Letters to the Editor

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Anisotropy of Diffusion in Grain Boundaries*

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THE structure and behavior of grain boundaries are subjects of much recent interest. One of the aspects which draws attention is the question to what extent the structure and property of a grain boundary depends upon the relative orientation of the two grains and upon the orientation of the grain boundary itself. The latter effect is rather small and will not be considered here. There is little doubt that the soap bubble analogy, where only the surface tension plays a role, is a rather rough approximation although it is very convenient for a description of the general aspects of grain boundaries, their topology, etc. In connection with a general study of diffusion along grain boundaries new evidence was obtained which indicates strongly that grain boundary tension or energy alone is not sufficient to describe its state and that crystallographic aspects play a vital role.

The experiment consisted in measuring diffusion of silver along grain boundaries of columnar copper (all grains having one cubic axis parallel to a common direction), the amount of penetration being observed by means of differential etching of silver-rich copper. As previously reported,[1] the preferential diffusion along grain boundaries in the columnar direction turned out to be negligible for angles (θ) between the two grains smaller than about 20 degrees, but increased rapidly for greater angles, reaching a maximum at 45°. Since columnar grains are often not ideally parallel and the deviation may reach values as high as 20–30°, in the above-mentioned study only those pairs of grains were considered which were columnar within 7–8°.

In many instances, at a junction of three grains, a grain boundary along which the columnar diffusion is high joins a grain boundary with low columnar diffusion. Such junctions were of particular interest, since it appeared that often silver supplied by the silver-rich boundary diffused into the silver-free boundary. Such diffusion, which occurred naturally in a direction perpendicular to the columnar direction, afforded a comparison of diffusion in the same grain boundary in two mutually perpendicular directions. The situation is best explained with reference to Fig. 1 (a) and (b), in which the plane represents the perspective view of a boundary between two grains. Each of the two grains has one cubic direction almost in the columnar direction (upward), with an angle α enclosed between them. The plane of that angle makes an angle β with the plane of the boundary (in the drawing it is assumed for simplicity that the two planes intersect along a columnar direction). Angle θ is the previously mentioned angle between two other cubic directions. The experiment indicates that whenever β is near a right angle, then for θ and α less than 20° there is no measurable grain boundary diffusion under the particular experimental conditions. For α small and $\theta>20°$ there is, as previously indicated, appreciable diffusion in the columnar direction but none perpendicular to it. Finally, for θ small and $\alpha>20°$ there is appreciable diffusion in the direction perpendicular to the columnar direction but none in the columnar direction. If α is large but β is small, i.e., in the case when the grain boundary has to be represented as an array of screw dislocations rather than edge dislocations,[2] the diffusion is very small. It follows that diffusion along a grain boundary is large along edge dislocations whenever the corresponding angle is large enough and is small perpendicular to these dislocations. The ideal directions of such edge dislocations are indicated by dashed lines in the lower portion of Fig. 1 (a) and (b).

It should be noted here that the large angle required to obtain appreciable grain boundary diffusion casts doubt whether there is any appreciable excess mobility of atoms along individual dislocations. At these large angles the distance between the dislocations is so small that the individuality of the dislocation is lost and one should rather imagine the dislocations being bunched up,

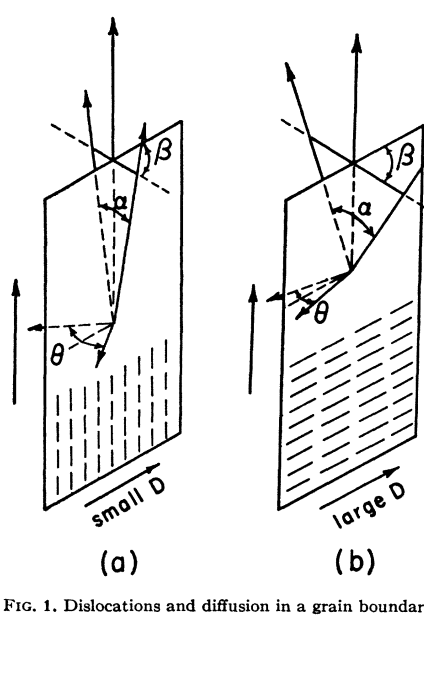

FIG. 1. Dislocations and diffusion in a grain boundary.

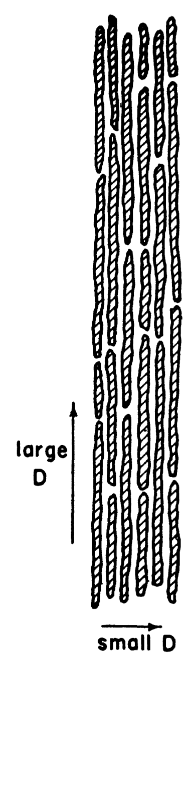

FIG. 2. "Islands of fit" and diffusion in a grain boundary.

forming atomic "channels." The experimental results can be explained perhaps even better by applying Mott's model of a grain boundary.[3] In this picture, which is particularly suitable for angles of the order of 20° and up, the grain boundary is made up of islands of fit surrounded by areas of misfit. The angle between the grains determines the distribution and shape of these islands, as is very schematically illustrated in Fig. 2. The diffusion would occur along the areas of misfit and would always be preferred in a direction parallel to the long axis of the generally elliptical areas of fit. This is, of course, also the direction of the edge dislocations in the other model and agrees with experiment.

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[3] N. F. Mott, Proc. Phys. Soc. (London) 60, 391 (1948).

Angular Distribution of Protons from $Li^6(d,p)Li^{7*}$, Li^7

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RECENT determinations[1,2] below 1-Mev deuteron energy of the angular distributions of the two groups of protons emitted in this reaction do not agree with one another. Since the forms of the distributions help in the allocation of spin to the excited state of Li^7 near 480 kev, it is important if possible to resolve this difference.

Ilford Type C2 photographic plates have been used in a camera previously described[3] to record the two groups of protons at all angles simultaneously. The total emission of protons at each of 10 angles between 13° and 167° is determined by counting the tracks with a $\frac{1}{4}''$ objective and ×6 eyepieces in a binocular microscope. At least two plates are exposed and some 20,000 tracks counted at each energy. The total emission is then divided into the long and short range groups by constructing representative histograms of 600 tracks at five of the ten angles of observation at each deuteron energy. The ratio of long to short range protons varies both with angle and energy. Typical angular distribution curves are shown in Fig. 1.

The angular distributions of the total emission and the long and short range groups are expressed in the form

$$N(\theta)=a_0P_0+a_1P_1+a_2P_2+\cdots+a_6P_6,$$

where $N(\theta)$ is the intensity at an angle θ, P_n is the Legendre polynomial of order n, and a_n is the coefficient of the polynomial of nth order. The coefficients, a_n, are evaluated from

$$a_n=\tfrac{1}{2}(2n+1)\int_{-1}^{+1}N(\theta)P_n d(\cos\theta),$$

by numerical integration using Simpson's rule. When expressions of this form are fitted to the results, it is found that terms as far as a_4P_4 are required to fit the long-range proton curves, while terms as far as a_2P_2 are sufficient for the short-range protons. The simpler expression for the short-range distribution may be partly due to the relatively poor statistics of these results. There is no evidence for the approximate spherical symmetry in the long-range proton distribution at low energies observed by Krone *et al.*[2] The results are of the same form as those of Whaling and Bonner[1] although the asymmetry of the short-range group is more marked in the present results.

The variations of the ratios a_1/a_0, a_2/a_0, a_3/a_0, $\cdots$, with energy for the total emission and the separate groups have been compared with other published results. The agreement between Whaling and Bonner[1] and the present results is in general satisfactory. The greatest discrepancies arise, as may be expected, in the short-range group. Except for a low value at 400 kev, the values of a_1/a_0 for the short-range protons obtained by Whaling and Bonner agree well with the present results, while only the 780-kev point of Krone *et al.* agrees with the other experiments. The values of a_2/a_0 for the short-range protons obtained by both Whaling and Bonner and Krone *et al.* are scattered between 0.2 and −0.2. The present values form a consistent set at about −0.06, however, and appear to be more probable. The decrease in a_4/a_0 observed in all three experiments suggests that the term a_4P_4 is, in fact, significant in the short-range distribution, although this is not substantiated on statistical grounds. The observed distributions indicate that the

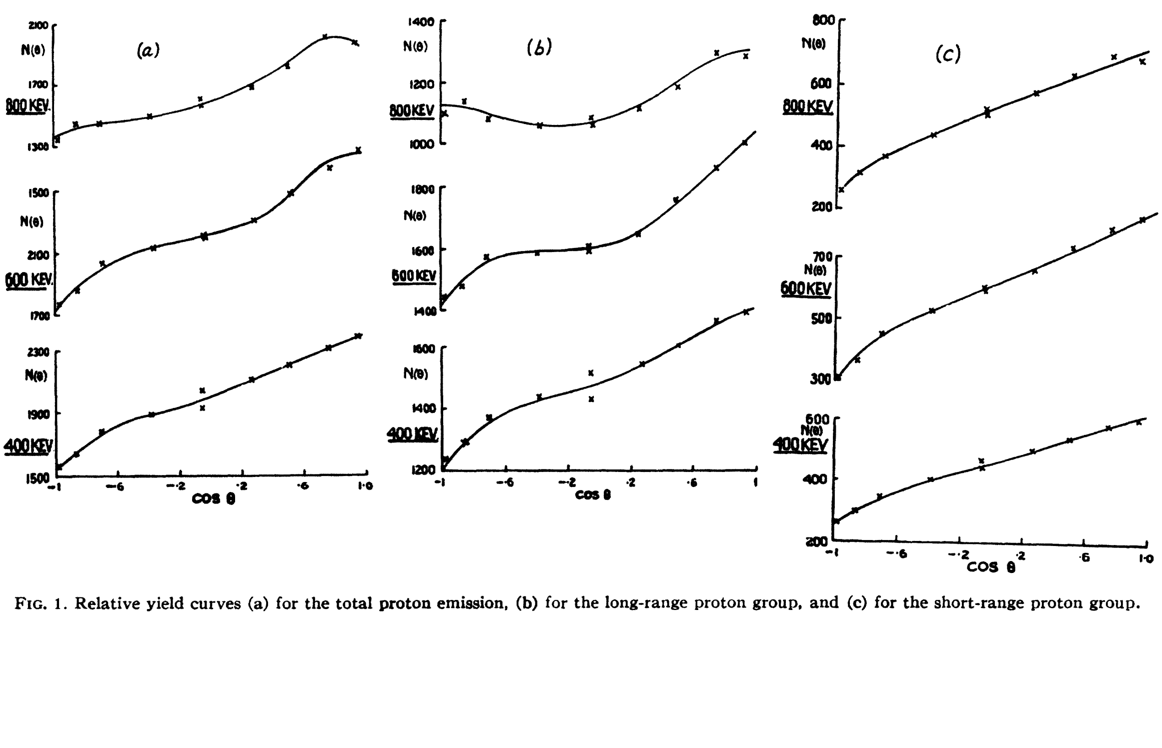

FIG. 1. Relative yield curves (a) for the total proton emission, (b) for the long-range proton group, and (c) for the short-range proton group.