Structural relaxation in amorphous metallic alloys

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We have made a microscopic investigation of the kinetics of high- and low-temperature structural relaxation of amorphous metals and alloys. We show that a nondiffusive mechanism of structural relaxation is possible in these systems. The mechanism is associated with cooperative barrier-free restructuring of atomic configurations accompanied by spatial redistribution of the electrons. The description of this mechanism of structural relaxation is based on the concept of dynamical concentration excitations, which makes it possible to take into account the characteristic structural state of the systems studied.

1. INTRODUCTION

Much important information on the structures and properties of amorphous metals and alloys that is uncharacteristic of crystalline materials and cannot be explained within classical solid-state physics has now been accumulated. The differences between the properties of metallic amorphous systems (ASs) and those of crystals, such as the unusual character of the low-energy dynamical structure factor,[1] anomalies of the kinetic and thermal properties at low temperatures,[2–4] characteristics of the electronic structure,[1,5] etc., are associated primarily with the structural state of the systems. The amorphous state is not unique; it incorporates significant and continuous change of the atomic structure. Structural studies and the reversibility of many properties of amorphous systems indicate that within the amorphous state there exist local atomic ordering processes which are not associated with a phase transition into a crystalline state via crystallization (see Ref. 4, Chapter 6). Such microscopic states are described by atomic short-range order. A basic problem is to incorporate such dynamical short-range order in the theoretical description of the physical properties and structure of amorphous systems.

In this work we have made a microscopic investigation of the kinetics of structural relaxation of amorphous metals and alloys, taking into account the characteristic structural states of these systems described by the dynamical concentration excitations (DCEs).[6–8] In Sec. 2 we review the existing experimental and theoretical information on structural relaxation of amorphous systems. In Sec. 3 we give a brief presentation of the concept of DCEs and on the basis of this concept we develop a microscopic theory of structural relaxation of amorphous metallic systems.

2. STRUCTURAL STUDIES OF METALLIC AMORPHOUS SYSTEMS

Structural studies of metallic amorphous systems, annealed or slowly heated up to temperatures below the vitrification point T_g, have shown that different local atomic configurations appear and decay in the structure of these materials. As a result of such structural changes, termed structural relaxation (SR), the density of amorphous systems increases and the metal transforms into a more stable amorphous state. Energy-resolved diffraction analysis (see Ref. 4, Chapter 6) has shown that in the structural relaxation process the position of the peaks and dips in the radial distribution function does not change significantly, and the positions of the atoms become more definite. The relative change in the heights of the first and second maxima is 2–3%, and the shoulder changes by $\sim 10\%$ from the second to the fifth maxima. Therefore, structural relaxation is due to the simultaneous motion of many atoms and not the diffusion of single atoms. In contradistinction to the crystallization process, when the height of the first peak in the structure factor $i(\mathbf{q})$ decreases and the shoulder transforms into a Bragg diffraction peak, in the course of structural relaxation the height of the second peak in $i(\mathbf{q})$ increases and the height of its shoulder decreases. This means that structural relaxation is not the process initiating crystallization. This feature of structural relaxation in amorphous metals makes it possible to introduce the structural relaxation parameter[4,9]

$$R(T_a, t_a) = \frac{1}{q_1 - q_2} \int_{q_1}^{q_2} |\Delta i(\mathbf{q})| \mathbf{q} d\mathbf{q},$$

where T_a and t_a are the annealing temperature and time and $q_1 = 5$ Å^{-1} and $q_2 = 6.15$ Å^{-1} are the wave vectors bounding the region of the second peak in $i(\mathbf{q})$.

The parameter $R(T_a, t_a)$ increases during structural relaxation, while during crystallization it decreases. For this reason, it clearly marks the difference between these two restructuring processes in amorphous systems.

Two types of structural relaxation are distinguished: low-temperature ($T_a < T_g - 150$ K) and high-temperature ($T_a \sim T_g$). In these two types of structural relaxation processes, different properties of the amorphous system behave differently. On plots of the volume, enthalpy, Young's modulus, positron lifetime, and resistivity versus the annealing temperature, the low- and high-temperature regions of structural relaxation are separated either by an inflection point or an extremum.[9] It is conjectured that in the case of low-temperature structural relaxation in a more or less rigid matrix some local atomic order (short-range atomic ordering) forms. In the second case cooperative processes which establish long-range order occur, decreasing the structural

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nonuniformity of the amorphous system.[4,9]

Energy-resolved x-ray diffraction with energy dispersion (see Ref. 4, Chapter 6) is a method for investigating structural relaxation in amorphous systems directly. However, this method does not make it possible to determine the physical reasons for this phenomenon. It can only establish that the structural factor has changed in the process of structural relaxation. The mechanisms of structural relaxation are determined by indirect methods for studying amorphous systems. These methods involve measurement, for example, of the resistivity combined with differential scanning calorimetry,[10,11] using different electrochemical, microcalorimetric, x-ray diffraction, and others. The results of these experiments indicate that low-temperature structural relaxation in amorphous alloys is accompanied by chemical (or compositional) short-range ordering, and topological changes of the geometric structure are manifested to a high degree at higher annealing temperatures.

On the basis of analysis of the experimental data on the heat capacity, positron lifetime, resistivity, etc. it can be conjectured (see Ref. 4, Chapter 6) that 1) structural relaxation, responsibile for the reversibility of some properties of amorphous systems, is due to localized structural relaxation over short distances, occurring in a stabilized amorphous matrix, and 2) irreversible structural relaxation, associated with corresponding properties of amorphous systems, is associated to either cooperative structural relaxation at moderate distances, encompassing only some of the amorphous matrix, or cooperative structural relaxation over large distances (the latter process, which encompasses the entire system, can usually be observed at $T_a \sim T_g$).

Thus, for $T_a < T_g$ the relaxation of an amorphous system consists of reversible structural relaxation at short distances and irreversible cooperative structural relaxation at moderate distances. At T_g and with prolonged annealing structural relaxation precedes in the form of the cooperative process over large distances. The accompanying increase of positron lifetime τ and resistivity ρ is connected with reversible structural relaxation and the decrease in τ and ρ is connected with irreversible structural relaxation, the latter process being due to the change in the degree of heterogeneity as a result of annealing at different temperatures T_a.

Computer experiments designed to study relaxation of amorphous systems[9,12] have shown that relaxation of a geometric structure is a process in which the amorphous metal is stabilized while the atoms strive to occupy positions as close as possible to the geometric centers of the polyhedra. As a result, the degree of local short-range order increases gradually. The change in the positions of the atoms as a result of structural relaxation is only 1/10 of the average interatomic distance, but almost all atoms undergo a displacement. Therefore, in the process of structural relaxation the atoms move in local regions and this motion results in atomic short-range ordering.

Using the model of multilevel systems in amorphous metals,[13] it has been shown by the method of relaxation of atomic positions that structural changes in the relaxed state occur mainly as a result of simultaneous displacement of many particles over short distances (~ 0.1 of a particle diameter).

Different models are employed to describe the mechanism of local restructuring of atomic configurations.[3,4,14–18] For example, in Refs. 3 and 4 it is suggested that these structural changes in amorphous systems be described in terms of the vanishing of structural defects during annealing. Structural defects are regions containing 10–20 atoms with high stress and low symmetry. They coexist with clusters of the same size, but low stress and high symmetry. Removal of structural defects in this case occurs by recombination of regions with low atomic density and regions with high atomic density. Local "motion" of defects over distances of the order of several interatomic separations is also possible. This motion can be described in terms of two-level systems (TLS).[19,20] This type of atomic motion is more likely, since in this case the atoms undergo tunneling between states with close energies.[1] However, the use of the two-level model to describe the properties of amorphous metals and alloys undergoing low-temperature structural relaxation is still problematical.[1,3] Many authors therefore conclude that in such systems there are other low-energy excitations, whose spectrum is bounded by a frequency which is an order of magnitude higher than the maximum frequency of the two-level system (~ 1 K).[21,22]

We propose a different approach to the problem of structural relaxation. Our approach is based on representing the amorphous structure as a quenched liquid, in which there can be a variety of short-range-ordered regions, many of which (with respect to the type of short-range order) are not encountered in the crystalline state of this system.[18] In this case, the interaction potential of the amorphous system typically contains several minima, of which the deepest (the principal minimum) corresponds to the crystalline state of the system and all other minima correspond to one or another type of short-range order. The short-range-ordered regions, forming the secondary minima of the interaction potential, are clusters, in which the interatomic bond determined by the spatial distribution of the electrons is different from the crystalline bond. This bond is of a dynamical (resonant) character and, correspondingly, it is formed by "resonance" $d(f)$ electrons. The short-range-ordered formations are maintained stationary by the fluctuation electronic states formed by them. In this sense the electronic states can be called autolocalized.

The last stage of the relaxation process in the structure described above is configurational rearrangement of a typical short-range-ordered regions via a transition of the electrons and, correspondingly, ions into a more favorable spatial position. In the process, a new chemical bond is formed between atoms in the cluster. Such restructuring is not of a vibrational or tunneling character, since it is associated with collective motion of atoms resulting from spatial redistributions of electrons with formation of a new (more favorable) chemical bond. This cooperative atomic motion is nondiffusive, and it is evidently similar to the motion observed in alloys during martensite transformations.

Thus in metallic amorphous systems another mechanism of structural relaxation, besides the known mechanisms based on diffusion, drift, or tunneling of atoms, is possible. It corresponds to virtually barrier-free, cooperative, nondiffusive restructuring of atomic configurations.[18] The proposed mechanism of structural relaxation actually indicates local atomic ordering. For this reason, it can be described in a manner similar to Ref. 23, where a microscopic theory of ordering in alloys is proposed.

3. DESCRIPTION OF STRUCTURAL RELAXATION KINETICS OF AMORPHOUS METALS AND ALLOYS

The kinetics of the structural relaxation of amorphous metals and alloys is described by the scheme proposed in Ref. 23 in terms of the equations of motion (averaged over a nonequilibrium statistical ensemble and describing changes in the electronic subsystem in the process of structural relaxation) for the electronic polarization and the population difference as well as for the creation and annihilation operators for quasiparticles generated or absorbed by the electronic subsystem as a result of structural relaxation. The electronic structure of disordered metallic alloys is characterized[24] by the presence of a zone of a crystalline phase (ZCP), to which the system relaxes under certain conditions, and a collection of so-called fluctuation zones (FZ), corresponding in the amorphous system to different types of short-range order (SRO) realized in the amorphous structure. In this case the structural relaxation corresponds to configurational rearrangement of a typical short-range-ordered regions owing to transition of ions and, correspondingly, electrons into an energetically more favorable spatial position. Relaxation of the fluctuation zones can occur both directly into ZCP and successively from one fluctuation zone into another.

The quasiparticles generated or absorbed by the electron-ion system in the process of structural relaxation correspond to excitations (DCEs), associated with the dynamical short-range order owing to microscopic concentration fluctuations. A quantum-mechanical description of DCEs is given in Refs. 8 and 18, and a microscopic theory of electron transfer in amorphous metals and alloys, which is based on the concept of DCEs and describes low-temperature anomalies of the resistivity, thermo-EMF, and thermal conductivity, is proposed in Refs. 6–8 and 18.

The diagonalized Hamiltonian of the DCEs has the form[8,18]

$$H_{\mathrm{DCE}}=\sum_{\mathbf{k}} E(\mathbf{k}) b_{\mathbf{k}}^{+} b_{\mathbf{k}}, \tag{1}$$

where

$$E(\mathbf{k})=\sum_{l}^{N}\left[A_l^2+2A_l\mathcal{M}_l(\mathbf{k})\right]^{1/2}, \tag{2}$$

$$A_l=-\frac{1}{c^2(1-c)^2M_l^3\mathcal{R}_l^2\alpha_l}, \tag{3}$$

$$\mathcal{M}_l(\mathbf{k})=\sum_{l'}\frac{c(1-c)}{4}W(|\mathbf{R}_l-\mathbf{R}_{l'}|)\alpha_l\alpha_{l'}\exp[i\mathbf{k}(\mathbf{R}_l-\mathbf{R}_{l'})]. \tag{4}$$

Here $b_{\mathbf{k}}^{+}$ and $b_{\mathbf{k}}$ are Bose creation and annihilation operators for DCEs, α_l is a short-range-order parameter, and M_l is the mass of an ion located at the point $\mathbf{R}_l$. Next, $\vec{\mathcal{R}}_l$ is the static component of the displacement vector $\xi^N=\vec{\mathcal{R}}_l\delta c(\mathbf{R}_l^N,t)$ of an ion from an uncharacteristic position in the Nth cluster into a more "suitable" position (the displacement ξ^N is caused by dynamical fluctuations of the concentration $\delta c(\mathbf{R},t)=c(\mathbf{R},t)-c$, where $c(\mathbf{R},t)$ is the microscopic and c is the macroscopic concentration of the components of the amorphous system).

The magnitude of the static component of the displacement can be determined from the condition, derived in Ref. 8, for the existence of undamped low-energy DCEs:

$$\mathcal{R}_l^2\lesssim 2\{c^2(1-c)^2M_l^3\alpha_l^2\sum_{l'}W(|\mathbf{R}_l-\mathbf{R}_{l'}|)\times\alpha_{l'}\exp[i\mathbf{k}_s(\mathbf{R}_l-\mathbf{R}_{l'})]\}^{-1}, \tag{5}$$

where $\mathbf{k}_s$ is the vector of the "superstructure" corresponding to the short-range-order parameter α_l.

The "force constants" $W(|\mathbf{R}_l-\mathbf{R}_{l'}|)$, determining the change in the bonding forces due to δc, have the form

$$W(|\mathbf{R}_l-\mathbf{R}_{l'}|)=\left.\frac{\partial^2u(\mathbf{R}_l-\mathbf{R}_{l'})}{\partial(\delta c_l)\partial(\delta c_{l'})}\right|_{\delta c\to0}=\frac{\partial^2u(\mathbf{R}_l-\mathbf{R}_{l'})}{\partial\mathbf{R}_l\partial\mathbf{R}_{l'}}\left[\frac{\partial(\delta c_l)\partial(\delta c_{l'})}{\partial\mathbf{R}_l\partial\mathbf{R}_{l'}}\right]^{-1}_{\delta c\to0},$$

where $u(\mathbf{R}_l-\mathbf{R}_{l'})$ is the pair interaction potential energy of the ions located at the points $\mathbf{R}_l$ and $\mathbf{R}_{l'}$ of the Nth cluster.

Since[8,18]

$$\delta c_l=\frac{1}{2}\sqrt{\frac{c(1-c)\alpha_l}{N}}\{b_{\mathbf{k}_s}\exp[i(\mathbf{k}_s\mathbf{R}_l-\omega(\mathbf{k}_s)t)]+\text{c.c.}\}, \tag{6}$$

we derive from Eq. (5)

$$\mathcal{R}_l^2\leq\left\{\frac{2k_s^2\delta c_l}{c^2(1-c)^2M_l^3\alpha_l^2}\left[\sum_{l'}\frac{\partial^2u(\mathbf{R}_l-\mathbf{R}_{l'})}{\partial\mathbf{R}_l\partial\mathbf{R}_{l'}}\frac{\alpha_{l'}}{\delta c_{l'}}\times\exp(i\mathbf{k}_s(\mathbf{R}_l-\mathbf{R}_{l'}))\right]^{-1}\right\}_{\delta c\to0},$$

whence it is easily seen that $\vec{\mathcal{R}}_l\to0$ as $\delta c_l\to0$. Therefore the displacement of ions owing to the dynamical fluctuations of the concentration takes place over distances shorter than the interatomic separations.

The complete Hamiltonian of the electron-ion system described above is[24]

$$H=\sum\varepsilon(\mathbf{k})a_{\mathbf{k}}^{+}a_{\mathbf{k}}+\frac{c(1-c)}{8}\sum_{\mathbf{q}}\{\omega(\mathbf{q})[2b_{\mathbf{q}}^{+}b_{\mathbf{q}}+b_{-\mathbf{q}}b_{\mathbf{q}}+b_{\mathbf{q}}^{+}b_{-\mathbf{q}}^{+}]-\mu b_{\mathbf{q}}^{+}b_{\mathbf{q}}\}+\sum_{\mathbf{k},\mathbf{q}}g(\mathbf{q})[a_{\mathbf{k}+\mathbf{q}}^{+}a_{\mathbf{k}}b_{\mathbf{q}}+a_{\mathbf{k}}a_{\mathbf{k}+\mathbf{q}}^{+}b_{\mathbf{q}}^{+}], \tag{7}$$

where the first term is the electronic part of the Hamiltonian (the operators $a_{\mathbf{k}}^{+}$ and $a_{\mathbf{k}}$ are the creation and annihilation operators for electrons in the state $\mathbf{k}$), the second term corresponds to the nondiagonalized Hamiltonian of the DCEs,[8,18]

$$\omega(\mathbf{q})=\sum_{l,l'}^{N}W(\mathbf{R}_l-\mathbf{R}_{l'})\alpha_l\alpha_{l'}\exp[i\mathbf{q}(\mathbf{R}_l-\mathbf{R}_{l'})],\quad\mu\equiv\sum_l A_l$$

and, finally, the last term in Eq. (7) describes the interaction of the electronic and ionic subsystems [$g(\mathbf{q})$ is the Fourier transform of the function $g(\mathbf{R})=V_A(\mathbf{R})-V_B(\mathbf{R})$, where $V_{A(B)}(\mathbf{R})$ are the "site" potentials of ions of type $A(B)$].

It is well known that the microscopic description of the kinetics of structural relaxation of metallic amorphous systems can be constructed by solving the system of the corresponding equations of motion. In our case the structural relaxation parameters are the population inversion in the FZ and ZCP $\sigma_{\mathbf{kq}}=a_{\mathbf{k}+\mathbf{q}}^{+}a_{\mathbf{k}+\mathbf{q}}-a_{\mathbf{k}}^{+}a_{\mathbf{k}}$, the electronic polarization $d_{\mathbf{kq}} = a^+_{\mathbf{k}} a_{\mathbf{k}+\mathbf{q}}$, $d^+_{\mathbf{kq}} = a^+_{\mathbf{k}+\mathbf{q}} a_{\mathbf{k}}$, and the creation and annihilation operators $b^+_{\mathbf{q}}$ and $b_{\mathbf{q}}$ for DCEs generated or absorbed by the electronic subsystem in the process of structural relaxation.

We write the corresponding equations of motion for the structural relaxational parameters indicated above with the help of the Hamiltonian (7). For simplicity we consider the process of separation, during annealing, of only one type of short-range order:

$$\begin{aligned} \dot{b}^+_{\mathbf{q}} &= i\left\{\left[\frac{c(1-c)}{4} W(\mathbf{q}) - \mu\right] b^+_{\mathbf{q}} \right. \\ &\quad \left. + \frac{c(1-c)}{8} W(\mathbf{q}) b_{-\mathbf{q}} + \Delta(\mathbf{q}) \sum_{\mathbf{k}} d^+_{\mathbf{kq}}\right\} - \varkappa_{\mathbf{q}} b^+_{\mathbf{q}}, \\ \dot{d}^+_{\mathbf{kq}} &= i\omega_{\mathbf{kq}} d^+_{\mathbf{kq}} - \Gamma_{\mathbf{q}} d^+_{\mathbf{kq}} - i\Delta(\mathbf{q})\sigma_{\mathbf{kq}} b^+_{\mathbf{q}}, \\ \dot{\sigma}_{\mathbf{kq}} &= -\sigma_{\mathbf{kq}} t_\sigma^{-1} + 2i\Delta(\mathbf{q})\,[d_{\mathbf{kq}} b^+_{\mathbf{q}} - d^+_{\mathbf{kq}} b_{\mathbf{q}}], \end{aligned} \tag{8}$$

where $\omega_{\mathbf{kq}} = \varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_{\mathbf{k}}$ and $b_{\mathbf{q}} = (b^+_{\mathbf{q}})^+$, $d_{\mathbf{kq}} = (d^+_{\mathbf{kq}})^+$. After averaging over the ensemble (in the secular approximation) in the case of exact resonance

$$\omega_{\mathbf{kq}} = \frac{c(1-c)}{4} W(\mathbf{q}) - \mu$$

we obtain

$$\dot{\tilde{b}}^+_{\mathbf{q}} = i\Delta(\mathbf{q}) \sum_{\mathbf{k}} \tilde{d}^+_{\mathbf{kq}}, \tag{9a}$$

$$\dot{\tilde{d}}^+_{\mathbf{kq}} = -\Gamma_{\mathbf{q}} \tilde{d}^+_{\mathbf{kq}} - i\Delta(\mathbf{q}) b^+_{\mathbf{q}} \sigma_{\mathbf{kq}}, \tag{9b}$$

$$\dot{\tilde{\sigma}}_{\mathbf{kq}} = -\sigma_{\mathbf{kq}} t_\sigma^{-1} + 2i\Delta(\mathbf{q})(\tilde{d}_{\mathbf{kq}} \tilde{b}^+_{\mathbf{q}} - \tilde{d}^+_{\mathbf{kq}} \tilde{b}_{\mathbf{q}}) \tag{9c}$$

with the initial conditions

$$\tilde{b}^+_{\mathbf{q}}\big|_{t=0} = 0, \quad \sigma_{\mathbf{kq}}\big|_{t=0} = \sigma^0_{\mathbf{kq}}, \quad \tilde{d}^+_{\mathbf{kq}}\big|_{t=0} = \tilde{d}^{+0}_{\mathbf{kq}}.$$

In Eq. (9a) $\dot{\tilde{b}}_{\mathbf{q}}$ is the rate of change of the amplitude of the concentration field. The right-hand side of the expression (9a) is the polarization of the electrons, causing $b_{\mathbf{q}}$ to be time-dependent in the case of resonance and in the absence of damping; $\Gamma_{\mathbf{q}} d^+_{\mathbf{kq}}$ is the damping of $d^+_{\mathbf{kq}}$ due to the interaction of the electrons with their environment (but without any interaction with the concentration field). The second term on the right-hand side of Eq. (9b) takes into account the polarization generated by the concentration field. The sign of the population $\sigma_{\mathbf{kq}}$ appearing here indicates increase or decrease of the polarization, depending on whether or not the electrons are excited. In Eq. (9c) $\sigma_{\mathbf{kq}} t_\sigma^{-1}$ is the population-inversion relaxation caused by incoherent relaxation processes. The second term on the right-hand side of Eq. (9c) is the interaction of the concentration and polarization fields. Summation over k transforms this term to $dN_{\mathbf{q}}/dt$, where $N_{\mathbf{q}}$ is the product of the operators $b^+_{\mathbf{q}}$ and $b_{\mathbf{q}}$, i.e., it determines the rate of change of the population inversion due to a coherent process (condensation).

Equations (9) describe a nonequilibrium "phase transition" process and resemble the laser equations, with everything this similarity implies.

The system of equations Eqs. (9) is strongly nonlinear and can only be solved numerically with the appropriate values of the microscopic parameters. In the approximation of exponential relaxation of $\sigma_{\mathbf{kq}}$, however, the third equation of the system (9) takes the form

$$\dot{\sigma}_{\mathbf{kq}} = -\sigma_{\mathbf{kq}} \gamma_{\mathbf{q}} \tag{10}$$

and the system reduces to the differential equation

$$\ddot{\tilde{b}}^+_{\mathbf{q}} + \Gamma_{\mathbf{q}} \dot{\tilde{b}}^+_{\mathbf{q}} - [\Delta^2(\mathbf{q}) \sigma^0_{\mathbf{q}} \exp(-\gamma_{\mathbf{q}} t)]\tilde{b}_{\mathbf{q}} = 0 \tag{11}$$

with the initial conditions

$$\tilde{b}^+_{\mathbf{q}}\big|_{t=0} = 0, \quad \dot{\tilde{b}}^+_{\mathbf{q}}\big|_{t=0} = i\Delta(\mathbf{q}) d^{+0}_{\mathbf{q}},$$

where

$$d^{+0}_{\mathbf{q}} = \sum_{\mathbf{k}} d^{+0}_{\mathbf{kq}}, \quad \sigma^0_{\mathbf{q}} = \sum_{\mathbf{k}} \sigma^0_{\mathbf{kq}}$$

is a phenomenological parameter which takes into account, besides dissipative processes, the dynamical change of the population inversion due to changes in the order parameter.

The solution of Eq. (11) for $\eta(t) = \sqrt{N_{\mathbf{q}}/N}$, where $N = \Sigma N_{\mathbf{q}}$, has the form

$$\begin{aligned} \eta(t) = \eta_\infty^{-1} \frac{2\Delta(\mathbf{q}) d^{+0}_{\mathbf{q}} \exp[-\Gamma_{\mathbf{q}} t/2)}{\gamma_{\mathbf{q}} \sqrt{N}} & [I_\nu(z_0) K_\nu(z_0 \exp[-\gamma_{\mathbf{q}} t/2]) \\ & - I_\nu(z_0 \exp[-\gamma_{\mathbf{q}} t/2]) K_\nu(z_0)], \end{aligned} \tag{12}$$

where

$$\eta_\infty = \Delta(\mathbf{q}) d^{+0}_{\mathbf{q}} (z_0/2)^{-\nu} I_\nu(z_0) \Gamma(\nu)/\gamma_{\mathbf{q}} \sqrt{N},$$

I_ν and K_ν are modified Bessel functions of order $\nu = \Gamma_{\mathbf{q}}/\gamma_{\mathbf{q}}$, $z_0 = 2\Delta(\mathbf{q})\sqrt{\sigma^0_{\mathbf{q}}}$, and $\Gamma(\nu)$ is the gamma function.

Numerical analysis of the expression (12) indicates that there are three stages to the relaxation process, differing by how rapidly η increases at short, moderate, and long times. In addition, the form itself of the dependences $\eta(t)$ is determined by the quantities $\Delta(\mathbf{q})\sqrt{\sigma^0_{\mathbf{q}}}$ and $\Gamma_{\mathbf{q}}$ (in units of $\gamma_{\mathbf{q}}$) and characterizes three different relaxation processes [the three typical curves *1*, *2*, and *3* in Fig. 1 (Ref. 24)]. For small $\Delta(\mathbf{q})\sqrt{\sigma^0_{\mathbf{q}}} \sim 1$ and large $\Gamma_{\mathbf{q}}$ (curve *1*) the function $\eta(t)$ grows rapidly for a short time and then slowly approaches its equilibrium value. The decrease in $\Gamma_{\mathbf{q}} \sim 1$ for the same values of $\Delta(\mathbf{q})\sqrt{\sigma^0_{\mathbf{q}}}$ (curve *2*) results in a smooth decrease of $\eta(t)$ and as in the first case we have $\dot{\eta} \propto \eta$, i.e., the relaxation is exponential with $\dot{\eta}$ dropping linearly. For large $\Delta(\mathbf{q})\sqrt{\sigma^0_{\mathbf{q}}} \sim 20$ (curve *3*, $\Gamma_{\mathbf{q}} \sim 10$) the relaxation curve is *S*-shaped with $\eta(t)$, $\dot{\eta}(t)$, and $\ddot{\eta}(t)$ varying nonmonotonically, which is connected with the increase in the initial population inversion $\sigma^0_{\mathbf{q}}$ of the electronic states $\mathbf{k} + \mathbf{q}$ and $\mathbf{k}$ and indicates that the phenomenon is of a cooperative character. A decrease of $\Gamma_{\mathbf{q}} \sim 1$ results in a smoother change in $\eta(t)$ and $\dot{\eta}(t)$ and a shift in the curves into the region of long times. The large values of $\sigma^0_{\mathbf{q}}$ in turn correspond to small values of the initial order parameter $\eta_0 \ll 1$, starting from which the further relaxation is considered. Therefore, the conditions for the curve *1* correspond to large $\eta_0 \sim 1$, the conditions for the curve *2* correspond to average values $\eta_0 \sim 0.5$, and the conditions for curve *3* correspond to small values of η_0. The rate of

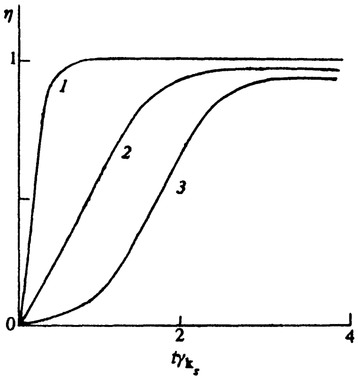

FIG. 1. Time dependence of the order parameter:[24] *1*) limit of small $\Delta(\mathbf{q})\sqrt{\sigma^0_\mathbf{q}}$ and large $\Gamma_\mathbf{q}$; 2) small $\Delta(\mathbf{q})\sqrt{\sigma^0_\mathbf{q}}$ and small $\Gamma_\mathbf{q}$; and, *3*) large $\Delta(\mathbf{q})\sqrt{\sigma^0_\mathbf{q}}$ and $\Gamma_\mathbf{q}$.

change of $\eta(t)$ for each of the three cases is determined by $\Gamma_\mathbf{q} \sim \tau_e^{-1}$, and the smaller the value of τ_e, the more rapidly η changes and the steeper the curve $\eta(t)$ is.

In the case when the FZ is separated from the ZCP by an energy interval

$$\omega_{\mathbf{kq}} = \varepsilon_{\mathbf{k+q}} - \varepsilon_\mathbf{k} > \frac{c(1-c)}{4} W(\mathbf{q}) - \mu,$$

the kinetic equations in the approximation of exponential relaxation of $\sigma_{\mathbf{kq}}(t)$ reduce to an equation differing from Eq. (11) in that $\Gamma_\mathbf{q}$ is replaced by $\Gamma = \Gamma_\mathbf{q} + i\Omega_\mathbf{q}$, where $\Omega_\mathbf{q} = \omega_{\mathbf{kq}} - \omega_\mathbf{k}$ is a measure of the deviation from resonance, and the solution for $\eta(t)$ has the form

$$\eta(t) = \frac{2\Delta(\mathbf{q}) d^{+0}_\mathbf{q} \exp[-\Gamma t/2]}{\gamma_\mathbf{q}\sqrt{N}} [I_\nu(z_0) K_\nu(z_0 \exp[-\gamma_\mathbf{q} t/2]) - I_\nu(z_0 \exp[-\gamma_\mathbf{q} t/2]) K_\nu(z_0)], \tag{13}$$

where $\nu = \Gamma/\gamma_\mathbf{q}$; the rest of the notation remains the same. For $\Omega_\mathbf{q} \gg \Gamma_\mathbf{q}$ we have

$$\eta(t) = \frac{2\Delta(\mathbf{q}) d^{+0}_\mathbf{q}}{\sqrt{N(\Gamma^2_\mathbf{q} + \Omega^2_\mathbf{q})}} [\exp(-\Gamma_\mathbf{q} t/2) \sin^2 \frac{\Omega_\mathbf{q} t}{2} + \frac{1}{4}(1 - \exp(-\Gamma_\mathbf{q} t/2))^2]^{1/2}, \tag{14}$$

whence one can see that the function $\eta(t)$ oscillates around its initial value.

Under nonequilibrium conditions, for example, in the presence of a temperature gradient, the electrons undergo population inversion. For this reason, transitions of electrons with a change in the population inversion become possible. In some of these transitions DCEs will be emitted. The larger $\Delta(\mathbf{q})$, the greater the number of transitions occurring in this channel will be. If the number of pairs of population-inverted states having the same difference of the wave vectors $\mathbf{q}' = \mathbf{k} - \mathbf{k}'$ is macroscopic in both the fluctuation and main zones, then a condensate of DCEs with $\mathbf{q}' = \mathbf{k} - \mathbf{k}'$ can arise as a result of lasing. Such states can arise only against the background of the equilibrium state examined above. We note that the appearance of the $\mathbf{q}'$ condensate will prevent damping $\varkappa_{\mathbf{q}'}$ of DCEs, but for sufficiently large gradients and therefore sufficiently large population inversion two structural states with $\mathbf{q}$ and $\mathbf{q}'$ can exist in the amorphous system.

In the general case several states with $\mathbf{k} = \mathbf{q}, \mathbf{q}', \mathbf{q}'', \ldots$ can appear due to generation of DCEs of the nonequilibrium electronic subsystem, i.e., complicated dissipative superstructures will be formed. We now construct the microscopic description for the appearance of such states. For simplicity we confine our attention to a single condensate with $\mathbf{k} = \mathbf{q}'$, i.e., we consider the interaction of electrons only with $\mathbf{q}'$-DCE and we neglect the interaction of $\mathbf{q}$- and $\mathbf{q}'$-condensates.

Let nonequilibrium conditions (for example, a temperature gradient) be created in the amorphous system with an equilibrium value (as small as desired) of $\eta(t)$. We maintain the degree of nonequilibrium over some time interval. Under these conditions there arises in the electronic subsystem a population inversion $\sigma^0_{\mathbf{kq}}$ which is constant as a function of time. In order to describe the appearance of a dissipative structure we write, as before, the Heisenberg equations of motion for the operators $b^+_{\mathbf{q}'}$, $b_{\mathbf{q}'}$, $d^+_{\mathbf{kq}'}$, $d_{\mathbf{kq}'}$, $\sigma_{\mathbf{kq}'}$. In contrast to Eqs. (9), the population inversion $\sigma^0_{\mathbf{kq}'}$ and the damping $\varkappa_{\mathbf{q}'}$ of DCEs must be included in these equations. Transformations similar to those made in deriving Eqs. (9) give

$$\begin{aligned}
&\varkappa_{\mathbf{q}'} \tilde{b}^+_{\mathbf{q}'} - i\Delta(\mathbf{q}')\alpha \sum_\mathbf{k} \tilde{d}^+_{\mathbf{kq}'} = 0,\\
&\varkappa_{\mathbf{q}'} \tilde{b}_{\mathbf{q}'} + i\Delta(\mathbf{q}')\alpha \sum_\mathbf{k} \tilde{d}_{\mathbf{kq}'} = 0,\\
&\Gamma_{\mathbf{q}'} \tilde{d}^+_{\mathbf{kq}'} + i\Delta(\mathbf{q}') \tilde{b}^+_{\mathbf{q}'} \sigma_{\mathbf{kq}'} = 0, \qquad (15)\\
&\Gamma_{\mathbf{q}'} \tilde{d}_{\mathbf{kq}'} - i\Delta(\mathbf{q}') \tilde{b}_{\mathbf{q}'} \sigma_{\mathbf{kq}'} = 0,\\
&[\sigma^0_{\mathbf{kq}'} - \sigma_{\mathbf{kq}'}] t_\sigma^{-1} + 2i\Delta(\mathbf{q}') [\tilde{b}^+_{\mathbf{q}'} \tilde{d}_{\mathbf{kq}'} - \tilde{b}_{\mathbf{q}'} \tilde{d}^+_{\mathbf{kq}'}] = 0.
\end{aligned}$$

The stationary solution $\sigma_{\mathbf{kq}}$ corresponds to compensation of the amplification and losses, and for this reason it plays the role of the threshold population difference $\sigma^{\text{th}}_{\mathbf{kq}'}$. From the condition for the existence of a nonzero solution $\tilde{b}^+_{\mathbf{k}'}$ and $\tilde{b}_{\mathbf{q}'}$ we find

$$\sum_\mathbf{k} \sigma^{\text{th}}_{\mathbf{kq}'} = \varkappa_{\mathbf{q}'} \Gamma_{\mathbf{q}'} / \Delta^2(\mathbf{q}')\alpha.$$

In the presence of a macroscopic number of population-inverted states with $\mathbf{k} - \mathbf{k}' = \mathbf{q}$ we can write

$$\sigma^{\text{th}}_{\mathbf{q}'} \approx \Gamma_{\mathbf{q}'} \varkappa_{\mathbf{q}'} / n_{\mathbf{q}'} \Delta^2(\mathbf{q}')\alpha, \tag{16}$$

where $\sigma^{\text{th}}_{\mathbf{q}'}$ is the threshold population of pairs of states between which the transition proceeds with emission of DCEs with wave vector $\mathbf{q}'$; $n_{\mathbf{q}'}$ is the number of pairs of such states. According to Eq. (16), the threshold decreases with increasing $\Gamma^{-1}_{\mathbf{q}'}$, $\varkappa^{-1}_{\mathbf{q}'}$, $\Delta(\mathbf{q}')$, α, as well as the number of population-inverted pairs $n_{\mathbf{q}'}$. Using the last three equations of the system (15) and $\tilde{b}^+_{\mathbf{q}'} \tilde{b}_{\mathbf{q}'} = N_{\mathbf{q}'}$, we obtain

$$N_{\mathbf{q}'} = \frac{\Gamma_{\mathbf{q}'}}{4 t_\sigma \Delta^2(\mathbf{q}')} \left(\frac{\sigma^0_{\mathbf{q}'}}{\sigma^{\text{th}}_{\mathbf{q}'}} - 1 \right). \tag{17}$$

For $\sigma^0_{\mathbf{q}'} < \sigma^{\rm th}_{\mathbf{q}'}$ the stationary state with a condensate does not arise, whereas for $\sigma^0_{\mathbf{q}'} > \sigma^{\rm th}_{\mathbf{q}'}$ a condensate will exist, i.e., $n_{\mathbf{q}'}$ and $N_{\mathbf{q}'}$ will be macroscopic.

In order to analyze how $\eta_{\mathbf{q}'}$ depends on the parameters determining the behavior of the system, we rewrite the expression (17) in the following form:

$$\eta^2_{\mathbf{q}'} = \sigma^0_{\mathbf{q}'} n_{\mathbf{q}'} \frac{1 - 2c + \eta^2/2}{4 t_0 \varkappa_{\mathbf{q}'} N} - \frac{\Gamma_{\mathbf{q}'}}{c(1-c)\Delta^2(\mathbf{q}) t_\sigma}. \qquad (18)$$

Hence one can see that $\eta_{\mathbf{q}'}$ is, in general, a nonlinear function of η. If t_σ^{-1}, $\varkappa_{\mathbf{q}'}$ and $\Gamma_{\mathbf{q}'}$ are of the same order of magnitude, then for $\sigma^0_{\mathbf{q}'} \gg \sigma^{\rm th}_{\mathbf{q}'}$

$$\eta^2_{\mathbf{q}'} \sim \frac{\sigma^0_{\mathbf{q}} n_{\mathbf{q}'}}{N} [1 - 2c + \eta^2/2]. \qquad (19)$$

Therefore, in order for dissipative structures to exist $n_{\mathbf{q}'}$ must be a macroscopic quantity, the population inversion must be large, and we must have $\eta \neq 0$. Dissipative structures of this kind can also form during quenching: They can be frozen and exist even in the absence of external nonequilibrium conditions, since such "frozen" states are nonequilibrium states and their relaxation time at low temperatures is very long.

CONCLUSIONS

The relaxation processes described above correspond to high-temperature ($T \sim T_g$) and low-temperature ($T < T_g - 150$ K) structural relaxation in the amorphous system. In the first case relaxation results in the formation of long-range-ordered regions and in the second case local short-range-ordered regions form. The reversibility of the relaxation of local regions is determined by the dynamical conditions under which they appear (structural states). It is interesting to note that if $\eta \neq 0$ holds, then $\eta_{\mathbf{q}'}$ increases [see Eq. (19)], i.e., reversible relaxation stimulates irreversible relaxation.

Thus we can conjecture that structural relaxation in metallic glasses is caused by relaxation of a large set of weakly interacting clusters and this relaxation is matched with relaxation of the fluctuation electronic states corresponding to these clusters. As mentioned above, fluctuation zones can relax either gradually or directly into ZCP. However, it is obvious that gradual relaxation is much more likely to occur than direct relaxation. In this sense, there is a hierarchy of structural relaxation in amorphous metallic systems.

In this connection we note that our analysis is similar to that in Ref. 25, where the hierarchical levels of structural relaxation were regarded as relaxational excitations of a system with structural nonuniformity. Dynamical concentration excitations, which we introduced previously for describing low-temperature anomalies in the kinetic properties of metallic glasses,[6–8] are excitations of precisely this type.

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[1] H.-J. Guentherodt and H. Beck [Eds.], *Glassy Metals: Atomic Structure and Dynamical and Magnetic Properties,* Springer-Verlag, N.Y., 1981, Vol. 2.

[2] B. Vasvari, Physica B **159**, 79 (1989).

[3] H.-J. Guentherodt and H. Beck [Eds.], *Glassy Metals: Ionic Structure, Electron Transport, and Crystallization,* Springer-Verlag, N.Y., 1981, Vol. 1.

[4] F. E. Lyuborskii [Ed.], *Amorphous Metallic Alloys* [in Russian], Metallurgiya, Moscow, 1987.

[5] P. Housler, F. Baumann, J. Krieg *et al.*, J. Non-Cryst. Solids **61–62**, 1249 (1984).

[6] V. E. Egorushkin and N. V. Melnikov, J. Phys. F **17**, 1379 (1987).

[7] V. E. Egorushkin and N. V. Melnikov, J. Phys. F **17**, 2389 (1987).

[8] V. E. Egorushkin and N. V. Mel'nikov, Zh. Eksp. Teor. Fiz. **103**, 189 (1993) [JETP **76**, 103 (1993)].

[9] K. Suzuki, H. Fujimori, and K. Hasimoto, *Amorphous Metals* [Russian translation], Metallurgiya, Moscow, 1987, Chap. 3.

[10] H. S. Chen, J. Appl. Phys. **52**, 1868 (1981).

[11] B. Marcello, Phil. Mag. B **56**, 177 (1987).

[12] K. Suzuki and T. Fukunaga, Sci. Rep. RITU A **27**, 110 (1979).

[13] E. H. Brandt and H. Kronmuller, J. Phys. F **176**, 1291 (1987).

[14] W. Gotze, Phys. Scripta **34**, 60 (1986).

[15] K. Yeong-Hwan, I. Akihasha, and M. Tsuyoshi, J. Non-Cryst. Solids **127**, 233 (1991).

[16] M. Francois, *Geometry Condensed Matter Physics*, Singapore, 1990, p. 233.

[17] A. I. Olemskoi and E. A. Toropov, Fiz. Met. Metalloved., No. 9, 5 (1991).

[18] V. E. Egorushkin and N. V. Mel'nikova, Preprint No. 36, Tomsk Science Center, Siberian Branch of the Russian Academy of Sciences, Tomsk (1990).

[19] P. W. Anderson, B. J. Halperin, and C. M. Varma, Phil. Mag. **25**, 1 (1972).

[20] W. A. Phyllips, J. Low-Temp. Phys. **7**, 351 (1972).

[21] A. Gupta, R. Gupta, S. Lal *et al.*, Mater. Sci. Eng. A **133**, 101 (1991).

[22] P. Doussineau, Helv. Phys. Acta **56**, 269 (1983).

[23] V. E. Egorushkin, A. I. Murzashev, and V. E. Panin, Izv. Vyssh. Uchebn. Zaved., Fiz., No. 1, 41 (1984).

[24] V. E. Egorushkin, A. I. Kul'ment'ev, E. V. Savushkin *et al.*, *Electrons and Phonons in Disordered Alloys* [in Russian], Siberian Branch of the Russian Academy of Sciences, Nauka, Novosibirsk, 1989.

[25] A. O. Velchev, A. I. Gusarov, and V. A. Mashkov, Zh. Eksp. Teor. Fiz. **101**, 579 (1992) [Sov. Phys. JETP **74**, 307 (1992)].

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