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Probability Method Applied to the Analysis of Recrystallization Data

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Probability equations are developed for the purpose of analyzing recrystallization data to determine what mechanisms may operate during recrystallization processes. The equations allow for inexact variations in orientation changes provided the variations are small. $P(E)=1.43\alpha^3$ gives the probability that a nucleation will result in an orientation falling within α radians of a specified one A on a chance basis. Other equations are given for the probability of occurrence of nearly common orientations for various types of groupings. Values of probabilities are given in tables.

INTRODUCTION

NEW crystals are produced whenever a single crystal is deformed a small amount and heat-treated above its recrystallization temperature. In general, the changes in orientation that occur cannot be described in terms of simple mechanisms such as twinning or as the rotation of the lattice about a single axis. Furthermore, if a mechanism is postulated that involves a large number of transformations, it may be of little use in predicting changes in the crystal lattice unless appropriate selection rules are also introduced to limit the number of final orientations. Such rules would depend upon experimental conditions.

In an attempt to overcome some of these difficulties, the writer has found it useful to analyze recrystallization data with the aid of probability equations. These equations are developed in the present paper. The first relationship, Eq. (1), gives the probability that a single nucleation will produce an orientation falling within α radians of a specified one A assuming all possible orientations as equally likely. Any nucleation that satisfies this condition is called event E and its probability, $P(E)$. The reciprocal of $P(E)$ will be called N. It is the maximum number of events similar to E. We might say that there are N ways for an orientation to occur and if each way is equally likely, then the probability that it is E is $1/N$. Call each of the N configurations a state (a classified orientation). These states, instead of orientations, may be used in considering mechanisms of recrystallization. The number of states allowed for a given mechanism, however, must be considerably less than N if the mechanism is to have much meaning. In this connection, an illustration is given for a mechanism that would produce high order twins. Finally, an application is made of $P(E)$ to obtain Eqs. (2a) and (2b) for the probability of occurrence of new crystals having nearly common orientations.

PROBABILITY $P(E)$ OF OCCURRENCE OF AN ORIENTATION IN A GIVEN STATE

Consider all orientations that agree within α radians of A, defined by three mutually perpendicular poles A_1, A_2, A_3 of $\{100\}$ planes, as belonging to the set E, i.e., in a state E. An orientation B belongs to E if no $\{100\}$ pole of B departs from A by more than α radians. We ask, "What is the probability of occurrence of event E if an orientation is selected at random from a group of random orientations?" If E is to occur, B must be taken from a subset of the group of random orientations having one pole within α radians of one pole of A. Consider the subset for pole A_1 and call a selection from it event F. Complete a set F by taking all such orientations. From this set make further selections, each having a pole within α radians of A_2, and thus obtain a set G. Finally, all orientations of this group that have a pole within α radians of A_3 may be taken to form a set H.

The probability of E (event E) will be $P(E)=P(F)P(G)P(H)$ where $P(F)$ is the probability of F, $P(G)$ is the probability of G after F has occurred, and $P(H)$ is the probability of H after F and G have occurred.[1,2a]

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[1] Arne Fisher, *Mathematical Theory of Probabilities*, (The MacMillan Company, New York, 1922), p. 29.

[2] Thornton C. Fry, *Probability and Its Engineering Uses* (D. Van Nostrand Company, Inc., New York, 1928), (a) p. 116; (b) pp. 19, 20.

In order to obtain $P(E)$, the original group of random orientations will be represented by a plot of $\{100\}$ poles on the surface of a hemisphere of radius R. Let k be the number of poles per unit area, thus giving a total of $2\pi R^2k$ poles and $2\pi R^2k/3$ orientations. Computing the area near A_1, we find that there are $2\pi(1-\cos\alpha)R^2k$ poles within α radians of A_1. Each pole belongs to a unique orientation. Consequently, there are $2\pi(1-\cos\alpha)R^2k$ orientations that belong to the set F. Expressing probability in the usual way, we get at once for low values of α:

$$P(F)=\frac{2\pi(1-\cos\alpha)R^2k}{2\pi R^2k/3}=3(1-\cos\alpha)\doteq\tfrac{3}{2}\alpha^2,$$

the error being only $\frac{3}{10}$ of one percent for α equal to 10°.

Figure 1 is a stereographic projection of the plot of set F. The poles have a density k in the large circle about A_1. The distribution of poles in the band of width $2\alpha R$ containing A_2 and A_3 is assumed to be uniform along the band, but the distribution across the band must be found. Divide the large circle about A_1 into rings of width $Rd\beta$. Consider one of radius $R\beta$. It contains approximately $2\pi R\beta Rd\beta k$ poles, the error being $\frac{1}{2}$ of one percent for α equal to 10°. Twice this number of associated poles are spread uniformly along 180° arcs that fall within a band of width $2\beta R$ (see Fig. 1). These arcs produce a uniform distribution of the poles. Considering every value of β, it may be seen that the distribution across the band, to a good approximation, is linear, varying from zero for β equal to α to a maximum at the center of the band. It may be represented by $a(\alpha-\beta)$ and must satisfy the following equations, the integration being carried out over $\frac{1}{2}$ the band along a 90° arc:

$$\pi\alpha^2R^2k=2\int_0^\alpha a(\alpha-\beta)R\pi/2\ Rd\beta.$$

$R\pi/2\ 2\alpha R$ gives the approximate area wherein one-half the associated poles fall. Consequently, $a=2k$.

We must now obtain all the poles in the circle about A_2 in order to calculate $P(G)$. Consider an arc where the density is $2k(\alpha-\beta)$. To a good approximation the circle intercepts a length of arc equal to $2[(R\alpha)^2-(R\beta)^2]^{\frac{1}{2}}$. Therefore,

$$P(G)=\frac{2\int_0^\alpha 2k(\alpha-\beta)2[(R\alpha)^2-(R\beta)^2]^{\frac{1}{2}}Rd\beta}{2\int_0^\alpha 2k(\alpha-\beta)\pi/2\ R\,Rd\beta}$$

$$=2\alpha(1-4/3\pi)=1.15\alpha.$$

The remaining poles of set G near A_3 are distributed within an approximate square of dimensions $2\alpha R$ in a rather complicated way. Consequently, the integration required to obtain $P(H)$ would be difficult to carry out. However, we can say definitely that

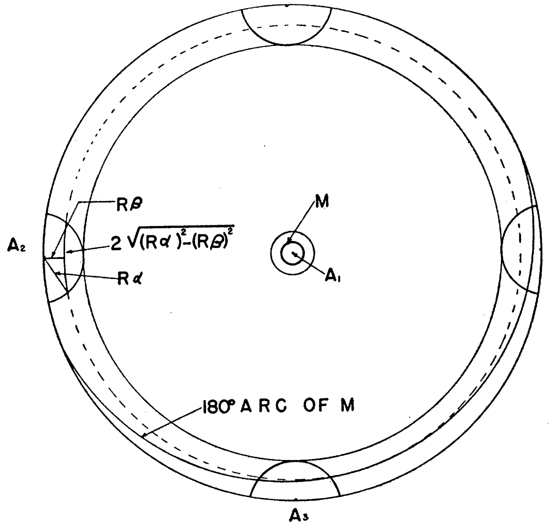

FIG. 1. Stereographic projection of the plot of set F together with diagrams used in calculating $P(G)$.

$$\frac{\pi\alpha^2R^2}{(2\alpha R)^2}<P(H)<1,$$

or $P(H)$ is between $\pi/4$ and 1. Substituting the values for $P(F)$, $P(G)$, and the limits of $P(H)$ in the equation for $P(E)$, we find that

$$1.35\alpha^3<P(E)<1.72\alpha^3.$$

Although this range is sufficiently accurate for most applications, a more definite value of $P(E)$ may be obtained as follows:

$$\text{write } P(E)=P(F)P(I).$$

The set I is to be obtained from F in such a way that all poles fall within the circles about

A_2 and A_3. Since a lengthy derivation is needed in this case, only the result will be given, namely:

$$P(I)=\frac{32}{\pi^2}(1-\sqrt{\tfrac{1}{2}})\alpha=0.95\alpha$$

(as before, approximations have been made for length of arc). Substituting the values for $P(F)$ and $P(I)$, we get:

$$P(E)=1.43\alpha^3. \tag{1}$$

As an illustration, Eq. (1) gives $P(E)=1/1140$ for α equal to 5°. In this case, the maximum number of states (N) is 1140.

PROBABILITY OF OCCURRENCE OF AN ORIENTATION IN ONE OF SEVERAL GIVEN STATES

Case I: Two states, K and L, in which all orientations are uniquely classified. (We may have overlapping circles in this case, but one of the three circles for one state must not overlap a circle of the second state). The probability that an orientation will occur in state K by chance is:

$$P(K)=1.43\alpha^3.$$

The probability that it will occur in state L is also $1.43\alpha^3$. The probability that it will occur either in state K or L is:

$$P(K \text{ or } L)=P(K)+P(L)=2\times 1.43\alpha^3.$$

Case II: Two states, S and T, overlap so that a unique classification of all orientations is impossible and some have to be described as being in states S and T. In this case, we should think of each as a state only when it is alone; together, we should think of them as being less than two states.

The probability that an orientation will occur either in state S or T by chance is less than the value obtained for Case I. We note that if S and T are allowed to merge, the probability drops from $2\times 1.43\alpha^3$ toward $1.43\alpha^3$, corresponding to a transition from two states (Case I) toward one state. A correction owing to the amount of overlapping area might be made for the circle having the smallest amount of overlap, but the non-uniform distribution of poles within a circle for a state would make this correction difficult to determine. Nevertheless, there would be a number f such that $P(S \text{ or } T)=f1.43\alpha^3$, and $1<f<2$.

Case III: When data for standard twin groups through three generations are plotted on a stereographic net,[3] it is found that no overlapping occurs among the 52 orientations until α becomes equal to about $2\frac{1}{2}°$. The probability that a new crystal will occur in one of the 52 states, when all N states are equally likely, is:

$$P=52/N=52P(E)=52\times 1.43\left(\frac{2.5\pi}{180}\right)^3$$
$$=0.00619=1/161.$$

When 5° is taken for α, the number of states N is 1140, but the maximum number of states allowed on the basis of a mechanism that produces only three orders of twins is 52. Because of overlap, there is some degeneracy among the states and their effective number is reduced as pointed out in Case II. Consequently,

$$P<\frac{52}{1140} \quad\text{or}\quad \frac{1}{22}.$$

This result means that recrystallization without any mechanism or preferment should not result in a 5° type fit more than once in every 22 times if we restrict a fit to one of the 52 first-, second-, and third-order twins. A mechanism of recrystallization of this degree of complexity should not be hard to test experimentally.[4]

PROBABILITY OF OCCURRENCE OF ORIENTATIONS FOR VARIOUS TYPES OF GROUPINGS

Consider a group of random orientations existing in N states, $H_1, H_2, H_3\cdots H_N$ ($N=1/P(E)$). Select n orientations ($n\leqslant N$) in an independent manner and suppose that these fall into l states in such a way that m_1 belong in one state, m_2 in another state, etc., up to m_k in a kth state ($m\geqslant 2$), and one each belongs in the remaining $l-k$ states. Suppose further that some of the k states contain an identical number of orientations. Designate the number of equal size groups by r_1, r_2, etc. We ask, "What is the probability of occur-

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[3] Data on four generations of twins have been obtained at the Pittsfield Works' Laboratory and are now being prepared for publication.

[4] In this connection, considerable data have already been accumulated at the Pittsfield Works' Laboratory of the General Electric Company.

rence of such a group?" The group in this case may be represented as follows:

$$H_{x(1)}^{m(1)}H_{x(2)}^{m(2)}H_{x(3)}^{m(3)}\cdots H_{x(k)}^{m(k)}H_{x(k+1)}^{1}H_{x(k+2)}^{1}\cdots H_{x(l)}^{1},$$

where the superscript* gives the number of orientations in a particular state. We do not, however, specify the states in advance. As an example, consider the case of throwing three dice to obtain a pair. In one throw we use three orientations (n) out of six (N), but to get a pair one orientation must occur twice. Therefore, l equals 2, k equals 1, and m_1 equals 2. Figure 2 gives an illustration of a more general orientation group existing in five states with n, l, k; m_1, m_2, m_3; r_1 and r_2 equal to 9, 5, 3; 3, 2, 2; 2 and 0, respectively.

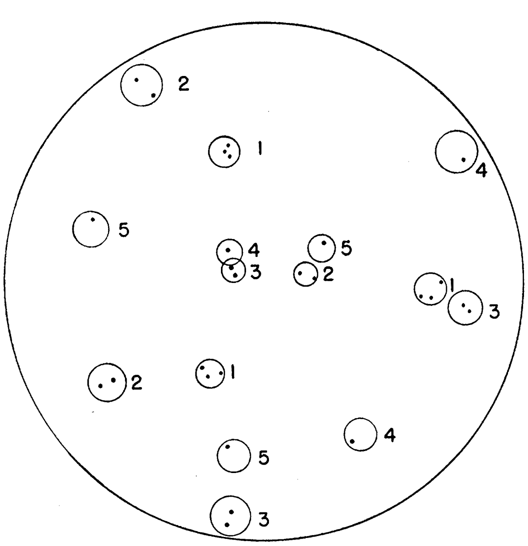

FIG. 2. Stereographic diagram showing states 1, 2, 3, 4, and 5 containing 3, 2, 2, 1, and 1 orientations, respectively. α is 5°. $N\leqq 1000$.

To obtain the probability of occurrence for the general case, consider first any group of k states of the following type:

$$H_{x(1)}^{m(1)}H_{x(2)}^{m(2)}H_{x(3)}^{m(3)}\cdots H_{x(k)}^{m(k)}.$$

The number of combinations of N states taken k at a time for a group where

$$m_1=m_2=m_3\cdots=m_k \quad \text{is} \quad \frac{N!}{(N-k)!k!}.$$

The number of combinations, however, is increased if all the m's are not the same. Suppose one of the m's occurs r_1 times, another r_2 times, etc. The number of unique arrangements[2b] of m_1, $m_2\cdots m_k$ is the factor needed. It is $k!/r_1!r_2!\cdots$. The number of combinations leading, therefore, to a

$$H_{x(1)}^{m(1)}H_{x(2)}^{m(2)}H_{x(3)}^{m(3)}\cdots H_{x(k)}^{m(k)}$$

type group is:

$$\frac{N!}{(N-k)!k!}\times\frac{k!}{r_1!r_2!\cdots} \quad \text{or} \quad \frac{N!}{(N-k)!r_1!r_2!\cdots}.$$

We may also write combinations for the $l-k$ states that are occupied by only one orientation each. Since k states of the N have been used in forming the group $m_1m_2\cdots m_k$, there are $N-k$ remaining to select from to get the $l-k$ singly-occupied states. The number of combinations is:

$$\frac{(N-k)!}{[N-k-(l-k)]!(l-k)!} \quad \text{or} \quad \frac{(N-k)!}{(N-l)!(l-k)!}.$$

Any one of the combinations containing n orientations could have been selected in a number of unique ways, namely,

$$\frac{n!}{m_1!m_2!\cdots m_k!}.$$

Therefore, the total number of ways to form a specified type of group is:

$$\frac{N!}{(N-k)!r_1!r_2!\cdots}\times\frac{(N-k)!}{(N-l)!(l-k)!}\times\frac{n!}{m_1!m_2!\cdots m_k!}.$$

Since the total number of ways to make n selections is N^n, the probability of getting the specified type of group is:

$$P_{m(1)m(2)\cdots m(k)}^{k}$$
$$=\frac{N!n!}{m_1!m_2!\cdots m_k!(N-l)!(l-k)!N^n r_1!r_2!\cdots}. \quad \text{(2a)}$$

When $l=n$, this equation reduces to:

$$P^0=\frac{N!}{(N-n)!N^n},$$

an expression giving the probability that all n orientations occur in different states.

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* In superscripts and subscripts m_1 is written as $m(1)$; m_2 as $m(2)$; m_3 as $m(3)$; etc.

TABLE I. Probability of occurrence of orientations for various types of grouping.

k	Type of group m_1	m_2	m_3	m_4	Probability from Eqs. (2a) and (2b)	Probability
0					$P^0=\dfrac{N!}{(N-n)!N^n}$	P^0
1	2				$\overset{1}{P}_2=\dfrac{P^0}{2!}\dfrac{(N-n)!n!}{(N-n+1)!(n-2)!}$	$\overset{1}{P}_2=\dfrac{P^0}{2}\dfrac{n(n-1)}{N-n+1}$
2	2	2			$\overset{2}{P}_{22}=\dfrac{P^0}{2!2!}\dfrac{(N-n)!n!}{(N-n+2)!(n-4)!2!}$	$\overset{2}{P}_{22}=\dfrac{\overset{1}{P}_2}{4}\dfrac{(n-2)(n-3)}{N-n+2}$
1	3				$\overset{1}{P}_3=\dfrac{P^0}{3!}\dfrac{(N-n)!n!}{(N-n+2)!(n-3)!}$	$\overset{1}{P}_3=\dfrac{\overset{1}{P}_2}{3}\dfrac{(n-2)}{N-n+2}$
3	2	2	2		$\overset{3}{P}_{222}=\dfrac{P^0}{2!2!2!}\dfrac{(N-n)!n!}{(N-n+3)!(n-6)!3!}$	$\overset{3}{P}_{222}=\dfrac{\overset{1}{P}_3}{8}\dfrac{(n-3)(n-4)(n-5)}{N-n+3}$
2	2	3			$\overset{2}{P}_{23}=\dfrac{P^0}{3!2!}\dfrac{(N-n)!n!}{(N-n+3)!(n-5)!}$	$\overset{2}{P}_{23}=\dfrac{\overset{1}{P}_3}{2}\dfrac{(n-3)(n-4)}{N-n+3}$
4	2	2	2	2	$\overset{4}{P}_{2222}=\dfrac{P^0}{(2!)^4}\dfrac{(N-n)!n!}{(N-n+4)!(n-8)!4!}$	$\overset{4}{P}_{2222}=\dfrac{\overset{2}{P}_{23}}{32}\dfrac{(n-5)(n-6)(n-7)}{N-n+4}$
1	4				$\overset{1}{P}_4=\dfrac{P^0}{4!}\dfrac{(N-n)!n!}{(N-n+3)!(n-4)!}$	$\overset{1}{P}_4=\dfrac{\overset{1}{P}_3}{4}\dfrac{(n-3)}{N-n+3}$
1	5				$\overset{1}{P}_5=\dfrac{P^0}{5!}\dfrac{(N-n)!n!}{(N-n+4)!(n-5)!}$	$\overset{1}{P}_5=\dfrac{\overset{1}{P}_4}{5}\dfrac{(n-4)}{N-n+4}$
At least two in one state					$1-P^0$	$1-P^0$

TABLE II. Values of $\overset{k}{P}_{m(1)m(2)\cdots}$ for $N=1000$.

					$n=20$		$n=10$		$n=5$	
k	Type of group m_1	m_2	m_3	m_4	$\overset{k}{P}_{m(1)m(2)\cdots}$	$\Sigma \overset{k}{P}_{m(1)m(2)\cdots}$	$\overset{k}{P}_{m(1)m(2)\cdots}$	$\Sigma \overset{k}{P}_{m(1)m(2)\cdots}$	$\overset{k}{P}_{m(1)m(2)\cdots}$	$\Sigma \overset{k}{P}_{m(1)m(2)\cdots}$
0					0.8259284	0.8259284	0.9558606	0.9558606	0.9900350	0.9900350
1	2				0.1599657	0.9858941	0.0434044	0.9992650	0.0099401	0.9999751
2	2	2			0.0124616	0.9983557	0.0006125	0.9998775	0.0000149	0.9999900
1	3				0.0009773	0.9993330	0.0001166	0.9999941	0.0000099	0.9999999
3	2	2	2		0.0005070	0.9998400	0.0000030	0.9999971	——	
2	2	3			0.0001352	0.9999752	0.0000024	0.9999995	9.9×10^{-9}	
4	2	2	2	2	0.0000117	0.9999869	4.5×10^{-9}		——	
1	4				0.0000042	0.9999911	0.0000003	0.9999998	5.0×10^{-9}	
1	5				1.4×10^{-8}		3.2×10^{-10}		9.9×10^{-13}	
At least two in one state					0.1740716		0.0441394		0.0099650	

If we substitute P^0 in Eq. (2a), we get:

$$\overset{k}{P}_{m(1)m(2)\cdots m(k)}=\frac{P^0(N-n)!n!}{m_1!m_2!\cdots m_k!(N-l)!(l-k)!r_1!r_2!\cdots}. \tag{2b}$$

Successive applications of Eq. (2b) give the probabilities listed in Table I.

If a small value of n is taken, it can be shown readily for any N whatsoever that the sum of the probabilities for all possible groups is one.

For instance,

$$P^0+P_2^1+P_{22}^2+P_3^1+P_{32}^2+P_4^1+P_5^1=1,$$

when n is 5 and $N \geqslant 5$.

The values of $N!$, etc., in the expression for P^0 may be obtained by using Stirling's formula. If n is small, however, it is easy to compute P^0 directly with the aid of either logarithms or an electrical computing machine.

Table II gives some numerical results on probabilities for one value of N and three values of n.

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The Photoconductivity of Sodium Chloride in the Far Ultraviolet

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Measurements have been made on the wave-length dependence of the photoconductivity of an uncolored sodium chloride crystal in the far ultraviolet region of 900 to 1350 angstroms in order to test the theories of Peierls, Frenkel, and Mott regarding the existence of discrete energy levels, called exciton levels, lying just below the conduction bands. A region was found between 1300 and 1350 angstroms in which there was large absorption but very small if any photoconductivity or external photoelectric effect indicating the existence of exciton states. At wave-lengths shorter than 1300 angstroms both the photoconductivity and the photoelectric effect began to set in and these showed a doublet structure. The photoconductivity rises abruptly at the second absorption peak in the absorption spectrum and shows structure which locates energy levels above the ground state. The experiments of Podubnij on the iodides are a contradiction to this experiment inasmuch as the alkali halides should reasonably be expected to behave similarly.

INTRODUCTION

PEIERLS,[1] Frenkel,[2] and Mott[3] have introduced the concept of non-photoconductive absorption in crystalline insulators because of the possible existence of discrete energy levels lying just below the conduction bands. The withdrawal of an electron by light of quantum energy corresponding to the distance AB, Fig. 1, leaves a hole in the filled band below A. This electron, termed an "exciton" by Frenkel, is then thought to be in the electric field of its positive hole, giving rise to discrete energy levels. Absorption of light of quantum energy corresponding to the distance AE would be a photoconductive absorption. A test for the existence of these exciton states would be to compare the dependence of photoconductivity and absorption on wave-length for an alkali halide crystal. Experimental data on the photoconductivity of pure alkali halides are very meager. To the author's knowledge the only previous work is by Podubnij[4] in which potassium and sodium iodide were illuminated over a wave-length range of 2500 to 1900 angstroms. The data showed photoconductive currents which depend in the same way on wave-length as does the absorption, and Podubnij concluded that all the absorbed energy is used to produce photoconductivity. There is no evidence that any care was taken to separate the primary photoconductive currents from secondary currents which Gudden and Pohl[5] have shown must be done in order to obtain interpretable results.

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[1] R. Peierls, Ann. d. Physik **13**, 905 (1932).

[2] J. Frenkel, Physik. Zeits. Sowjetunion 9, 158 (1936).

[3] N. F. Mott, Trans. Faraday Soc. **34**, 500 (1938).

[4] Podubnij, J. Exper. and Theo. Phys. **8**, 410 (1939).

[5] Hughes and DuBridge, *Photoelectric Phenomena* (McGraw-Hill Book Company, Inc., New York, 1931), p. 291.