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NEW DIFFUSION MECHANISM FOR HIGH TEMPERATURE DIFFUSION IN SOLIDS

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ABSTRACT

A new atomic transport mechanism in solids at high temperatures has been discovered by Molecular Dynamics computer simulation. It can be described as a ring sequence of atomic replacements induced by unstable Frenkel pairs. This transport process takes place without stable defects, the atomic migration occurring indeed by simultaneous creation and migration of unstable defects. Starting from the analysis of this mechanism in different solids at high temperature (CaF_2, Na, Ar) and in irradiated copper by subthreshold collisions, we discuss the role of this mechanism on various diffusion controlled phenomena and also on the atomic processes of defect creation.

INTRODUCTION

A new atomic diffusion mechanism has been discovered by the computer simulation of Calcium Fluoride and can be described as a ring sequence of atomic replacements induced by an unstable Frenkel pair (figure 1).
As this process is very similar in its dynamical aspect to the ring sequence with replacements created by subthreshold collisions observed in simulation works on Copper [1,2], we have tried to know if it can occur also in other crystals like Sodium, chosen as a model system due to the reliability of the available interatomic potentials and the suitable experimental values of diffusion parameters.

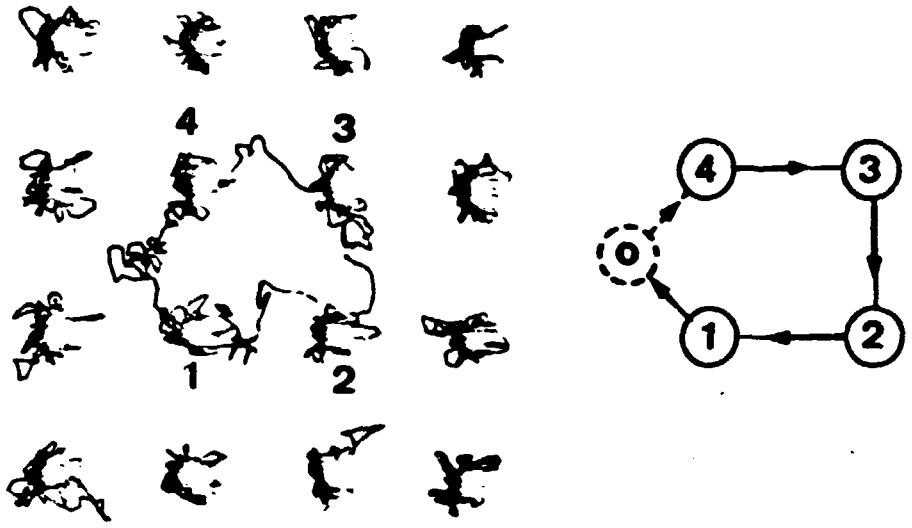

Fig. 1 : New diffusion mechanism : the sequence is initiated by an unstable Frenkel pair (vacancy at 1 and interstitial at 0), followed by jumps of atoms 2,3,4 and finally ended by a recombination jump of the interstitial to site 4.

MODEL AND METHODS OF ANALYSIS

The model used for the simulation is a cubic microcrystallite bounded by {100} planes containing N atoms arranged in an appropriate lattice. Periodic boundary conditions are applied in the usual way so that the system is surrounded by images of itself. In order to simulate thermal vibrations, an initial maxwellian distribution was assigned to the velocity components of the atoms in a random fashion. The initial temperature of the microcrystallite was adjusted so that at equilibrium the lattice was maintained at constant temperature . Additional details of the model are given in [3].
The particles interact via the Born-Mayer-Huggins potentials in CaF_2, the Dagens-Rasolt-Taylor potentials in Na and the Lennard-Jones potential in Argon. The values of different parameters used in these potentials are given in [4,5,6]. In order to take into account the long range coulombic forces summed over neighboring boxes and to improve the accuracy of the calculation, effective pair potentials are actually used according to [7,8]. The procedures used to follow the trajectories of atoms, to identify the jump events (catalogue of site occupancy) and to analyse the time interval between jumps or their simultaneousness are described in details in [3].

RESULTS

The new mechanism presented schematically in the introduction results from a

detailed analysis of runs in CaF_2 and Na. Attention has been paid to the qualitative aspects of the jump events and particularly to their cooperative process. For this purpose, it is necessary to make runs at appropriate temperatures, so as to observe some atomic jumps in the usual simulation time typically of a few psec. On the other hand, the simulation temperature should not be too high because the high number of events would make the jump analysis too complicated. For this reason, the examples presented hereafter are taken from runs at 0.73 T_m in CaF_2 and 0.78 T_m in Na.

- Calcium Fluoride. In this superionic conductor, we are interested only in the behaviour of F^- anions, because at 0.73 T_m the Ca^{++} cations are practically immobile. We shall analyse more carefully the cooperative process of F^- jumps in the example given in the introduction. Figure 2 shows some snapshots of the movement of four F^- anions involved in this event. Though we should keep in mind that other neighbors of these anions could participate to some degree in the process, we can describe the latter as a ring sequence of four quasi-simultaneous and cyclic jumps induced by an unstable Frenkel pair created at site 1. From the outset, the ion 1 is displaced to an octahedral position (site 0) (figure 2b), after that the ions 2, 3, 4 jump into the vacant site and replace each other (figure 2c and d) and finally the loop is ended by the last jump of ion 1 into the site 4. This sequential analysis is on the other hand corroborated by the catalogue of site occupancy at different timesteps and the relative displacement diagram (figure 3).

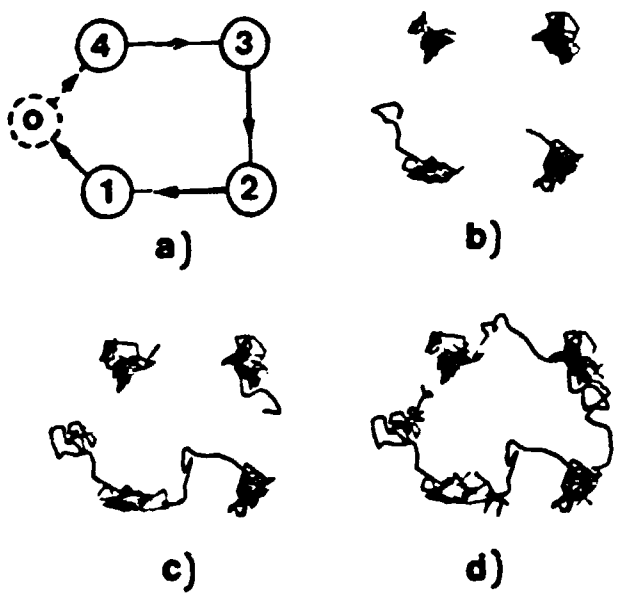

Fig. 2 : Example of F^- cyclic jumps in CaF_2. Trajectories of F^- ions at different timesteps ($\Delta t = 0.5\ 10^{-14}$s): a) schema, b) 40 Δt, c) 120 Δt, d) 250 Δt.

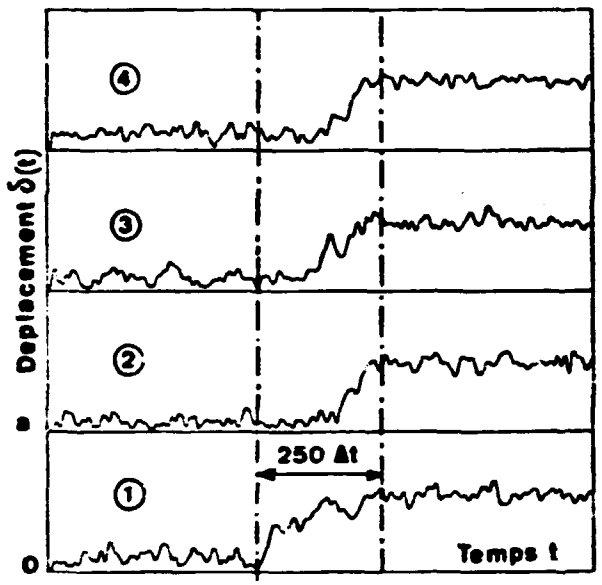

Fig. 3 : Diagram representing relative displacements of F^- ions from their initial position during the sequence of Fig. 2. The jump distance is given by a/2.

Other examples of this ring mechanism with more ions and jumps in one or different planes are also observed [3]. As the simulation temperature increases, the loops become more complex and begin to overlap each other as their number increases rapidly.

- Sodium. In order to examine the generality of the new mechanism, we have carried out similar simulations in bcc Sodium. The results show clearly that, in the absence of preexisting defects, atomic migration takes place by the same mechanism as in CaF_2. It is illustrated in figure 4 by a simple sequence of six cyclic atomic jumps, induced by an unstable Frenkel pair formed by a vacancy at site 1 and a dissociated interstitial at site 2. A careful examination of the occupancy catalogue at successive timesteps shows in fact that the process takes place by three jumps of the dissociated interstitial from site 2 to site 5 and in the same time by a vacancy jump from site 1 to site 6 and finally by a vacancy-interstitial recombination at site 6. It is noticed in this event that both vacancy and interstitial are mobile.

In order to check that the new mechanism is not an artifact related to the small size of the microcrystallite and their periodic boundary conditions, some runs are made on boxes with 3456 atoms. Despite the fact that, a priori, a larger box gives rise to larger atomic mean squared displacements [6] and therefore is more favorable to the creation of unstable Frenkel pairs, the results are quite similar to those obtained in smaller box. On the other hand, if a vacancy is introduced in the box during simulation, it can be displaced to some distance to a neighboring site by a process similar to the vacancy migration induced by subthreshold collisions [9].

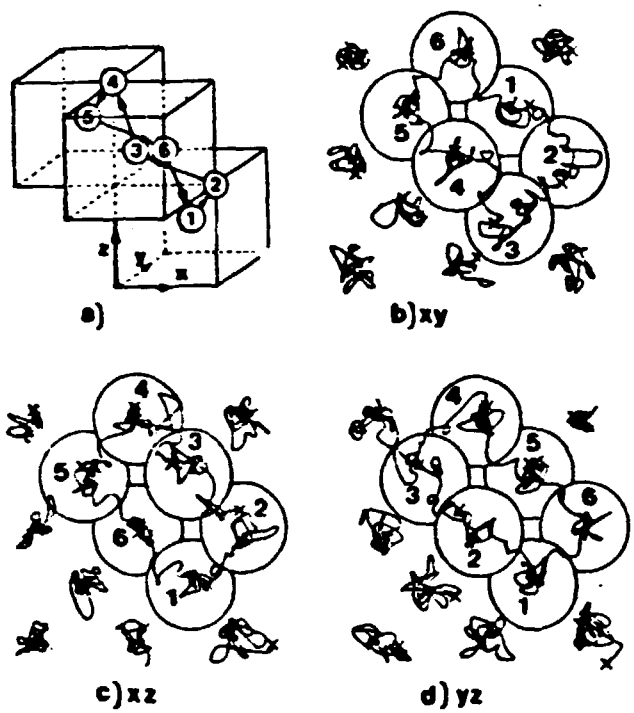

Fig.4 : Ring sequence of atomic jumps in Na viewed from different directions.The arrows in theschema a) represent the jump directions and the circles in b) c) d) define lattice sites in b.c.c. structure with arbitrary radius a$\sqrt{3}$/4

- Argon. From the previous observations, one is tempted to state that the new mechanism is correlated to sufficiently low energy values for Frenkel pair creation and defect migration. This means also that in a f.c.c. structure like solid Argon, similar events should not be observable in equivalent conditions. As we shall see later, Argon is chosen for this test because of interesting results obtained in recent simulation works [6,10,11]. As expected, simulation done in this system shows no such event, even for temperatures up to 0.95 T_m.

DISCUSSION AND CONCLUSION

The new mechanism can play an important role in solids where the atomic mobility is high enough (for example in superionic conductors, in b.c.c. metals, etc...) or enhanced by irradiation. In the presence of stable defects, it could enhance their diffusion by a process similar to the defect migration induced by subthreshold collisions. Its importance on various diffusion controlled phenomena and particularly on those observed under irradiation is under study. On the other hand, this new mechanism could also take an important part in the atomic process of defect creation. To make this point clear, additional arguments are needed. They are mainly based on the following results taken from simulation works and experimental observations:

- vacancies on surfaces [10] and in grain boundaries [11] in solid Argon are generated from vacancy-interstitial pairs ; in the latter, the interstitials

are trapped at particular sites while, on the surfaces, the adatoms are eliminated at jogs ;
- unstable Frenkel pairs are observed in Argon at some layers below the surface [10] while they are not seen in the bulk as mentioned above ; in other words, this would mean that the energy necessary to create unstable Frenkel pairs is probably much less in the vicinity of a surface than in the bulk ;
- vacancy injection from the surface into the bulk observed in Au foils irradiated by electrons at subthreshold energies [12].

Taken together, these results suggest that the creation of unstable Frenkel pairs in the vicinity of planar or linear defects (surfaces, grain boundaries, dislocations) would be the starting point in the creation process of stable defects in solids : the defects would be generated in pairs and either of them (for example the interstitials in the case of dense structures) trapped at surfaces or eliminated at jogs so as to maintain the thermodynamic equilibrium.

Acting directly on the efficiency of defect sources and sinks, this process would control all the transient effects related to defect concentrations (effects of impurities, defect injection...) which are responsible for most of important phenomena in thin films behaviour.

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