Theory of Grain Boundary Diffusion*

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The previously proposed dependence of the structure of grain boundaries upon the angle of disorientation of the two grains is used as a basis of a quantitative consideration of diffusion along grain boundaries and in particular of the apparent activation energies. At small angles in the dislocation range the diffusion is controlled by volume diffusion mechanism. At high angles near 45° the model of a uniform grain boundary is applicable. In the intermediate range an array of rod-like areas of distorted lattice leads to low or even negative apparent activation energies. The theory is in good agreement with experiment.

ON the basis of an experimental study of grain boundary diffusion Achter and the author have suggested[1] the following sequence of structures of a grain boundary: At small angles of disorientation θ of the two grains the grain boundary can be described as an array of single dislocations as proposed by Burgers[2] and quantitatively discussed by Read and Shockley.[3] With increasing θ the dislocations increase rapidly in density and collect in bunches which are properly described as areas of highly distorted lattice rather than in terms of individual dislocations. The critical angle θ_R at which this occurs depends upon grain orientation, crystal structure, elastic characteristics of the material, etc. For copper, with grains having one cubic direction in common, the angle θ_R is in the proximity of 15 degrees which for a face-centered cubic lattice corresponds to an average distance between dislocations of about two lattice constants. The rod-like regions of highly distorted crystalline lattice are separated by relatively undistorted areas. With further increase in θ their density increases and finally at θ_S they coalesce into flat areas perhaps several tens or hundreds of atoms broad. This corresponds to the "island" model proposed by Mott.[4] Figure 1(a) illustrates schematically the structure of the grain boundary for the three different ranges of orientation of the grains.

This structure of grain boundaries explains in a qualitative manner the absence of a preferential, rapid grain boundary diffusion at small angles where the average number of neighbors and the space available for the diffusing atom in the grain boundary are not much different from the conditions inside of the grain characteristic of volume diffusion. In that connection it seems certain that the various discrepancies in experimental volume diffusion data[5] cannot be blamed on diffusion along mosaic block boundaries since there the disorientation angle is much smaller than one degree. Only high angle grain boundaries could act as "short circuits."

Grain boundary diffusion becomes observable at an angle θ_C [Fig. 1(b)], when the rods of bunched-up dislocations provide a sufficient volume of disordered crystal and the flux of the diffusing material is big enough to compensate sufficiently for its loss from the grain boundary by volume diffusion into the two neighboring grains. The maximum grain boundary diffusion is reached at 45 degrees. As pointed out elsewhere[1] this structure of grain boundaries is also in agreement with the numerous measurements[6] of grain boundary energy [Fig. 1(c)] and with the observed anisotropy of diffusion in a given boundary.[7] The purpose of this paper is to deduce from this picture a quantitative description of the grain boundary diffusion process and in particular to evaluate the activation energies and their dependence on orientation. We assume that the highly distorted areas possess a diffusion coefficient and an activation energy independent of orientation. The variation of the depth of diffusion and of the apparent activation energy with angle will follow from the influence of orientation of the grains upon the structure of the grain boundary itself.

THE DIFFUSION EQUATION

As yet no general solution of the diffusion equation for diffusion along grain boundaries has been obtained. Fisher[8] derived an approximate solution assuming that (a) the grain boundary is a zone of uniform width δ across which the concentration does not vary and (b) the material diffusing along a grain boundary (direction y) is being lost into the two grains by volume diffusion in a direction perpendicular to the grain boundary only (direction x). The second assumption eliminates the possibility of calculating the shape of the well-known "cusp" for small y, i.e., in the proximity of the intersection of the grain boundary with the original interface, since there the concentration gradient (and the direction of diffusion) is approximately perpendicular to the outline of the cusp. This may seriously affect the various attempts to estimate the ratio of the volume

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[1] M. R. Achter and R. Smoluchowski, Phys. Rev. **76**, 470 (1949); Proc. Natl. Research Council Conference, Pocono Manor, October, 1950; and J. Appl. Phys. **22**, 1260 (1951).
[2] J. M. Burgers, Proc. Phys. Soc. (London) **52**, 23 (1940).
[3] W. T. Read and W. Shockley, Phys. Rev. **78**, 275 (1950).
[4] N. F. Mott, Proc. Phys. Soc. (London) **60**, 391 (1948).
[5] A. S. Nowick, J. Appl. Phys. **22**, 1182 (1951).

[6] See, for instance, Dunn, Daniels, and Bolton, Trans. Am. Inst. Mining Met. Engrs. **188**, 1245 (1950) or K. T. Aust and B. Chalmers, Proc. Roy. Soc. (London) **204**, 359 (1950).
[7] M. R. Achter and R. Smoluchowski, Phys. Rev. **83**, 163 (1951).
[8] J. C. Fisher, J. Appl. Phys. **22**, 74 (1951).

diffusion coefficient to the grain boundary diffusion coefficient from the angle of the cusp.[9] Besides this theoretical difficulty there is also the question of an unambiguous determination of the cusp angle as well as the problem of anisotropy of etching, which foiled the original efforts in that direction on the copper-silver system.[1]

Fisher's approximation is satisfactory whenever the grain boundary diffusion coefficient D_B is much greater than the volume diffusion coefficient D_V. It can be easily shown that it is also self-consistent since the calculated concentration gradient in the grain and the direction normal to the grain boundary make an angle δ/y_B, where y_B is the average depth of penetration along the grain boundary.[10] For experimental reasons, y_B is usually greater than 10^{-3} cm while δ is of the order 10^{-8} cm.

(a) Uniform Grain Boundary

The assumption that the grain boundary is a uniform slab of material of high diffusivity is applicable only at $\theta > \theta_S$, where the distance f between the areas of misfit is small compared to their size b as shown in Fig. 1(a). The average concentration $\bar{C}(y)$ in a grain boundary at a distance y from the original interface is then equal to $C(y)b/(b+f)$, where $C(y)$ is the concentration in the region of misfit. The latter can be obtained from the equation

$$\partial c/\partial t = D_B \partial^2 c/\partial y^2 + (2/\delta)D_V(\partial c/\partial x)_{x=0} \quad (1)$$

in the grain boundary and the equation

$$\partial c/\partial t = D_V \partial^2 c/\partial x^2 \quad (2)$$

in the grains. Fisher has shown that this can be done in an analytical manner because his original assumptions mentioned above lead to the following additional simplifications: (c) In calculating the volume diffusion into the grains the concentration in the grain boundary can be assumed constant and equal to its value at time t and (d) it can be assumed that $\partial c/\partial t = 0$ in the grain boundary at time t. The solution is then of the form

$$C = \phi(y, t)\psi(x, t), \quad (3)$$

which with the boundary condition $C = 1$ at $y = 0$ gives

$$C = \exp(-2^{\frac{1}{2}}D_V^{\frac{1}{4}}y/\pi^{\frac{1}{4}}\delta^{\frac{1}{2}}D_B^{\frac{1}{2}}t^{\frac{1}{4}}) \operatorname{erfc}(x/2D_V^{\frac{1}{2}}t^{\frac{1}{2}}). \quad (4)$$

It is easily seen that condition (d) is extremely strong and makes a solution in this form not applicable when D_V is zero since then (4) should go over into

$$C = \operatorname{erfc}(y/2D_B^{\frac{1}{2}}t^{\frac{1}{2}}). \quad (5)$$

However, for most experimental conditions for which

[9] A. D. Le Claire, Phil. Mag. (7), **42**, 468 (1951).
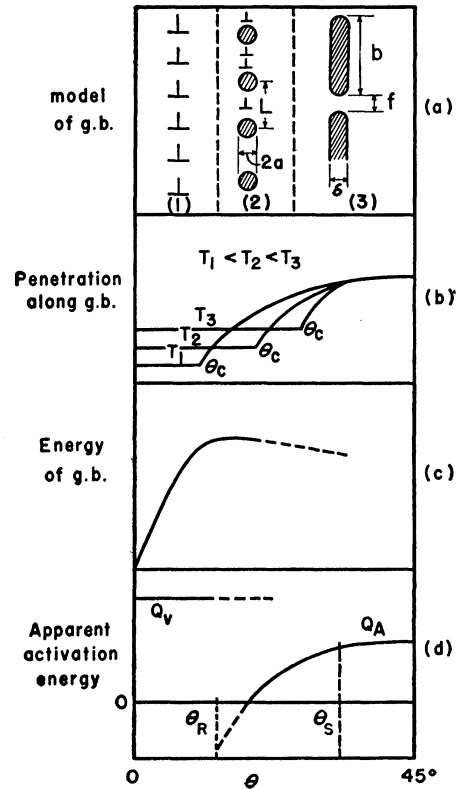[10] Similar to $x_V \cong 2(D_V t)^{\frac{1}{2}}$ for volume diffusion.

FIG. 1. Structure and properties of grain boundaries as a function of the angle of disorientation.

both y_B and x_V are measurable it is probably the best solution now available.

(b) Widely Spaced Rods of Misfit

If the grain boundary consisted of an array of very widely spaced rods of misfit (such as shown in region 2 of Fig. 1(a), for large L), then we could consider diffusion along an isolated rod, diameter $2a$, and neglect the influence of neighboring rods. Instead of Eqs. (1) and (2) we would have then

$$\frac{\partial c}{\partial t_1} = \frac{\partial^2 c}{\partial y_1^2} + 2\left(\frac{\partial c}{\partial r_1}\right)_{r_1=1} \quad (6)$$

in the rod, and

$$\frac{\partial c}{\partial t_1} = \frac{1}{r_1}\frac{\partial}{\partial r_1}\left(r_1\frac{\partial c}{\partial r_1}\right) \quad (7)$$

outside of the rod, in which

$$r_1 = r/a, \quad t_1 = tD_V/a^2 \quad \text{and} \quad y_1 = y/(a^2 D_B/D_V)^{\frac{1}{2}} \quad (8)$$

are dimensionless. The simplifying assumptions and the boundary conditions are analogous to those for the uniform grain boundary. Equation (7) is transformed by $C = v \exp(-\alpha^2 t_1)$ into a Bessel equation of zero order, which for the boundary conditions $C = 0$ at $r_1 > 1$ for

$t_1 = 0$ and $C = 1$ at $r_1 = 1$ for all t_1 gives[11]

$$C(r_1, t_1) = 1 + \frac{2}{\pi} \int_0^\infty \exp(-u^2 t_1)$$

$$\times \frac{J_0(ur_1)Y_0(u) - Y_0(ur_1)J_0(u)}{J_0^2(u) + Y_0^2(u)} \frac{du}{u}, \quad (9)$$

where J_0 and Y_0 are Bessel functions of first and second kind, respectively. Similarly to (3) we put

$$C = \phi(y_1, t_1)\psi(r_1, t_1), \quad (10)$$

in which $\psi(r_1, t_1) = C(r_1, t_1)$ as given by (9). Condition (d) is expressed now as

$$\partial^2 c/\partial y_1^2 + 2\partial c/\partial r_1 = 0 \quad \text{at} \quad r_1 = 1, \quad (11)$$

which with (9) and (10) gives

$$\frac{\partial^2 \phi}{\partial y_1^2} - (8\phi/\pi^2) \int_0^\infty \exp(-u^2 t_1)$$

$$\times (J_0^2(u) + Y_0^2(u))^{-1}\frac{du}{u} = 0 \quad (12)$$

as an equation for ϕ. Since t_1 is of the order $(x_V/a)^2$ which in most experiments is very large ($10^8 - 10^{10}$), we can use the corresponding series expansion[11] of the integral in (12) and obtain

$$\partial^2 \phi/\partial y_1^2 - 4\phi[(\log 4t_1 - 2\gamma)^{-1}$$
$$- \gamma\,(\log 4t_1 - 2\gamma)^{-2} + \cdots] = 0, \quad (13)$$

where γ is Euler's constant $0.577\cdots$. Retaining only the first term we have

$$\phi = \exp[-2y_1\,(\log 4t_1 - 2\gamma)^{-\frac{1}{2}}],$$
or finally

$$C = \exp\{-(2yD_V^{\frac{1}{2}}/aD_B^{\frac{1}{2}})$$
$$\times [\log(4D_Vt/a^2) - 2\gamma]^{-\frac{1}{2}}\}\psi(r_1, t_1). \quad (14)$$

If in (12) we expand the integral in a series[11] valid for small t_1, we obtain

$$\partial^2 \phi/\partial y_1^2 - \phi[2(\pi t_1)^{-\frac{1}{2}} + 1 - \frac{1}{2}(t_1/\pi)^{\frac{1}{2}} + \cdots] = 0, \quad (15)$$
and
$$\phi = \exp\{-y_1[2(\pi t_1)^{-\frac{1}{2}} + 1 - \cdots]^{\frac{1}{2}}\}, \quad (16)$$

which, retaining only the first term and putting δ for a in relations (8), are identical with Fisher's equations; in particular (16) becomes the first factor of (4). This is satisfactory since small t_1 corresponds to a large a which should approximate a uniform, flat boundary.

(c) Intermediate Case

It is clear that the assumption of a negligible influence of neighboring rods on diffusion is not tenable when the distance between rods L is small compared to the aver-

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[11] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Clarendon Press, Oxford, 1947).

age depth of volume diffusion away from the rods. Then the concentration of the diffusing material in the areas between the rods increases so rapidly that soon the majority of the flux from the rods is in the direction perpendicular to the grain boundary rather than radial. This concentration ridge between rods will be built up by a volume diffusion process since in the grain boundary the dislocations will then be perpendicular to the direction of diffusion.[7] The amount of this volume penetration depends of course on the concentration at the grain boundary and will be large for small y and small for large y. The character of grain boundary diffusion will therefore change from that of a uniform boundary, near the original interface, to that typical of rod diffusion for large y. It follows also that for a particular y with increasing time the diffusion will approach that of a uniform boundary. A complete solution of the diffusion equation in the case of such an array of parallel, equally spaced rods is obtainable but is very complicated. It seemed therefore more advisable to obtain an approximate solution which would lend itself to an intuitive interpretation.

The solution is obtained by putting for the gradient $(\partial c/\partial r_1)_{r_1 = 1}$ in Eq. (11) a linear combination of the gradients for a single rod and for a uniform boundary. We obtain then from Eqs. (13) and (15)

$$\partial^2 \phi/\partial y_1^2 - 2\phi[2q(\log 4t_1 - 2\gamma)^{-1} + (1-q)(\pi t_1)^{-\frac{1}{2}}] = 0. \quad (17)$$

On the basis of the preceding discussion the parameter q should be, in general, a function of $\phi(y)$, however, as it will appear later, a constant q (i.e., some sort of an average over y) leads to satisfactory results. We have thus from (17)

$$\phi = \exp\{-y_1[4q\,(\log 4t_1 - 2\gamma)^{-1} + 2(1-q)(\pi t_1)^{-\frac{1}{2}}]^{\frac{1}{2}}\}, \quad (18)$$

where q varies from 0 for a uniform boundary to 1 for a single rod. A theoretical interpretation of the parameter q is given in a later section.

THE APPARENT ACTIVATION ENERGY

It is reasonable to suppose that the diffusion coefficients in the grain boundary material and in the volume of the grain obey the usual exponential law at least in the relatively narrow range of temperatures in which measurements of diffusion along individual grain boundaries are feasible. We have thus

$$D_B = D_{B0} \exp(-Q_B/RT)$$
and
$$D_V = D_{V0} \exp(-Q_V/RT). \quad (19)$$

With increasing temperature both D_B and D_V increase; however, since $Q_V > Q_B$, the increase of D_V is more rapid. This has the following important consequence: With increasing temperature the rate of loss of the diffusing material from the grain boundary into the two grains increases more rapidly than the increase of its flux in the grain boundary itself. The apparent activa-

tion energy for grain boundary diffusion Q_A, i.e., the activation energy of the flux along the grain boundary is therefore lower than Q_B and may even become negative. This, as we will see, depends upon the structure of the grain boundary as a function of the angle θ.

The only experimental data which are suitable for comparison with theory were obtained by observing the depth of penetration along individual boundaries[12] at various temperatures. The experimental technique indicates the limit y_L beyond which the concentration is lower than a certain well reproducible, though only approximately known, critical value. The apparent activation energy is then conveniently defined by

$$y_L{}^2 = f(t, T) \exp(-Q_A/RT), \qquad (20)$$

where $f(t, T)$ is a slowly varying function of T or independent of it. For volume diffusion we have, of course,

$$y_V{}^2 = kt \exp(-Q_V/RT), \qquad (21)$$

where k is a constant. For a "uniform" grain boundary or "slabs" at high θ, i.e., when the islands are wide and thin, we put $x=0$ in (4) and the exponent equal to a constant. We have then, using (19),

$$y_S{}^2 = kt^{\frac{1}{2}} \exp[-(Q_B - \tfrac{1}{2}Q_V)/RT]. \qquad (22)$$

For a grain boundary described in terms of widely separated rods we put $r_1 = r/a = 1$ in (14) (thus $\psi(r_1, t_1) = 1$) and equate the exponent to a constant. This gives

$$y_R{}^2 = k[\log(4D_V t/a^2) - 2\gamma] \exp[-(Q_B - Q_V)/RT], \qquad (23)$$

in which the influence of temperature on the first factor is negligible compared to the exponential. Finally in the intermediate case we have from (18)

$$y_I{}^2 = kt^{\frac{1}{2}} D_B D_V{}^{-\frac{1}{2}}[\log(4D_V t/a^2) - 2\gamma]$$
$$\times \{2q\pi^{\frac{1}{2}}(D_V t)^{\frac{1}{2}} + (1-q)a[\log(4D_V t/a^2) - 2\gamma]\}^{-1}, \qquad (24)$$

which cannot be put in form (20) valid at all temperatures. However, grain boundary diffusion experiments usually can be made only over a rather narrow range of temperatures, and thus in proximity of a particular temperature T' an approximate expression is obtainable from (24),

$$y_I{}^2 = (y_I{}')^2 \exp\{[(Q_B - \tfrac{1}{2}Q_V) + qA(Q_B - Q_V)]$$
$$\times [R(1+qA)]^{-1}(1/T' - 1/T)\}, \qquad (25)$$

where

$$A = (4\pi D_V{}' t)^{\frac{1}{2}} a^{-1}[\log(4D_V{}' t/a^2) - 2\gamma]^{-1}$$

and the prime indicates values at T'.

Equations (21), (22), (23), and (25) give thus the apparent activation energies expressed in terms of Q_B and Q_V, Table I, for various ranges of θ corresponding to grain boundaries made up of individual dislocations, rods, and slabs of distorted crystal lattice. The low apparent activation energy for an array of rods and especially for a single rod is due to the fact that the

concentration gradient at a convex surface is greater than at a flat surface. It follows that the loss of the diffusing material from the grain boundary into the grains will be more rapid for an array of rods than for a uniform grain boundary, and thus an increase of temperature will be more effective in lowering the concentration and the apparent activation energy at a boundary made up of rods than at one made up of flat slabs. If $Q_V > 2Q_B$, there will be only negative apparent activation energies, except of course, at small angles where only the usual volume diffusion occurs. Even for $Q_V < 2Q_B$ negative apparent activation energies may occur at low T near θ_R. It should be noted, however, that $\theta_R > \theta_C$, and that below θ_C no characteristic grain boundary diffusion is observable.

Negative apparent activation energies in diffusion processes have been found in other instances. Barrer[13] studying the flow of gases through zeolites which provide a whole network of capillary channels of molecular size found that in certain cases an increase in temperature actually reduced the flux. This is explained as an overcompensation of the increase of mobility of gas molecules in the channels by a decrease of the interstitial density and thus by a decrease of the concentra-

TABLE I. Apparent activation energies.

Angle	Structure	Q_A
$0 < \theta < \theta_R$	Dislocations	Q_V
$\theta \sim \theta_R$	Single rods	$Q_B - Q_V$
$\theta_R < \theta < \theta_S$	Array of rods	$[(Q_B - \tfrac{1}{2}Q_V) + qA(Q_B - Q_V)](1+qA)^{-1}$
$\theta_S < \theta < 45°$	Slabs	$Q_B - \tfrac{1}{2}Q_V$

tion gradient of sorbate molecules. In grain boundaries this decrease is due to an increased loss into the neighboring grains.

COMPARISON WITH EXPERIMENT

As mentioned before, experimental data suitable for comparison with theory have been recently obtained[12] on grain boundary diffusion of zinc in copper. They are reproduced schematically in Fig. 1(b) in which the depth of penetration along grain boundaries is plotted against angle θ for various temperatures assuming that the times of diffusion were so adjusted as to give the same depth of penetration at 45°. Using Eqs. (21)–(25) we can calculate the experimental apparent activation energies. For small θ, that is the region of simple volume diffusion, one obtains $Q_A = Q_V = 34,000$ cal/mole. At 45° the ratio of the penetration depths Eq. (22) gives $Q_A = Q_B - \tfrac{1}{2}Q_V = 7500$ cal/mole or $Q_B = 24,500$ cal/mole. In the intermediate range, that is for $\theta_R < \theta < \theta_S$ where the rodlike structure predominates, we obtain q as a function of θ from the ratio of penetrations as given by Eq. (24). The effective diameter of the rod was put equal to 10^{-8} cm. From these experimental values of q one

[12] R. Flanagan and R. Smoluchowski, Bull. Am. Phys. Soc. **27**, 23 (1952) and J. Appl. Phys. (to be published).

[13] R. M. Barrer, Trans. Faraday Soc. **45**, 358 (1949).

TABLE II. Apparent activation energy Q_A, distance between rods L, and parameter q for various angles of disorientation.

Angle θ	25°	30°	35°	40°	45°
q(exp)$\times 10^6$	14	4.4	0.2	0	0
Q_A(exp) cal/mole	1960	4050	7210	7500	7500
L(exp) A	16	8.5	5.2	slab	slab
L(th) A	10	6.8	5.1	slab	slab
q(th)$\times 10^6$	12.5	4.5	0.2	0	0
Q_A(th) cal/mole	2160	4000	7200	7500	7500

can calculate now (with $T'=600°C$) the apparent activation energies from the corresponding formula in Table I. The results are given in Table II. It appears thus that in accord with expectations the apparent activation energy begins to drop as soon as there is not enough distorted material available along the grain boundary to form more or less continuous slabs. This occurs around 35 degrees. The apparent activation energy is measurable until it drops to such low values at $\theta=\theta_C$ that the volume diffusion overshadows any preferential grain boundary penetration. It is important to note that q is of the order 10^{-5} which agrees with the assumption that the concentration between the rods is high and that a small contribution of the rod-like diffusion is sufficient to lower appreciably the apparent activation energies.

THEORETICAL CALCULATION OF THE APPARENT ACTIVATION ENERGIES

It should be pointed out that the experimental values of the apparent activation energies in Table II are obtained without assuming any constants (apart from a plausible value for the effective radius of the rods) or making any specific assumption about a probable relation between q and other quantities. Such a relationship, however, is necessary to complete the theory. From the
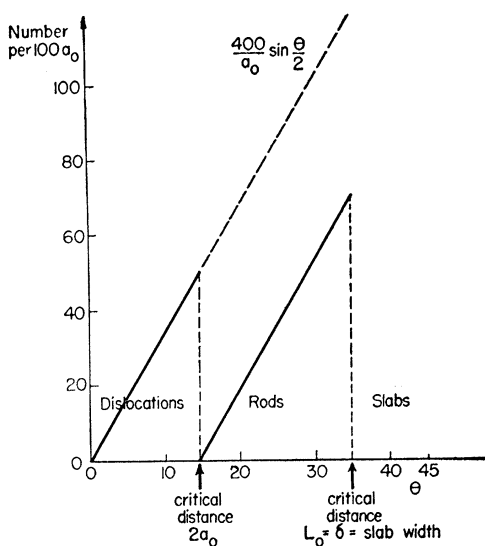
FIG. 2. Density of dislocations and of rods of distorted crystal lattice in grain boundaries as a function of the angle of disorientation.

previously discussed roles of L and of the average depth of penetration it seems natural to put

$$q=K'(L(\theta)-L_0)(D_V't)^{-\frac{1}{2}}, \qquad (26)$$

where $L(\theta)$ is the average distance between rods as a function of θ, L_0 is the critical distance at which the rods coalesce to form slabs and K' is a proportionality factor. The prime indicates, as previously, the values of K and of the diffusion coefficient at some intermediate temperature T' within the range of temperatures over which the apparent activation energies are being determined. In view of the dependence of q on T' rather than on T, the latter does not enter in the derivation of the apparent activation energy in Eq. (25). L_0 is probably of the order of a few angstroms while $L(\theta)$ can be determined from the known expression[3] for the density of dislocations. For a face-centered lattice and one common cubic direction this density is given approximately by

$$\rho=(4/a)\sin\frac{1}{2}\theta. \qquad (27)$$

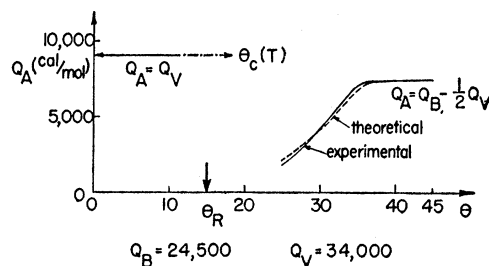As mentioned previously, at $\theta_B=15°$ the average dis-

FIG. 3. Experimental and theoretical apparent activation energies for diffusion of zinc in grain boundaries of copper as a function of the angle of disorientation.

tance between dislocations is about two lattice constants, and so we can assume that every additional dislocation produces a rod. This is illustrated in Fig. 2 where the number of dislocations and rods per 100 lattice constants is plotted against angle θ. In this figure the critical distance L_0 has been put equal to 5A, the slab width suggested by Fisher,[8] with the result that from about 35° on the grain boundaries consist only of slabs. One could evaluate $L(\theta)$ taking into account lattice strains and a certain degree of randomness of the spacing of dislocations, but the results do not seem to warrant the much more complicated assumptions.

It is of interest to check the validity of Eq. (26), which ties in the apparent activation energy with the known density of dislocations along a grain boundary. First of all, since L is the order of 10^{-8} cm and $(D_V't)^{\frac{1}{2}}$ of the order 10^{-3}, it is clear that whatever specific assumptions we make about L_0, Eq. (26) gives the right order of magnitude of q and thus the constant K' is of the order unity. This is important since it indicates that the model underlying the theoretical formulas and the approximate solution of the diffusion equation for an

array of rods are satisfactory within the limits of the available experimental material. The very small values of q obtained from experiment make the value of its upper limit rather unimportant and it is sufficient that for L of the order of 10^{-3} cm, q is of the order of one. If we put $K'=2$, then the experimental values for L shown in Table II are in good agreement with the theoretical L calculated on the basis of Eq. (27). Consequently the same applies to the calculated values of q and Q_A. The latter are compared with experiment in Fig. 3. Of course the surprisingly good agreement with experiment does not indicate that the specific values assumed for the critical distances between dislocations and between rods or the diameter of the latter are uniquely correct. Rather it indicates that with reasonable values for these quantities the suggested structure of grain boundaries is in accord with experimental observations.

In discussing the intermediate case it was pointed out that the character of the diffusion will depend upon time due to the increasing concentration between the rods. As evident from Eq. (26) and Table I the apparent activation energy will gradually increase with increasing time. However, as experiment shows, this gradual local approach to a uniform grain boundary does not overshadow the basic role of the rod-like structure and the resulting striking variation of Q_A with θ. It is clear that the early idea that a grain boundary varies in a gradual manner from an array of dislocations at small θ to a slab of highly distorted material at high θ, with a gradual decrease of the activation energy from Q_V to Q_B, is in disagreement with experimental data here discussed.

The author wishes to express his appreciation to Dr. F. Adler and Dr. E. G. Olds for help and discussion of some of the mathematical problems.

Note added in proof: C. S. Smith in his discussion to the paper by H. Brooks in the 1951 A.S.M. Seminar on Metal Interfaces points out that the difference between low angle and high angle grain boundaries is easily seen in soap bubble models shown on p. 167 of the above reference. In his paper Brooks indicates schematically, in Fig. 4b, the area of plastic deformation surrounding a dislocation. Formation of a rod would correspond to merging of such areas, of neighboring dislocations, with a concurrent formation of vacancies. The stability of a regular array of such rods is now being investigated. The author is indebted to Dr. F. Seitz for a discussion of these matters.

Slow Neutron Crystal Spectrometry: The Total Cross Sections of Co, Er, Hf, Ni⁵⁸, Ni⁶⁰, Ho, and Fission Sm†

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A focusing spectrometer using a variable curvature quartz crystal has been developed for measuring total cross sections *versus* energy of small samples of rare elements, separated isotopes, and radioactive isotopes in the energy region 0.03 ev to about 1.5 ev. Samples having macroscopic cross sections from 0.1 to 1.0 square millimeters have been used as absorbers. The main features of the new instrument are described, and performance curves are given. The instrument was first used to show that a sample of rare earth fission product material has a resonance at an energy corresponding to the known resonance of Sm^{149}. Test runs were made on normal cobalt, whose total cross section was found to fit the formula, σ(barns) $=5.0+6.1(E$ in ev$)^{\frac{1}{2}}$. A resonance at about 1 ev, attributed in the literature to zirconium, was found to belong to hafnium. Erbium was found to have a neutron resonance at about 0.5 ev. Ni^{58} was found to be the isotope primarily responsible for the anomalously high scattering cross section of normal nickel, confirming results from neutron diffraction studies made simultaneously by other observers. Results are given also for Ni^{60}. Analysis of the holmium measurements give a scattering cross section that is strongly energy dependent. Paramagnetic scattering is suggested as a possible explanation of the variation.

I. INTRODUCTION

FOR the past several years we have been interested in the measurement of total cross sections of very small samples of elements rare in the highly pure state and of separated stable isotopes. We have been interested also in the possibility of measuring the cross sections of radioactive isotopes. For these, of course, only microscopic quantities of sample can be made available. In order to achieve acceptable values of transmission the sample and the neutron beam must necessarily be of very small cross-sectional area. Also, because of the intense radiations emitted by the sample, adequate shielding of personnel during the long periods of observation becomes of paramount importance. For this program we have adapted the focusing spectrograph described below, which has been in use for the past several years. This report covers some of the measurements made with it during this period.