" vacancy mechanism of Kidson, but smaller than would normally be expected for simple vacancy diffusion in bcc metals. It is concluded that diffusion in β-titanium most probably proceeds via a combination of vacancy and short-dislocation-path diffusion, known as the Hart mechanism. Non-Gaussian penetration profiles were observed in some of the runs. This has been interpreted in terms of oxide holdup of the tracer at the surface and possible diffusion of the tracer as an oxide along dislocation pipes or grain boundaries near the surface prior to dissociation.

I. INTRODUCTION

A. General

Diffusion in metals has been investigated quite extensively over the past many years. Studies of both self- and impurity diffusion have shown that the diffusion coefficient quite accurately obeys the Arrhenius relation

$$D = D_0 e^{-Q/RT} , \tag{1}$$

where D is the diffusion coefficient, D_0 the frequency factor, Q the activation energy, R the gas constant, and T the absolute temperature.[1]

For most metallic systems, D_0 and Q are found to be independent of temperature over wide ranges of temperature.′ Furthermore, certain empirical relationships have been found which correlate these parameters for many different materials. These relationships are

$$Q = 34 T_m \text{ cal/mole (within about 20\%)} , \tag{2a}$$

$$D_0 = 1 \text{ cm}^2\text{/sec } (\times 10^{\pm 1}) , \tag{2b}$$

and

$$Q \simeq 16.5 L_m , \tag{2c}$$

where T_m is the absolute melting temperature and L_m is the latent heat of melting.[2] Because these relationships are found to be followed so nearly universally, this behavior has come to be regarded as "normal."

On the other hand, a small number of bcc metals, namely, β-Ti,[3,4] β-Zr,[5,6] β-Hf,[4,7] and γ-U,[8] are notable for their drastic violation of most or all of these "rules," and have come therefore to be known as the "anomalous" bcc metals. Thus β-Ti and β-Zr exhibit marked curvature in the Arrhenius plots for self- and impurity diffusion and all four of these materials have very low values of Q and D_0 by comparison with the semiempirical rules. The two previous studies of self-diffusion in β-Ti are shown in Fig. 1. It may be noted that the data of de Reca and Libanati may be fitted with a straight line within the accuracy of the experimental points. One other bcc metal, vanadium, may perhaps be included in the "anomalous" group, since it apparently exhibits a two-slope Arrhenius plot rather than being continuously curving.[9] The values of Q and D_0 for the low-temperature region of V are in the normal range, however, whereas the high-temperature values are significantly larger.

In addition to departure from the semiempirical rules, there are several other features of diffusion in the anomalous bcc metals which may be regarded as anomalous. First, the absolute value of the self-diffusion coefficients, considered on a relative temperature scale, ranges from one to three orders of magnitude larger than what is observed in normal metals.[10] Second, the range of values of diffusivity for various impurities in β-Ti and γ-U is quite large, as much as a factor of 10^3.[8,11] In normal metals this range seldom exceeds a factor of 10.

A third additional apparent anomaly in these metals is found in the pressure dependence of diffusion reported for self-diffusion in γ-U[12] and impurity diffusion of Fe in β-Ti.[13] In both of these cases, D's were reported to increase initially with pressure, although in γ-U, D was found to decrease with pressure above 4 kbar. Attempts have been made to interpret the apparent negative activation volume

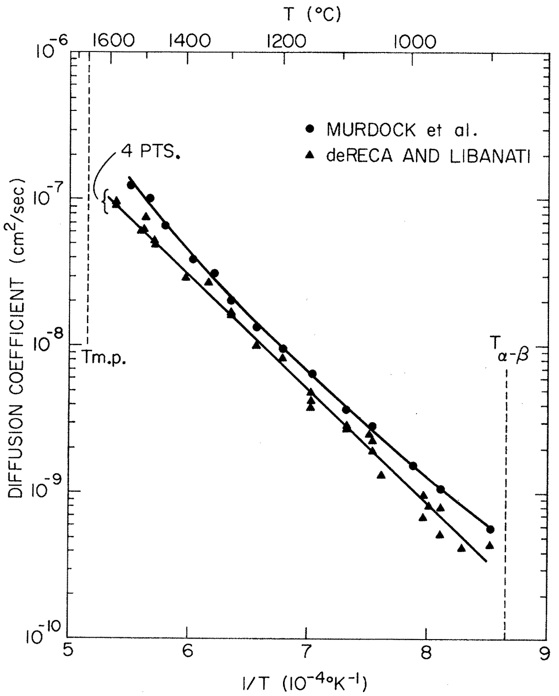

FIG. 1. Self-diffusion in β-Ti. Circles: Murdock, Lundy, and Stansbury, Ref. 3; triangles: de Reca and Libanati, Ref. 4.

obtained in these two studies in terms of supposed variation of the elastic constants.[14] However, the technical difficulties involved in these pressure experiments make it seem hardly justifiable to take the results so seriously. It was shown, for instance, that grain boundary effects in polycrystalline Ag may cause an initial increase of D with pressure,[12] although Lazarus has suggested that both of these results (γ-U and Ag) may be caused by impurities in the Ar gas used as a pressure medium.[15] The situation is further complicated by a reported time dependence of the measured D values for short times.[12,16] The fact that the Fe-in-Ti pressure study was for anneal times of only 30–60 min thus makes that result subject to serious question. An important purpose of the present experiment was to resolve, if possible, the question of the supposed anomalous pressure dependence of D.

Several different theories have been advanced to explain the diffusion behavior in the anomalous bcc metals. A single temperature-dependent activation energy would explain the curved Arrhenius plots, but would fail to account for the several other aspects of anomalous diffusion, and is further discounted by the Zr thermomigration and electromigration results of Campbell and Huntington.[17] Other theories, based on the assumption of two competing mechanisms, have been concerned with specifying the mechanisms supposed to be dominant in the high- and low-temperature regions. Kidson[18] proposed that the usual vacancy mechanism is operative at high temperature, but that at low temperatures, diffusion is dominated by "extrinsic" vacancies introduced by gaseous impurities in the lattice. The high concentration of dissolved O_2 and N_2 required to explain the magnitude of D, the high vacancy-impurity binding energy needed to explain the low Q's, coupled with negative results of an environmental study conducted by Askill,[19] tend to discount this "intrinsic-extrinsic" model.

Grain boundary or dislocation enhancement at low temperatures has also been suggested as the second mechanism. A high density of short interpenetrating dislocations would be required to account for the observed Gaussian penetration profiles, with diffusion presumably proceeding via the so-called Hart mechanism.[20] The dislocation density deduced from the curved Arrhenius plots depends largely on the assumptions made in fitting to the sum of exponentials.[21,22] However, it is possible that a moderately high dislocation density could be "locked in" in these metals by impurities which are impossible to remove completely. The fact that the α phases of Ti, Zr, and Hf also give low values of D_0 and Q seems to lend support to this possibility.[23]

Peart and Askill[24] have proposed that vacancies and divacancies are competing mechanisms for all metals, and have applied this theory to explain the vanadium results. This model would require that vacancies be responsible for diffusion at low temperatures. However in Ti and Zr, where the low-temperature values of Q and D_0 are so much lower than expected for normal vacancies, this is not a particularly satisfactory explanation.

Experimentally, diffusion mechanisms may be inferred from a few key experiments.[25] (a) The Simmons-Balluffi-type experiment[26] determines the net defect concentration at high temperatures and allows one to deduce the dominant type of defect. (b) The observation that an initially inhomogeneous specimen may be homogenized by annealing at high temperatures implies the operation of a bulk diffusion mechanism. (c) Observation of a Kirkendall effect shows that the bulk diffusion involves defects such as vacancies or interstitialcies, that can be created or annihilated locally in the lattice. (d) The isotope effect reveals the degree of nontracer atom participation in the jump process and, in fcc metals, substantiates the single-vacancy mechanism. (e) The activation volume obtained from the pressure dependence of diffusion determines the degree of relaxation around lattice defects.

In fcc metals, diffusion has been shown to proceed via the vacancy mechanism on the basis of consistency of all or most of the observations listed above. Of the bcc metals, only sodium has been studied by all of the above experiments.[27-29] In that case it is thought that self-diffusion occurs by a very relaxed vacancy mechanism. In the bcc transition metals, including the anomalous metals, only experiments (b) and (c) have been performed. Thus, while a vacancy mechanism is a strong possibility, it is by no means firmly established. The hope of the present experiment was to determine ΔV for one of the anomalous metals, β-Ti, and hence hopefully to further elucidate the diffusion mechanism in these metals.

B. Activation Volume

The activation volume for diffusion, ΔV, is defined from the Gibbs free energy of formation and motion of defects[30]:

$$\Delta V = \left(\frac{\partial \Delta G}{\partial P}\right)_T \tag{3a}$$

$$= \Delta V_F + \Delta V_m \tag{3b}$$

$$= -RT\left(\frac{\partial \ln D}{\partial P}\right)_T + RT\left(\frac{\partial \ln \gamma a^2 \nu f}{\partial P}\right)_T . \tag{3c}$$

In most fcc metals, ΔV for self-diffusion is found to lie between 0.65 and $0.90 V_m$,[31–35] where V_m is the molar volume. Thus in fcc metals, which are known to diffuse via the vacancy mechanism, there is evidence of considerable relaxation around the vacancies. In bcc metals, measured values of the ratio $\Delta V/V_m$ are about 0.5 ± 0.1,[29,36,37] which is evidence of even greater relaxation about the defect (vacancy).

If diffusion in titanium is via a relaxed vacancy mechanism, as is found for other bcc metals, $\Delta V/V_m$ should be about 0.5. If it is via extrinsic vacancies, as originally proposed by Kidson, only the motional term should enter, and the measured ΔV is expected to be small, $\Delta V_{\text{ext}} \simeq 0.1 V_M$.[38] For diffusion along grain boundaries or dislocations where less work must be done for an atom to migrate, the measured activation volume should be slightly less than the vacancy migration volume: $\Delta V_{\text{dis}} = \Delta V_{\text{gb}} \lesssim \Delta V_m \lesssim 0.1 V_M$.

Hart[20] has shown that when diffusion is through bulk plus short interpenetrating dislocation paths, Gaussian penetration profiles result and an effective D value is obtained which is given by

$$D_{\text{eff}} = g\langle l^2\rangle_{\text{av}}/2\tau + (1-g)D_v , \tag{4}$$

where $\langle l^2\rangle_{\text{av}}$ is the mean-square projected distance over which an atom migrates along a dislocation in a mean-stay time τ, and g is the fraction of the time an atom spends in a dislocation or, equivalently, the fraction of all atoms which are "in dislocations." Writing $\langle l^2\rangle_{\text{av}}/2\tau = D_d$, we may evaluate the pressure dependence of D_{eff} and obtain

$$\Delta V_{\text{eff}} = \frac{D_v}{D_{\text{eff}}}\,\Delta V_v + \frac{gD_d}{D_{\text{eff}}}\,\Delta V_d - RT\,\frac{gD_d}{D_{\text{eff}}}\,\frac{\partial \ln g}{\partial P} , \tag{5}$$

since $D_d \gg D_v$.

The magnitude of the enhancement factor gD_d/D_{eff} will then determine the value of ΔV_{eff}. The last term of Eq. (5) is expected to be negligible, since it would seem, qualitatively, that so long as the specimen environment remains perfectly hydrostatic, the dislocation density *per se* should not vary with pressure, although the actual value of g may vary randomly from sample to sample. The measured value of ΔV_{eff} may then also give a rough indication of the size of the enhancement factor gD_d/D_{eff} by comparing ΔV_{eff} with predicted values of ΔV_v and ΔV_d.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

A. High-Pressure Equipment

The high-pressure diffusion runs were carried out using an internally heated pressure vessel which was allowed to heat during the run to help limit the furnace power requirements. Thermocouple and power leads were brought out through frozen-oil seals. The thermocouple reference junction was within the pressurized region, with chromel wires used as extension leads for the Pt|Pt-10% Rh thermocouple wires. The chromel wires were brought through the frozen-oil seals and connected inside a thermal-free brass box to lengths of coaxial cable, the outer conductors of which were used as part of the potentiometer guard circuit.

Standard gas high-pressure generating equipment was employed, consisting of an Autoclave separator and Harwood intensifier. Pressures were measured on a Heise 100 000-psi bourdon gauge whose linearity and absolute calibration were checked against a manganin gauge (based on previous calibration of wire from the same spool against the freezing point of mercury[39]). High-purity argon gas was used as the pressure medium, with helium used for leak detecting.

The furnace was made from Alsimag 222 or 997 alumina parts. The latter were found to be superior in their strength and ability to resist thermal and pressure shocks. For the first series of diffusion runs at 1000 °C, the Alsimag furnace core was wound uniformly, 12 turns per in., with 0.020-in. Pt-10% Rh thermocouple-resistance wire. The Pt|Pt-10% Rh thermocouple bead was positioned so that it was touching an 0.050-in. Ti cap placed over the active face of the specimen (discussed in more detail below). It was subsequently found that quite sizeable temperature gradients existed inside the furnace with this configuration, resulting in a pressure-dependent error in reading the sample temperature.

Using a differential thermocouple arrangement, the temperature difference between inside and outside the sample was determined along the axis of the furnace. Differences of as much as 10 °C were found at 1000 °C at low pressures. The difference decreased rapidly with pressure, however, so that above about 2 kbar the difference was 2 °C or less. Part of the temperature error arises from the fact that the center of the metal sample reaches a higher mean temperature than a parallel point along the axis of the ceramic furnace parts. In addition, because the thermocouple wires were brought out through a steep temperature gradient, some heat flow down the wires results, causing a drop in the actual temperature of the thermocouple bead. The measurements made with the differential thermocouple arrangement probably do not reveal the full extent of the gradients actually in existence during a diffusion run, since, with the differential arrangement, some heat from inside the sample is conducted out to the second junction, raising its temperature. Thus, temperature errors as large as 10–15 °C might be expected at low pressures with this configuration.

The longitudinal temperature gradients along the axis of the furnace can be greatly reduced by winding the core nonuniformly. This was accomplished using a uniformly grooved core, but with a few turns of smaller-diameter wire at the ends of the winding. This procedure gave a temperature distribution which was essentially flat over the central 2–3 in. of the $5\frac{1}{4}$-in.-long winding. Gradients measured in the nonuniformly wound furnace with the differential thermocouple arrangement were found to be greatly reduced and became negligible above 1 kbar.

Because of the problem caused by the temperature gradients, it was evident that the thermocouple should be embedded inside the metal sample or a dummy in order to read the correct sample temperature. Because it was necessary to use separate thermocouples for the controller and potentiometer, the design finally used was a sandwich thermocouple arrangement with two separate Pt|Pt-10% Rh thermocouples spot welded to a Pt foil disk, measuring over crossed portions of the disk. The disk thermocouple setup was then sandwiched between the Ti sample and a Ni dummy, with the four leads brought through the Ni inside four-hole alumina tubing. (Calibration of these working couples after the completion of the series-II diffusion runs showed a possible gradient and/or calibration offset in this arrangement. Apparently any calibration offset occurred during the first 2–3 h at 1000 °C, however, so that subsequent runs after the first would still be at the same relative temperatures.)

The effect of pressure on the thermocouple emf was also taken into account. Measurements by Hanneman and Strong[40] yielded a value of $\partial T_{PR}/\partial P = 0.96$ °C/kbar for Pt|Pt-10% Rh couples at 1000 °C and pressures below 10 kbar, while measurements by Getting and Kennedy[41] gave a value of 0.52 °C/kbar at 1000 °C. Both of these measurements employed somewhat indirect measurements of the pressure effect, using solid-media high-pressure systems with the thermoelements brought out through the pressure seals. Dickerson,[42] in this laboratory, has made direct measurements of the emf difference between two Pt|Pt-10% Rh couples, one under pressure and the other not, using the thermoelectric power apparatus of Bourassa *et al.*[43] Extrapolating Dickerson's data to 1000 °C from 800 °C (the highest temperature successfully run), a value of $\partial T_{PR}/\partial P = (0.50 \pm 0.05)$ °C/kbar is obtained. Since Dickerson's experimental setup most closely resembles that of the present diffusion runs, the value of $\partial T_{PR}/\partial P$ from Dickerson's work has been used. The sign of the correction indicates that the true temperature is higher by $0.5P$, where P is in kbar, than read from the thermocouple table.

B. Sample Preparation

The titanium used for the first series of diffusion runs was from a bar of iodide Ti (99.99%—not including gases), which was zone refined by the Materials Research Corp. The second series used titanium purchased from MRC in the form of a $\frac{3}{8}$-in.-diam rod of triple-zone-refined Ti (99.97%). Specimens $\frac{3}{8} \times \frac{1}{2}$ in. were spark cut from the rod. The specimens were readily machinable with specially shaped Vasco Supreme lathe tools after most runs, indicating a minimal pickup of interstitial gases during the runs, although it was frequently necessary to resharpen the tool after the first few sections. (Specimens diffused during one or two runs were much harder, however, and could be sectioned only with tungsten carbide or diamond-tipped lathe tools.)

After being spark cut, the specimens were hand polished through 4/0 emery paper and etched in $HF:HNO_3:H_2O = 1:1:10$ acid solution. The isotope[44] was applied to the polished specimen face by drying under a heat lamp after first neutralizing the acid solution with NH_4OH. (The resulting NH_4F and NH_4Cl salts sublime below 500 °C, and hence did not interfere with the diffusion.) As a reliability check, two or three runs were made with the isotope dried directly onto the face, but with the drying accomplished by blowing a stream of cool dry air onto the specimen face. No systematic variation of the measured D values with drying method was found.

Attempts at electroplating the Ti^{44} proved completely unsuccessful. A saturated ammonium oxalate solution, which is useful for many other tracers, gave no electrodeposition of Ti^{44}. A similar result was obtained using dimethyl sulfoxide, which reportedly has been used for this purpose by Libanati and Dyment.[23] In a private communication, Dyment related that the electroplating technique worked only when the tracer was in the chloride form, and would not work from the fluoride.[45] Since the tracer used in the present work was in the form of fluoride and chloride, no electroplating was achieved.

C. Run Procedure

The Ti specimen was enclosed in a capsule made from three layers of 0.001-in. Ti foil wrapped tightly onto the end of one of the furnace plugs. A 0.050-in.-thick cap machined from Ti, having an 0.015-in. recess where it faced the plated end of the specimen, was spot welded into the end of the Ti foil sleeve. The specimen was inserted plated face down into this capsule and pushed tight against the end cap. The entire capsule assembly was then fitted onto the end of one furnace plug, which served to move the sample in and out of the furnace. The thermocouple bead was simply pushed up against the sample assembly in the first series of runs. In the second series, the sample assembly was positioned snugly against the Pt disk thermocouple, forming a sandwich with Pt between Ni and Ti. The Ti capsule served to "getter" any residual gas and/or carbon impurities and allowed the specimen itself to remain relatively clean during the run.

Before beginning a run, the pressure was built up in the bomb and the system carefully checked for leaks. Only very small leaks could be safely tolerated in this experiment, since the pressure had to be maintained constant for 5–10 h, and, in addition, gas leaking out had to be immediately replaced by fresh gas. Contamination, in the form of carbon in the oil, which frequently got into the gas from the separator, and oxygen from the compressed gas tanks or from back diffusion into the bomb from the air, caused blackening of both the alumina furnace parts and the Ti capsule (and sometimes the specimen itself). It was therefore essential that the gas be maintained, as nearly as possible, perfectly clean—free from oil and atmospheric contaminants—and that all leaks be eliminated before beginning a run.

After it was determined that pressure could be maintained, the temperature in the furnace was increased. As the temperature increased, the pressure increased, so that it was necessary to lower the intensifier simultaneously to maintain a constant pressure during warmup. The temperature was stabilized at around 800–850 °C for a few minutes before the final warmup through the α-β phase transformation (882 °C) to the anneal temperature. The anneal time was corrected for the time above 882 °C only, since $D(\alpha \text{ phase}) \ll D(\beta \text{ phase})$ at the transformation.[4] Standard warmup time corrections were then applied.

For the first series of diffusion runs, the temperature was controlled manually using a Variac and series rheostat to provide fine control. The temperature was measured on an L & N K-3 potentiometer and null detector, and the control was done by observing deflections on the null detector. Control of the furnace temperature was generally better than ± 1 °C.

For the second series of diffusion runs, a Thermac TC-5192 solid-state temperature controller was used to control the temperature. One thermocouple of the sandwich-couple pair was used for control and the other was used for precise measurement of temperature on the potentiometer. This arrangement was necessary to avoid interaction between controller and potentiometer which resulted when a common thermocouple was used.

Standard lathe-sectioning techniques were employed for sectioning the specimens following the diffusion anneal.[46] A specially designed tool bit, made of Vasco Supreme vanadium steel, was made to give optimal quality chips. One run had to be sectioned with a diamond tool when it was too hard even for the Supreme tool.

III. RESULTS

The high-pressure Ti diffusion runs may conveniently be discussed in groups according to the nominal temperature at which the series was run. The first series was run at 1000 °C apparent thermocouple temperature, using the Alsimag furnace assembly, uniformly wound furnace core, manual temperature control, and the zone-refined Ti. Series II was run nominally at 1007 °C, with the alumina furnace, nonuniformly wound core, Thermac temperature controller, and the MRC triple-zone-refined Ti.

A. First Series

The results obtained during the first series of runs are shown in Fig. 2 and summarized in Table I. The sample-number designation is simply the order in which the sample was run. Certain of the specimens in the first series were used twice, with the back side used for the second run. These are designated by the numbers in parentheses. [For example, I-11(4B) means the back side of sample 4 was used for series I, run 11.]

The penetration plots for some of the samples deviate from a perfect Gaussian behavior. Others are linear on a plot of log(concentration) vs x^2 over two or more decades of activity. Since this feature is common to both series, a full discussion will be deferred until after the second-series data are discussed. The diffusion coefficients given in Table I correspond to the best fit of the penetration plots to Gaussian profiles.

The variation with pressure at 1000 °C of the diffusion coefficients of series I is shown in Fig. 3.

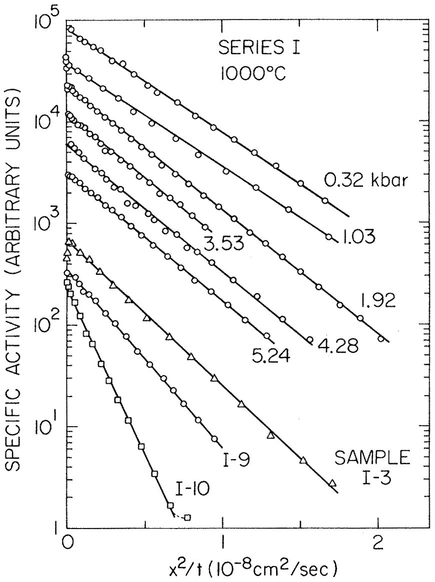

FIG. 2. Penetration profiles for diffusion of Ti^{44} into β-Ti for series I at approximately 1000 °C.

Those runs where large experimental uncertainties were encountered have not been included in this plot. The error bars represent the rms error in the slope determination. One prominent feature seen in this figure is the high D values at $P \leq 1$ kbar compared to the higher-pressure values. This is seen qualitatively to be caused by the pressure-dependent temperature error discussed in Sec. II. If the points at 0.32 and 1.03 kbar are corrected by 10 and 7 °C, respectively, corresponding to a slightly larger correction than found using the differential thermocouple arrangement, the points marked by triangles in Fig. 3 are obtained. A least-squares analysis gives an activation volume of $3.2 \pm 0.7\ \text{cm}^3/\text{mole}$.

B. Second Series

The results of the second series of Ti diffusion runs are shown in Fig. 4 and Table II. Sample II-2 was cycled eight times through the phase transformation prior to the diffusion anneal, due to repeated overloading of the 20-A circuit breaker. A special 40-A line was finally installed to provide the high currents needed by the temperature controller. Sample II-3 had a somewhat concave surface after the diffusion anneal, resulting in some uncertainty in the proper reference plane for the sectioning. A two-step source solution was tried as a first approximation to the actual surface. Such a correction gave a slight change of slope (D decreased by approximately 5%), but the break in the Gaussian was not removed. The value given in the table is from the raw data, uncorrected.

TABLE I. Diffusion coefficients for series I.

Sample	P (kbar)	T_{TC} (°C)	T_{corr} (°C)	t_{eff} (10^4 sec)	D_{meas} ($10^{-9}\text{cm}^2/\text{sec}$)	D_{1000} ($10^{-9}\text{cm}^2/\text{sec}$)
I-4	1.03	1000	1000.5[a]	1.810	1.06	1.055[a]
I-5	0.32	1000	1000.2[a]	1.298	1.062	1.059[a]
I-6	4.28	1000	1002.1	1.835	0.863	0.845
I-7	3.53	1000	1001.8	2.819	0.862	0.846
I-11(4B)	5.24	1000	1002.6	1.889	0.864	0.841
I-12(5B)	1.92	1000	1001.0	2.191	0.886	0.877

[a] Not including error caused by temperature gradient.

Run II-4 showed the most dramatic break in penetration plot of any of the samples in either series. The only difference between this and other runs was the time of the anneal, which was only 3 h rather than 5 or more (caused by another blown fuse). Whether the shorter anneal time could produce such a break is not fully understood. As a check, another sample was run at 5 kbar for 10 h. This sample was so hard, because of impurities absorbed during the anneal, that it had to be sectioned with a diamond lathe tool. The result, subject to some uncertainty due to impurities, does not show as large a break as the 3-h run, but does show some tracer hold up near the surface. The linear portion of this curve extends over two decades of activity, however.

The pressure variation of the series-II diffusion coefficients is shown in Fig. 5. The error bars indicate the approximate range of values for "near" and "far" regions of the curved penetration plots, whereas the points represent best fits to a Gauss-

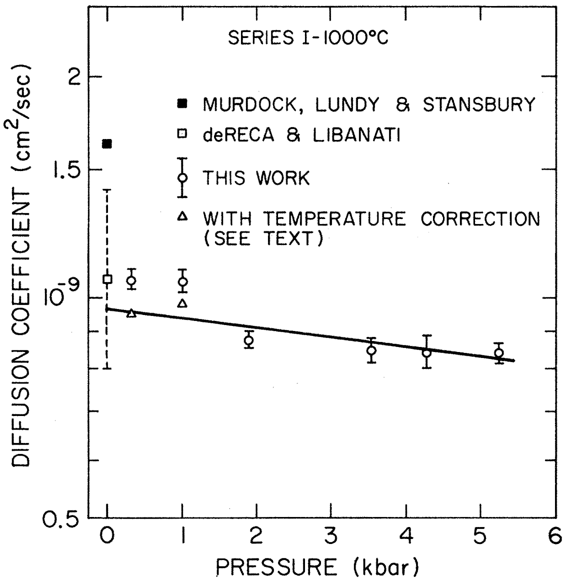

FIG. 3. Diffusion coefficient vs pressure for series I at 1000 °C. The circles represent the best fit to Gaussian penetration profiles and the flags are rms deviation plus 2 °C temperature uncertainty. Filled square, Ref. 3; open square, Ref. 4.

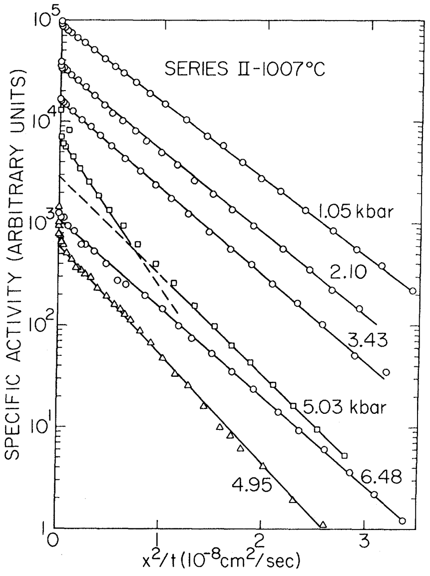

FIG. 4. Penetration profiles for diffusion of Ti^{44} into β-Ti for series II at nominally 1007°C.

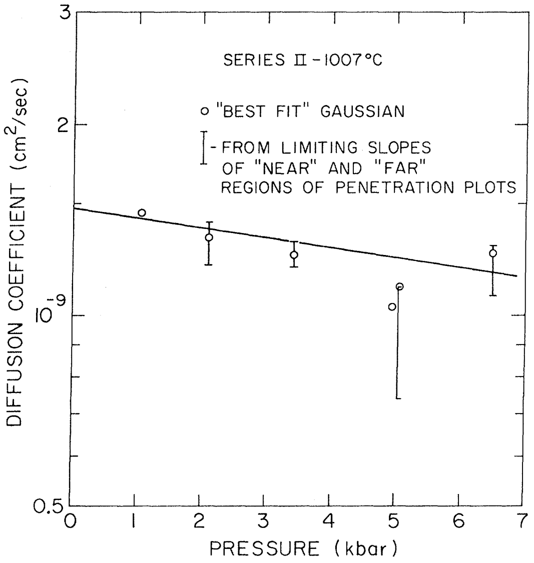

FIG. 5. Diffusion coefficient vs pressure for series II at 1007°C. The points represent best fits to Gaussian profiles and the flags give the approximate range of initial and limiting slopes.

ian. The activation volume calculated by the method of least squares from these data is 3.9 ± 1.8 cm³/mole. The "far" part of run II-4 has been used, and run II-7 has not been used in computing ΔV because of the obviously high impurity level in the latter sample.

Taking a weighted average of the two values for the activation volume determined in the two series, an average value of $\Delta V = 3.5 \pm 1.0$ cm³/mole is obtained. (The indicated error limits do not take account of possible systematic temperature errors beyond those discussed earlier.) The molar volume of titanium at room temperature and atmospheric pressure is 10.6 cm³/mole. Thus, $\Delta V/V_M = 0.33 \pm 0.09$ cm³/mole.

A correction term should be included in calculating ΔV.[47] Since the sectioning and counting procedures are carried out at room temperature, the D value actually determined is related to the value at high-pressure and high-temperature conditions by

$$D'(T,P)/a_0^2 = D(T,P)/a^2(T,P), \qquad (6)$$

where $D'(T,P)$ is the value actually measured and a_0 is the room temperature and pressure lattice constant. Substituting this relation into the expression for the activation volume, Eq. (3c), we have

$$\Delta V = -RT\frac{\partial \ln D'}{\partial P} + RT\frac{\partial \ln \gamma a_0^2 \nu f}{\partial P}. \qquad (7)$$

Now, since a_0 is a constant, the correction term is simply $RT\partial \ln\nu/\partial P$; ν is a vibrational frequency, of the order of the Debye frequency, so we may take

$$\frac{\partial \ln\nu}{\partial P} = \frac{\partial \ln\nu}{\partial \ln V}\,\frac{\partial \ln V}{\partial P} = (-\gamma_G)(-K_T),$$

TABLE II. Diffusion coefficients for series II.

Sample	P (kbar)	T_{TC} (°C)	T_{corr} (°C)	t_{eff} (10^4 sec)	D_{meas} (10^{-9} cm²/sec)	D_{1007} (10^{-9} cm²/sec)
II-2[a]	3.43	1006.3	1008.0	1.607	1.26	1.247
II-3[b]	2.10	1006.0	1007.1	1.890	1.33	1.329
II-4[c]	5.03	1004.5	1007.0	1.073	(0.74–1.11)	(1.11)
II-5	1.05	1005.8	1006.3	1.805	1.434	1.444
II-6	6.48	1003.5	1006.8	1.832	1.252	1.255
II-7[d]	4.95	1002.5	1005.0	3.65	1.012	1.032

[a] Went eight times through phase transformation prior to anneal.

[b] Sample had slightly concave face before sectioning.

[c] Has pronounced break in pentration profile—only deep part used to calculate ΔV.

[d] Specimen had to be sectioned with diamond tool—not used to calculate ΔV.

where γ_G is the Grüneisen constant and K_T is the isothermal compressibility. Thus,

$$\Delta V = -RT\,\frac{\partial \ln D'}{\partial P} + RT\gamma_G K_T \;. \qquad (8)$$

From the elastic constants measurements of Fisher and Dever,[48] the compressibility of β-Ti at 1000 °C is approximately 1.10×10^{-3} kbar^{-1}. The Grüneisen constant for β-Ti is approximately 1.04, based on the Grüneisen relation[49] $\alpha = \gamma_G C_V K_T / 3V$, and taking $C_V = 8.28$ cal/mole °K $(= C_p - 9\alpha^2 VT/K_T)$,[50,51] $\alpha = 12\times10^{-6}\,{}^\circ\text{C}^{-1}$,[52] and $V = 10.9$ cm^3/mole (at 1000 °C, taking $a = 3.308$ Å).[52] The correction factor then is $RTK_T\gamma_G = 0.12$ cm^3/mole. The final value for the activation volume thus is $\Delta V = 3.6 \pm 1.0$ cm^3/mole. Using the high-temperature molar volume 10.9 cm^3/mole gives the ratio $\Delta V/V_M = 0.33 \pm 0.09$.

C. Nonlinear Penetration Plots

The penetration profiles of several of the Ti diffusion runs departed from a perfect Gaussian. In most cases this amounted to only a slight break in the plot of log(concentration) vs x^2, or simply a gentle curvature. The 3-h run at 5 kbar, however, gave a very large break. The penetration plot for this run does not fit any of the current models of grain boundary diffusion,[53–56] but can be quite accurately represented by a sum of two Gaussians, corresponding to values of $D = 0.53\times10^{-9}$ cm^2/sec and 1.11×10^{-9} cm^2/sec.

The remaining runs showing slight breaks in the penetration plots have also been analyzed in terms of the sum of two Gaussian exponentials. However, the uncertainties involved in making such a breakdown of the penetration plots are quite large, so that such a procedure may not be very meaningful. The near-surface D values did seem to be consistent, however, and appeared to vary with pressure at about the same rate as the "far" values. Furthermore, the ratio of far and near D values was roughly constant at 2.1–2.4.

It has thus been shown that the far-slope region of the nonlinear penetration plots most probably is not due to grain boundary diffusion, since the logarithm of the concentration falls off as x^2, indicating either pure bulk or Hart-mechanism diffusion. The near-surface behavior may be due simply to tracer holdup. If the tracer were tied up in an oxide, for example, it could well result in a time-dependent release of tracer into the bulk. In that case the deep-penetration regions should represent the true bulk diffusion. The fact that it is the deep-penetration regions which do not exhibit structure sensitivity bears out this conclusion.

IV. DISCUSSION

The aim of the present experiment was twofold: (i) to determine the sign of ΔV for self-diffusion in β-titanium and (ii) to determine the magnitude of ΔV. The reported anomalous pressure dependence of D in β-Ti and γ-U should be resolved if the sign of ΔV can be determined. The magnitude of ΔV has a direct bearing on the mechanism of diffusion and needs to be determined with some precision if the mechanism is to be specified with any certainty.

The routine errors in this experiment have been kept to a minimum. Counting errors have been kept to $\frac{1}{2}\%$ or less by accumulating at least 40 000 counts for each section. The deep sections, having count rates closer to background, have a proportionately higher absolute uncertainty, however. By use of a microbalance to weigh the sections, weighing errors are estimated to be less than 1%. (The sections weighed about 1–3 mg each.) Some uncertainties in weight are caused by occasionally picking up a piece of lint or fragment of bristle from the brush used to collect the chips, or possibly by not collecting 100% of the chips. The fact that the weight loss of the specimens equaled the total weight of side cuttings and sections within a fraction of a percent indicates nearly 100% chip collection efficiency. Measurement of the section diameter was possible to 0.5% with a micrometer. Possible variation of specimen density due to surface impurities might result in measured D's which were slightly smaller than the true D's. (The density of thick oxide scales on Ti metal is about 4.2 gm/cm^3, compared to 4.51 for the pure metal.[57] Hence, any surface density variation in the actual Ti diffusion specimens is expected to be at most a few percent, based on its machinability.)

Errors in determining the pressure were small, less than 2% on an absolute scale. The pressure was held constant during each run to ± 0.03 kbar. The temperature measurement constitutes the largest single source of error in these experiments. The problems involved in measuring the temperature accurately have been discussed in detail in Sec. II. While every effort was made to ensure reproducibility of the temperature measurements to at least 1 °C, it appears unlikely that such accuracy was actually achieved. Uncertainties of 3–5 °C seem to be indicated by the scatter of the data, even for series II, where the control was better and, hopefully, the thermocouple geometry was more favorable. The possibility of Ni contamination of the Pt disk thermocouple arrangement casts some doubt on the absolute accuracy of the series-II temperatures. The indications are, however, that any such possible calibration offset occurred early in the first run so that subsequent runs were performed at the same relative temperatures. This effect may explain qualitatively why the actual D values of the two series are displaced from one another, even when referred to a common temperature. The two series have been considered separately in determining the activation volume.

The value of the activation volume determined in this work is relatively small, but definitely positive. One may, without greatly stretching either the imagination or the data, obtain a slope of $\ln D$ vs P giving activation volumes ranging from 2 to 8 cm^3/mole. In any case, ΔV is *not* negative. Thus, the earlier reports of anomalous negative ΔV's in β-Ti[13] and γ-U[12] seem to be refuted.

The average value of ΔV determined in this work is $\Delta V = 3.6 \pm 1.0$ cm^3/mole $= 0.33 V_M$. This is to be compared with values for other bcc metals discussed in Sec. I, namely, $\Delta V/V_M$'s of roughly 0.5.

Several empirical models have been suggested for estimating activation volumes. Keyes[58] first obtained the relation

$$\Delta V = 4K_T \Delta H, \tag{9}$$

relating the compressibility K_T and activation energy ΔH to the activation volume. Taking $\Delta H = 33$ kcal/mole and $K_T = 1.10 \times 10^{-3}$ kbar^{-1} for Ti, this relation gives $\Delta V \simeq 6.1$ cm^3/mole. Based on a continuum elastic model,[59] Keyes obtained the relation

$$\Delta V = 2(\gamma_G - \tfrac{1}{3}) K_T \Delta G. \tag{10}$$

Taking the entropy term $\Delta S/R \simeq -3$,[4] we find for the increment in Gibbs free energy $\Delta G \simeq 40$ kcal/mole, which gives $\Delta V \simeq 2.6$ cm^3/mole. Lawson *et al.*[60] derived an approximate relation between the formation volume and molar volume

$$\Delta V_f / V_M = 1/(\gamma_G - \tfrac{1}{3}), \tag{11}$$

which gives reasonable agreement for several materials. For Ti, however, the result is $\Delta V_f/V_M \simeq 1.41$, far larger than the measured value.

Johnson[61] has calculated various defect properties for bcc iron on the basis of an atomic model. This model predicts zero for the vacancy motional volume and just slightly less than unity for the formation volume, again indicating a large value for $\Delta V/V_M$.

The lack of agreement between the various theoretical or semiempirical models and the activation volume determined here is certainly not surprising. The models are themselves only very approximate, and, as discussed below, the measured ΔV is very likely not to be identified with the actual value of the activation volume for vacancies.

In addition to resolving the discrepancy concerning the sign of ΔV, the present work may provide some useful insight into the mechanism or mechanisms of diffusion in the anomalous metals, although this must remain mostly qualitative because of insufficient accuracy in the experimental data. The value $\Delta V = 0.33 V_M$ appears to be far too large to be consistent with the extrinsic vacancy mechanism of Kidson.[18] If self-diffusion in β-Ti proceeds via a simple vacancy mechanism, the activation volume is expected to be approximately 0.5, as found for other bcc metals. If diffusion is via the Hart mechanism, the effective volume will be given approximately by

$$\Delta V_{\text{eff}} = \frac{D_v}{D_{\text{eff}}} \Delta V_v + \frac{g D_d}{D_{\text{eff}}} \Delta V_d, \tag{12}$$

as derived in Sec. I. A relatively small value of ΔV_{eff} may thus indicate a significant contribution from dislocation enhancement. Taking $\Delta V_v \simeq 0.5 V_M$, $\Delta V_d \simeq 0.1 V_M$, and $\Delta V_{\text{eff}} \simeq 0.33 V_M$, we obtain $D_v/D_{\text{eff}} \simeq 0.58$, indicating that about one-half the actual diffusion may be via short, connected dislocation paths.

This result may be qualitatively related to the curved penetration plots on the basis of the following model. It has been shown that both near and far regions of the penetration plots determined in this work follow an x^2 dependence, indicative of either bulk or Hart diffusion. If we suppose that the dislocation density is occasionally reduced near the surface for certain samples, but has its normally high value in the bulk, then diffusion near the surface would proceed predominantly via vacancies, while deeper in it will be via the Hart mechanism. The uncertainty in resolving the penetration plots precludes making a comparison of the activation volumes for the two regions. However, rough agreement with the value $D_v/D_{\text{eff}} \simeq 0.58$ may be seen from the ratios of the near and far diffusion coefficients, i.e., $D_{\text{near}}/D_{\text{far}} \simeq 0.55 \pm 0.05$. If this argument is reversed, and it is assumed that $D_{\text{near}}/D_{\text{far}} \simeq 1/2.2$ actually represents D_v/D_{eff}, then the value calculated for ΔV for vacancy diffusion is $0.61 V_M$.

One objection to this model is the *ad hoc* assumption of a spatially varying dislocation density. Even if this were possible, the solution would not necessarily follow the sum of two Gaussians. The sum of two Gaussians requires the operation of two independent mechanisms over the entire diffusion zone. The operation of vacancy and dislocation pipe diffusion processes could produce this; however, then the ratio of D's found for $D_{\text{near}}/D_{\text{far}}$ is not nearly large enough (more typically, $D_d/D_v \simeq 10^5$), although D_d would still be moderated by the multiplicative factor g. This model also fails to explain the very large absolute value of D_{near} if it is supposed to represent D_v.

The results of the present experiment indicate the following. The penetration profiles are not all perfect Gaussians. Some runs give greater deviation from Gaussian behavior than others. The deep part of the profiles seems to represent the "intrinsic" behavior of the material, in that it is roughly the same for all samples, and varies as the square of the penetration distance. The near part also varies as x^2, but seems to depend on the time and/or pressure of the anneal, and varies in extent from specimen to specimen.

There are several possible explanations for this curvature which can be dismissed immediately. It is not caused by a time-dependent D (as might arise if the dislocation density decreased with time due to annealing, for example). It may easily be shown by differentiation that the penetration profile from a thin source for a time-varying D is still a Gaussian. (The effect is similar to varying the temperature during the anneal.) The curvature is also not due to having a moderately thick source rather than the usual thin source solution. For a finite source of thickness $2b$, located between $-b$ and $+b$, diffusion into an infinite medium is given by[62]

$$C(x,t)=\tfrac{1}{2}C_0\left(\operatorname{erf}\frac{b-x}{(4DT)^{1/2}}+\operatorname{erf}\frac{b+x}{(4DT)^{1/2}}\right), \qquad (13)$$

where the error function is defined by $\operatorname{erf}(z)=(2/\sqrt{\pi})\times\int_0^z e^{-\eta^2}d\eta$. Expanding the error functions to the first nonvanishing order, the concentration is given by

$$\ln C=\ln(\text{const})-(x^2/4DT)(1-b^2/6Dt). \qquad (14)$$

The plot of $\ln C$ vs x^2 is thus still a straight line, although with a slightly different slope. Carrying the expansion to the next nonvanishing order gives a term $b^4x^4/(120\times 256D^4t^4)$ as the first x-dependent term. The source would thus have to be unreasonably thick before any departure from a Gaussian would appear.

An alternative explanation for the curvature may be seen by considering the following model. If a sizeable amount of the tracer becomes tied up in the form of an oxide, during plating or when first heated, it will not be available immediately to diffuse as Ti. The TiO_2 (or whatever form the oxide may take) may, because of its extreme stability, remain intact for a sufficiently long time that it actually diffuses into the sample down dislocation pipes or grain boundaries. The mobility of the molecule down the pipes would probably be relatively small, but if the dislocation density shortly after going through the phase transformation is high, as seems to be suggested by the results of Gregory and Askill,[16] appreciable diffusion might take place. Eventually, as the molecules get trapped in the dislocations or grain boundaries, they will dissociate, with both tracer and oxygen going into solution. From there the tracer would diffuse as a single ion, by the mechanism operative in the bulk, presumably the Hart mechanism. The dislocation density in the bulk probably reaches some "irreducible minimum" after a short time, so that the enhancement is the same from run to run.

This model explains qualitatively the observed lower values for D_{near} relative to D_{far}. One objection to such a model is the assumption that a sizeable fraction of the tracer atoms becomes oxidized. When first dried onto the sample, the tracer is in the form of a fluoride or chloride. Subsequently, when the sample is heated up and oxidation begins to take place, it would seem to be as likely for matrix atoms to oxidize as tracer atoms, or the oxygen may simply go directly into solution without attaching to single atoms. However, if single-atom attachment does occur by the oxygen, it might do so preferentially to the relatively free tracer atoms rather than to the bound matrix atoms at the surface.

In discussing the effective activation volume for the Hart mechanism above, the dislocation activation volume has been assumed to be small. The argument for this given in Sec. I is that less work is required for an atom to migrate down a dislocation or grain boundary; hence ΔV should be of the order of or less than the migration volume ΔV_m. This may or may not be a valid assumption. Martin, Blackburn, and Adda[63] have reported measurements of the effect of pressure on grain boundary self-diffusion in bicrystals of silver. They find quite large changes with pressure, giving $\Delta V_{gb}/V_M = 1.1 \pm 0.2$. Although this result does not correlate well with simple atomic models, it is difficult to simply dismiss out of hand. If the ΔV_d for Ti is indeed larger than the $0.1 V_M$ estimated, the enhancement factor gD_d/D_{eff} deduced from ΔV_{eff} will be accordingly larger. The Hart mechanism might therefore give a ΔV_{eff} of the order of that determined in this work, with little or no contribution from normal vacancy diffusion.

V. CONCLUSIONS

In conclusion, the activation volume for self-diffusion in β-titanium has been found to be positive, and equal to approximately 3.6 ± 1.0 cm^3/mole at 1000 °C. Determination of the sign of ΔV refutes earlier reports of negative ΔV's for diffusion of Fe in β-Ti and possibly also that for self-diffusion in γ-U.

The magnitude of ΔV is not very precisely determined due to the multitude of problems encountered in measuring diffusion in titanium at high pressures and high temperatures. Any significant improvement of the data would require much improved experimental conditions over those achieved here. The thermometry might be improved somewhat. The high-pressure gas should be kept absolutely clean and free from oil or atomspheric contaminants. Pressure leaks, which were a constant problem in this work, should be eliminated completely to avoid back diffusion of oxygen from the air. Such conditions would be extremely difficult to achieve in practice.

It is concluded that diffusion in β-Ti most probably proceeds via a combination of vacancy and short-dislocation-path diffusion, known as the Hart mechanism. Non-Gaussian penetration plots were observed in some of the runs. This has been interpreted in terms of oxide holdup of the tracer at the surface and possible diffusion of the tracer as an oxide along dislocation pipes or grain boundaries near the surface before dissociation takes place.

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Helmholtz Free Energy of an Anharmonic Crystal to $O(\lambda^4)$[*]

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All of the diagrams contributing to the Helmholtz free energy to $O(\lambda^4)$, for a crystal in which every atom is on a site of inversion symmetry, have been evaluated. The expressions given are valid for finite temperatures, and separate expressions are given for all cases where the double occurrence of phonon lines is important. Numerical calculations have been carried out for all the diagrams for a nearest-neighbor central-force model of a face-centered-cubic lattice in the high-temperature limit and in the leading-term approximation. Two separate techniques, a scanning method and the plane-wave expansion method, were used for the evaluation of each diagram. When applied to a Lennard-Jones potential it is found that none of the diagrams makes a negligibly small contribution and that the convergence of the perturbation expansion appears poor for $T > \frac{1}{3} T_m$.

I. INTRODUCTION

A knowledge of the anharmonic contributions to the Helmholtz free energy of a crystal is necessary for a complete understanding both of the properties of the solid itself and of the phenomenon of melting. Most approaches to this problem are based initially on the use of perturbation theory, but the systematic application of this technique is not well defined. The difficulty is that the use of perturbation theory leads to an anharmonic contribution to the free energy which is an infinite series in the perturbing potential, while the perturbation is itself an infinite series expansion of the cubic, quartic, and higher-order terms in the Taylor expansion of the potential energy of the crystal.

The traditional approach is to use an ordering scheme devised by Van Hove.[1] He introduced an ordering parameter, here called λ, equal in magnitude to a typical atomic displacement divided by the nearest-neighbor distance, and showed how the order of the various terms in the double series expansion could be obtained. The lowest-order anharmonic contributions to the free energy are then found to be of order λ^2. The derivation of these contributions, and their evaluation for a simple model, has been described by Maradudin, Flinn, and Coldwell-Horsfall.[2] The contribution to C_v from these diagrams is found to be proportional to T at high temperatures, but it has been found that this temperature dependence is inadequate to describe the experimental results for several