Diffusion mobility of the hydrogen atom with allowance for the anharmonic attenuation of migrating atom state

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ABSTRACT

Evolution of vibration relaxation of hydrogen atoms in metals with the close-packed lattice at high and medium temperatures is investigated based on non-equilibrium statistical thermodynamics, in that number on using the retarded two-time Green function method. In accordance with main kinetic equation – the generalized Fokker-Plank- Kolmogorov equation, anharmonism of hydrogen atoms vibration in potential wells does not make any contribution to collision effects. It influences the relaxation processes at the expense of interference of fourth order anharmonism with single-phonon scattering on impurity hydrogen atoms. Therefore, the total relaxation time of vibration energy of system metal-hydrogen is written as a product of two factors: relaxation time of system in harmonic approximation and dimensionless anharmonic attenuation of quantum hydrogen state.

1. Introduction. Harmonic approximation

The mechanism of the elementary act of the hydrogen atom (H atom) diffusion in metals is determined by the configuration potential relief of the impurity center, which has a significant impact on both its diffusion mobility and quantum state. In [1–3] was shown that the main contribution to the potential relief of the H atom is made by the Coulomb interaction between the metal ions and the impurity center on a homogeneous background of free electrons. Upon that, an amendment describing the contribution of the electron gas polarization by a charged impurity atom is taken into account.

We confine ourselves to the movement of the H atom in metals with close-packed lattice. Recall that these lattices are formed from the same close-packed layers of atoms but with different means of their arrangement. However, we are further going to refer to the hexagonal close-packed (HCP) lattice more often since the octahedral positions in its structure are aligned along the hexagonal axis and form a periodic sequence of symmetrical wells having the potential minima near the octahedral positions. It is assumed that the barrier height is much greater than the average thermal energy of the H atoms. In case of HCP metals main contribution to the potential relief inserts contributes of metal atoms on the background free electrons, while the interaction with local strain field in a first approximation does not considered.

In this article we studied the influence of anharmonic effects on diffusion mobility of light atoms in metals with HCP lattice. Mostly in the scientific literature, the object of study is the action of anharmonicity on the lattice dynamics - the phonon dispersion throughout the Brillouin zone, the frequency shift and the damping of phonons [4]. In

the present article, we propose a different direction of research – the anharmonic potential impact on the relaxation kinetics of non-equilibrium process.

Using a system of units in which $(h/2\pi)=k_B=1$, the total Hamiltonian in the harmonic approximation can be written as

$$H_1 = H_{ph} + H_p^{(h)} + H_{int}, \tag{1}$$

where $H_{ph} = \sum_q \omega_q b_q^+ b_q$ is the lattice Hamiltonian (b_q^+ are b_q are the Bose operators, ω_q is the energy of an acoustic phonon); $H_p^{(h)} = \sum_s \omega_s a_s^+ a_s$ is the hamiltonian of the H atom in the harmonic approximation; H_{int} is the interaction hamiltonian the H atom with thermal lattice vibrations;; $\omega_s = \Omega s$ is energy of the H atom, that is the harmonic oscillator, oscillating in the x-direction, with the natural frequency Ω; a_s^+ and a_s are the Fermi operators. In the nearest neighbors approximation, it can be written as

$$H_{int} = \widetilde{\lambda} \sum_{\langle d \rangle} h(X) u(X + d), \tag{2}$$

where $\widetilde{\lambda}$ is the bond constant of a particle with lattice vibrations; u is displacement of the lattice atom with respect to the lattice nodal point; $h(X)$ is displacement of the H atom with respect to the minimum of the potential well with the coordinate X (chaotic variable); d - the distance between neighbor octahedral sites of the x −chain. In the second-quantization representation we have

$$H_{int} = \sum_{sq} \varepsilon_q(s, s+1) \exp[-i(q-k)X] a_s^+ a_{s+1}(b_q^+ + b_{-q}), \tag{3}$$

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where

$\varepsilon_q(s, s + 1) = I_q(s + 1)^{1/2}$, $I_q = -i\widetilde{\lambda}(\overline{N}M\omega_q m\Omega)^{-1/2}$, M is the mass of the lattice atom, m is the mass of the H atom, $\overline{N}$ is the number of atoms in the x-chain.

In order to describe the system in the framework of non-equilibrium statistical theory we must enter the statistical operator ρ_l (t). If the thermodynamic parameters of the system change slowly, we can be restricted to using by the stationary statistical operator ρ_l. Introduction to statistical operator allows us to define the two-time retarded Green's function, which is an amendment to the equilibrium distribution of the H atoms $n_s = \langle a_s^+ a_s \rangle$. and is written in the following form [5]

$$G_{ss'}(t) = \langle\langle a_s^+(t)a_{s'}, A\rangle\rangle = \frac{1}{i}\theta(t)\langle[a_s^+(t)a_{s'}, A]\rangle, \qquad (4)$$

where A is the external driving force,$\langle P\rangle = Sp(\rho_l P)$ is the average value; $[B, A] = BA - AB$.

In the harmonic approximation the Green's function (4) satisfies the equation, which is shaped similar to the finite-difference equation of the Fokker-Planck-Kolmogorov equation for the probability density

$$\left(i\frac{d}{dt} + \omega_{ss'}\right)G_{ss'}^{(h)}(t) - \delta(t)\langle[a_s^+a_{s'}, A]\rangle =$$
$$= 2\pi i\sum_q\{|\varepsilon_q(s, s + 1)|^2 S_1 G_{ss'}^{(h)}(t) - |\varepsilon_q(s - 1, s)|^2 S_2 G_{ss'}^{(h)}(t)\}\delta(\omega_q - \Omega), \qquad (5)$$

where $S_1 G_{ss'}^{(h)}(t) = (f(\xi) + 1)G_{s+1,s'+1}^{(h)}(t) - f(\xi)G_{ss'}^{(h)}(t)$,

$S_2 G_{ss'}^{(h)}(t) = (f(\xi) + 1)G_{s,s'}^{(h)}(t) - f(\xi)G_{s-1,s'-1}^{(h)}(t)$,

$\omega_{ss'} = \omega_s - \omega_{s'}, f(\xi) = (e^\xi - 1)^{-1}, \xi = \beta\Omega$. \qquad (6)

The analytical solution of the Eq. (5) implies that the Fourier component of the Green's function in the harmonic approximation has the form

$$G_{ss'}^{(h)}(E) = (2\pi)^{-1}\sum_{s''} B_{s''1}F_1(-s'', 1; s)\left[E + \omega_s - \omega_{s'} + is''\frac{1}{\tau^{(h)}}\right]^{-1}. \qquad (7)$$

Here

$$\sum_{s''} B_{s''1}F_1(-s'', 1; s) = 2n_s, \qquad (8)$$

$$\frac{1}{\tau^{(h)}} = 2\pi\sum_q \widetilde{\lambda}^2 NM\omega_q m\Omega\delta(\Omega - \omega_q) \qquad (9)$$

is the reciprocal relaxation time in the harmonic approximation;$_1F_1(-s'', 1; s)$ is the confluent hypergeometric function; $\frac{1}{\beta}$ is the lattice temperature. The explicit form of the function $B_{s''}$ calculated with consideration of the Eq. (8) is given in [5].

2. The equation of motion for the Green's function. The vibrational energy relaxation in the system of anharmonic oscillators

The theory presented above is formulated in the harmonic approximation. As will be shown below (see part 5), the using harmonic potential, we actually exclude from consideration the area in which the fluctuation fields acting on the migrating particles are located. This raises concerns that the resulting picture is thus not fully in line with the physical situation. Therefore, it is of interest to approach the problem in a more realistic model including anharmonic potential in the initial definitions.

As a model potential we shall use the standard potential of impurity particles in a crystalline solid [6]

$$V(X) = \frac{1}{2}V_0\left[1 - \cos\frac{2\pi}{d}h(X)\right].$$

Restricting in the terms of the fourth order of the displacements of the impurity atom, we can write the total Hamiltonian of the system as

$$H_2 = H_{ph} + H_p^{(h)} + H_p^{(anh)} + H_{int}, \qquad (10)$$

where

$$H_p^{(anh)} = \lambda^2 \sum_{lmfg}\sum_{\eta\nu\rho\sigma}\varphi_{lmfg}^{\eta\nu\rho\sigma}V_0 e^{ik\Lambda X}a_l^+a_{l+\eta}^+a_m^+a_{m+\nu}a_f^+a_{f+\rho}a_g^+a_{g+\sigma}. \qquad (11)$$

In the formula (11) indexes $\eta, \nu, \rho, \sigma; l, m, f, g$ are discrete variables that takes two values of 1 and -1; $\Lambda = \eta + \nu + \rho + \sigma$. The summation with respect to η, ν, ρ, σ in (11) and in all subsequent equations is performed for $\Lambda \neq 0$. In addition in the formula (11) k is reciprocal lattice vector and the dimensionless (formal) parameter λ, which indicates the order anharmonism contribution in the final expression is superseded with 1. The length in the theory of harmonic oscillators is written in terms of setting $x_0 = (m\Omega)^{-1/2}$, the fourth-order relation can be represented as

$$I = -\frac{2}{3}\left(\frac{\pi}{c_1 x_0}\right)^4\varphi_{lmfg}^{\eta\nu\rho\sigma} = I\langle l|\delta x|l + \eta\rangle\langle m|\delta x|m + \nu\rangle\langle f|\delta x|f + \rho\rangle\langle g|\delta x|g + \sigma\rangle,$$

where $\langle l|\delta x|l + \eta\rangle$ is the matrix element of the H atom displacement, $d = c_1 \times_O$, and c_1 is a numerical coefficient.

Now we are writing the equation of motion for the Green's function (4) taking into account the combined effects on migrating particle inelastic phonon scattering (3) and anharmonic potential (11). Complete calculation of the equation of motion is presented in the Appendix A. Substituting equation (A2)–(A4) in the original equation (A1), we obtain the desired equation. Since the resulting equation is obtained rather cumbersome, we confine ourselves to writing the equation only for the amendment to the Green function on the effect of anharmonicity $\delta G_{ss'}(t) = G_{ss'}(t) - G_{ss'}^{(h)}(t)$.

After the transition to the Fourier components of the Green functions we obtain the equation of motion describing at the same time both dynamic effects of H atom collisions of the and anharmonic effects that are realized in condition of H atom vibrations in the wells of configuration potential. We obtain

$$(E + \omega_{ss'})\delta G_{ss'}(E) = -4\pi\sum_q\{|\varepsilon_q(s, s + 1)|^2 J(s, s + 1; s', s' + 1; E) -$$
$$- |\varepsilon_q(s - 1, s)|^2 J(s - 1, s; s' - 1, s'; E)\}\delta(\omega_q - \Omega), \qquad (12)$$

where

$$4J(s, s + 1; s', s' + 1; E) = \{f(\xi)\sum_{\eta\nu\rho\sigma}w_s^{\eta\nu\rho\sigma} - (f(\xi) + 1)\sum_{\eta\nu\rho\sigma}w_{s+1}^{\eta\nu\rho\sigma}\}$$
$$G_{ss'}^{(h)}(E), \qquad (13)$$

$$w_s^{\eta\nu\rho\sigma} = \sum_{\eta'\nu'\rho'\sigma'}(s, s + \eta, s + \eta + \nu, s + \eta + \nu + \rho; s + \Lambda)$$
$$(s, s + \eta', s + \eta' + \nu', s + \eta' + \nu' + \rho'; s + \Lambda')\overline{\delta}_{\Lambda,\Lambda'}.$$
$$(s, s + \eta, s + \eta + \nu, s + \eta + \nu + \rho; s + \Lambda) =$$
$$= \langle s|\delta x|s + \eta\rangle\langle s + \eta|\delta x|s + \eta + \nu\rangle\langle s + \eta + \nu|\delta x|s + \eta + \nu.$$
$$+ \rho\rangle\langle s + \eta + \nu + \rho|\delta x|s + \Lambda\rangle \qquad (14)$$

In the above equation $\overline{\delta}_{\Lambda,\Lambda'}$ is the Kronecker delta function.

3. The two-level (two-zone) model of the upper states and attenuation of the quantum state under the influence of anharmonism

We shall use the potential of double-cell well with a barrier V_0 that separates the left and right octahedral positions (p and p' in Fig. 1) as the simple configuration of the relief of the impurity atom. For maximum simplification of the problem is convenient to use a two-level model for the upper states of migrating atom which includes only the level of the potential barrier s_0 and the lower over-barrier $s_0 + 1$ level.

It is assumed that the subsystem, including the two upper levels,