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COMPUTER SIMULATION OF INTERSTITIAL DIFFUSION IN TUNGSTEN

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COMPUTER SIMULATION OF INTERSTITIAL DIFFUSION IN TUNGSTEN

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ABSTRACT

A fully dynamic computer model employing ~150 atoms interacting through an empirical pair potential is used to follow the diffusion of a self-interstitial atom in tungsten. The dynamics of the jump process have been fully explored over a wide range of temperature. The results show that dynamic calculations must be run for times long enough to establish diffusion coefficients from macroscopic motion of the defect since methods based on discrete jump counting can lead to serious error.

INTRODUCTION

Because of the technological importance of radiation induced damage and because self-interstitial atoms are the immediate consequence of a damage event, they have received, over the years, considerable investigation. The temperature independent static relaxation method has most often been used in computer simulations. In only one case, to the best knowledge of the authors, has the motion of an interstitial been followed to the extent that a diffusion coefficient could be measured.

Tsai, Bullough and Perrin[1] (TBP) used a dynamic model to investigate interstitial and vacancy diffusion in b.c.c. α-Fe and found good agreement with the static model calculations for interstitial diffusion. In our parallel investigation of tungsten a major improvement in statistics has been achieved as well as a clearer delineation of the kinematics.

MODEL

The code employs a block of 2×9^3 atoms, corresponding to $10 \times 10 \times 10$ cubic cells with periodic boundary conditions. Atoms interact through a pair potential[2] which accurately reproduces experimentally measured phonon dispersion data and reasonably matches thermal expansion, elastic constant temperature dependence and shock compression data. The shape of the fundamental unit was varied in test calculations to insure the absence of nonphysical boundary effects. Operating the code in a relaxation mode, the split <110> configuration was found to correspond to equilibrium. Statically, an enthalpy of 0.38 eV is required for diffusion of the self-interstitial.

A centered first order finite difference scheme is used to solve the equations of motion in successive time steps. The time step, Δt, is taken equal to 1/15 the value of the reciprocal of the maximum lattice vibrational frequency ν_{max}. This time interval is sufficiently large to complete the problem in a reasonable period of time, yet small enough to give accurate results, e.g., one obtains the same jump rate by reducing the time step by a factor of ten.

The system is initialized by giving each atom random velocity components and then allowing sufficient time for the entire system to attain equilibrium. The volume is adjusted to maintain constant pressure at the desired temperature. Calculation of the diffusion coefficient then proceeds by recording all changes in position of the split interstitial.

CALCULATION OF THE DIFFUSION COEFFICIENT

It is difficult to establish the discreteness of a diffusive jump, since large center of mass motions occur which do not necessarily give rise to diffusion. TBP divided their lattice into "Wigner-Seitz" cells and defined the cell which contained two atoms longer than one free period of oscillation as the position of the interstitial. This method is unsatisfactory, yielding spuriously low values for ΔH_m, the enthalpy

of motion. We used two additional methods of calculating D; one relies upon the movement of the center of mass of the split interstitial and the other upon the root mean-square distance of travel of the defect. Sites at which no atom is within 1/3 of a lattice constant, a_o, are defined as vacant. A jump is recorded when both the vacant center of mass, thus defined, and the additional atom transfer to an adjacent site; there is no residence requirement in any location.

The diffusion coefficient can be calculated from the mean jump rate, Γ, as given by Eq. (1),

$$D = \Gamma a_o^2/8. \tag{1}$$

In the absence of correlation effects, this value should agree with that calculated from a macroscopic continuum definition, i.e.

$$D = \langle R^2 \rangle / 6t_o \tag{2}$$

where $\langle R^2 \rangle$ is the mean squared displacement after a lapse of time t_o. It is this latter value which is of interest, since it is independent of the choice of jump criterion as long as $t_o > \Gamma^{-1}$. Because of the necessarily ad hoc nature of any attempt to define the diffusion of an extended defect in terms of a series of discrete displacements, we feel that the macroscopic approach is required if we wish to make a valid comparison between dynamic and static calculations.

Calculations were made at five temperatures from .08 to .3 eV ($.25 < T/T_m < .95$). At each temperature the interstitial was allowed to diffuse until 1000 or more jumps (defined by the criteria given above) were accumulated. Each run was arbitrarily divided into 200 segments of equal duration and $\langle R^2 \rangle$ computed. The values of the diffusion coefficient D, from Eq. (2) are shown in Fig. 1 as a function of T_m/T.

The line corresponds to

$$D = D_o \exp(-\Delta H_m/kT), \tag{3}$$

with $D_o = 1.50 \times 10^{-3}$ cm^2/sec and $\Delta H_m = .33$ eV. Arrhenius behavior is observed over the whole range of temperatures investigated.

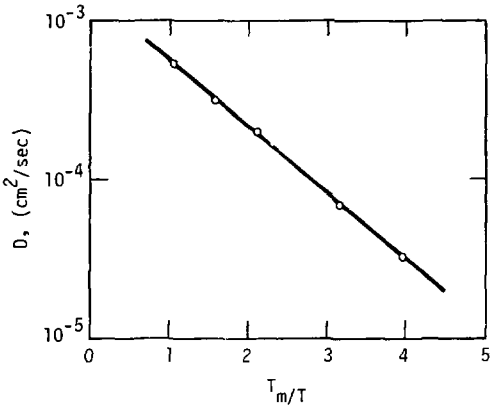

Fig. 1. Interstitial diffusion coefficient as a function of $(T/T_m)^{-1}$.

COMPARISON OF COUNTING METHODS

TBP obtained Arrhenius behavior, but only over the higher temperature portion of their work. In their lowest temperature run they obtained more than twice as many jumps as expected from an extrapolation of the high temperature points. We observe a similar behavior when their method of jump counting is employed.

Since we have no reason to expect any correlation in self-interstitial diffusion, jump rates calculated by both our method and that of Tsai et al. are compared to that expected from Eq. (1). In Fig. 2 the solid line corresponds to the jump rate calculated by substituting the measured diffusion coefficient in Eq. (1). The crosses correspond to the method of Tsai et al., the open circles to our method of counting.

At lower temperatures the method of TBP gives anomalously high values for the jump rates. While our method gives values much closer to those expected from $\langle R^2 \rangle$, agreement is still poor at lower temperatures.

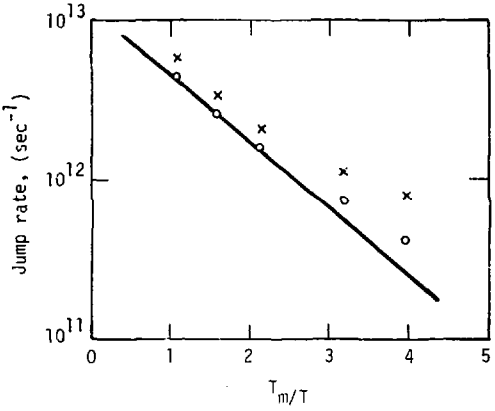

Fig. 2. Comparison of jump rates as a function of $(T/T_m)^{-1}$. See text.

By increasing the residence requirement the TBP method can produce a reasonably good fit to the Arrhenius equation, but yields much lower values of ΔH_m and D_o, than those obtained from $\langle R^2 \rangle$.

HIGH TEMPERATURE CORRELATION

An interesting temperature dependent correlation, specifically a tendency for the interstitial to continue along a <111> axis, is revealed by the dynamic calculations. This correlation is not the result of a dynamic crowdion or a persistence of motion as discussed by Alder et al.[3] A detailed analysis of jumps in all such sequences is consistent with a random one-dimensional walk.

Some degree of correlation is expected for a split <110> interstitial, due to the presence of an energy barrier opposing rotation. We would expect that the probability, P_c, of two successive jumps being along the same axis would lie somewhere between the value of 1/2, corresponding to forbidden rotation, and 1/4, corresponding to random diffusion. P_c can

be inferred from the diffusion data from the average number of jumps, $\langle n_d \rangle$, between changes in <111> axes, since

$$\langle n_d \rangle \approx 1/(1 - P_c). \qquad (4)$$

As is evident from Table 1., only at the lowest temperature does P_c even approach a value as low as 1/2, while at high temperatures values as high as .84 are observed.

Table 1. Jump sequences.

T(eV)	$\langle n_d \rangle$	P_c
0.082	2.18	0.54
0.102	2.45	0.59
0.153	5.59	0.82
0.196	6.11	0.84
0.297	4.79	0.79

The effect can be understood as a result of the diffusion geometry and the high temperatures involved. In the b.c.c. lattice it is possible for the <110> split-interstitial to diffuse back and forth along a given <111> axis without returning to the equilibrium configuration. A change of axis requires that the dumbbell pass through a configuration near equilibrium. At high temperatures the entropy term dominates the energy term so that the dumbbell passes through the equilibrium position only infrequently, and diffusion tends to continue along the same axis. At low temperatures, the energy term is dominant, and the dumbbell spends most of its time near the equilibrium position, changing axis more often between diffusion jumps.

CONCLUSIONS

The activation enthalpy of .33 eV determined dynamically is ~15% lower than the value .38 eV determined by the static relaxation method. This difference appears to be outside the uncertainty of either calculation. At present the source of this difference is not clear.

Dynamic calculations must be extended to times long enough to define macroscopic diffusion coefficients, since no completely satisfactory method has been found to describe the interstitial motion as a series of discrete jumps. This may be due in part to the extended nature of the defect, and the fact that the reference coordinate system against which

motion is measured is based upon the undistorted perfect lattice.

The observed high temperature correlation should prove to be a general feature of split <110> interstitial diffusion in the b.c.c. lattice, arising as it does from an entropy effect. Macroscopically, the effect is of little consequence. Locally, on a 100 angstrom scale, the one-dimensional nature of the diffusion could substantially modify expected recombination and recovery kinetics.

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