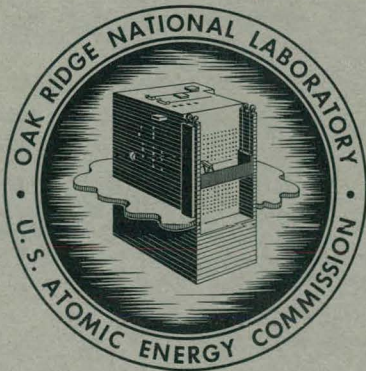


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Be
SELF-DIFFUSION OF BERYLLIUM IN BeO
UNIRRADIATED, COLD-PRESSED AND
SINTERED BERYLLIUM OXIDE

H. J. de Bruin
G. M. Watson



OAK RIDGE NATIONAL LABORATORY

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ABSTRACT

Diffusion of beryllium-7 through polycrystalline unirradiated specimens of BeO was studied as a preliminary step to a study of diffusion in irradiated material. Beryllium-7 was deposited on one end of cylindrical specimens by exchange and adsorption from aqueous solution. The depth of penetration perpendicular to the surfaces of deposition was determined after annealing the specimens at pre-determined conditions. A simple lapping device of high precision was developed to determine penetration depths.

For the polycrystalline cold-pressed and sintered BeO studied, the diffusion behavior between 1150 and 1800°C is described by the empirical relation:

$$D = 2.49 \times 10^{-3} \exp \left(- \frac{62.5 \times 10^3}{RT} \right) \text{ cm}^2/\text{sec.}$$

A diffusion model is proposed based on vacancy migration which suggests identical activation energies for diffusion in both a

and c directions in single crystals and predicts an activation energy of the correct order of magnitude. Furthermore, the model predicts that the frequency factor in the direction perpendicular to the c axis should be about 50 percent higher than that parallel to the c axis.

INTRODUCTION

Beryllium oxide is of interest as a moderator for nuclear reactors because of its attractive nuclear properties and its general excellence as a high-temperature ceramic, although the possible failure of beryllium oxide to resist radiation damage remains as the most serious obstacle to its use in power reactors. It is an established fact, however, that some of the radiation damage by fast neutrons to the crystal lattice of BeO is subject to recovery by annealing at high temperatures. The annealing process is probably due to self-diffusion of beryllium and of oxygen ions in the lattice to fill the vacancies created by particle collision during irradiation. Accordingly, the object of the present investigation is to study the self-diffusion of beryllium out-of-pile and in-pile in compacts of beryllium oxide. The present paper describes out-of-pile experiments with unirradiated specimens.

Knowledge of the self-diffusion behavior of beryllium in beryllium oxide is of importance for several reasons:

1. The mechanical properties of polycrystalline compacts such as creep, sintering, conductivity, and annealing rates, are fundamentally dependent on the diffusion behavior of the ions in the lattice which, in turn, depend greatly on the history of the specimen, such as density, method of fabrication, grain size, and purity. It is hoped that data on self-diffusion can aid in the prediction of the mechanical behavior of compacts from different sources and with different histories.

2. Irradiation of beryllium oxide brings about anisotropic growth of the crystal lattice and the formation of gases due to nuclear reactions. The diffusion processes responsible for the recovery of the damage due to anisotropic growth are functions of temperature, purity, previous history of the specimen, concentration of additives, neutron spectrum, dosage and flux. Studies of self-diffusion may reveal the relative importance of the factors controlling the recovery processes and may be of significant help in the choice of optimum operating conditions for beryllium oxide in nuclear power reactors.

Previous investigations to study the self-diffusion of beryllium and/or oxygen in beryllium oxide have been performed by Austerman^{1,2} and by Holt.³ Self-diffusion coefficients have also been obtained indirectly by calculation from measured values of various physical properties and a

correlation has been made by Rothman.⁴ Figure 1 shows a summary of the self-diffusion results and includes the previous and present work. Very large differences in the results are immediately apparent. The large differences observed may be due to the variable quality of material which was available for the earlier investigations and to possible weaknesses in the theoretical models used to calculate the self-diffusion coefficients from other physical properties.

The present report presents the results of diffusion experiments on cold-pressed and sintered beryllium oxide of the UOX-type and is restricted to data from unirradiated specimens. The experimental procedures include the development of a precision lapping device, the deposition of Be^7O on the surface of a specimen of Be^9O from aqueous solution by exchange and/or adsorption, and the application of γ -autoradiography as a possible alternate procedure for precision lapping in the determination of penetration depths. The theoretical portion includes the postulation of a diffusion model based on vacancy migration which appears to be consistent with the experimental observations.

EXPERIMENTAL PROCEDURES

In summary, a cylindrical BeO specimen was selected on the basis of macroscopic and microscopic examinations. It was annealed for two hours at 1800°C and one of its surfaces was ground flat. Be^7 was deposited on the flat surface and

the sample brought to the diffusion temperature for 5 minutes only. The surface activity was removed by grinding. In sound specimens, the activity would be completely removed within 10 to 15 microns. If the specimen was chipped, cracked, or had holes, the activity could not be removed within the stipulated thickness and the specimen was discarded. Sound specimens were activated again and annealed at predetermined diffusion temperatures for periods ranging from one day to two months. The fractions of the original activity which remained in the specimen were then determined as functions of depth by precision lapping or by γ -autoradiography of a wedged sample. From the penetration profiles, self-diffusion coefficients were calculated.

Material, Fabrication, and Selection of Specimens

The BeO pellets used were made from UOX-grade powder by cold-pressing and sintering in a hydrogen atmosphere for 60 hours at 1750°C. Final densities were between 96 and 98% of theoretical. Two different batches were used, one with grain size 20 to 30 microns and another between 60 and 70 microns. The total metallic impurity content was less than 1000 ppm. The results of typical analyses for this material are given in Table 1. Samples were selected on the basis of macroscopic and microscopic inspections of their surface in search of flaws and the soundness of the specimens was tested by the presence of a sharp concentration profile of Be⁷ after initial placement on the ground end of the cylinder prior to

annealing. The difference between a sound and an unsound specimen is illustrated in Fig. 2.

Table 1. Typical Concentrations of Impurities
in BeO Specimens

Impurity	Concentration (ppm)	Impurity	Concentration (ppm)
Al	15	Cu	2
B	1	Fe	200
Ba	5	Mg	9
Ca	<10	Pb	20
Cr	2	Sn	250

Application of Surface Activity

Exchange between Be^7 in solution and Be^9 at the surface of the highly sintered ceramic was found to be a most efficient method for the application of an infinitely thin layer of diffusant on the sample. The process can be made to proceed in either direction by pH and Be ion concentration control of the contacting solution.

To apply the initial source of Be^7 , a pellet was placed inside tightly fitting silicone tubing and one of its end surfaces was covered with the required amount of Be^7Cl_2 solution to give a surface activity of about 5×10^4 counts per minute on a γ -scintillation counter. After making slightly alkaline by the addition of ammonia, the surface was allowed to contact the solution for 24 hours. The

pellet was then thoroughly washed before removing the silicone tubing. The placement of Be^7 on the surface was so effective that grinding was required for its removal as only a minor fraction of activity could be removed by vigorous washing. After the sample was dried for 2 hours at 110°C in a drying oven, the sides were lapped down on a lathe approximately 2×10^{-4} inch, and it was then ready for the annealing stage.

Annealing Procedure

The sample was annealed in a vacuum graphite resistance furnace.⁵ The temperature was measured with an optical pyrometer directed at the sample inside the graphite coil. Allowance for emissivity was made by calibrating the pyrometer with thermocouples up to 1700°C . For the calibration 60/40 and 80/20 platinum-rhodium⁶ thermocouples were inserted in a hole drilled in a BeO pellet identical to the normal samples.

Precision Lapping

To determine penetration profiles, a simple precision lapping device was developed⁷ to accommodate cylindrical samples of diameters ranging between 1/4 and 0.8-in. (Fig. 3). The BeO specimen, (D), was placed in the conically-shaped Teflon washer, (E), and was locked inside the main body of the instrument, (F), parallel to the base, (A), within 2.5 microns across its diameter. As the specimen was locked in position, the parallel alignment was constantly checked by means of an "Electrolimit Gauge," which has a full scale

deflection of 1.2×10^{-3} inch or 5×10^{-5} inch per scale division.

The depths of penetration were measured by means of the enlarged micrometer on the side of the grinder. The magnification obtained by enlarging the scale allowed lappings to be measured accurately to ± 1.5 microns.

The grinder was fabricated so that its base, (A); and the surface, (B), which slides along the stone base, (C), were lapped flat and parallel to each other within 2×10^{-6} inch, as measured by interference fringes under an optical flat with monochromatic light. All metal parts were case-hardened and dull-chrome-plated to improve wear. The width of the grinding stone was limited to 3/16-inch, since a small area of contact between sample and stone proved beneficial in reducing friction and capping.¹ Because of the circular geometry of the device, a rotational motion during grinding guaranteed the removal of layers parallel to the original one.

In order to avoid the BeO dust hazard during grinding, the stone was wetted with a drop of glycerine. This also facilitated removal by washing of the active powder from the stone after each grinding.

No hardening plastics were used to accommodate a sample, and it was possible to remove it from and replace it in the device at different stages of the experimental procedure. That is, the specimen was lapped flat in preparation of activity placement, it was tested by examination of the

"blank" concentration profile before the actual diffusion anneal, and finally it was replaced in the device to determine the actual depth of penetration after diffusion had taken place. The grinder, however, was not limited to specimens with circular cross-section and it allowed samples of a variety of shapes to be handled by setting them in Wood's metal inside the Teflon washer. This has already proven convenient for experiments with single crystals.

Radiochemical Analysis

Most of the samples were analyzed by direct γ -counting of the 0.48 Mev Be^7 peak on a scintillation counter with a single channel differential analyzer. No correction for self-shielding by the BeO sample was needed, since the depth of penetration for 99% of the activity was never more than 0.5 mm, and the energy of the observed radiation is high.

In order to have an independent means of analysis, a γ -autoradiographic technique was developed. After annealing, the sample was placed in the lapping device at a slight angle and its relative thickness was mapped with respect to the base of the grinder. A wedge of precise and known dimensions was then removed and the sample was placed in a γ -collimating rig, over a photographic emulsion, as shown in Fig. 4. The emulsion, Kodak AR-50 autoradiographic strippable film, had previously been placed on a microscope slide. Contact was made for two to three days, and after developing the film, the optical density was analyzed on a Joyce Micro-densitometer.

RESULTS

The penetration profiles obtained by the methods previously described are shown in Figs. 5 and 6. The fraction of the original activity remaining is plotted in Fig. 5 as a function of penetration along with the theoretical curves corresponding to the indicated values of the product Dt . Figure 6 shows a dimensionless plot of the fraction remaining versus $x(Dt)^{-\frac{1}{2}}$. By this technique, the experimental data from all the specimens could be compared to a single theoretical curve.

Figure 7 shows an analysis of a BeO sample by γ -autoradiography. This method has been abandoned now because of its lower accuracy in the low temperature region of interest in this work; it is suggested, however, that efficient collimation of γ -radiation from a sample makes autoradiography possible. Since resolution is a function of collimating efficiency, which in the mechanical method employed is very low, relatively thick photographic emulsions (12μ) suffice for the purpose.

Diffusion coefficients were calculated using the mathematical relations given in the Appendix, and the results have been summarized in Table 2 which also lists the temperatures, the standard deviations, the length of annealing, and the mean displacement⁸ of the cation estimated for one year at the given temperature. Diffusion coefficients as a function of temperature are shown in Fig. 8, and are compared with some

Table 2. Self-Diffusion Coefficients of Beryllium
in Beryllium Oxide

Annealing Conditions		Diffusion Coefficient		Mean Displacement for Be Ion
Temperature (°C)	Time (sec)	(cm ² /sec)	% Deviation	Microns/Yr
1180	4.212 x 10 ⁶	5.64 x 10 ⁻¹³	29	60
1245	1.639 x 10 ⁶	3.02 x 10 ⁻¹²	26	138
1273	2.340 x 10 ⁵	2.71 x 10 ⁻¹²	24	131
1273	2.340 x 10 ⁵	6.83 x 10 ⁻¹²	16	207
1410	3.300 x 10 ⁵	1.42 x 10 ⁻¹¹	39	299
1500	1.602 x 10 ⁵	6.01 x 10 ⁻¹¹	25	616
1515	2.516 x 10 ⁶	1.00 x 10 ⁻¹⁰	42	795
1600 ^a	2.509 x 10 ⁶	5.85 x 10 ⁻¹¹	39	608
1663 ^b	2.340 x 10 ⁵	3.42 x 10 ⁻¹⁰	22	1472
1663 ^c	2.340 x 10 ⁵	2.21 x 10 ⁻¹⁰	-	-
1795	8.640 x 10 ⁴	4.41 x 10 ⁻¹⁰	15	1665
1795	8.640 x 10 ⁴	5.96 x 10 ⁻¹⁰	20	1940

^aSample A in Fig. 8

^bSample B in Fig. 8

^cAnalysis by γ -autoradiography.

of Austerman's results^{1,2} on hot-pressed beryllium oxide. The constants for Arrhenius' equation were determined using a method of least squares. The resulting equation:

$$D = 2.49 \times 10^{-3} \exp(-62,500/RT) \text{ cm}^2/\text{sec} \quad (1)$$

summarizes the experimental results between 1150 and 1800°C within the experimental error of the present investigation.

DISCUSSION

Experimental Uncertainties

As will be briefly discussed below, the uncertainty in the magnitude of the diffusion coefficients is estimated to be approximately 40 to 65% in most of the experiments performed. The uncertainty becomes much larger for experiments of long duration at temperatures sufficiently high for grain growth to occur appreciably. These conditions, however, were purposely avoided.

Uncertainties in the measurement of temperature and in the determination of penetration profiles were found to be the principal sources of error. An uncertainty of δ_T in the temperature measurement can be shown to cause an uncertainty of δ_D in the absolute value of the diffusion coefficient as given by the relation:

$$\delta_D = (Q/RT)\delta_T \quad (2)$$

where Q is the activation energy of the process in cal/mole. Since the temperatures were measured correctly to within 1.5%, corresponding uncertainties of 25% are expected from

this source. In addition, uncertainties ranging from 15 to 40%, as indicated in Table 2, were introduced in the determination of the penetration profiles. Accordingly, the total uncertainty is estimated to be approximately 40 to 65%. The results plotted in Fig. 8 correlate within this estimate of error.

There is a significant lack of agreement between the present data and Austerman's values as may be seen from Fig. 8. The large differences are perhaps due to diversity in fabrication techniques, in densities and in purity.

The activation energy for the self-diffusion of beryllium in beryllium oxide was found to be $62 (\pm 4)$ kcal/mole. Again this value is significantly different from Austerman's values of 91 kcal/mole below 1725°C and 36.6 kcal/mole above this temperature for his 1961 data. The abrupt change in activation energy just above 1700°C suggested by Austerman was not noted in the present investigation, but the data do not cover sufficiently the high temperature range to make a more definite statement. However, at high temperatures, the length of annealing appeared to have an effect on the final value of the diffusion coefficient. This is illustrated by the results from Samples A and B in Fig. 8. Sample A was annealed for four weeks while Sample B, at only slightly higher temperature, for only two days. It appears that with increasing time, the value of the diffusion coefficient decreases. The effect seems more marked at higher temperatures. Photomicrographs of Samples A and B (Fig. 9)

show a significant grain growth in A which may account for the large differences obtained in the results from the two samples. In order to improve the self-consistency of the results, relatively short annealing periods were used at the higher temperatures.

Another source of uncertainty exists in the penetration profiles at the deeper penetrations containing approximately 15% or less of the original activity. As is apparent from Figs. 5 and 6, the points deviate significantly from the theoretical curve at the deeper penetrations. This is probably due to the existence of additional mechanisms for diffusion besides volume diffusion assumed in the present calculations. Accordingly, only the data from samples containing more than 15% of the activity were used in the calculations.

Diffusion Model

A diffusion mechanism is suggested, based on the movement of beryllium ions via the interstices of the Wurtzite geometry to a vacancy. Figure 10 is a perspective drawing of the approximate physical shape of the spaces between the closed packed anion in the BeO lattice showing the four types of interstices: triangular (shaded in the figure), positive tetrahedral (+T), here containing Be ions, negative tetrahedral, (-T), and octahedral, (Oct).

The interstices have been drawn apart to improve clarity. They fit together by joining them at the shaded

triangular interfaces. The non-shaded curved surfaces are those in contact with the oxygen ions, which have been removed in this drawing. The significance of this diagram is to show the increased complexity of the diffusion path for the cation in contrast to the simple situation commonly used to depict vacancy and interstitial diffusion mechanisms in metals. If it is assumed that site A is occupied and sites B and D are vacant, then the diffusion paths in the c and a directions, as shown in the figure, will give rise to the qualitative energy diagram in Fig. 11. The peaks represent the energies as the Be passes through triangular holes before moving into energy minima corresponding to octahedral (O) or negative tetrahedral (-T) interstices.

The activation energy can be taken to be the sum of two terms, firstly, the increase in crystal energy per ion pair as the distance of the beryllium changes from its value at the equilibrium position, (1.646 Angstroms if ideal Wurtzite geometry is assumed), and decreases to 1.552 Angstroms for the Be ion at the center of the triangle formed by three oxygen ions. Secondly, the energy change due to polarization. The crystal energy per ion pair of charge number z , at a distance R_1 from each other is given by⁹

$$\phi_1 = -\frac{z^2 A \epsilon^2}{R_1} + \frac{z^2 A \epsilon^2 R_0^{n-1}}{n R_1^n} \quad (3)$$

Here A is the Madelung constant, a parameter allowing for the effect of all other ions in the crystal lattice, and R_0 the equilibrium distance in Angstroms; ϵ is the electronic

charge; n is a constant dependent on the compressibility of the crystal. For an ion with a helium configuration (Be^{2+}), $n = 5$, for one with a neon structure (O^{2-}), $n = 7$, and for the actual crystal BeO , n is the arithmetic mean.¹⁰

The first term in Eq. (3) represents Coulombic forces, the second is an interaction term for electron orbital overlap. The crystal energy per mole is therefore:

$$V_1 = -z^2 AN\epsilon^2 \left(\frac{1}{R_1} - \frac{R_0^{n-1}}{nR_1^n} \right), \quad (4)$$

The activation energy for diffusion by the interstitial mechanism is suggested to be the $V_1 - V_0$, where V_0 is the equilibrium crystal energy for $R_1 = R_0$. Using the following values:

$$N\epsilon^2 = 329.7 \text{ kcal-Angstrom}$$

$$z = 2$$

$$A = 1.641 \text{ for Wurtzite}^{9,10}$$

$$R_1 = 1.552 \text{ Angstrom}$$

$$R_0 = 1.646 \text{ Angstrom}$$

the activation energy was found to be 39.2 kcal/mole for the diffusion of Be in BeO . No attempt was made here to estimate the effect of polarization. It is suggested, however, that this value of 39.2 is not inconsistent with the actual value of 62.5 kcal/mole.

Diffusion Coefficients in Single Crystals

The vacancy diffusion model in which the passage of Be ion through a triangular hole determines the activation

energy, also suggests an estimate of the ratio of diffusion coefficients in the directions parallel and perpendicular to the crystallographic c axis at any given temperature.

In the equation proposed by Eyring¹¹

$$D = \lambda^2 \frac{kT}{h} \exp \left(\frac{\Delta S^*}{R} \right) \exp \left(- \frac{\Delta H^*}{RT} \right) , \quad (5)$$

λ is the jump distance, i.e., the distance between the position on either side of a triangular hole; ΔS^* and ΔH^* are the entropy and the enthalpy of activation, k and h are the Boltzmann and the Planck constants, respectively. In the c direction, the activated complex is formed four times, in the a direction, twice before the cation reaches the closest possible vacancy. Although the distances between valleys in the energy diagram are unlikely to be as equally spaced as Fig. 11 suggests, and the energies represented by subsequent peaks are not necessarily equal to that of the first, it is not unreasonable to assume that

$$\lambda_c \cong \frac{c_0}{4} , \text{ and } \lambda_a \cong \frac{a_0}{2} . \quad (6)$$

Therefore, at the same temperature T :

$$\frac{D_a}{D_c} \cong \left(\frac{a_0/2}{c_0/4} \right)^2 = 1.5 , \quad (7)$$

assuming that the thermodynamic equilibrium constant for the formation of the activated complex is the same in a and c directions. Since the activation energies for diffusion in both directions are the same, the ratio of the frequency factors D_a^0 and D_c^0 has this same value 1.5. That is, in single crystals, the model predicts diffusion coefficients

in the a direction to be about 50% higher than in the c direction.

Thermodynamics of Activation

Comparison of Eq. (5) with the parameters in the Arrhenius Eq. (1) gives values for the enthalpy and entropy of activation. The relations between these thermodynamic quantities and the experimentally obtained values for the frequency factor and activation energies are available elsewhere.¹² The relevant equations from the theory of absolute reaction rates are found to be:

$$D_0 = \lambda^2 \frac{kT}{h} \exp \left(\left(\frac{\Delta S^*}{R} \right) + 1 \right) , \quad (8)$$

and

$$\Delta H^* = Q - RT . \quad (9)$$

It is assumed that the vacancy model is predominant, i.e., the time spent by a beryllium ion in the interstices is small compared with the time for it to move to the nearest vacancy. In polycrystalline BeO, with perfectly random orientation of the crystallites, the jump distance, λ , can be taken as the average between the a and c distance.

Using the data by Klein,¹³ namely $a = 2.74$ and $c = 4.45$ at 1500°C , then $\lambda = 3.59 \times 10^{-8}$ cm; consequently $\Delta S^* = -7.8 \pm 2.5$ eu, and $\Delta H^* = -59.0 \pm 4.0$ kcal/mole.

CONCLUSIONS

1. By the use of a precision lapping device which was developed for the purpose of studying self-diffusion of

beryllium in BeO, very small diffusion coefficients could be obtained (as low as 5×10^{-13} cm²/sec) making possible to perform experiments at temperatures as low as 1150°C well within the practical operating region of advanced gas-cooled power reactors.

2. By an aqueous exchange-adsorption technique, suitable infinitely thin layers of Be⁷ could be deposited on the surfaces of the specimens to provide the source for diffusion.

3. A γ -autoradiographic technique was developed to determine penetration profiles of the Be⁷. However, it was used only to a limited extent as an independent check.

4. Self-diffusion coefficients of beryllium in polycrystalline cold-pressed and sintered beryllium oxide have been found to exhibit an activation energy of 62 (± 4.0) kcal/mole and a frequency factor of 2.5×10^{-3} cm²/sec.

5. The entropy and enthalpy of activation for the self-diffusion process were found to be -7.5 (± 2.5) eu and 59.0 (± 4.0) kcal/mole, respectively.

6. A proposed mechanism based on movement of beryllium ions via interstices to the nearest vacancy does not contradict the experimental data. This model predicts, for single crystals, identical activation energies for diffusion in both the a and c directions and the relative magnitude of the frequency factor in the a direction to be about fifty percent higher than in the c direction.

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APPENDIX

Mathematical Treatment

The differential equation which describes one-dimensional diffusion of a substance and assumes a constant diffusion coefficient is the well known expression:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (10)$$

The boundary conditions which approximate more closely the experimental procedure used are:

- a. Zero initial concentration of Be^7 for all penetrations greater than zero, or

$$C(x,0) = 0 \text{ for } x > 0 \text{ and } t = 0.$$

- b. A source containing an amount M_0 of Be^7 which remains constant throughout the diffusion period and is initially deposited in an infinitely thin layer in the plane $x = 0$ at $t = 0$. Accordingly:

$$\int_0^{\infty} C(x,t) dx = M_0 \quad .$$

- c. Specimens of "semi-infinite length."

The solution of Eq. (10) corresponding to the specified boundary conditions is readily available¹⁴ as follows:

$$C(x,t) = \frac{M_0}{(\pi Dt)^{\frac{1}{2}}} \exp \{-x^2/4Dt\} \quad (11)$$

However, in actual experiments, it is not convenient to determine directly the concentrations of Be^7 at different penetrations, but rather to measure the fractions of the original activity remaining in the specimens at different stages of grinding. The appropriate expression is readily obtained if we let:

$M(x,t)$ be the quantity of Be^7 remaining at penetration x , and $F(x,t)$ the corresponding fraction of the original activity. Accordingly,

$$F(x,t) = \frac{M(x,t)}{M_0} = \frac{\int_x^\infty C(x',t) dx'}{M_0} \quad (12)$$

Substituting Eq. (11) in Eq. (12) gives

$$F(x,t) = \frac{2}{(\pi)^{\frac{1}{2}}} \int_x^\infty \exp \{-x'^2/4Dt'\} \frac{dx'}{2(Dt')^{\frac{1}{2}}} \quad (13)$$

It is advantageous to change the variables of integration with the result:

$$F(x,t) = \frac{2}{(\pi)^{\frac{1}{2}}} \int_u^\infty \exp(-u^2) du = \text{erfc}(u) \quad (14)$$

where:

$$u = x/2(Dt)^{\frac{1}{2}} \quad (15)$$

Convenient tabulations of the complementary error function, $\text{erfc}(u)$, are available in the literature¹⁵ and are used in the numerical calculations. Specifically, the fractions remaining, $F(x,t)$, are determined experimentally, the corresponding values of u are obtained from the tabulations and the diffusion coefficients are calculated from Eq. (15) after substitution of the proper values of t which are also experimentally dependent.

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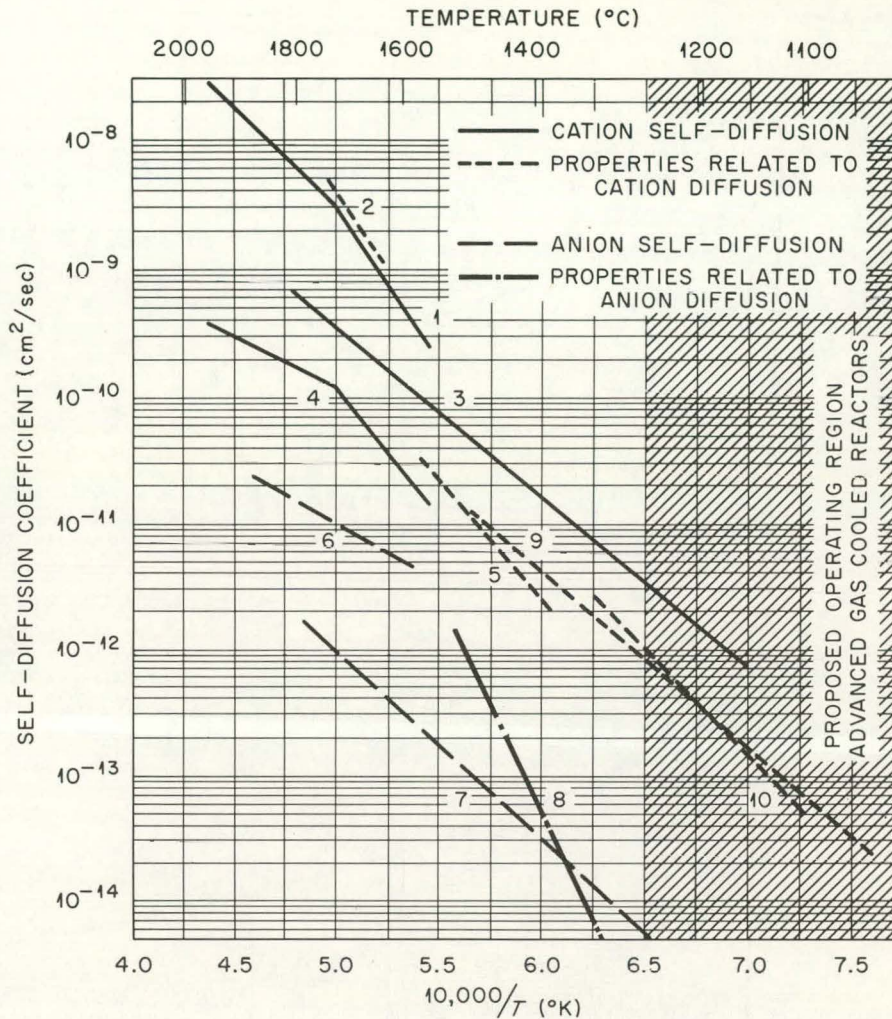
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FIGURE CAPTIONS

- Fig. 1. Self-Diffusion Coefficients in Beryllium Oxide. Direct measurements and calculated values from transport properties.
- Fig. 2. Blank Concentration Profiles.
- Fig. 3. Hand-Lapping Device.
- Fig. 4. Collimator of γ -Radiation for Autoradiography.
- Fig. 5. Fraction of Original Activity Remaining versus Penetration.
- Fig. 6. Fraction of Original Activity Remaining versus $x/(Dt)^{\frac{1}{2}}$.
- Fig. 7. γ -Autoradiographic Analysis of Wedge Ground From Specimen (A-17-4) After Annealing at 1663°C for Two Days.
- Fig. 8. Self-Diffusion Coefficient of Be in BeO as a Function of Temperature.
- Fig. 9. Microstructure of Polycrystalline BeO After Diffusion.
- Fig. 10. Types of Interstices in an Ideal Wurtzite Type Crystal.
- Fig. 11. Energy Diagram for Self-Diffusion of a Cation in a Wurtzite Type Crystal.



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Fig. 1. Self-Diffusion Coefficients in Beryllium Oxide. Direct measurements and calculated values from transport properties.

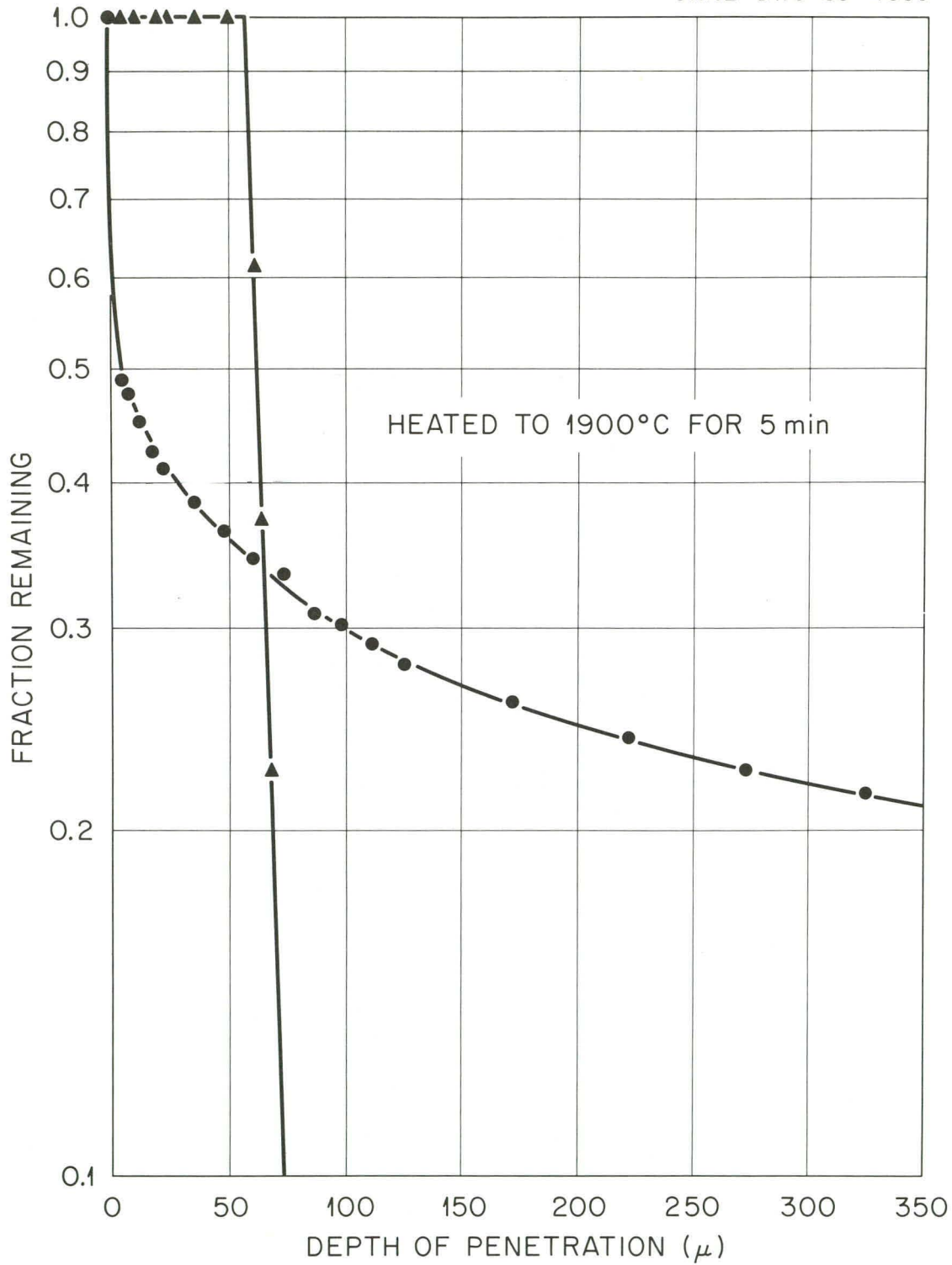
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Fig. 2. Blank Concentration Profiles.

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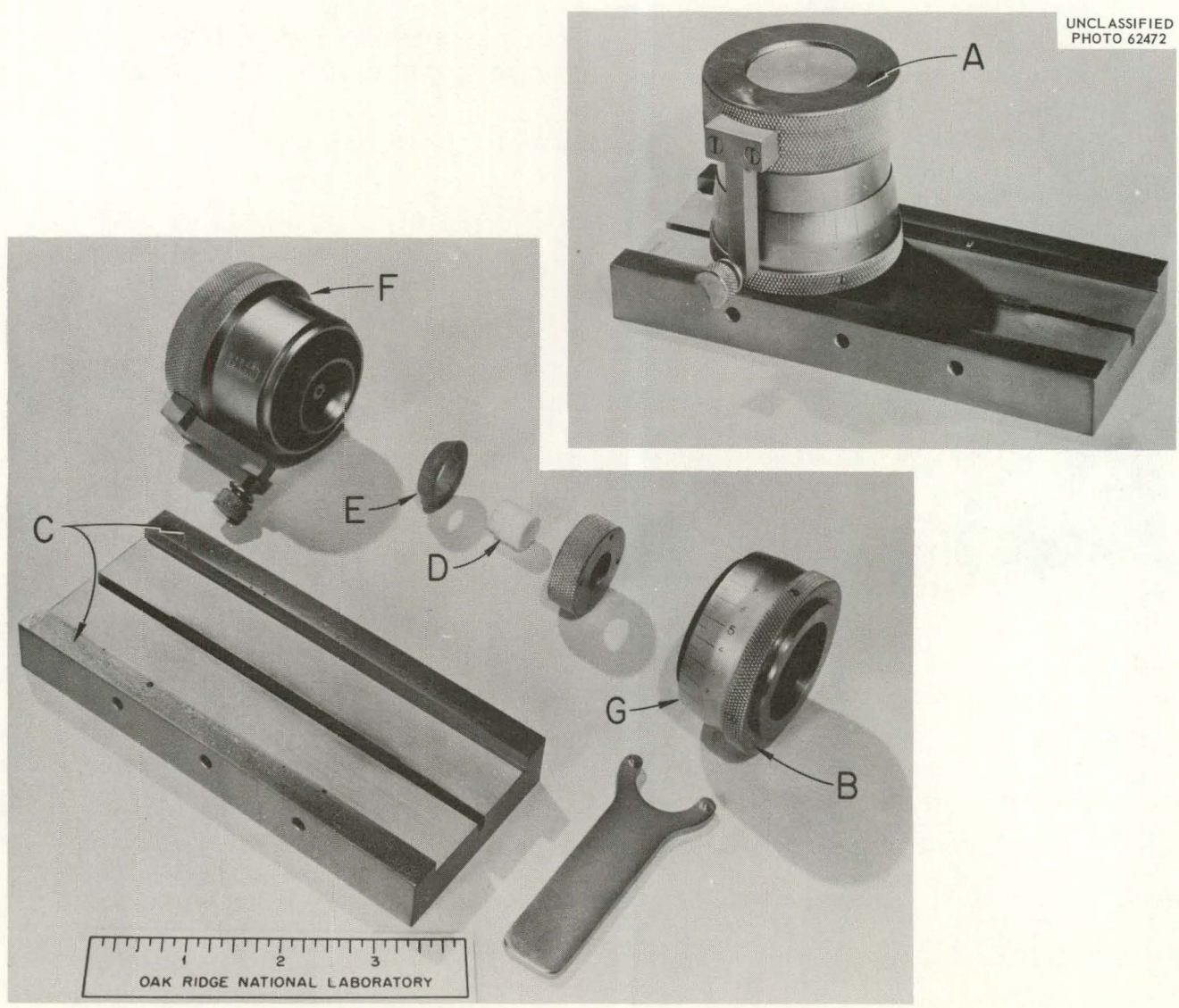


Fig. 3. Hand-Lapping Device.

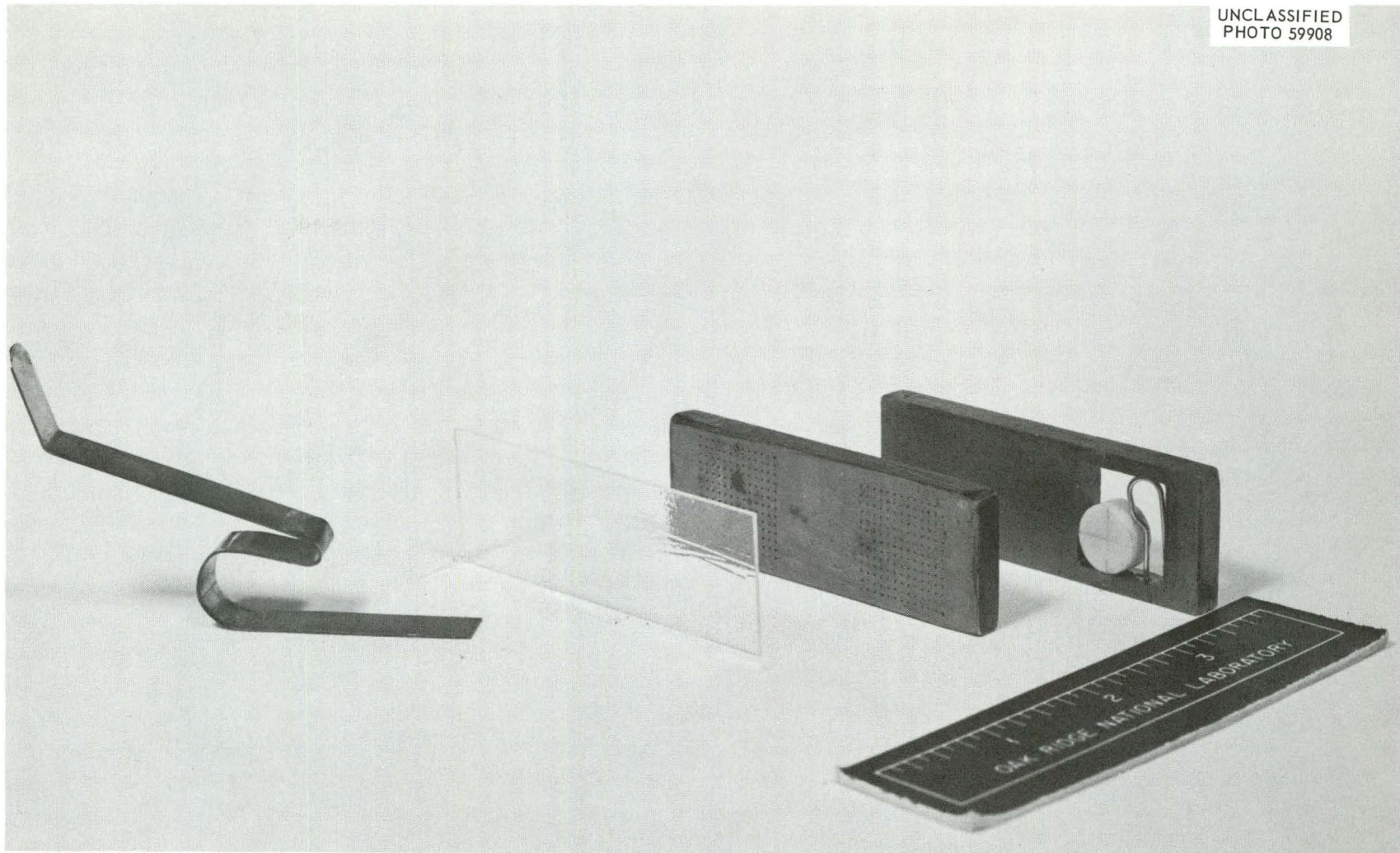


Fig. 4. Collimator of γ -Radiation for Autoradiography.

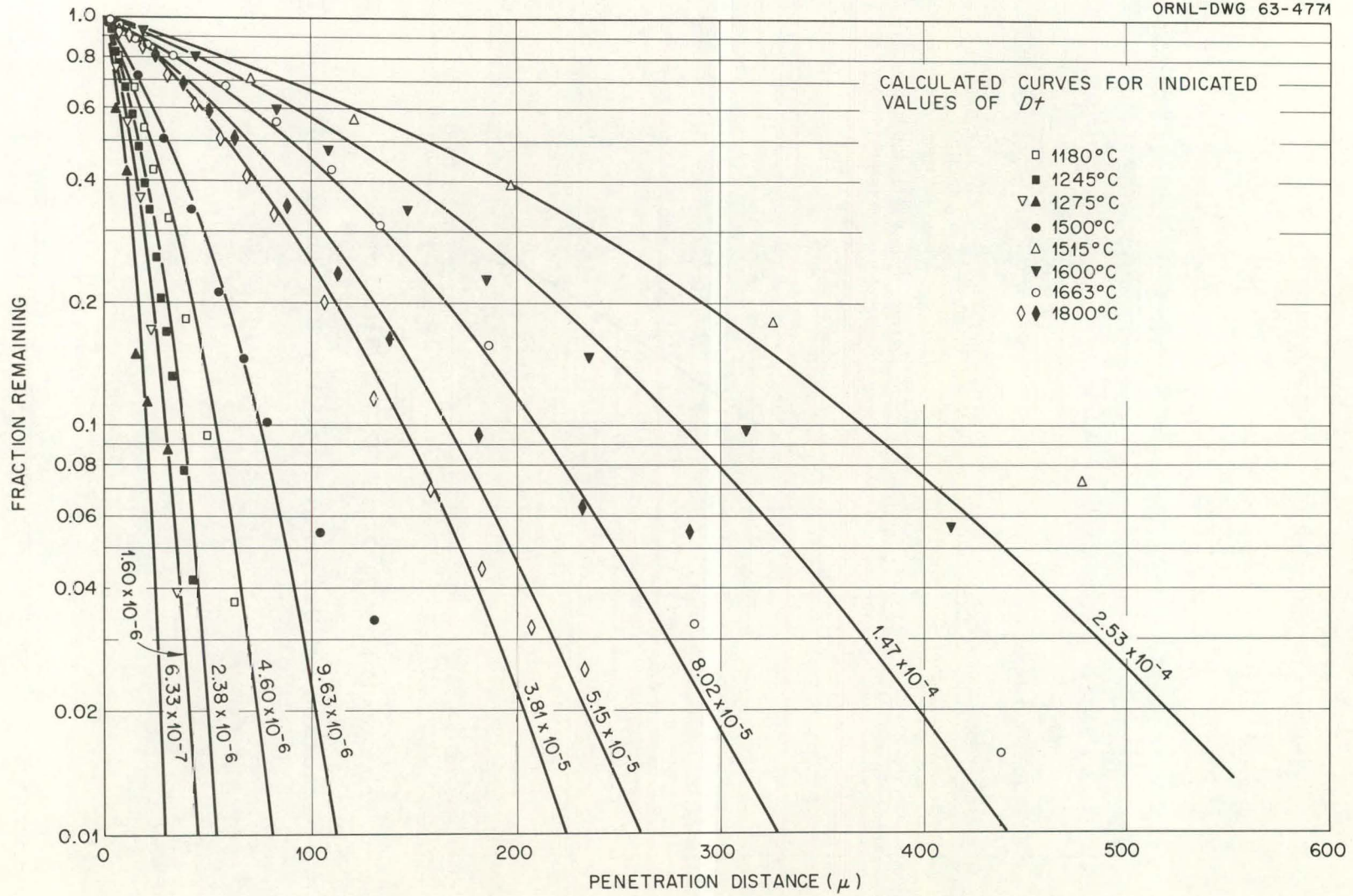


Fig. 5. Fraction of Original Activity Remaining versus Penetration.

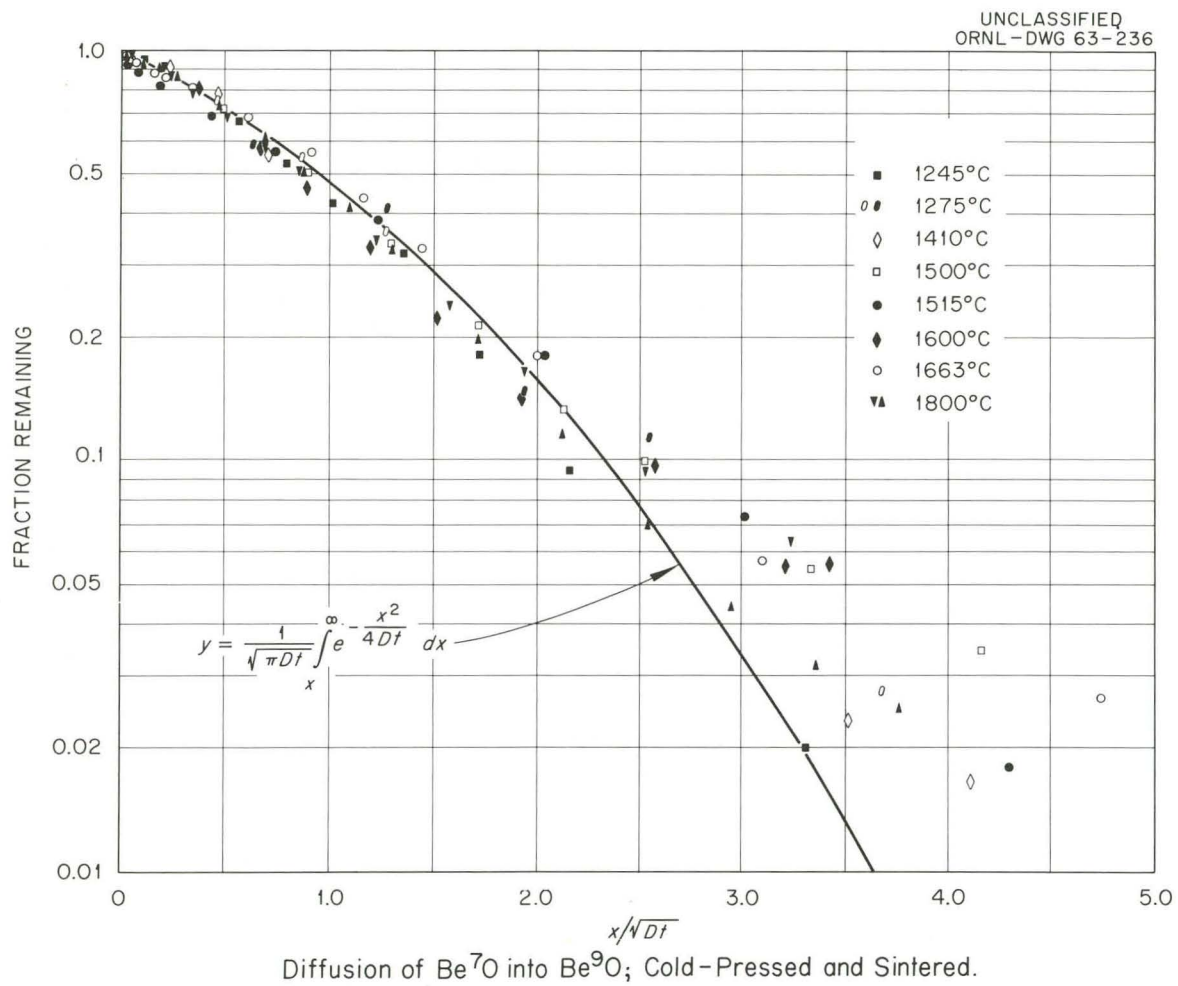


Fig. 6. Fraction of Original Activity Remaining versus $x/(\text{Dt})^{\frac{1}{2}}$.

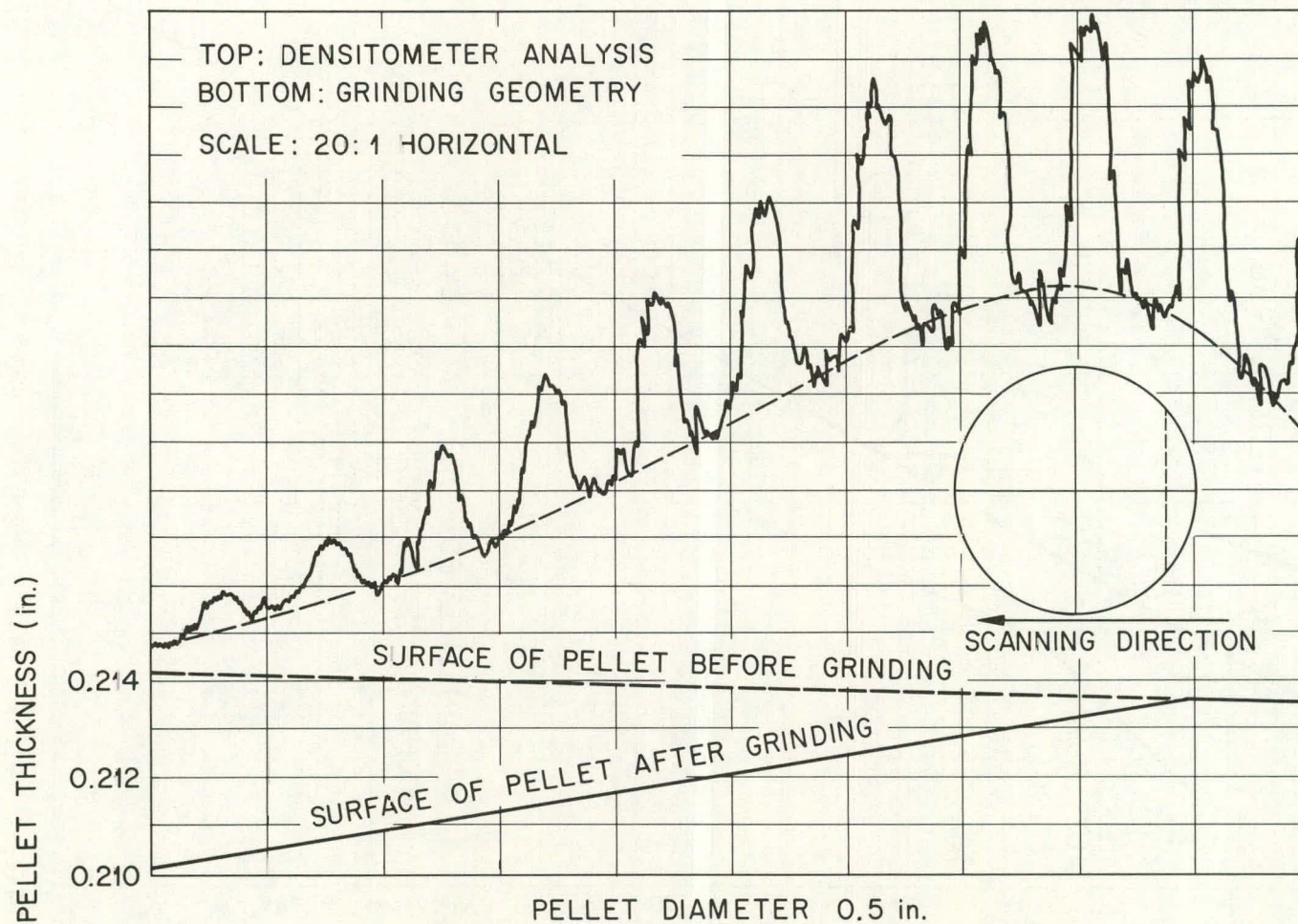


Fig. 7. γ -Autoradiographic Analysis of Wedge Ground From Specimen (A-17-4) After Annealing at 1663°C for Two Days.

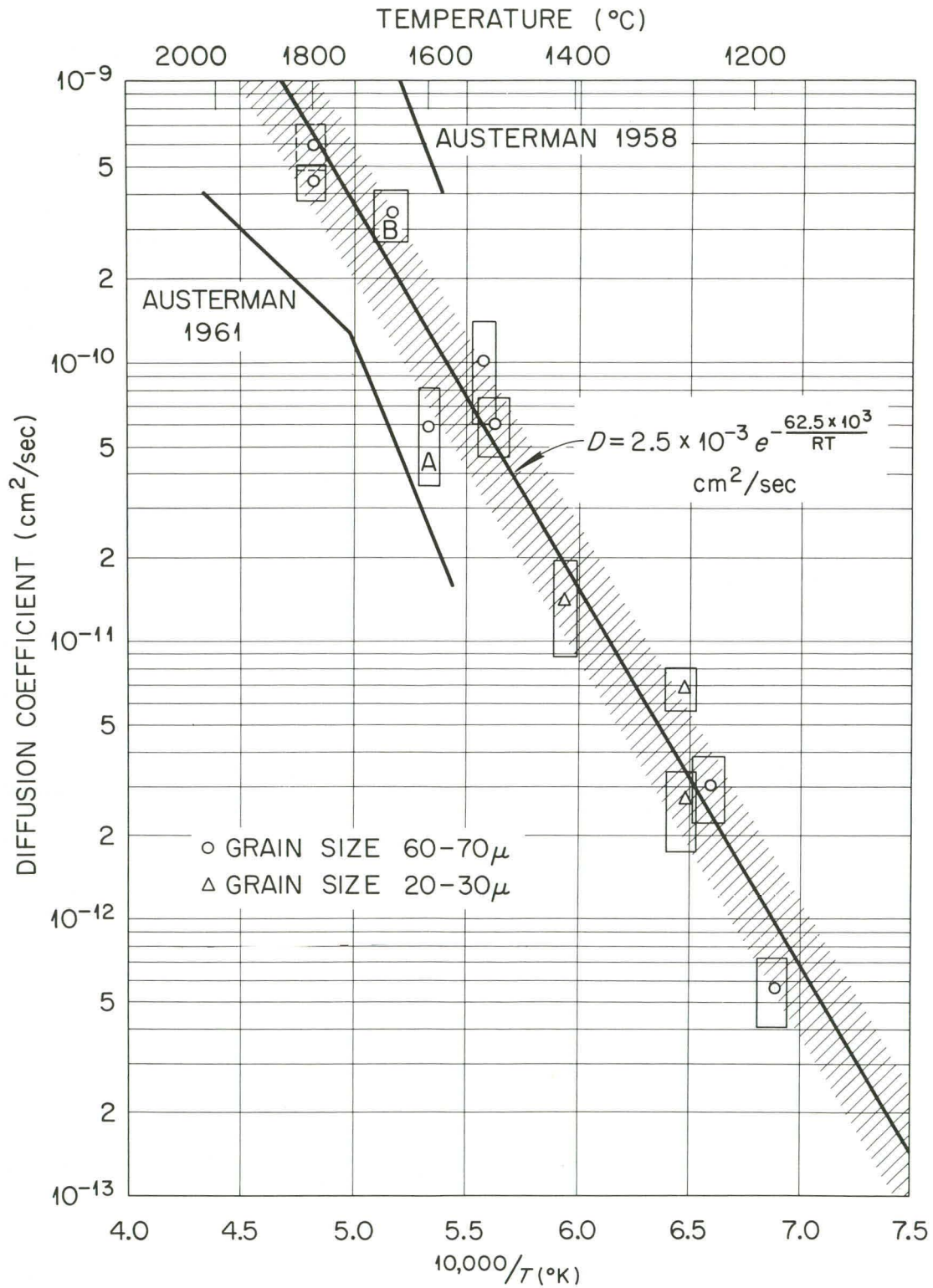


Fig. 8. Self-Diffusion Coefficient of Be in BeO as a Function of Temperature.



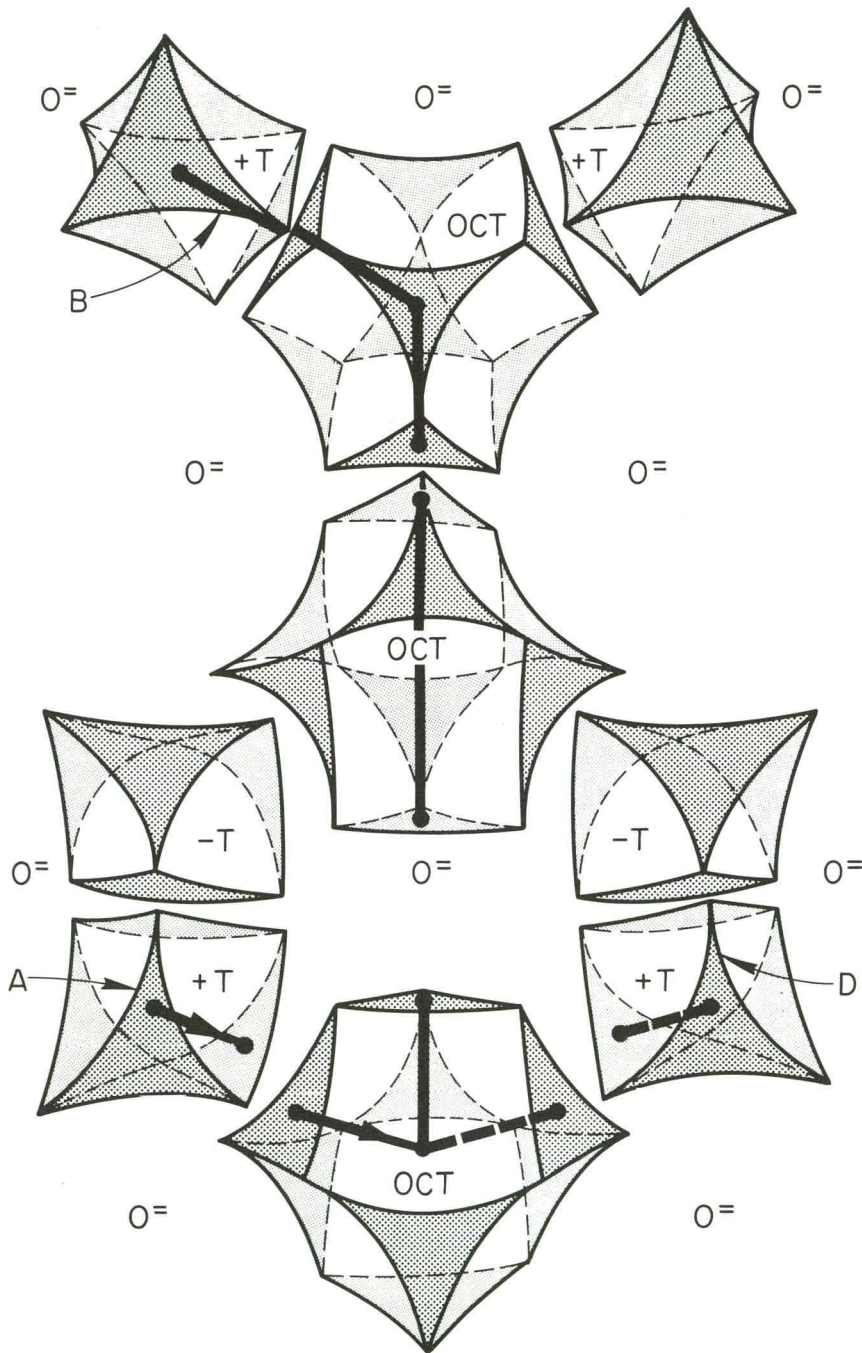
INCHES
0.02
0.03
100X
0.05



17-3 1663°C $D = 34.3 \times 10^{-11}$ sq cm/sec

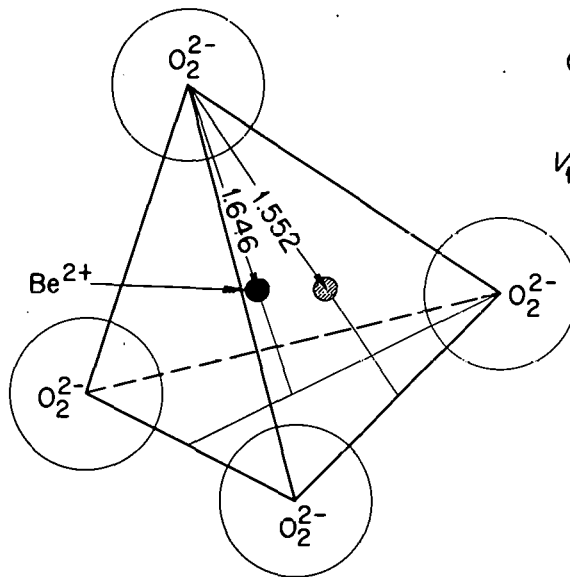
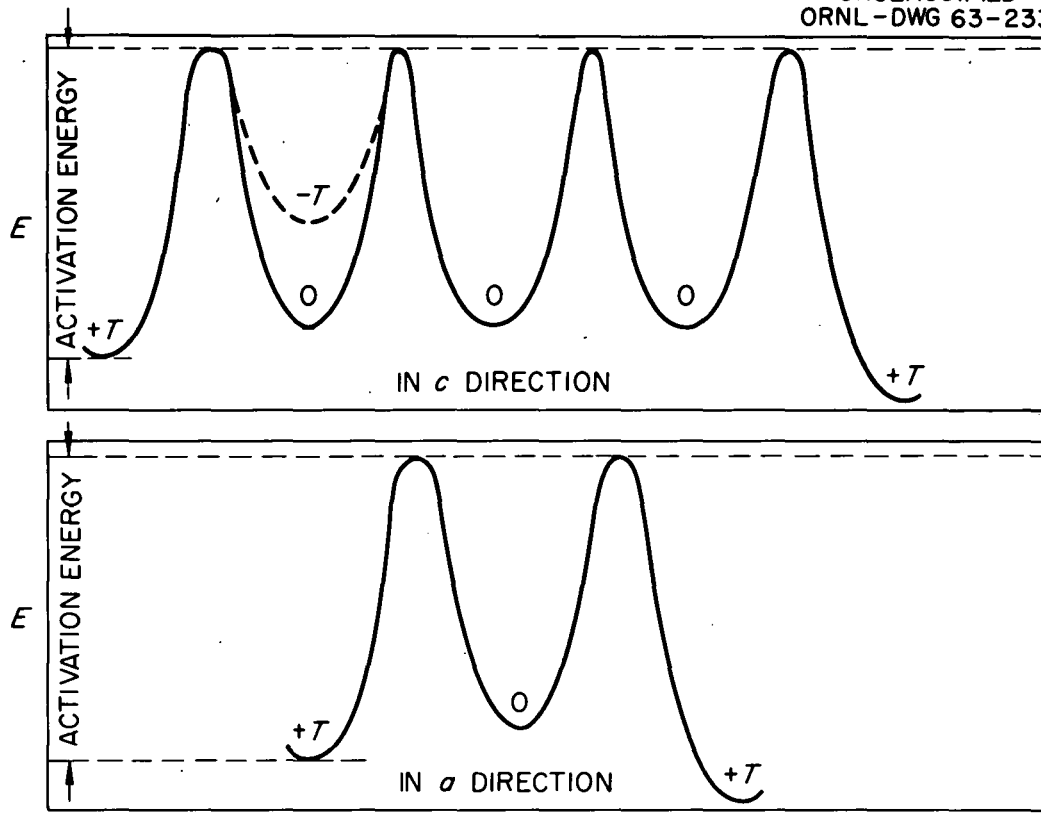
A-1735 1600°C $D = 5.8 \times 10^{-11}$ sq cm/sec

Fig. 9. Microstructure of Polycrystalline BeO After Diffusion.
Reduced 30%.



Exploded View Interionic Space in BeO.
Oxygen Ions Removed.

Fig. 10. Types of Interstices in an Ideal Wurtzite Type Crystal.

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CRYSTAL ENERGY CHANGE

$$= V_1 - V_0$$

$$V_1 = AZ^2 N \epsilon^2 \left\{ \frac{1}{R_1} - \frac{R_0^{n-1}}{n R_1^n} \right\}$$

A = MADELUNG CONSTANT
= 1.641 FOR WURTZITE LATTICE

R_0 = EQUILIBRIUM Be-O DISTANCE
= 1.646 Å (CENTER OF TETRAHEDRON)

R_1 = Be TO O DISTANCE AT CENTER
OF TRIANGLE
= 1.552 Å

n = CONSTANT DETERMINED FROM
COMPRESSIBILITY OF THE CRYSTAL
= 6 FOR BeO

Fig. 11. Energy Diagram for Self-Diffusion of a Cation in a Wurtzite Type Crystal.

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