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Atomic Particle Delocalisation Effect in Disordered Media

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Possible reasons are given of the higher diffusion rates of atoms (comparatively to crystals) in disordered condensed media (in metallic and oxide glasses, polycrystalline and amorphous semiconductors). It is shown, that the diffusion coefficient exponentially depends on the disordering degree of the media. A quantum-chemical simulation of the diffusion processes in amorphous silicon is made, the results of which corresponds to the delocalisation atom effect obtained in random fields. The most characteristic experimental features of the activation processes in disordered media are analysed.

Рассмотрены возможные причины повышенных (по сравнению с кристаллами) скоростей диффузии атомных частиц в неупорядоченных конденсированных средах (металлических и оксидных стеклах, поликристаллических и аморфных полупроводниках). Показано, что коэффициент диффузии экспоненциально зависит от степени неупорядоченности среды. Проведено квантово-химическое моделирование диффузионных процессов в аморфном кремнии, результаты которого качественно согласуются с обнаруженным эффектом делокализации атомов в случайном поле. Проанализированы наиболее характерные экспетиментальные особенности активационных решеточных процессов в неупорядоченных конденсированных средах.

1. Introduction

Recently disordered condensed media have attained more attention. This is connected with their non-trivial physical properties, many of which are of practical use. Thus, oxide glasses possess high ionic conductivity and expel traditional liquid electrolytes [1]. Metallic glasses evidence unique magnetic properties [2]. Amorphous and polycrystalline semiconductors are of more use in electronic engineering [3].

Many significant properties of disordered condensed media are determined by activated lattice processes, which are investigated for some years as competing with electronic processes [4]. From the experimental data we may come to the following conclusions concerning the peculiarities of these processes:

1. Diffusion coefficients in disordered media are higher than in crystals.
2. There exist indications that there are no Arrhenius relationships for the activation energy [6].
3. Diffusion properties are, as a rule, of high sensitivity to structural relaxation [1, 6, 13].

The present paper studies possible causes of such a behaviour of disordered condensed media.

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2. The Theory of Diffusion Processes in Disordered Condensed Media

The essential peculiarity of non-crystalline solids is the absence of long-range order in the spatial arrangement of atoms. Consequently, the potential energy $E(\boldsymbol{r})$ at any point $\boldsymbol{r}$ is a random variable, so it makes sense to suppose the atom to have an energy in some interval $(E, E + \mathrm{d}E)$ determined by a functional $F(E)$. Thus, contrary to a crystal, having a constant barrier for a diffusional atom jump E_a^c, in disordered media there is a variable barrier distribution (Fig. 1).

Let us write down the diffusivity of atoms in disordered media as follows:

$$D = D_0 \exp\left(-\langle E\rangle/kT\right), \tag{1}$$

where D_0 is a pre-exponential factor not depending on $\langle E\rangle$, T the absolute temperature, k the Boltzmann constant, and $\langle E\rangle$ an average activation energy.

We demonstrate now that the calculation of $\langle E\rangle$ is the problem of atom percolation in a random potential field. For a formal convenience and comparison with known results [15] we discern the ionic conductivity

$$\Omega = \Omega_0 \exp\left(-\langle E\rangle/kT\right), \tag{2}$$

containing the same exponential term as the diffusivity (1) [1].

The theory of transfer processes in non-homogeneous media has been developed by Miller and Abrahams while investigating hopping conductivity [16]. Starting with atoms localized in separate sites, we calculate the transition probability of atoms between two states i and j and count the number of transitions $i \to j$ per unit time. Without an electric field the same number of atoms make inverse transitions. In weak field direct and inverse transitions become non-balanced, so there appears a current proportional to the electrical field. Having calculated the current, we determine the given transition resistance R_{ij} and the random resistance equivalent to the net condection,

$$R_{ij} = R_{ij}^0 \exp\left(g(\boldsymbol{r})\right),$$

where $g(\boldsymbol{r}) = E_{ij}/kT$, E_{ij} is the activation energy of the transition, R_{ij}^0 a constant multiplier.

In [15] the effective conduction exponent of media with local specific conduction $\Omega(\boldsymbol{r})$, whose non-homogeneity is exponentially large, is calculated,

$$\Omega(\boldsymbol{r}) = \Omega \exp\left(-g(\boldsymbol{r})\right).$$

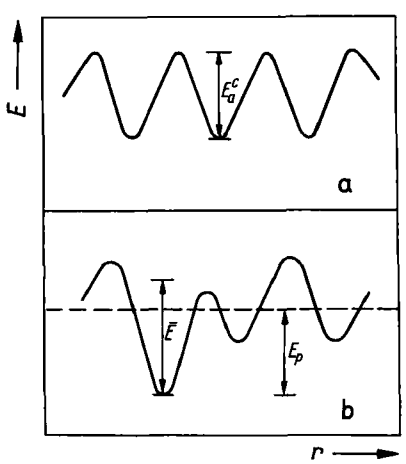

Fig. 1. Potential energy scheme: a) in crystal, b) in disordered media. $\bar{E}$ is the average energy value, E_p the percolation level, E_a^c the activation energy of diffusion in crystal

If elements of the medium in order of increasing resistance are consistently included, the exponent $\Omega(r)$ will be determined by elements creating an endless connected region, providing current percolation. In this case $g(r)$ is equal to a critical value g_c, being found by the percolation formalism.

Therefore, instead of $\langle E \rangle$ into the expression for the effective ionic conductivity (2) a critical value E_p called percolation level should be inserted. Because of including the same exponential factor into (1) and (2) the diffusion coefficient (1) may be rewritten as follows:

$$D = D_0 \exp(-E_p/kT) . \tag{3}$$

Let us calculate the percolation level. It is the minimal energy possessed by an atom moving in space with potential energy profile $E(r)$. It is possible to determine E_p if the volume fraction $V_p(E)$, occupied by regions possessing energy $E \leqq E_p$ at percolation threshold level, is equal to the so-called Scher-Zallen invariant [15]:

$$V_p(E) = \int_{-\infty}^{E_p} F(E)\, dE = f x_c . \tag{4}$$

Here f is the package density, x_c the percolation threshold for the site problem. The product $f x_c$ is constant and equal to 0.15 ± 0.01 for all three-dimensional lattices.

Calculation of the integral in (4) is also simple, for known distributions $F(E)$ (uniform, normal, and exponential types) we have [18]

$$E_p = \overline{E} - m\sigma , \tag{5}$$

where $\overline{E}$ is the average energy, σ the corresponding distribution dispersion, m a constant equal to 1.04 for normal, 0.84 for exponential, and 1.47 for uniform distributions.

Let us compare now the atomic process transfer efficiency in crystalline and disordered media. Let in a crystal the average diffusion barrier value be equal to E_a^c and in a disordered medium $\overline{E}$. Moreover, we suppose them to be equal: $E_a^c = \overline{E}$. The conservation of short-range order and chemical binding type in disordered media, similar optical and other characteristics prove this [4]. Thus, as it follows from (5), in disordered media the activation energy of diffusion would be by $m\sigma$ less than that in a crystal. Physically it corresponds to the diffusion along with paths lower mean barriers in disordered media. At $\sigma \to 0$ (ordering of the structure) $E_p \to \overline{E} \to E_a^c$, i.e. one obtains a limiting transition, corresponding to the transition from disordered phase to crystalline state. If $m\sigma = \overline{E}$, then $E_p = 0$ and atom diffusion becomes athermic.

Thus, from (5) one obtains the quite common conclusion: the higher the disorder degree σ in a medium is, the less is the activation energy of diffusion. It may be supposed that the peculiarities of diffusion processes in disordered condensed media are due to this effect.

It should be noticed that this delocalisation effect of atoms in random field is evidenced not only in originally disordered systems but also in crystalline media, whose structure is disturbed in any way (by introduction of structural defects at radiation impacts and others, by admixtures, and so on). Here the modification of the potential pattern $E(r)$ is essential, providing activation barrier dispersity.

3. Computer Simulation of Diffusion Processes in Amorphous Silicon

As an additional test for checking the obtained results a computer calculation of self-diffusion in amorphous silicon (a-Si) was performed. Results were obtained by the quantum-chemical simulation method [17].

The system energy was indicated as follows:

$$E = \sum_{i,j} \langle \Psi_{ij} | \hat{H} | \Psi_{ij} \rangle + E_1 + E_2 ,$$

where Ψ_{ij} is the molecular orbital for an electron pair (i, j) forming a covalent bond, $\hat{H}$ is a two-electron Hamiltonian, and E_1, E_2 are corrections to energy due to wave function non-orthogonality of valence and core electrons (E_1) and wave functions of individual bonds (E_2). Basic wave functions were elected in the form of Slater functions with variable orbital exponent $\alpha(\boldsymbol{R})$.

The angular part of the wave functions are sp^3-hybridized,

$$Y_i = \sum_j a_{ij} Y_j .$$

Here $Y_{i,j}$ are the angular parts of s- and p-functions, a_{ij} is the hybrid coefficient, which for non-equilibrium configurations are determined from conditions of orthonormalization and the greatest orbital overlap for neighbour atoms.

A fragment simulation of a-Si was made for an ideal microcrystal consisting of two coordination spheres (Fig. 2). Random displacements within $\Delta r = (0.05 - 0.15)\, a_0$ (a_0 is the equilibrium interatomic distance) were imparted to atoms of the second coordination sphere and were later recorded. The position of the central atom being fixed, the equilibrium positions of the first sphere were determined. Next the first sphere being fixed, the position of the central atom was determined. Such a procedure was repeated until self-adjustment of coordinates of the central atom and the first sphere took place. The resulting radial distribution function and angular distortions satisfactorily coincide with experiment [4].

The calculation was performed as follows. At time $t = 0$ coordinates X_i, total energy E, forces $\boldsymbol{F}_i$, and velocities $\boldsymbol{V}_i$ in the system were known. The central atom 1 (Fig. 2) was given an impulse corresponding to an energy of 3 to 5 eV in a direction close to $\langle 111 \rangle$, and recalculation of hybrid coefficients, E, $\boldsymbol{F}_i$, $\boldsymbol{V}_i$, X_i was made in steps of $\Delta t = 2 \times 10^{-14}$ s. The maximum of the obtained data E was elected as a barrier quantity for atom migration.

Table 1

Activation energy of diffusion (relative value) in crystalline E_a^c and amorphous silicon E_a^a depending on the dispersion of barrier distribution σ at different values Δr. Results were obtained by quantum-chemical simulation

Δr	σ	$E_a^c/\overline{E}$	E_a^c/E_a^a
0.05	0.32	0.96	1.70
0.10	0.77	0.70	3.00
0.15	2.11	0.63	−0.70

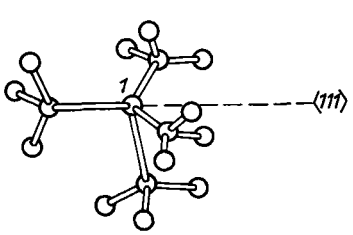

Fig. 2. Diamond lattice fragment as a model of an amorphous silicon "quasi-molecule". 1 is the central atom

We carried out three series of computer experiments with $\Delta r = (0.05, 0.10, 0.15)\, a_0$ and selected a value equal to 50 barriers for every Δr. The obtained barriers are distributed normally. For comparison the migration barrier in Si crystal is calculated. From Table 1 with calculation results it follows that the larger the σ value is the smaller is the activation energy of diffusion E_a^a in amorphous media. A negative value of E_a^c/E_a^a means potential barrier inversion and athermic atomic jump.

Thus, the effect of atom delocalisation with increasing dispersion of the examined system is approved by the example of a-Si.

It is worth while mentioning that with increasing σ the "quasi-molecule" a-Si is less stable, and with $\sigma \geqq 2$ it is impossible to get an energetically stable structure. This fact was used in the discussion given below to explain the known effect of "big doses" observed in ion-implanted diamond-like semiconductors [19].

4. Discussion of Results

The peculiarities of activation processes in disordered condensed media given at the beginning of our paper should be interpreted.

1. Let us substitute $\langle E \rangle$ by E_p in the diffusion coefficient (1). Now we have

$$D = D_0 \exp\left(-(\bar{E} - m\sigma)/kT\right) = D_0 \exp\left(-\bar{E}/kT\right) \exp\left(m\sigma/kT\right).$$

It follows at $\bar{E} = E_a^c$ that in disordered media the diffusion coefficient is $\exp(m\sigma/kT)$ times larger than in the corresponding crystalline phases.

In Table 2 there are collected known data of comparative diffusion investigations in different types of disordered media and their crystalline counterparts. It appears that the activation energy of diffusion in disordered media is less than in crystals.

While investigating internal friction in metallic glasses $Pd_{80}Si_{20}$, Gorsky relaxation connected with hydrogen migration was revealed [8]. While measuring the frequency dependence of the internal friction peak, it was found that the average relaxation time is as follows:

$$\tau_R = \bar{\tau}_{0R} \exp\left(\bar{E}/kT\right),$$

where $\bar{\tau}_{0R} = 1.4 \times 10^{-14}$ s, $\bar{E} = 0.33$ eV, hydrogen migration activation energy $E_m = 0.25$ eV. For the interpretation of experimental data a barrier distribution for diffusing hydrogen $F(E)$ is supposed as given in Fig. 3. In our opinion, the experimental results [8] prove expression (5). Really, at $\bar{E} = 0.33$ eV, $\sigma = \sigma_1/2 + \sigma_2/2 = 0.075$ eV the activation energy of hydrogen diffusion is 0.25 eV.

2. The non-Arrhenius behaviour of E_a^a is investigated in detail in [7]. The observation of hydrogen migration in metallic glasses $TiCuH_x$ ($1.27 \leqq x \leqq 1.35$) at 100 to

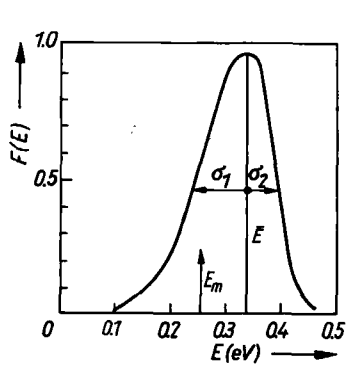

Fig. 3. Density probability function $F(E) = \exp\left(-(E_m - \bar{E})^2/\sigma^2\right)$ for hydrogen migration energy in $Pd_{80}Si_{20}$ [8]. It consists of two semi-Gaussians with dispersions $\sigma_1 = 0.092$ eV and $\sigma_2 = 0.057$ eV; $\bar{E} = 0.33$ eV, $E_m = 0.25$ eV

Table 2
Activation energies of diffusion in crystalline and disordered condensed media

material	state*)	diffusing atom	activation energy (eV)	ref.
α-$TiCuH_{1.3-1.35}$	A	H	0.05	[6]
α-$TiCuH_{1.3-1.35}$			0.11	
α-$TiCuH_{1.3-1.35}$			0.18	
α-$TiCuH_{1.3-1.35}$			0.40	
$TiCuH_{0.94}$	C	H	0.79	
$TiCuH_{1.81-1.91}$	A	H	0.51	
$Pd_{77.5}Cu_6Si_{16.5}$	A	Au	0.75—1.82	[5]
$Pd_{80}Si_{20}$	A	H	0.25	[8]
$Pd_{80}Si_{20}$	A	Au	1.90	[9]
$Pd_{81}Si_{19}$	A	Ag	1.63	[7]
Pd	C	Pd	3.42	[7]
$Fe_{40}Ni_{40}B_{20}$	A	Au	2.04—2.09	[5]
$Fe_{40}Ni_{40}P_{14}B_6$	A	Fe	2.00	[10]
$Fe_{40}Ni_{40}P_{14}B_6$	C	Fe	2.36	[10]
$Fe_{79}B_{11}Si_{10}$	A	Ni	1.04	[7]
Fe	C	Ni	3.19	[7]
$Gd_{16}Co_{84}$	A	Co	1.20	[9]
$(Li_2O)_{25}(Al_2O_3)_{25}(SiO_2)_{50}$	A	Li	0.72	[1]
$(Li_2O)_{25}(Al_2O_3)_{25}(SiO_2)_{50}$	C	Li	0.84	
$(Li_2O)_{33.3}(SiO_2)_{66.7}$	A	Li	0.70	
$(Li_2O)_{33.3}(SiO_2)_{66.7}$	C	Li	1.43	
$(Li_2O)_{50}(Nb_2O_5)_{50}$	A	Li	0.44	
$(Li_2O)_{50}(Nb_2O_5)_{50}$	C	Li	1.90	
Si	PC	Al	1.69	[11]
Si	C	Al	3.45	[11]
Si	PC	As	3.90	[12]
Si	C	As	4.10	[12]
Si	A	P	0.46	[14]
Si	C	P	3.66	[14]
Al	PC	Al	0.30—1.20	[13]
Al	C	Al	1.40	[13]

*) A amorphous, C crystalline, PC polycrystalline.

450 K by nuclear magnetic resonance is proposed. Four activation energies of diffusion are discovered, while in the crystalline state E_a^c is constant in a wide temperature range. With increasing temperature E_a^a approaches E_a^c (see Table 2).

We can easily comprehend the results if we assume that the degree of glass ordering increases when the temperature increases, σ decreases, and E_a^a tends to E_a^c with approaching the "glass-crystal" transformation point [18].

3. The considerable dependence of activation processes upon the relaxation degree in disordered condensed media is evidently determined by the exponential dependence of activation energy on σ. Really, structural relaxation processes change the barrier distribution characterized by σ. Due to relaxation dispersion decreases, leading to an activation energy increase.

In conclusion we examine the mentioned "effect of big doses". While investigating the kinetics of amorphisation and annealing of ion-implanted semiconductors, we

observe not only amorphisation of the layers where ions penetrate, but also crystal structure restoration in amorphised regions beginning with some doses. The recrystallisation process is an athermic phenomenon.

As mentioned above in the quantum-chemical simulation of a-Si stability loss of amorphous media with increasing disorder degree was determined. This result made us suppose that recrystallisation begins at the moment, when disorder is so considerable, that $m\sigma = \bar{E}$ and $E_a^a = 0$. Diffusion processes become athermic and the amorphous phase turns to the crystalline state [19].

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