Vacancy Double Jumps and Atomic Diffusion in Aluminum and Sodium

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The relevance of a high-temperature mechanism for vacancy migration, the double jump, has been established by molecular dynamics in Al and Na. Migration energies for single jumps are 0.42 ± 0.1 eV and 0.12 ± 0.02 eV, respectively, while for double jumps they are about five times larger. Second-near-neighbor jumps are found in Na near melting. Comparison with lattice statics and experiments indicates the adequacy of a monovacancy description. The inclusion of double jumps explains the anomalous diffusion of Na at high temperature.

One of the most remarkable experimental facts in solid-state diffusion is the linearity often exhibited by Arrhenius plots of the diffusion coefficient D, over wide temperature ranges.[1] This fact has led workers to regard the activation enthalpy H as constant with respect to temperature for a given defect type, since $-d(\ln D)/d(1/K_B T) = H$; and to ascribe eventual curvatures to the competition of two or more defect types. On the other hand, some authors have insisted that anharmonicity and lattice expansion can bring about variations for the activation parameters with temperature,[2] therefore causing the curvature observed in some cases. A controversy has thus originated about the interpretation of diffusion experiments in a number of metals.

The relative importance of various diffusion mechanisms and their temperature dependence can be investigated by computer simulation. While lattice statics has been widely employed, the relevance of dynamical simulation of atomic diffusion is perhaps insufficiently recognized. Dynamical correlations in the defect diffusion process have been revealed in this way.[3] Furthermore, when other than simple nearest-neighbor exchanges between atoms and defects contribute to diffusion, the description of the migration process is complicated by the presence of more than one activation energy and jump length.[4] In these conditions it is clear that lattice-statics evaluation of migration energy and entropy of the most obvious migration channel is not exhaustive.

The experimental Arrhenius plots of Al and Na show measurable curvatures. Their interpretation has received much attention in recent years.[2,5] In addition, Na shows a high-temperature anomaly, referred to as the premelting phenomenon,[2] also exhibited by other alkali metals (e.g., Li): The diffusion coefficient has a sharp rise above $T = 0.9T_m$ and the isotope effect abruptly decreases, in the same region, from the value apropriate to normal monovacancy diffusion.

The purpose of this Letter is to report a classical molecular-dynamics (MD) simulation of monovacancy diffusion in a 256-site fcc crystal model with an interaction pair potential appropriate to Al, and in a 250-site bcc model appropriate to Na, with periodic boundary conditions. Calculations were carried out at three temperatures within a 100-K interval in Al and four temperatures within a 45-K interval in Na. The system was followed for a time of the order of 10^{-9} sec to collect approximately 500 jump events for each run for Na and about a half of this for Al. We present here the results of this study. A comprehensive report will be published in due course, including a study on potassium.

The interaction pair potentials we have used are due to Dagens, Rasolt, and Taylor.[6] They are *ab initio* potentials, i.e., not fitted to empirical crystal properties. Previous studies of solid- and liquid-phase properties of Al,[7] K,[8] and Li[9] have shown that they give very good account of the experimental bulk behavior. Vacancy energies and volumes have been also computed with these potentials,[7,10] including anharmonic effects of lattice vibrations neglected in all existing calculations have given for the first time the correct positive sign[1] of the variation of defect formation and migration energies with increasing temperature. The formation energy for a vacancy in Na is found to be 0.25 and 0.28 eV at $T = 0$ and $T = T_m$ with formation volume ΔV_f of 0.6 atomic volume[10]; the migration energies in Al are found to be 0.42

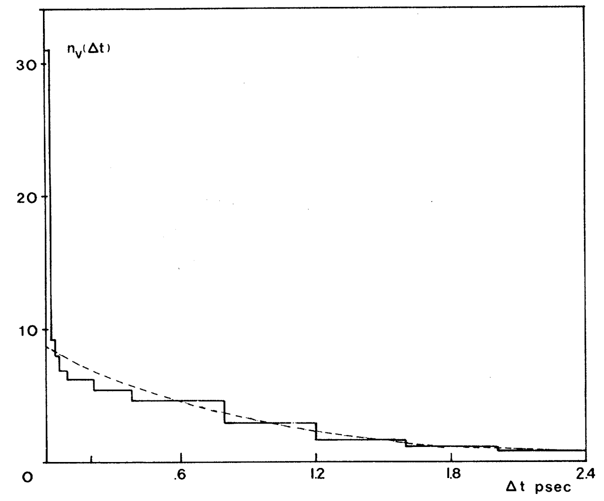

FIG. 1. Distribution of vacancy jumps in Al at melting vs their time delay Δt. The broken line represents the exponential distribution appropriate to a random process with the same overall jump rate. The histogram is much higher than the broken curve at very short times because of the double-jump events, and then becomes lower at intermediate times because of the suppression of backward jumps.

TABLE I. Migration parameters of the vacancy. E_m', E_m'', and E_m (in eV) correspond to SJ, DJ, and atomic mean-square displacement, respectively.

Metal	E_m'	E_m''	E_m	S_m'
Na	0.12 ± 0.02	0.55 ± 0.1	0.18 ± 0.02	$\sim K_B$
Al	0.42 ± 0.1	~ 2	0.5 ± 0.1	$\sim K_B$

and 0.70 eV, with migration volume ΔV_m of 0.6 atomic volume.[7]

The analysis of the jump events of our MD simulation indicates the following:

(1) The distribution $n_V(\Delta t)$ of the time delays of successive jumps of the vacancy departs at short times (a few vibration periods of the lattice) from the exponential distribution appropriate to a random process (see Fig. 1).

(2) The huge peak occuring in n_V at short times grows rapidly with temperature: It is connected with simultaneous (within a vibration period of the lattice) forward-correlated jump events. The temperature dependence of their occurrence frequency indicates a migration energy much higher than for single-jump (SJ) events by about a factor of 5. Thus we must regard the double jump (DJ) as a second diffusion mechanism involving two atoms that jump at the same time collinearly, with the vacancy jumping to a non-nearest-neighbor site. Vacancy jumps to second near neighbors (SNNJ) have also been found in Na (5% at the melting point). They exhibit a migration energy also much higher than the SJ.

The defect jump rate Γ for the two mechanisms is obtained by counting the respective jump events observed in the various runs. For SJ we can write $\Gamma' = z\tilde{\nu}\exp(S_m'/K_B)\exp(-E_m'/K_BT)$, where z is the coordination number of the lattice. The slope of $\ln\Gamma'(T)$ versus $1/K_BT$ gives the value of E_m'. This quantity represents the migration enthalpy, that reduces to the migration energy at zero pressure. The migration enthropy S_m' is then deduced by inserting appropriate values of the attempt frequency $\tilde{\nu}$, which are 5×10^{12} sec^{-1} and 2×10^{12} sec^{-1} in Al and Na, respectively. Similarly, letting $\Gamma'' = \Gamma_0\exp(-E_m''/K_BT)$, a value of the migration energy for DJ is defined. We note that the value of Γ_0 is puzzlingly high if one tries to interpret it in the traditional way. Results are given in Table I, along with the overall migration energy E_m derived from the temperature variation of the asymptotic slope of the mean-square atomic displacement versus time.

The values of the migration parameters need an important specification. The MD technique imposes constant energy (CEC) and constant volume (CVC) conditions on the atomic system in the atomic system in the periodic cell, in contrast to experiment, during the migration process—the volume changes, however, with temperature as that of the real solid at room pressure.

The CEC does not affect the results in a substantial way. The probability of occurrence of fluctuations of a given amplitude of the potential energy is somewhat reduced in our CEC microcanonical system with respect to the canonical distribution. Lower jump frequencies are then expected. An investigation of these distributions shows that the reduction is, however, negligible for SJ, but is nonnegligible for DJ and for SNNJ found in Na, since both processes show a migration energy of the order of 5 times E_m'. The occurrence frequency of these events is probably reduced by over 10%. Their migration energy should not be altered appreciably, however.

The Gibbs free energy of migration (and formation) of the defect is not altered by CVC, i.e., $H^P - TS^P = E^V - TS^V$ with P and V referring to constant-pressure or -volume conditions.[11,12] So that the value of Γ is not altered either, and (the constant) E_m' is directly comparable with the (high-temperature) value of H^P ($\sim E^P$) given by experiment. S_m' corresponds in turn to S^P. The effect of CVC must, however, be explicitly considered in static calculations.[7,10-12] Here E^P is obtained by adding to E^V the entropic contribution consisting essentially in the lattice entropy increase upon volume expansion[13]:

$$E^P \simeq H^P = E^V + T(S^P - S^V) \simeq E^V + T(\alpha/K_T)\Delta V^P .$$

For SJ in Al, at melting, static calculations give[7] $E^V = 0.3$ eV and $\Delta V^P = 0.6$ atomic volume Ω; the corresponding entropic term is 0.4 eV. The value of E_m' from Table I is then to be compared to the static result $E^P = 0.7$ eV and to the high-temperature experimental value $E^P > 0.62$ eV.[5] The difference between E^V and E^P for the migration of Na is instead very small. This is because ΔV^P must be small; in fact, the static evaluation of the formation volume[10] 0.6Ω is already larger than the measured activation volume 0.5Ω,[14] which is the sum of the two. In any case the entropic correction is only about 0.015 eV for each increase of 0.1 in $\Delta V^P/\Omega$.[10]

The dynamical result obtained for E_m' in Al is somewhat lower than the static evaluation E^P, which is close to the experimental value. The rather large variation of the static value E^P with temperature and a corresponding variation of the formation energy[7] suggest that there is no need to invoke divacancies to explain the curvature of the experimental Arrhenius plot in Al.

For Na we can add the migration energy E_m obtained in the present work, i.e., 0.18 eV at melting and 0.12 eV at low temperature (where only SJ contribute), to the static formation energies 0.28 and 0.25 eV to obtain 0.46 and 0.37 eV. These values are in excellent agreement with the temperature dependence of the measured self-diffusion coefficient.[14] By taking the slope of the best-fit formula of Mundy's self-diffusion data one obtains, in fact, 0.45 and 0.37 eV. Monovacancies, then explain, the curvature of the Arrhenius plot in Na.

At the melting point of Na, DJ contribute more than one fourth of the atomic migration processes. As a consequence near T_m the slope of Arrhenius plot, E_m, is substantially increased with respect to E_m'. Furthermore, the collective character exhibited by DJ causes a reduction of the isotope effect.[15] This is strong evidence that DJ are responsible for the premelting phenomenon observed in Na.

A preliminary study of K shows similar values for the migration parameters, and an accord with experimental data[16] just as good. The DJ in K are found to contribute a smaller amount to diffusion at melting than in Na; the same is true for SNNJ.

The DJ can be revealed by an accurate comparison of experimental results on mass diffusion with those of tracer diffusion. SNNJ can be instead revealed by incoherent neutron scattering. Their effect on the self-diffusion function $S_s(K, \omega)$ has been computed on the basis of the present data.[17] Experiments are indeed under way, and in preliminary runs it looks as if an interpretation of the data in term of nearest-neighbors jumps only is not possible.[18]

The overall agreement of the results of this work with static calculations and experiment indicate the following: (1) The pseudopotential pair interaction of Dagens, Rasolt, and Taylor is quite adequate for defect dynamics in Na and K. The situation is less conclusive for Al. (2) A description of atomic diffusion in these systems based on monovacancies only is able to give account of experimental results and explain the observed anomalies and curvatures.

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Negative Magnetoresistance in Very Strong Accumulation Layers on ZnO Surfaces

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Negative transverse magnetoresistance was observed in quantized accumulation layers on the $(000\bar{1})$ face of ZnO single crystals. The results are interpreted in terms of surface scattering center with giant magnetic moments, possibly due to the formation of charged clusters. Good quantitative agreement is found between theory and experiment.

We report on magnetoresistance (MR) measurements in very strong accumulation layers on ZnO surfaces. The measurements were carried out at low temperatures T (2–80 K), with the magnetic field B perpendicular to the surface (transverse MR) and in the range of surface electron concentrations ΔN of 8×10^{12} to 7×10^{13} cm^{-2}. In this range the electrons in the accumulation layer become a quasi two-dimensional degenerate electron gas.[1,2] The MR was found to be negative over the entire experimental range. It depends quadratically on B/T for small B/T, and saturates at high B/T. The results are interpreted in terms of magnetic scattering centers with giant magnetic moments, of the order of $100\mu_B$ (where μ_B is the Bohr magneton). The agreement between theory and experiment is considered good.

Bulk negative MR has been observed by several workers[3-7] in doped semiconductors. Most of these workers concluded that the MR is caused by the presence of huge effective magnetic moments, up to $(50-100)\mu_B$. Measurements on surface channels,[8] on the other hand, almost always show the presence of only positive transverse MR and only in a very few instances was a negative effect found.[9-11] The most comprehensive work on negative transverse MR in surface channels is that of Eisele and Dorda[10] on silicon inversion layers, at relatively low electron concentrations ($\sim10^{12}$ cm^{-2}). These authors assume, somewhat arbitrarily, that the effective magnetic moment of the scattering centers is about $2\mu_B$. The negative effect they found, however, was partially masked by the sumultaneous presence of positive MR and thus it was difficult to compare their data to a theoretical model. Such a positive effect is absent in our samples up to the highest fields used (~60 kG).

The measurements were performed on the $(000\bar{1})$ polar face of ZnO grown by Airtron Co. The samples were cut, mechanically polished, and chemically etched. The bulk resistivity at the temperature range studied was effectively infinite. Small contacts were attached to the sides of the sample to serve as voltage probes for conductivity and Hall-effect measurements. The strong accumulation layers were obtained by exposing the surface to helium ions produced by an electrical discharge in helium atmosphere.[12]

Figure 1 shows semilog plots of the transverse MR, $\Delta\rho/\rho$, at 4.5 K vs B for different ΔN values. The straight lines in the figure were drawn with a slope of 2. We see that the negative MR is proportional to B^2 at low fields and tends to saturate at higher fields. The deviation from quadratic behavior occurs at lower fields the higher the value of ΔN, and $-\Delta\rho/\rho$ increases with increasing ΔN.

Figure 2 shows the dependence of $\Delta\rho/\rho$ on B/T for a fixed $\Delta N=6.5\times10^{13}$ cm^{-2}. The points corresponding to different temperatures follow the same curve, thus showing that $\Delta\rho/\rho$ is a function of B/T. At low B/T values, $\Delta\rho/\rho$ is proportional to $(B/T)^2$; it deviates from this square dependence for $B/T\gtrsim100$ G/K, and saturates (see below) at very high magnetic fields.

To explain our results one has to assume, similarly as in the semiconductor bulk, that part of the scattering is due to localized magnetic mo-