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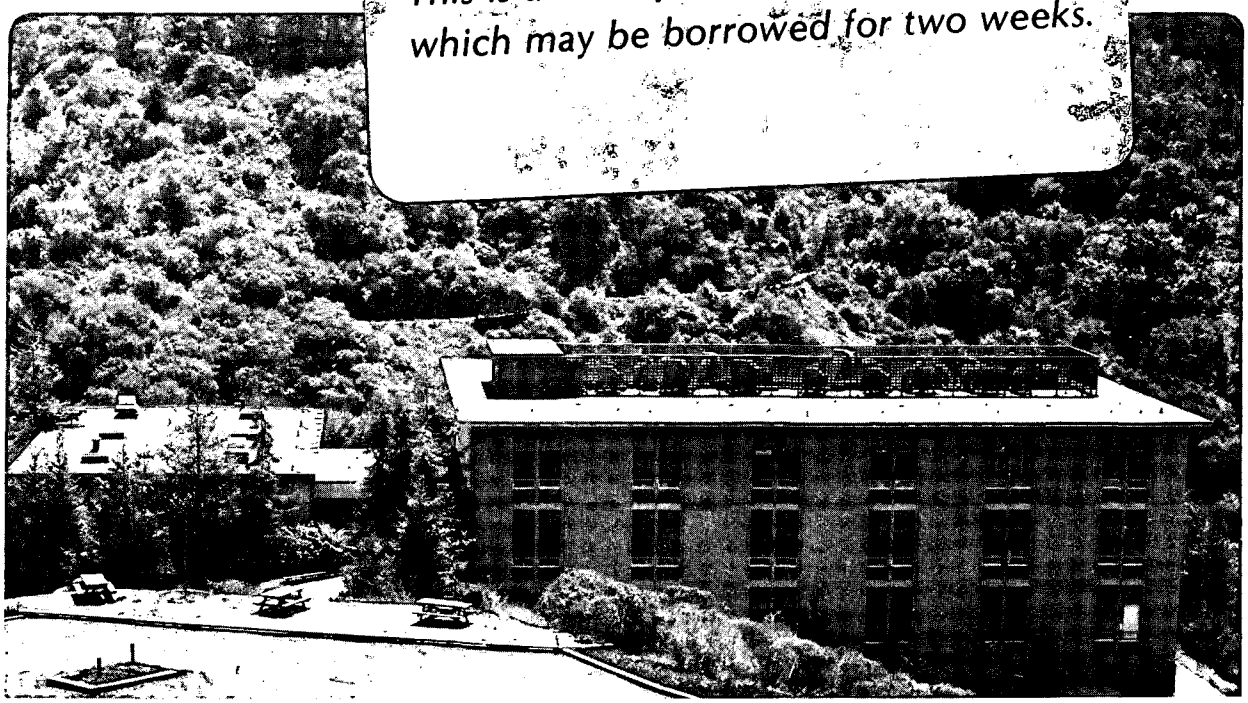

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The Structure Dependence of Grain Boundary Corrosion in Niobium Bicrystals

X. R. Qian,* Y. T. Chou,* and E. A. Kamenetzky+

*Department of Materials Science and Engineering

Lehigh University, Bethlehem, PA 18015 (U.S.A.)

+Materials and Molecular Research Division

Lawrence Berkeley Laboratory

University of California, Berkeley, CA 94720 (U.S.A.)

Abstract

Grain boundary corrosion of oriented niobium bicrystals with symmetrical tilt boundaries has been investigated using interference microscopy. It is shown that the depth of penetration, d, increases with misorientation angle, θ, except near some coincidence-site-lattice boundaries where minimum cusps appear. For small-angle boundaries, d depends on θ following a Read-Shockley-type relationship. The structure dependence of grain boundary corrosion is explained in terms of variations of free volume. The local expansion at large-angle grain boundaries was calculated using a soft-sphere model.

1. Introduction

The structure of a grain boundary influences its corrosion susceptibility. Indications of this relationship have been demonstrated by several authors using bicrystal samples with well-determined crystallographic factors [1-3]. Since the crystallography is controlled, it remains to separate the effects of structure and composition. By resorting to studying pure metals, the effects of composition can be minimized. Most of the structural grain boundary corrosion studies have been carried out in FCC metals; representative publications are those on aluminum [4-6]. In a recent paper Qian and Chou [7] reported a correlation between grain boundary corrosion (measured by the depth of penetration) and grain boundary energy for BCC niobium bicrystals with symmetrical tilt boundaries. It was found that the penetration distance, d, increases with the misorientation, θ, except near coincidence-site-lattice (CSL) boundaries, where d dips into a local minimum. It was also found that for bicrystals with small-angle tilt boundaries the θ-dependence of d follows a linear relationship of the Read-Shockley type, a well-known correlation describing the θ-dependence of γ, the energy of the boundary, based on a dislocation model [8]. In this paper it will be shown that a direct correlation exists between grain boundary corrosion and the amount of free volume at the grain boundary. The grain boundary free energy also correlates with grain boundary free volume and, thus, the present effort is a more precise pinning down of structural effects. The current understanding on grain boundary structure has been

reviewed recently by several authors [9,10].

In the previous study on niobium bicrystals [7], the results were obtained from the set of bicrystal samples with [011]/[100] and [011]/[0$\bar{1}$1] type of tilt boundaries. Here, the first vector represents the pair of vectors that span the misorientation angle θ and the second refers to the tilt axis of the bicrystal [11]. In this paper, the study is extended to a new set of bicrystals with symmetrical tilt boundaries having the [001]/[100] and [001]/[110] orientations.

2. Experimental

Niobium bicrystals with symmetrical tilt boundaries were grown from bicrystal seeds using the method of Pande *et. al.* [12]. The growth process is described briefly as follows: A single crystal seed, 3 *cm* in length and 0.635 *cm* in diameter, is first grown from a polycrystalline rod in a vertical floating-zone electron-beam melting furnace. The top end of the single crystal is cut 1.5 *cm* along a central plane, thereby yielding two split sections which are then bent apart symmetrically with respect to the center plane of the crystal. This Y-shaped crystal is used as a bicrystal seed that will grow into a polycristalline rod placed above it. A schematic illustration is shown in Fig. 1.

In the present study, the single crystal seeds were grown in the [001] orientation. These seeds are, in practice, much more difficult to grow than the [011] type seeds since the later is the natural growth direction for niobium crystals. Again, two sets of symmetrical bicrystals were prepared based on the choice of

the cut planes. In the first set, the cut plane was (010) with the tilt axis along [100] (the [001]/[100] bicrystals); in the second set, the cut plane was $(1\bar{1}0)$ with the tilt axis along [110] (the [001]/[110] bicrystals). A typical bicrystal contains 7 p.p.m. nitrogen, 130 p.p.m. oxygen, 5 p.p.m. hydrogen, 20 p.p.m. carbon, 410 p.p.m. tantalum, and 65 p.p.m. tungsten. The orientation of the bicrystals were checked by Laue patterns at two perpendicular directions with an accuracy of $\pm 1^{\circ}$.

As in the previous study, the corrosion samples cut from the bicrystal stems were mounted in polyethylene molds and carefully polished. The polished surface was perpendicular to the boundary plane and parallel to the tilt axis. The samples were then corrosion treated at room temperature for 40 seconds in an acid solution containing 70% HNO_3 and 30% HF by volume.

The depths of the boundary grooves or the penetration depths, d, were measured using a Leitz multibeam interference microscope with a sodium light source. For each value of θ, a set of five readings of d values were recorded and averaged. The d values were then plotted as a function of θ.

3. Results and Discussion

The measured data is summarized in Figs. 2 and 3 which are a plot of penetration depth, d, *vs.* misorientation angle, θ. Shown in Fig. 2 is the plot of d *vs.* θ for the set of [001]/[100] bicrystals and in Fig. 3 the plot for the set of [001]/[110] bicrystals. The results unambiguously illustrate that the penetra-

tion depth increases with an increase in the misorientation of the bicrystals, except at and near CSL boundaries where minimum cusps appear. In addition, for small-angle tilt bicrystals, the θ-dependence follows a Read-Shockley relationship, *i.e.*, a linear relationship between d/θ and $\ln\theta$ (see the corner plots in Figs. 2 and 3). The general features of these variations are very similar to those for the [011]/[100] and [011]/[0$\bar{1}$1] bicrystals previously studied [7]. In fact, the previous results can be regarded as complimentary to the data presented here. The structure of a [011]/[100] grain boundary with misorientation θ is the same as the structure of a [001]/[100] boundary of misorientation 90°$-\theta$. Similarly, the structure of a [011]/[0$\bar{1}$1] grain boundary of misorientation θ is the same as the structure of a [001]/[110] boundary of misorientation 180°$-\theta$. For example, the boundary Σ17 [011]/[100]/28.07° has the same structure as Σ17 [001]/[100]/61.93°; in both cases the boundary plane is of the form {035}. However, the grain boundary structure of Σ17 [001]/[100]/28.07° is entirely different than that of Σ17 [001]/[100]/61.93°.

The two parameters that should influence the structural contribution to intergranular corrosion are the grain boundary energy and the grain boundary free volume, a measure of the heterogeneity of the boundary. In fact, the two factors are closely related. If the internal energy of a boundary is considered to be the energy used in creating the necessary vacancies and the entropy originates from the loss of normal environment of the boundary atoms, the grain boundary free energy can be estimated [2]. Aaron and Bolling [13] first pointed

out that the grain boundary free volume should be used as a criterion for studying grain boundary properties and evaluating grain boundary models.

The small-angle boundary data confirms the correlation established by Qian and Chou [7] between grain boundary corrosion and grain boundary energy. The variation of free volume with misorientation is also of the Read-Shockley type, since, like the energy, it depends only on the density of crystal lattice dislocations.

The high-angle data unexpectedly shows the same features as that previously reported for bicrystals with [011] span vectors. A close inspection of Fig. 2, however, indicates that the corrosion rate or the penetration depth d is slightly higher at the $\Sigma 13$ boundary than at the $\Sigma 17$ boundary. The differences are more pronounced in the previous study of the [011]/[100] bicrystals [7]. In another study concerning grain boundary hardening in [001]/[100] niobium bicrystals [11,14], the boundary hardness is higher in a $\Sigma 13$ bicrystal than in a $\Sigma 17$ bicrystal. In order to explain these results, the high-angle data must be compared also against free volume values. The excess volume data was obtained from a soft-sphere structural model described below.

A simple geometrical method has been developed [15] to calculate grain boundary translations that preserve first- and second- nearest neighbor coordination across the interface. These translations form interlocking polyhedral groups of atoms that define a mechanical stable boundary. Further individual atom relaxations can be easily recognized from the geometry of the atom

arrangements. The description of boundary structure that results from this model is equivalent to a soft-sphere description where a range of interatomic distances between the first- and second- nearest neighbors exists at the boundary. A number of possible structures (translations) exists for each boundary. The criterion that has been used in order to obtain the most likely occuring boundary structure is to look for the structure with the highest coordination and with the minimum excess volume. The excess volume is related linearly to the z-component (normal to the boundary) of the translation, t_z, and thus to minimize the excess volume, the lowest t_z is required. The excess volume is usually indicated by the expansion, e, that is, the difference between t_z and the interplanar spacing parallel to the boundary. Each boundary in the sequence of [100] symmetrical tilt boundaries between the perfect crystal and $\Sigma 5$ can be described as a sequence of structural units of the $\Sigma 5$ boundary and structural units representing the core of crystal lattice dislocations.

The energy of the [001]/[100] boundaries has been calculated by Vitek based on a central-force potential model [16]. This atomistic calculation also gives the values of the local expansion at the boundary. The soft sphere [17] and atomistic data are compared in Table 1. The authors believe that differences occur because the atomistic calculations are carried out at constant volume; the expansion is calculated by an extrapolation of the normal displacement of the last relaxed layers back to the interface. The soft-sphere data predicts correctly that the penetration depth of the $\Sigma 13$ boundary should be

higher than that at the $\Sigma 17$ boundary. The expansion , e, for other CSL boundaries between the perfect crystal and $\Sigma 13$ indicates that these boundaries should be highly corroded ($e = .42$ *at* $\Sigma 25$ $\theta = 16.26^\circ$ and $e = .38$ *at* $\Sigma 37$ $\theta = 18.92^\circ$ [17]). Thus, the cusps in Fig. 2 are correctly predicted. The variations around the cusps are similar to small-angle boundary variations, since they correspond to additions of displacement-shift-complete lattice dislocation of the favored boundaries (the perfect crystal and $\Sigma 5$) [18]. Small variations in corrosion rate may not only be related to the expansion, but also to the distribution of the free volume along the boundary plane. The preceding discussion proves that the correlation between penetration distance and grain boundary excess volume is also valid for the high-angle data.

No correlation can be found between penetration and the grain boundary energy data presented by Vitek *et.al.* [16]. A different energy calculation by Wolf concludes that no energy cusps are found which are associated with the CSL boundaries in symmetrical [001]/[100] bicrystals [19]. These inconsistencies in theoretical calculations of grain boundary energy can be due to the central-force potential used [20]. Further work is needed in this area.

The expansion data for the [110] symmetrical tilt boundaries [17] correctly predict a cusp in the penetration curve at $\Sigma 19$ ($e = .32$). Additional cusps can be predicted at $\Sigma 9$ $\theta = 38.94^\circ$ $e = .24$, $\Sigma 11$ $\theta = 50.48^\circ$ $e = .30$, and $\Sigma 3$ $\theta = 70.53^\circ$ $e = 0$ *or* $.04$. These predictions have not been checked experimentally because of the difficulty in growing niobium bicrystals with large misorien-

tation angles [9]. Experimental grain boundary energy data obtained by the method of thermal etching pits on silicon iron samples [21] show local minima in the energy *vs.* θ curve at $\Sigma 51$ θ=16.10 ° and at $\Sigma 19$. The local minimum at $\Sigma 51$ explains the dip in Fig. 3 around 16 °.

It has been shown conclusively that grain boundary corrosion in niobium bicrystals is directly related to the grain boundary free volume. Further work is needed in relating the grain boundary energy and other grain boundary properties such as impurity segregation to the amount and distribution of free volume along the grain boundary plane. These must be studied in well-characterized bicrystals such as the ones used in this report. Unfortunately, old data cannot be used because not all the grain boundary parameters were determined.

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Figure Captions

Fig. 1 Arrangement for the growth of symmetrical bicrystals from Y-shaped seeds by floating-zone melting technique.

Fig. 2 Variation of depth of penetration, d, as a function of misorientation θ, in niobium [001]/[100] symmetrical tilt bicrystals. Units of $d = \lambda/2$ ($\lambda = 589\ nm$, wavelength of sodium light source).

Fig. 3 Variation of depth of penetration, d, as a function of misorientation θ, in niobium [001]/[110] symmetrical tilt bicrystals. Units of $d = \lambda/2$ ($\lambda = 589\ nm$, wavelength of sodium light source).

Table 1

Computed Values of the Expansion for [001]/[100] Niobium Bicrystals

Σ	θ	Plane	Expansion[+]	
			Atomistic[†]	Soft-sphere[‡]
$\Sigma 5$	36.87	(013)	0.16	0.23
$\Sigma 13$	22.62	(015)	0.19	0.31
$\Sigma 17$	28.07	(014)	0.29	0.25

[+] In units of the lattice parameter a
[†] Data reported by Vitek *et.al.* [16]
[‡] Data reported by Kamenetzky [17]

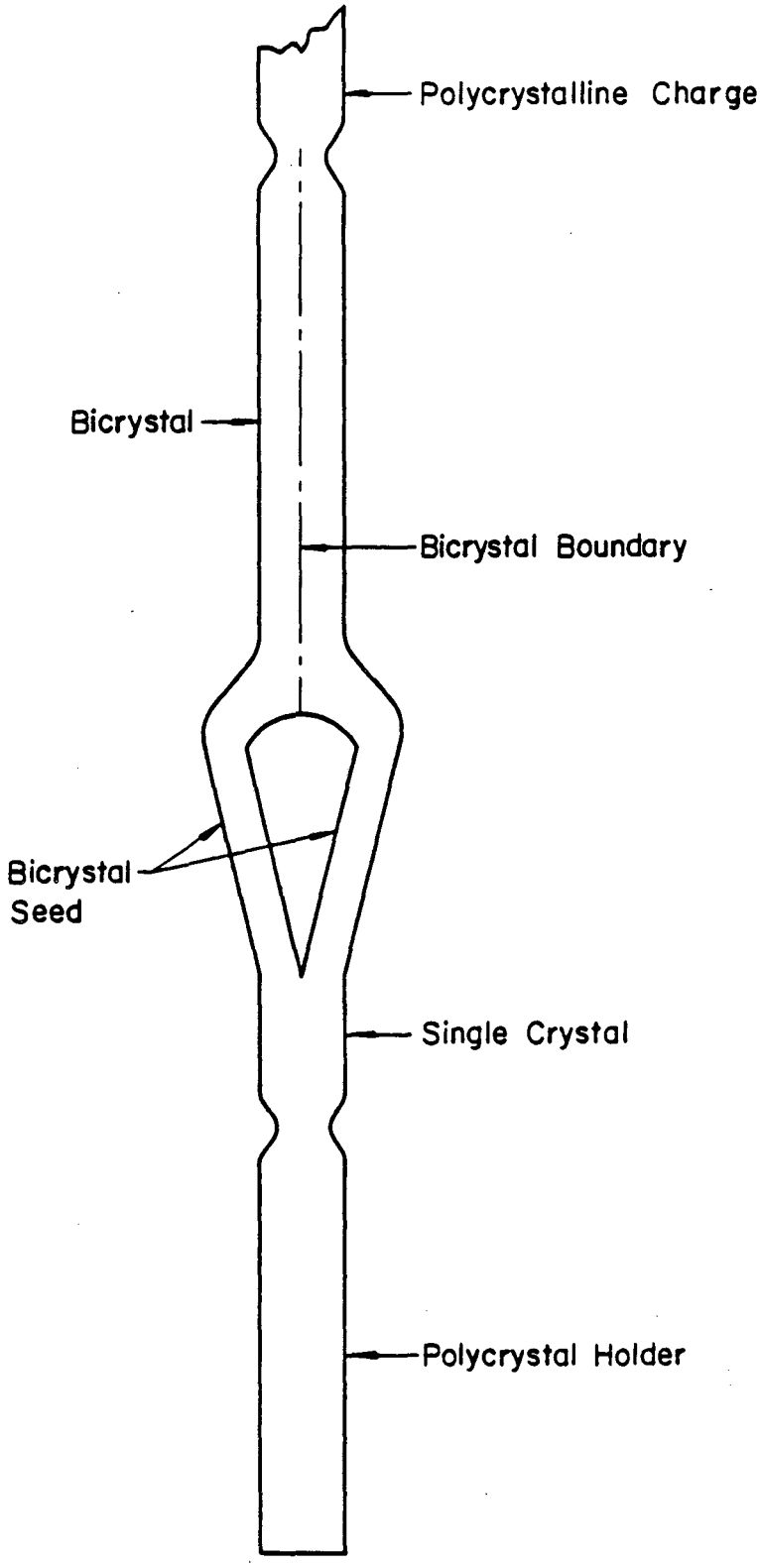

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Fig. 1

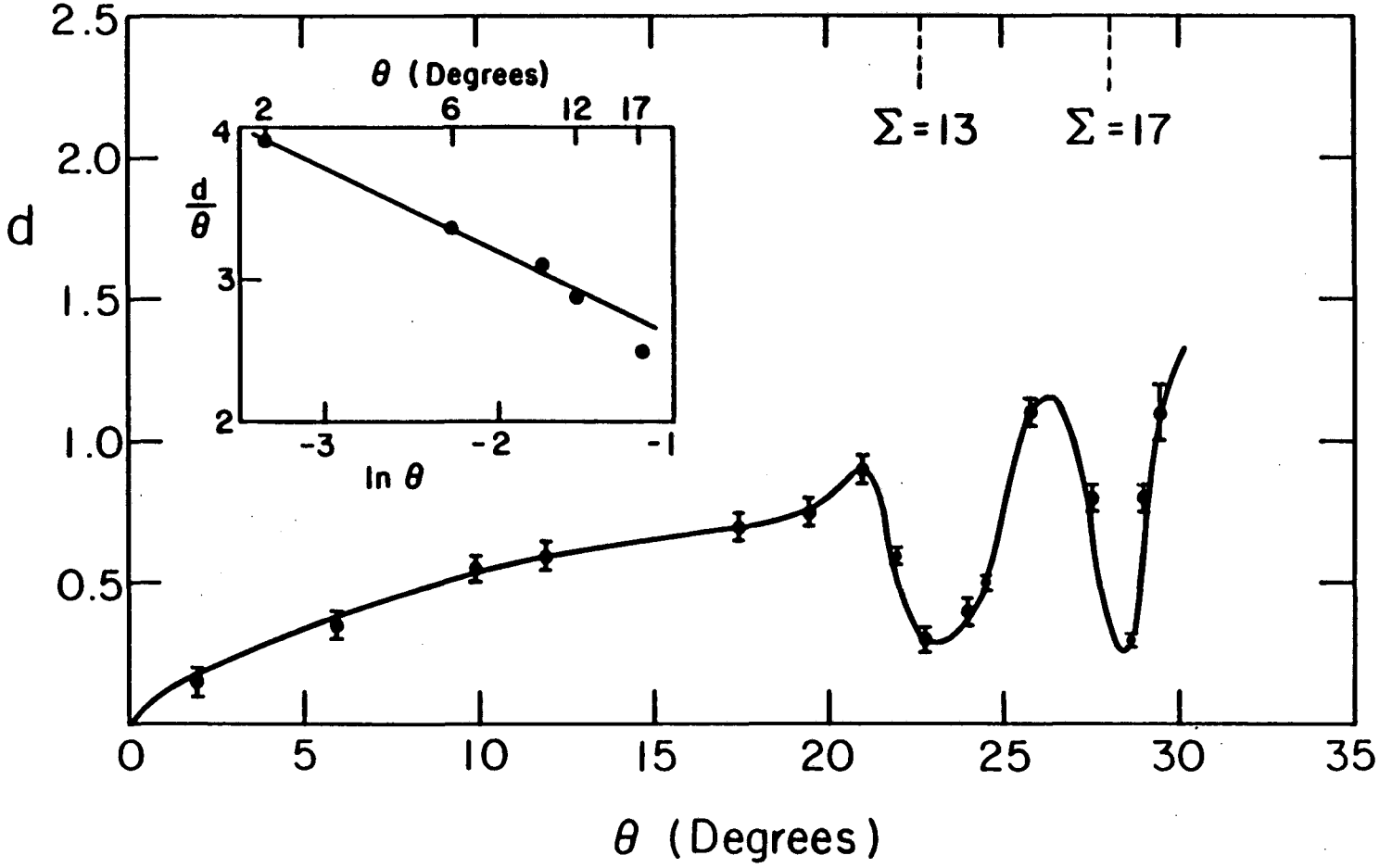

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Fig. 2

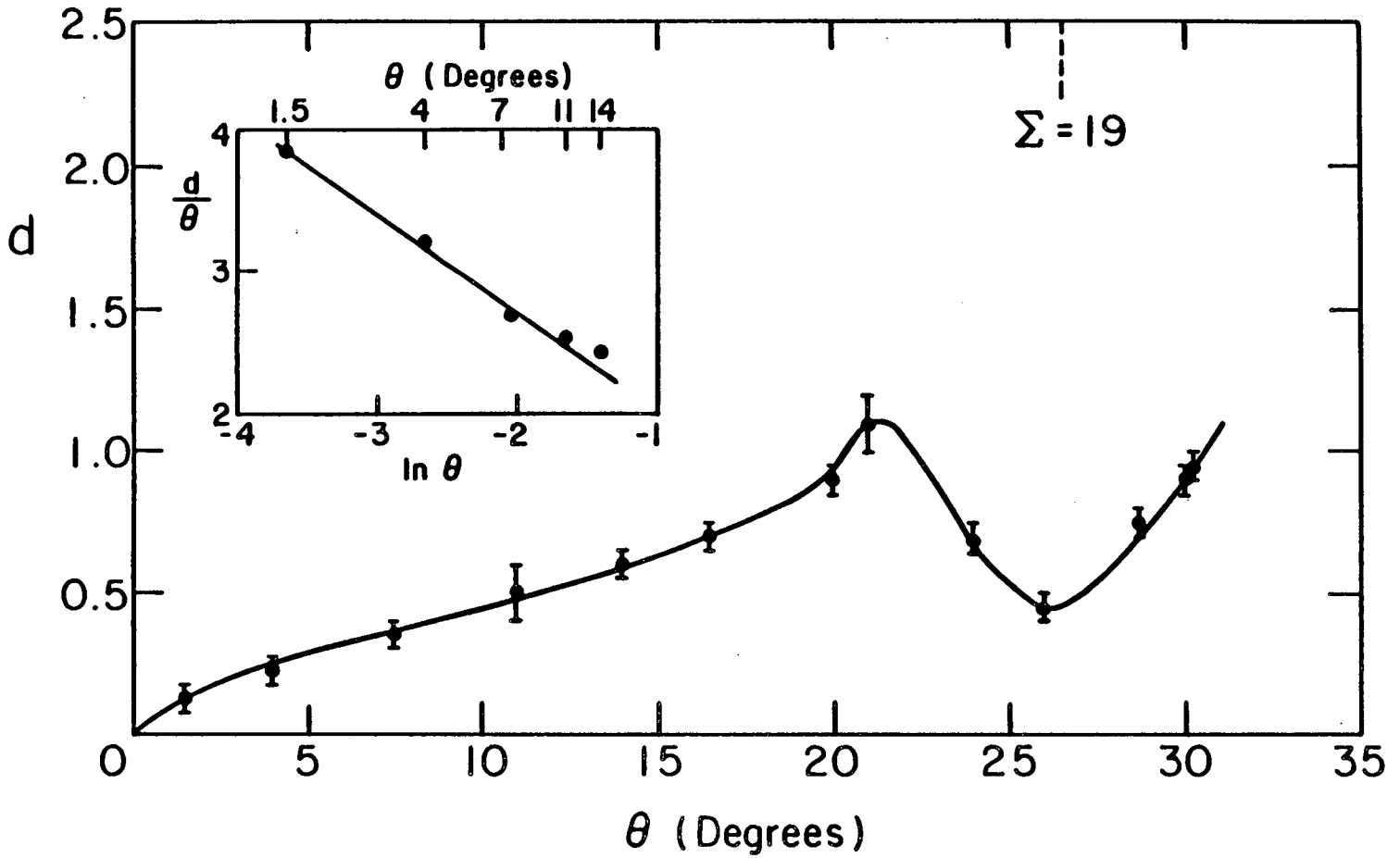

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Fig. 3

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