Atom Transport Under Varying Pressure *, **

D. Lazarus, D. N. Yoon †, and R. N. Jeffery ††

Department of Physics and Materials Research Laboratory
University of Illinois, Urbana, Illinois 61 801, U.S.A.

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Study of the effect of hydrostatic pressure on the rate of diffusion-limited processes gives information regarding the intrinsic volume changes associated with formation and motion of defects. While there are basic problems associated with interpretation of the motional volume, such effects may be measured directly in some cases and subtracted to give unambiguous results for the defect formation volume. Experimentally, precise measurement of specimen temperature within a high-pressure environment poses the most severe practical constraint. Results are given for measurements to pressures of 7 kilobars of ionic conductivity in a series of pure and doped alkali halides: NaCl, KCl, NaBr, and KBr, all of which are predominantly cationic vacancy conductors. The activation volumes are found to be pressure dependent in the intrinsic regions. In all cases the Schottky pair vacancy formation volume is found to be larger than the molar volume, the ratio being largest for NaCl and smallest for KBr. Results are also given for the total activation volume for diffusion of Ti^{44} in beta-Ti, a case of "anomalous" bulk diffusion. The tracer penetration plots do not follow a perfect gaussian profile. However, if the penetration plots are fit to a single gaussian, the activation volume derived is consistent with that expected for a vacancy mechansm in bcc metals.

1. Introduction

It has been well established that lattice defects, such as vacancies and interstitials, are primarily responsible for atom transport through the bulk of crystalline solids. Such diffusion processes are most frequently analyzed in terms of the familiar reaction-rate model, whereby the diffusion coefficient is expressed by the relation

$$D=\gamma\, a^2\, \nu_0\, f\cdot \exp\{-(\Delta G_{\mathrm{f}}+\Delta G_{\mathrm{m}})/k\,T\}\,. \qquad (1)$$

Here γ is a constant of order unity, a is the lattice parameter, ν_0 a characteristic frequency of the order of the Debye frequency, f the correlation factor which takes account of nonrandomness in successive jumps, and ΔG_{f} and ΔG_{m} are, respectively, the increments in Gibbs free energy required for formation and motion of the appropriate defect, k is Boltzmann's constant and T the absolute temperature.

Since the Gibbs function is expressible in terms of enthalpy and entropy changes: $\Delta G=\Delta H-T\,\Delta S$, eq. (1) may be rewritten as

$$D=\gamma\, a^2\, \nu_0\, f\cdot \exp\{(\Delta S_{\mathrm{f}}+\Delta S_{\mathrm{m}})/k\} \cdot \exp\{-(\Delta H_{\mathrm{f}}+\Delta H_{\mathrm{m}})/k\,T\}\,. \qquad (2)$$

Accordingly, the logarithmic temperature derivative of the diffusion coefficient gives the enthalpy changes associated with formation and motion of defects:

$$(\partial \ln D/\partial(1/T))_P = -(\Delta H_{\mathrm{f}}+\Delta H_{\mathrm{m}})/k + (\partial \ln \gamma\, a^2\, \nu_0\, f/\partial(1/T))_P\,. \qquad (3)$$

Since the second term on the right in (3) is generally very small, study of the variation of diffusion processes with temperature at constant pressure leads directly to evaluation of the enthalpy terms.

Additional information regarding the formation and motion of defects can be obtained by study of the variation of diffusion processes with pressure at constant temperature. Since, for the Gibbs function, $\mathrm{d}G=V\,\mathrm{d}P-S\,\mathrm{d}T$, the logarithmic pressure derivative of the diffusivity is

$$(\partial \ln D/\partial P)_T = -(\Delta V_{\mathrm{f}}+\Delta V_{\mathrm{m}})/k\,T + (\partial \ln \gamma\, a^2\, \nu_0\, f/\partial P)_T\,. \qquad (4)$$

Again, the second term on the right is generally very small, and the results permit direct evaluation of the volume changes associated with formation (ΔV_{f}) and motion (ΔV_{m}) of defects.

The validity of these identifications rests, of course, on the validity of the reaction rate model. There is little controversy about the significance of

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† Present address: Department of Chemical Engineering and Materials Science, Wayne State University, Detroit, Michigan, U.S.A.

†† Present address: Departement of Physics, Rensselaer Polytechnic Institute, Troy, New York, USA.

the defect formation terms $\varDelta H_\mathrm{f}$ and $\varDelta V_\mathrm{f}$, since these govern simply the *a priori* probability of existence of a defect at a site adjacent to a diffusing atom. However, the physical significance of the motional terms $\varDelta H_\mathrm{m}$ and $\varDelta V_\mathrm{m}$ is far less certain. C. P. FLYNN, in a companion paper at this conference, discusses a dynamical model for consideration of the jump process in terms of fluctuations in atom positions resulting from a random superposition of normal modes of the lattice. From this viewpoint, the terms $\varDelta H_\mathrm{m}$ and $\varDelta V_\mathrm{m}$ do not simply correspond to physical changes in enthalpy and volume of the lattice, but are related to more complicated derivatives of the normal modes.

Studies which determine the effect of pressure on bulk diffusion properties inevitably lead to a determination of the sum $\varDelta V_\mathrm{f} + \varDelta V_\mathrm{m}$. Where the term $\varDelta V_\mathrm{m}$, whatever its physical significance, can be determined separately, the term $\varDelta V_\mathrm{f}$ can be determined from the difference and compared with theoretical models for lattice defects. This is possible, for example, in studies of ionic conductivity in alkali halides. In the high-temperature intrinsic region in pure crystals, where only cations are mobile, the conductivity is governed by the term $(\varDelta G_\mathrm{f}/2 + \varDelta G_\mathrm{m})$, where $\varDelta G_\mathrm{f}$ is the free energy of formation of a Schottky cation-anion vacancy pair and $\varDelta G_\mathrm{m}$ is the motional energy of the cation vacancy. In the low temperature extrinsic region, or in heavily doped crystals, the conductivity is governed by $\varDelta G_\mathrm{m}$ alone. Thus, pressure measurements of the intrinsic conductivity yield values of $(\varDelta V_\mathrm{f}/2 + \varDelta V_\mathrm{m})$, while the extrinsic studies yield $\varDelta V_\mathrm{m}$ alone. From a difference of the two, the formation volume of the Schottky pair, $\varDelta V_\mathrm{f}$, can be derived.

In the present research, attention has been centred on studies of the effects of pressure on ionic conductivity of a series of pure and doped alkali halides, and on a study of tracer self-diffusion in bcc Ti, a familiar case of "anamalous" diffusion where marked deviations are found from the Arrhenius law, with atypically low activation energies and high diffusion coefficients. The alkali halides are well-known to be cationic conductors, so the defect responsible for diffusion and conductivity is the cation vacancy. By study of both pure and doped specimens, unambiguous values of the formation volume of Schottky vacancy pairs can be derived for comparison with theoretical models (see the companion paper in the conference by FAUX and LIDIARD). Because of its anomalous behavior, the mechanism for self-diffusion in bcc Ti is not well understood. The goal of the present research is to ascertain if the characteristic activation volume, $\varDelta V_\mathrm{f} + \varDelta V_\mathrm{m}$, is at all similar to the values found for other metals for which the vacancy mechanism has been well established.

2. Experimental

The present measurements were carried out in a large high pressure chamber with inside dimensions 3.8 cm diameter by 25 cm length. Specimens were maintained at constant temperature by a furnace inside the pressure chamber, the temperatures being controlled and measured by chromel-alumel (for the alkali halides) or platinum-platinum-rhodium (for the Ti) thermocouples which were brought out through frozen oil seals. Pressurization up to 7 kilobars was effected by filling the chamber with argon gas, assuring ideal hydrostaticity of the pressure environment.

Measurements within such a high pressure environment pose a number of technical problems, the bulk of which are of no concern here. In the present studies, the most serious problem is that of precise measurement of specimen temperature inside the high pressure chamber. Since the validity of the results depends in no small measure on the precision of the temperature measurement, it is necessary to dwell briefly on the techniques employed. As noted, the thermocouple leads were brought out through frozen oil seals. This method, while a bit cumbersome, at least has the virtue that it obviates the necessity for having any discontinuities in the thermocouple material between the specimen and an isothermal reference bath. In this method, the original platinum couple leads are brought, at constant high pressure, to an ice bath, where they are joined, isothermally, to chromel wires. The chromel pair is then brought out of the pressure system through frozen oil in an isothermal bath at liquid nitrogen temperature. The assured isothermal conditions at the point of transition of thermocouple materials to chromel and at the point of pressure gradient in the chromel leads obviate any spurious emf's which could arise from such discontinuities. In the ionic conductivity apparatus, the original chromel-alumel leads are brought directly through frozen oil seals to a reference ice bath at atmospheric pressure.

The thermoelectric powers of metals are generally not independent of pressure, and appropriate corrections must be made to the measured voltages to compensate for this effect. Such is the case for platinum-rhodium couples, the correction used being 0.5 °C per kbar at 1000 °C. Fortuitously, chromel-alumel couples exhibit a very small pressure coefficient of the thermoelectric power, and these couples may be used without correction up to temperatures of 720 °C, the maximum used for the alkali halide studies. However, chromel-alumel couples deteriorate very rapidly at temperatures above 800 °C, since a very small amount of diffusion can displace the effective hot junction by a short distance. In a region of very high temperature gradients, which are both unavoidable and strongly pressure dependent inside a high pressure chamber, such effects are catastrophic. Figure 1 shows the difference between temperatures measured by chromel-alumel and platinum-rhodium couples embedded inside the same metal block as a function of time and pressure at a relatively high temperature. Such studies indicate that diffusion-induced displacements of the effective hot junction by little more than a millimeter can cause several degrees error in temperature measurement. Since platinum vs. platinum-rhodium couples are far more resistant to diffusional contamination than chromel-alumel, they are essential for temperature measurement above 750 °C.

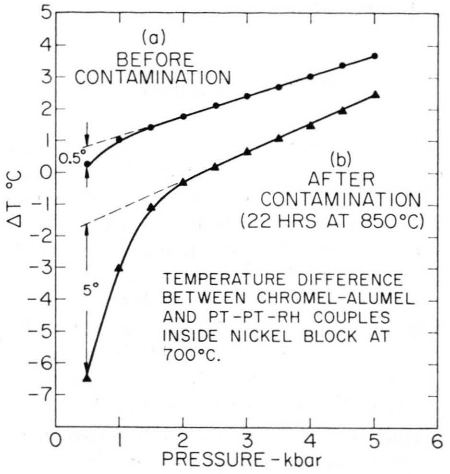

Fig. 1. Temperature difference measured as a function of pressure between a chromel-alumel couple and a platinum-platinum-rhodium couple embedded inside a single nickel block at 700 °C. a) Before contamination of the chromel-alumel couple. b) After contamination of the chromel-alumel couple by holding the system at 850 °C for 22 hours.

In addition to the above precautions, care must also be taken to assure excellent thermal contact between the measuring couple and the specimen itself. This is a far more serious problem in a high pressure system than in vacuum, particularly with speciments of poor thermal conductivity, since sizable temperature gradients are inescapable. In the present measurements, good thermal contact between the thermocouple and alkali halide specimens was assured by cementing the couple into a massive nickel electrode, coated with platinum at the contact surface. This electrode was forced, under spring tension, into tight physical contact with the thin crystal, which was sandwiched between two massive electrodes. Calibration measurements made for this system, shown in Fig. 2, indicate that the temperature difference between the measuring couple and another couple cemented between the electrodes to simulate a specimen, while pressure dependent, is reproducible and never amounts to more than a few degrees.

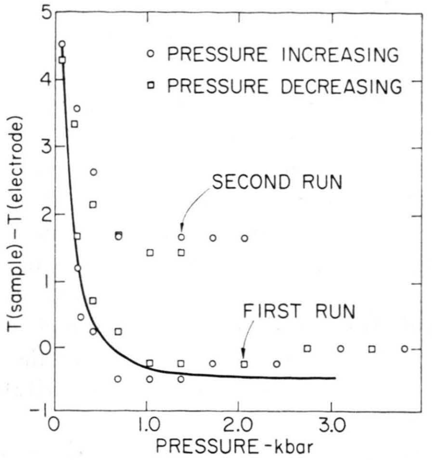

Fig. 2. Temperature difference measured at 700 °C as a function of pressure between chromel-alumel couple cemented into nickel electrode and a second couple embedded in dummy specimen in ionic conductivity apparatus.

In the case of the measurements on β-Ti, which were conducted at 1000 °C, platinum vs. platinum-rhodium couples were employed. Good thermal contact between the couple and the specimen surface containing the Ti^{44} tracer was insured by spot-welding the two thermocouple wires to a thin sheet of platinum which was sandwiched between the actual specimen and an adjacent nickel dummy.

Contamination of specimens was also a potentially serious problem in the present measurements. In the case of the ionic conductivity studies, considerable care had to be taken to insure against contamination of the pressure gas by residual oil from the pressurization apparatus. Breakdown of the oil at high temperatures could cause a thin layer of conducting material to be deposited around the specimen and electrodes, giving spurious conductivity measurements. In the case of the Ti diffusion studies, purity of the pressure gas was essential to avoid contamination of the specimen itself, due to the well known gettering properties of titanium. The system, at high pressure, had to be maintained essentially vacuum tight, as measured by a helium leak detector. In addition, the specimen was surrounded by titanium foil which served to getter residual impurities in the pressure gas. With such precautions, the specimens were generally found to be shiny and readily machinable following the diffusion anneals.

The techniques used for ionic conductivity and tracer diffusion measurements were conventional. Conductivity measurements were made using a conductance bridge connected to the electrodes inside the pressure system via leads brought through frozen oil seals. Tracer diffusion measurements in Ti were made by coating high-purity specimens of Ti with a thin layer of Ti^{44} tracer, diffusing at high pressure, and afterwards determining the value for the diffusion coefficient by the lathe-sectioning and counting technique. Ti^{44}, because of its exceedingly small specific activity, is a far from optimal tracer, but satisfactory results were obtained simply by drying a drop of tracer solution onto a hand-polished and etched specimen face.

3. Results

Experimental results for the series of alkali halides are shown in Figs. 3 and 4, and the activation volumes derived are given in Table 1. As shown in the figures, the slopes of the curves of log conductivity versus pressure are not constant, but have their maximum values at low pressures. The values for the activation volumes tabulated are taken from the low-pressure slopes. When the pressure system was maintained clean, no hysteresis was observed in cycling either pressure or temperature during successive runs on a single specimen. (However, some evidence of slight contamination was often found during the first warm-up, indicating possible diffusion of polyvalent impurities into the salt crystals from the platinum electrodes. No further changes occurred after the first warm-up.) The major error involved in these measurements, as noted before, is in precise determination of the specimen temperature. Such uncertainties are reflected in the error limits for the activation volumes indicated in Table 1.

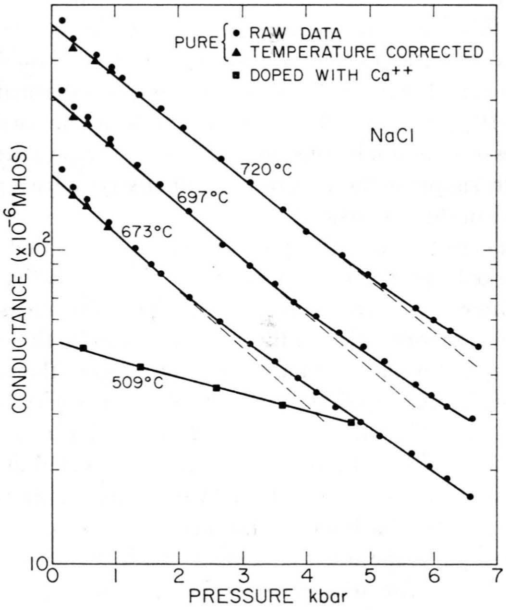

Fig. 3. Pressure dependence of the ionic conductivity of NaCl.

Table 1. Activation volumes for ionic conductivity in alkali halides (all volumes in cm^3/mole).

Material	$\Delta V_{\text{intrinsic}}$	$\Delta V_{\text{extrinsic}}$	ΔV_f *	V_{molar}	$\Delta V_f / V_{\text{molar}}$
NaCl	34 ± 3	7.5 ± 0.3	53 ± 5	29.7	1.8 ± 0.2
KCl	40 ± 3	9.2 ± 0.3	62 ± 5	41.4	1.5 ± 0.2
NaBr	31 ± 3	9.0 ± 0.2	44 ± 5	35.4	1.2 ± 0.1
KBr	39 ± 3	12 ± 0.3	48 ± 5	47.6	1.1 ± 0.1

* Formation volume for Schottky pair = $2(\Delta V_{\text{intrinsic}} - \Delta V_{\text{extrinsic}})$.

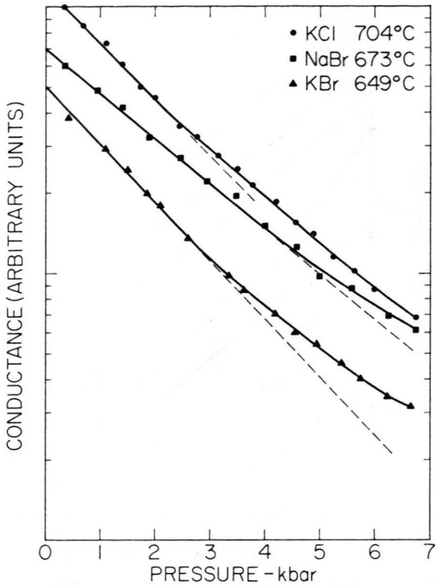

Fig. 4. Pressure dependence of the intrinsic ionic conductivities of KCl, NaBr, and KBr.

Experimental results for self-diffusion in beta-Ti for pressures to 7 kbar at 1007 °C are shown in Figs. 5 and 6 and in Table 2. The penetration curves are *not* precisely gaussian, as shown, the slope being consistently higher at short penetration distances. One sample shows a significant break between the two regions, while in all others only a very slight break is found. If the data are fit to a straight line in each case, ignoring the one case where a distinct break was found, the values of the diffusion coefficients thus derived are reasonably accurate.

All activation volumes given in Tables 1 and 2 are derived directly from the experimental values of the diffusion coefficients. They thus represent the total relaxations of the entire crystal, including the image terms[1] arising from the surface boundary condition. For comparison with atomic models which

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[1] J. D. ESHELBY, J. Appl. Phys. **25**, 255 [1954].

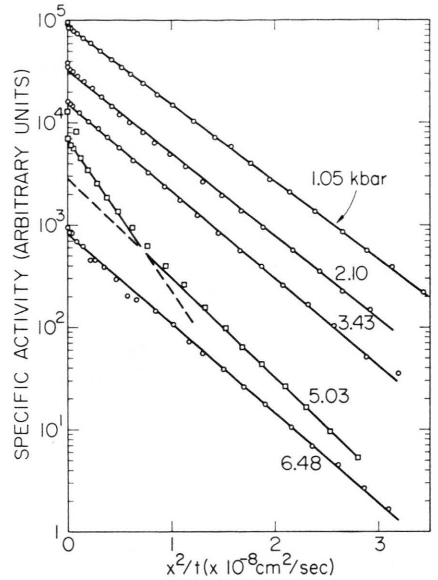

Fig. 5. Penetration profiles for diffusion of Ti^{44} into β-Ti at various pressures.

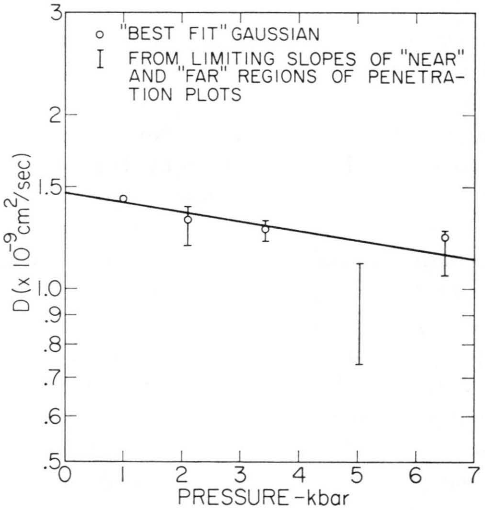

Fig. 6. Pressure dependence for self-diffusion in β-Ti.

Table 2. Effect of pressure on diffusion of Ti^{44} in β-Ti.

pressure k bar	temperature °C	time sec	D (best fit) cm^2/sec
1.05	1006	1.81×10^4	1.43×10^{-9}
2.10	1007	1.88×10^4	1.32×10^{-9}
3.43	1008	1.61×10^4	1.27×10^{-9}
5.03 *	1007	1.08×10^4	$(.74-1.1) \times 10^{-9}$
6.48	1007	1.85×10^4	1.26×10^{-9}

* Profile shows marked deviation from gaussian
Activation volume: $\Delta V = 4 \pm 1$ cm^3/mole;
Molar volume: $V_M = 10.6$ cm^3/mole;
$\Delta V / V_M = 0.4 \pm 0.1$.

treat only local deformations in an infinite lattice, the effect of the image terms should be taken into account.

4. Discussion

A) Alkali Halides

An important feature of the present results is the observation of a marked pressure dependence of the activation volume in the intrinsic region, as shown in Figs. 3 and 4. The "knee" between the low and high pressure portions of these curves moves to lower pressures at lower temperatures.

It appears most reasonable that this effect is due to a much more rapid suppression of the intrinsic conductivity with pressure (because of the large value of ΔV_f) than of the extrinsic conductivity. Thus, at high pressure where the intrinsic conductivity is considerably suppressed, the specimen is no longer in the true intrinsic region, but in a region of mixed intrinsic and extrinsic conductivity. In this case, the measured pressure dependence is characteristic of the mixed region, and should be associated with an activation volume intermediate to $\Delta V_{\text{intrinsic}}$ and $\Delta V_{\text{extrinsic}}$. In this sense, increasing pressure is analogous to decreasing temperature — both suppress the intrinsic conductivity more rapidly than the extrinsic.

There remains the possibility, however, that this marked pressure dependence of the activation volume arises from errors in temperature measurement. Errors sufficiently large to explain this curvature, however, would be far larger than the directly measured temperature difference shown in Fig. 2. It should be noted that in similar measurements for NaCl by the Saclay group reported at this conference (see paper by BEYELER and LAZARUS), no curvature is found in the pressure dependence of the high-temperature intrinsic conductivity at low pressures, for temperatures below 660 °C. In the Saclay work, the same slope as the present high-pressure slope (corresponding to $\Delta V_{\text{intrinsic}}$ of 27 cm^3/mole instead of 34 cm^3/mole) is found to persist at low pressures, even with an *externally* heated pressure vessel, which should minimize errors in temperature measurement. The reasons for this discrepancy are as yet unresolved, but may be attributable simply to the difference in temperature ranges ($T > 670$ °C for the present results, $T < 660$ °C for the Saclay results) in the two separate studies.

B) Beta-Ti

Previously reported values for the activation volumes for self-diffusion in anomalous bcc metals have been quite confusing. BEYELER and ADDA[2] reported an activation volume for self-diffusion in gamma uranium which was first negative and then positive with increasing pressure. PEART[3] reported a value for the diffusion of iron in beta titanium which was essentially negative for all pressures to 3 kbar. A negative value of ΔV, while not *a priori* impossible, would pose some rather unusual constraints on the basic diffusion mechanism, and would clearly be at variance with any sort of vacancy mechanism. However, it is not clear, *a posteriori*, that in either of these previous measurements the pressure system and pressurizing gas were sufficiently clean to preclude marked contamination of the specimens during the diffusion anneal, which could well have given rise to spurious results for the pressure dependence. In addition, the anneal times in Peart's work were relatively short, only 30 – 60 minutes, which may have been too short to allow equilibration of the dislocation structure[4].

The present results, while hopefully performed under more optimal conditions, do not give a completely unambiguous result. The reason, as noted earlier, is in the fact that the tracer penetration profiles, which are otherwise as precise as those measured on many other systems in this laboratory, do not follow the precise gaussian functional dependence expected for diffusion from a thin source. Experimentally, it has been shown that the curved profiles do not result from isotopic contamination of the Ti^{44} tracer nor to failure to take proper account of effects of surface diffusion, etc. The fact that one specimen showed a very pronounced break, while the break is much smaller in others, lends credibility to the hypothesis that this deviation may be structure sensitive. Nothing is, or can be, known about the dislocation density or grain structure of the specimens, since the metal transforms from hcp to bcc at about 120 °C below the diffusion temperature. It seems unlikely that impurities contribute directly to the anomaly, since the original Ti is nominally 99.99% pure. However, the presence of some atmospheric contaminants such as oxygen and nitrogen is certainly unavoidable in the present experiment, and these could play a role in enhancing either bulk or dislocation diffusion.

If one ignores the one profile which shows a distinct break (and there is no *a priori* reason to question the validity of this result), the other curves may be fit to a single gaussian without unreasonable errors. Diffusion coefficients may be calculated from these "best-fit" gaussians. The pressure dependence of these coefficients is found to be characterized by an activation volume of 4 cm^3/mole, which is consistent with that expected for a normal vacancy mechanism in bcc metals[5]. However, the departure from ideal gaussian profiles indicates that more than one mechanism must be operative in this system.

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[2] M. BEYELER and Y. ADDA, Physics of Solids at High Pressures, ed. by C. T. TOMIZUKA and R. M. EMRICK, Academic Press, New York 1965, p. 349.

[3] R. F. PEART, Phys. Stat. Sol. **20**, 545 [1967].

[4] A. G. GREGORY and J. ASKILL, Phil. Mag. **12**, 901 [1965].

[5] D. LAZARUS and N. H. NACHTRIEB, Solids Under Pressure, McGraw-Hill Book Co., New York 1963, p. 43–69.