STATISTICAL THEORY OF DIFFUSION. APPLICATION TO A VACANCY IN A LINEAR CHAIN OF ATOMS

Yu.A. Kashlev

The model of a vacancy in a lattice consists of a linear chain of atoms with one vacant site and a substrate potential. In the framework of this model, Kubo's expression for the transport coefficient is used to study the coefficient of diffusion of the vacancy. In the derivation of the coefficient, allowance is made for the distortion of the lattice around the vacancy and mass-difference scattering of phonons. Two mechanisms whereby the atom goes over into the neighboring vacant site are considered: 1) at high temperatures, through a nonlocalized intermediate state, which leads to an Arrhenius-type expression (classical picture) for the transition probability; 2) at low temperatures, through a tunnel transition. The phonon scattering is described by means of the t matrix and Green's functions.

In [1], the method of two-time Green's functions [2] was applied to the theory of the high-temperature mobility of a vacancy in a linear chain of atoms. The displacement of an atom was described in [1] as a transition from an excited (long-lived) state in the original potential well to a state with the same energy in the neighboring well. Many-phonon transitions of the atom from the ground state to a state with energy sufficient for a transition were not considered.

The basic ideas of the quantum theory of migration [1] have been developed further in the present paper, in which we consider the mobility of a vacancy not only at high temperatures, but also at low temperatures, at which the transitions occur through quantum-mechanical tunneling. In addition, we investigate a new mechanism (compared with [1,3,4]) of high-temperature mobility -- transition of an atom through an excited intermediate state, including many-phonon transitions in the case of thermal excitation of the state (Orbach-type process [5]).

Because of mathematical difficulties, we do not consider real crystals, but only a simplified model [6], in which the atoms form a linear chain and none of the N sites of the chain can be occupied by more than one atom. The site \(x_m=am\) (\(a\) is the lattice constant) is associated with the spin variable \(\sigma_m\), which takes the value \(\sigma_m=+1\) if the site is vacant and \(\sigma_m=-1\) if it is occupied. The exchange of a spin variable can be described by the operator \(T^A\) [6], which determines the probability of exchange between nearest-neighbor sites \(m\) and \(m'\) in the case \(\sigma_m=-\sigma_{m'}\). Introduction of the migration Hamiltonian \(hT^A\) into the total spin-phonon Hamiltonian of the system enables one to treat the diffusion mobility of the vacancy in the framework of linear response theory [2].

1. The operator of vacancy-migrating atom exchange has the form [6]

\[
T^A = \frac{1}{2} \sum_m T^A_{mm+1}, \quad T^A_{mm'} = w_A (I_{mm'} - 1) \Delta_{mm'},
\]

where \(w_A\) is the frequency of the transition \(m \rightarrow m'\), and the nondiagonal operator \(I_{mm'}\) satisfies the commutation relations [6]

\[
I_{mm}\sigma_m = \sigma_m I_{mm'} \quad I_{mm}\sigma_{m'} = \sigma_{m'} I_{mm'}, \quad I_{mm}\sigma_{m''} = \sigma_{m''} I_{mm'}, \quad I_{mm}\sigma_{mm'} = \sigma_{mm'} I_{mm'}, \quad I_{mm}^2 = 1, \quad \text{for } m'' \neq m, m'
\]

and the condition \(I_{mm'}^2 = 1\) for \(\sigma_m = -\sigma_{m'}\).
The operator \( I_{m,m'} \) defined by Eqs. (2) can be expressed in terms of the operators of a spin localized at a site:

\[
I_{m,m'} = S_m S_{m'} + S_m S_{m'}^* - S_{m'} S_m^*.
\] (3)

If we consider transitions as a result of which the number of nearest neighbors (and, therefore, the energy of the system) is conserved, then [6]

\[
\Delta_{m,m'} = -\frac{1}{2}(1 - \sigma_n \sigma_{m'}), \quad \sigma_n = -2S_n^*.
\] (4)

The total Hamiltonian of the system is

\[
\mathcal{H} = \mathcal{H}_{ph} + \mathcal{H}_{vac} + \hbar \mathcal{T}^A,
\]

where \( \mathcal{H}_{ph} \) is the Hamiltonian of an ideal chain of atoms on a substrate [1], \( \mathcal{H}_{vac} = \mathcal{H}_{vac}^{(1)} + \mathcal{H}_{vac}^{(2)} \) is the Hamiltonian of the vacancies [7]. The Hamiltonian \( \mathcal{H}_{vac}^{(1)} \) describes the rearrangement of the vibrations of the ideal lattice due to the new equilibrium positions of its atoms resulting from the formation of the vacant sites. This term is linear in \( Q(x_m) \), the longitudinal displacements of the atoms from the equilibrium position:

\[
\mathcal{H}_{vac}^{(1)} = -\sum_{m \neq m'} A(x_m - x_m') Q(x_m) \frac{1}{2}(1 - \sigma_n) \frac{1}{2}(1 + \sigma_m),
\] (5)

where \( A(x) = \partial V/\partial x \) is the gradient of the interatomic interaction potential, \( \frac{1}{2}(1 + \sigma_m) \) is the density of the gas of vacancies, and the summation over \( m \) and \( m' \) includes nearest-neighbor sites. The energy of the distant atoms corresponds to

\[
\mathcal{H}_{vac}^{(2)} = \frac{1}{2N} \sum_m p^2(x_m) \frac{1}{2}(1 + \sigma_m) + \frac{1}{2} \sum_{m \neq m'} \left( g(x_m - x_m') [Q(x_m) - Q(x_m')] \right)
\]

\[
+ \frac{1}{2} \sum_{m \neq m'} [Q(x_m) - Q(x_m')] \frac{1}{2}(1 - \sigma_m) \frac{1}{2}(1 - \sigma_m),
\] (6)

where \( p(x_m) \) is the momentum and \( M \) the mass of an atom, \( g(x) = -\partial^2 V/\partial x^2 \), and \( \bar{g} \) is the harmonic force constant corresponding to the substrate potential. The Hamiltonian (6) describes isotopic scattering of phonons on the mass fluctuations associated with the formation of vacancies at the sites \( x_m \).

2. The coefficient of diffusion of the vacancy (of the neighboring atom) is [1, 8]

\[
D = \frac{1}{\hbar} \int_\tau^\infty dt \langle \hat{d}(\hat{d}(-t)) \hat{S} \rangle \exp(-\epsilon t), \quad \epsilon \to +0,
\] (7)

where \( \hat{d} = [\mathcal{H}, \hat{d}] \) is the velocity operator, \( \hat{d} = \sum_m \frac{p_m}{\hbar}(1 + \sigma_m) \) is the operator of the dipole moment of the migrating atom, \( \langle \ldots \rangle_0 \) denotes statistical averaging over the equilibrium state with the Hamiltonian \( \mathcal{H}_0 = \mathcal{H}_{ph} + \mathcal{H}_{vac} \) (we ignore the operator \( \mathcal{T}^A \) compared with \( \mathcal{H}_0 \) [1, 3]). Going over in \( \hat{d} \) from \( \sigma_m \) to the Pauli operators \( \hat{a}_m \) and \( \hat{\bar{a}}_m \) [2], we obtain in the case of a chain with one vacancy

\[
\hat{d} = (a/2) \sum_m (\hat{a}_m + \hat{\bar{a}}_m)^{+} \sigma_m = \hat{a}_m \hat{\bar{a}}_m.
\]

We perform a unitary transformation of the expression in (7) under the symbol \( \langle \ldots \rangle_0 \) (or rather, under the trace symbol), using the unitary operator

\[
\exp S = \exp \left\{ \frac{1}{N} \sum_{k,h} (\hat{a}_h - \hat{\bar{a}}_h)^{+} \hat{a}_h \hat{\bar{a}}_h \exp(ikx_h) \right\},
\]

where \( u_k = -i\omega_k(2\omega_0)^{-N} \), \( \omega_k \) is the energy of the \( k \)-th vibrational mode, \( \omega_0^2 = (2\gamma/M)(1 - \cos k\gamma) + \omega_0^2 \), \( \omega_0^2 = \bar{g}/M \), \( f_k \) is the Fourier component of \( A(x) \), \( \hat{b}_k \) and \( \hat{b}_k \) are Bose operators. Taking into account the invariance

* Here and below, we use units for which \( \hbar = k_B = 1. \)