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Theory of Point Defect Annealing in Metals*

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ABSTRACT

The kinetics of the annealing of point defects, either by migration to sinks or by recombination, is complicated by the occurrence of a variety of simultaneous reactions. An extensive theoretical study of annealing processes is in progress at Brookhaven based on the isolation and combination of simple kinetic steps. When analytic solutions could not be found, computer solutions have been used to obtain useful approximations and to determine their regions of validity. Two migration reaction schemes have been studied; the simultaneous annealing of single and di-vacancies, and the annealing of single vacancies with impurity trapping. Three recombination reactions have been investigated; vacancy-interstitial annihilation with interstitial migration to sinks, di-interstitial formation, and interstitial trapping at impurities.

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DISCLAIMER

Introduction

Point defects tend to anneal out of any crystal that contains more defects than the thermodynamic equilibrium concentration, provided they have sufficiently high mobility to do so. Vacancies and interstitials can anneal out by migration to sinks and by recombination with each other. It is also known that single point defects can cluster or become attached to impurity atoms. The investigation of the kinetics and the measurement of the corresponding activation energy for the annealing of point defects are therefore complicated by the occurrence of a variety of simultaneous reactions. An extensive theoretical study of annealing processes is in progress at Brookhaven based on the isolation and combination of simple kinetic steps. When analytic solutions to the rate equations could not be found, computer solutions have been used to obtain useful approximations and to determine their regions of validity. The various migration and recombination reactions that have been studied are listed in Table I.

Migration Reactions

If a defect of only one type is present, recombination reactions do not take place and annealing occurs by migration to sinks. Although the kinetic formulations to be discussed are valid for any defect, the discussion will be given in terms of vacancies because there is a great deal of experimental information on quenched-in vacancies.

Table I

Migration Reactions

I. $V_1 + V_1 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} V_2$

$V_1 \xrightarrow{K_3}$ sinks

$V_2 \xrightarrow{K_4}$ sinks

II. $V_1 + I \underset{K_2}{\overset{K_1}{\rightleftharpoons}} C$

$V_1 \xrightarrow{K_3}$ sinks

III. clustering reactions

Recombination Reactions

IV. $V_1 + i \xrightarrow{K_1}$ annihilation

$i \xrightarrow{K_2}$ sinks

V. $V_1 + i \xrightarrow{K_1}$ annihilation

$i + i \underset{K_3}{\overset{K_2}{\rightleftharpoons}} i_2$

VI. $V_1 + i \xrightarrow{K_1}$ annihilation

$i + I \underset{K_3}{\overset{K_2}{\rightleftharpoons}} C$

V_1 = single vacancy, V_2 = divacancy, i = interstitial,

i_2 = di-interstitial, I = impurity, C = impurity-defect complex,

K's = rate constants.

In quenching experiments only vacancies and their simple clusters are introduced. The simplest idealized model of the subsequent annealing process involves the simultaneous migration of single and divacancies and the formation and decomposition of the divacancies (Case I, Table I). The overall annealing process is kinetically complex and exhibits five regions of different kinetic behavior as a function of annealing temperature, as illustrated in Fig. 1. The different regions arise from the different temperature dependence of the various K's. The range of validity of these regions is also a sensitive function of the defect concentration and, therefore, of the quench temperature. The characteristics of these five regions may be briefly described as follows.

In region I, i.e., at low temperature, the single vacancies are immobile and, therefore, the migration of the more mobile divacancies is observable if they are present in sufficient concentration. Such a decay would be simple exponential.

In regions II and III a steady state approximation for divacancies was found to be valid, i.e., $dV_2/dt = 0$. With this approximation the kinetic equations can be integrated to give a pure quadratic or a quadratic plus linear decay. The simple quadratic reaction is present in both regions and arises from the combination of single vacancies to form divacancies which then migrate to sinks. At higher temperatures (Region III) some of the divacancies dissociate and more of the annealing comes from single vacancy migration to sinks. This introduces an extra linear term.

In region IV an analytic approximation is valid but it

is too complicated to be useful for the analysis of experimental curves. In region V no analytic approximations have been found. The machine solutions show, under certain conditions, an initial delay in annealing related to the buildup of divacancy concentration.

When impurities are present, the migration of vacancies to sinks is complicated by the formation of immobile vacancy-impurity complexes (case II, Table II).[2] After an initial transient which establishes the equilibrium concentration of complexes, the reaction is governed by the dissociation of complexes and the subsequent migration of the vacancies to sinks. For these latter processes a steady state approximation is valid and the overall decay curve is an exponential. The decay constant is related, but not equal, to the rate constant for vacancy migration, since it involves the binding energy of the vacancy to the impurity atom. The annealing rate is always decreased by the presence of impurities and impurity concentrations as low as 10^{-5} can introduce an appreciable error in the determination of the migration energy for vacancies. However, from comparative annealing experiments on very pure and on carefully doped samples the impurity-vacancy binding energy can be directly evaluated.

Calculations indicate that clusters of vacancies are stable and immobile.[3,4] Cluster formation (Case III, Table I) can be important, particularly when a high concentration of vacancies is present. Preliminary computer solutions of an annealing scheme that allows the formation of clusters up to six vacancies, and the

same size clusters of vacancies attached to impurity atoms, show that the rate of this complicated process is controlled only by the energy of migration of the single vacancy. Annealing runs at different temperature, therefore, superpose by a time shift. Further detailed studies designed to test for analytic approximations are in progress.

Recombination Reactions

In irradiated metals the basic defects are the interstitial and the vacancy which can recombine, disappear at sinks, cluster, and interact with impurities. Three of these processes have been studied theoretically, all based on the assumption that the interstitial is the more mobile defect.

Random recombination of vacancies and interstitials is bimolecular and therefore obeys quadratic decay. If interstitials are permitted to disappear at sinks also, the simple quadratic behavior is changed to a much more complex decay, (Case IV, Table I).[5] The interstitials decay to zero but the vacancy concentration approaches a terminal value, V_∞, as illustrated in Fig. 2, Case IV. There is an analytic relation between the concentration of interstitials and vacancies, valid at all times and independent of the annealing temperature but a function of the sink concentration and initial defect concentration. The growth of defect concentration during irradiation at a temperature where the interstitials are mobile has also been studied. In this case the interstitial concentration goes through a maximum as a function of irradiation time.

Past this maximum a steady state approximation is valid and the subsequent growth of the vacancy concentration can be described by a simple relation. The vacancy growth in steady state is independent of the temperature and is only a function of the integrated exposure. Therefore, one can compare, on the basis of integrated exposure, the buildup of vacancies during continuous irradiation and during periodic irradiation (at low temperature) and annealing. This comparison is illustrated in Fig. 3 which shows clearly that the vacancy accumulation is decreased when the mechanism of accumulation involves periodic irradiation and annealing. In this case the accumulation curves depend on the size of the irradiation dose. It is seen in Fig. 3 that the accumulation is smallest for the largest irradiation dose. This is because the annihilation reaction is favored by a high concentration of defects.

At high interstitial concentration the formation of di-interstitials (assumed to be immobile) may be far more important than the escape of the interstitials to sinks. Vacancy interstitial annihilation with di-interstitial formation (Case V, Table I) was, therefore, investigated.[6] A computer solution is shown in Fig. 3, Case V, but no closed solutions and no simple analytic approximations have been found for this kinetic scheme. However, the computer solutions can be used to establish the range of temperature and binding energy where di-interstitial formation must be taken into account. Suitable approximations have been found for the high and low temperature regions. At high tempera-

ture, or for low binding energy, the di-interstitial concentration may be neglected and the resulting kinetics is the simple quadratic interstitial-vacancy annihilation governed by the interstitial migration energy. At low temperature, or for high di-interstitial binding energy, the decomposition reaction can be neglected and analytic approximations have been found which govern the growth of the concentration of di-interstitials.

When impurities are present the reaction of interstitial-impurity complex formation may be the dominant one.[7] The corresponding reaction scheme is Case VI, Table I. A complete analytic solution has been obtained for the kinetics of the above reaction scheme of vacancy-interstitial annihilation with impurity-interstitial trapping.[8] After an initial transient, which is a rather complex combination of exponentials, the decay is simple quadratic. This quadratic decay is governed by the decomposition of the interstitial-impurity complex and its effective activation energy is, therefore, the sum of the interstitial migration energy and its binding energy to the impurity. The complete decay is illustrated in Fig. 3, Case VI. The quadratic approximation is valid at times past the arrow.

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Figure Captions

Fig. 1 Schematic of the temperature dependence of a set of rate constants for the simultaneous annealing of single and divacancies (Case I, Table I).

Fig. 2 Comparison of the decay of vacancies and interstitials for Cases IV, V, and VI of Table I. In all three cases initial vacancy and interstitial concentration is 5×10^{-6}, the annealing temperature is 50°K, and the interstitial migration energy is 0.1 ev. The binding energy for i_2 in Case V and C in Case VI is 0.2 ev. The impurity concentration in case VI is 10^{-5}.

Fig. 3 Comparison of vacancy accumulation by continuous irradiation with vacancy accumulation by periodic irradiation (low temperature) and annealing.

Instructions to Editor

Table and all three figures should be 12 cm wide.

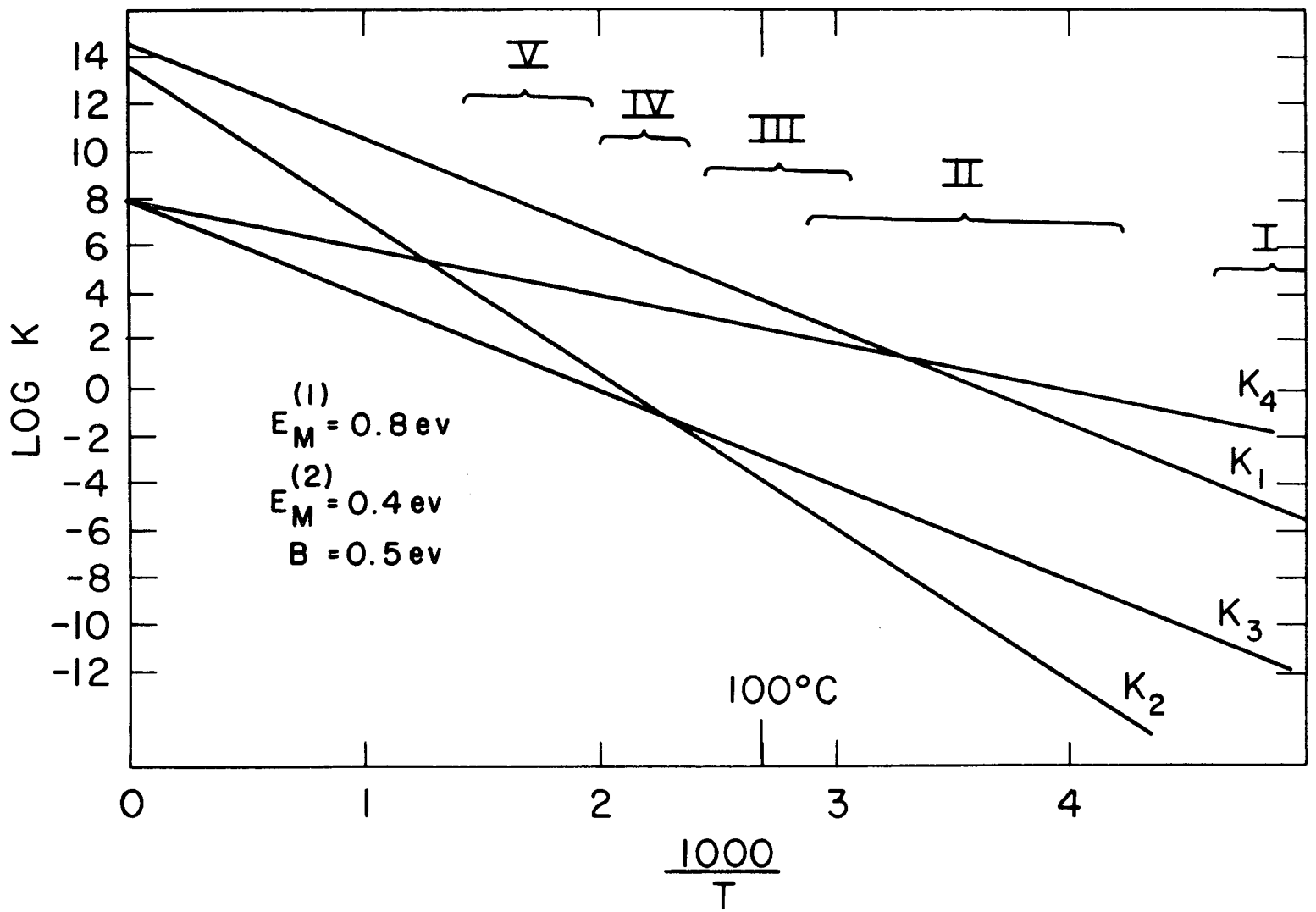

FIG. 1

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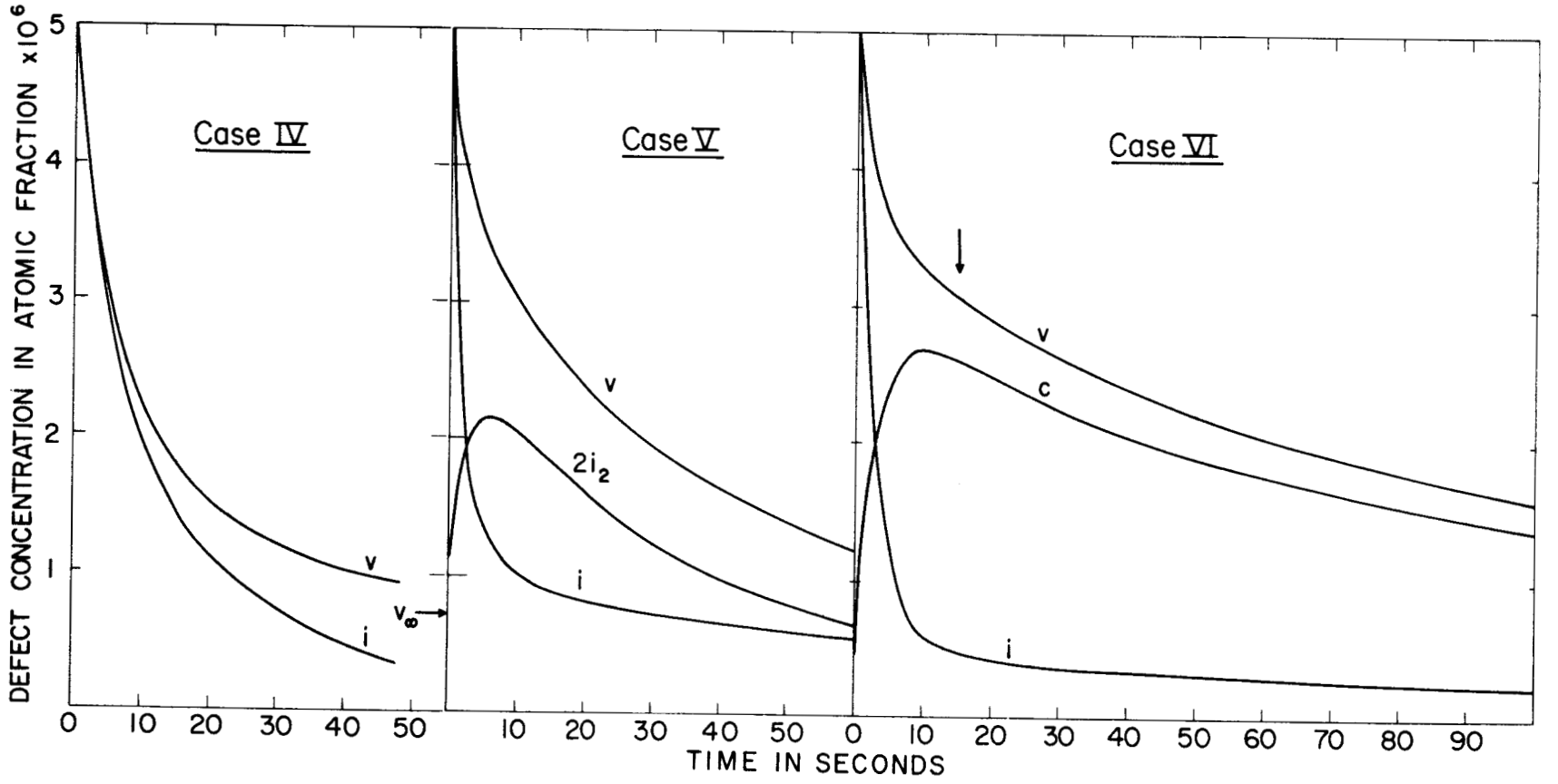

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FIG. 2

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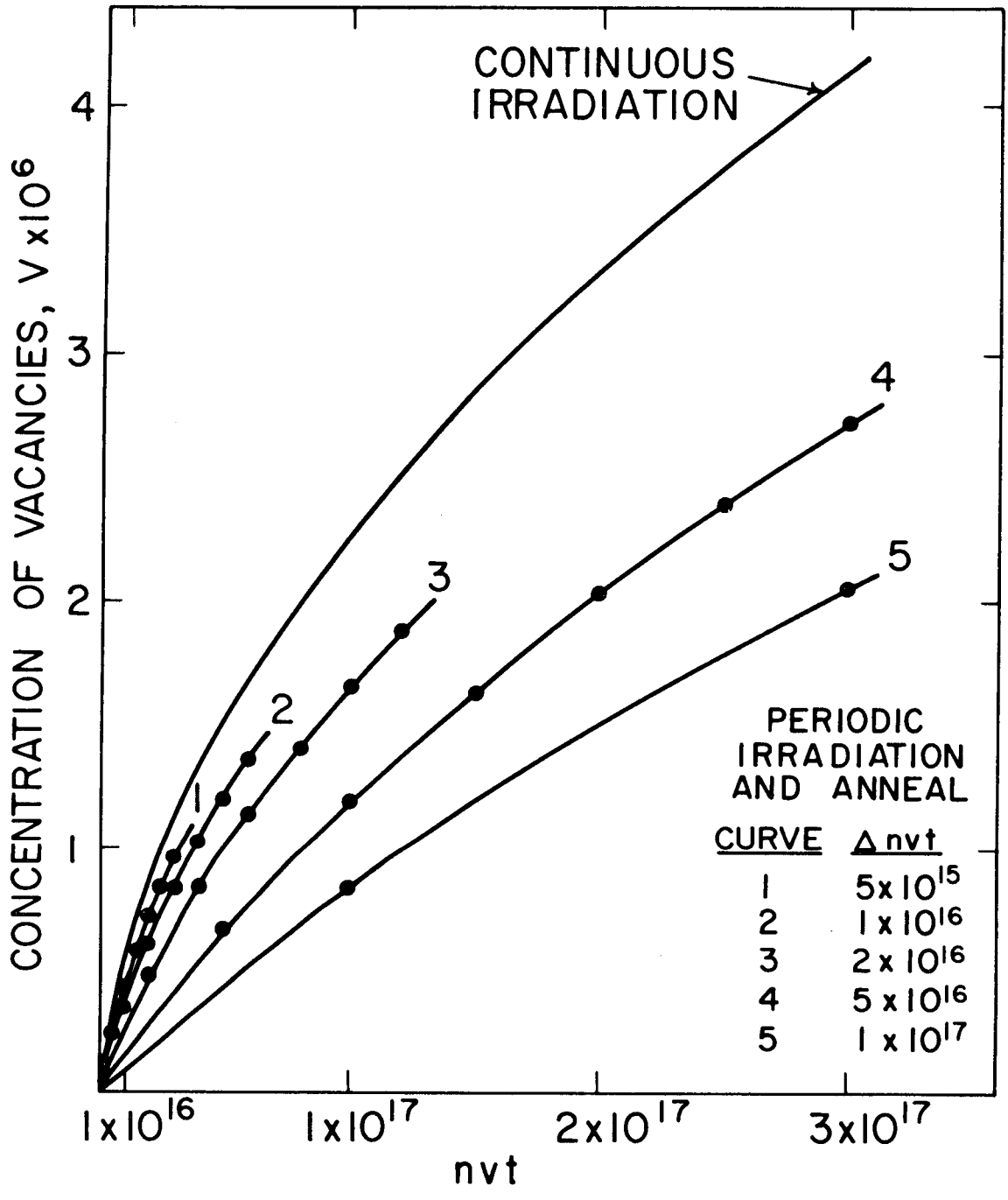

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FIG. 3

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