

MODELLING OF THE SOLID STATE AMORPHIZATION BY HIGH PRESSURE TREATMENT

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Abstract A simple nonlinear model has been proposed to describe the solid state amorphization by high pressure treatment. The model is based on the deformation field due to structural defects of the disordered matrix. A solution in the form of a self-sustaining wave is obtained. The influence of the deformation field parameters on the amorphization scenario and characteristic correlation length of the amorphous phase formed by amorphization was studied.

Keywords: solid state amorphization, structural forming defects, medium range order

Introduction

Solid state amorphization (SSA) can be attained by a high pressure treatments [1, 2]. This is a direct transition from the crystalline into the amorphous state without the necessity of quenching of a liquid or deposition on a cold substrate. The high-pressure technique is a promising method that allows to obtain new amorphous materials and solid solutions in the bulk form [3]. During this process a homogeneous high-pressure phase abruptly loses its stability and a disordered solid is formed. The different pressure-induced transformations have common features, namely a strong metastability of the initial state before the start of disordering and a similarity in the short-range order observed for the low-pressure crystalline phase and the formed disordered phase [4].

The first theoretical interpretation of SSA was based on an empirical model of "cold melting" [5] and it was rather controversial. In recent years, the considering of the lattice instability as a driving force for the amorphization becomes one of the most popular approaches [6, 7]. The molecular dynamics simulation shows a direct connection between amorphization and softening of the elastic constants [8]. The *ab-initio* pseudopotential calculations show that amorphization result from the overlap of disordered regions of defects having energy above a certain threshold, determined roughly by the difference in energy between the crystal and the amorphous phase [9]. The regions of these defects, called "grey zones", are supposed to be building blocks of amorphous matter and they are observed in experiments on transition electron microscopy [10]. The "grey zones" can be identified as "structural forming defects" (SFD), introduced previously in our model of SSA. A detailed description and the experimental background of our model are given elsewhere [11].

According to our model [11] SFD act as soft regions in the rigid network, which allow to vary the angle and distance of bonds adjacent to the SFD [12] and, hence, they are responsible for the disordering. From this point of view, amorphization is equivalent to the creation of a critical concentration of such disordered regions. The stationary value of the SFD concentration, $N(t)$, should define the order parameter of the amorphous matter, namely the medium range order length, L_{MRO} :

$$N(t \rightarrow \infty)^{-1/3} = L_{MRO} . \quad (1)$$

Note that at the beginning of the amorphization process the sample is in a strongly metastable stressed state [13] with energy higher than that of the amorphous state, i. e. far away from equilibrium. We suppose that this initial state, referred as the *excited state* [14, 15], is characterized by the absence of any type of long-range or medium-range order and can be described as a high-

energy localized vibrational state of the atomic network [15]. In general, the excess of energy, Q_{tr} , should be equal to sum of amorphization and crystallization energies: $Q_{tr} = Q_{cr} + Q_{am}$. Indeed, the relaxation of the stresses leads to the fact that the system goes to the nearest available phase, amorphous or crystalline. In the first case the energy $Q_{am} < Q_{tr}$ is released and SFD are formed. During a crystallization process, the energy Q_{cr} is delivered and long-range order is formed. Hence, and that is the central point of our approach, during amorphization the value Q_{cr} should be captured by SFD, which serve as traps for the energy. Then the SSA process is equivalent to the decay of the excited state accompanied by the creation of a noticeable concentration of the SFD and a finite medium-range order length.

Formalism

Mathematically, the amorphization process can be described by a system of rate equations for the concentration $N(r, t)$ and temperature $T(r, t)$ fields [16]. Here we consider the one-dimensional case and will search for a solution in the form of a self-sustaining phase transition wave with velocity v . For the autowave variable $\xi = x - vt$ we can write the rate equations in the form:

$$-v \frac{dy}{d\xi} = D_N \frac{d^2 y}{d\xi^2} - \frac{y}{\tau_0} e^{-\frac{\Delta}{\theta}} + \frac{b}{\tau_0} e^{-\frac{U(y)}{\theta}} \quad (2a)$$

$$-v \frac{d\theta}{d\xi} = D_T \frac{d^2 \theta}{d\xi^2} + \frac{v k_B}{c \rho a^3 b} \frac{d}{d\xi} (y U(y)), \quad (2b)$$

where $y = Nr_0^3$, $\theta = k_B T$, $b = r_0^3/a^3$. k_B is the Boltzman constant, D_N and D_T are the thermal and defect diffusion coefficients, respectively, c is the specific heat, ρ is the density and a is lattice parameter. $\tau_0 \approx a/v_{ph} \approx 10^{-13}$ s is a characteristic transition time and Δ is the activation energy of the defect annihilation, that is equal to the activation energy of crystallization, E_{cr} . The experimental values representing the case of a typical semiconductor which undergoes solid state amorphization by a high pressure phase retention were taken for modelling [16]. We define the temperature of the sample after amorphization as θ_0 and choose zero flux boundary conditions for y and θ at $\xi \rightarrow \pm\infty$. Therefore, no exact values of $y(\xi \rightarrow \pm\infty)$ are involved.

We assume that the SFD interact via a stress field on the way to make easier the creation of new defects, as it is typical for the standard defects in solids [17]. In the mean-field approximation the corresponding activation energy is

$$U = \langle U(r) \rangle = U_0 - \left\langle \sum_i \varphi(r - r_i) \right\rangle \approx U_0 - n_0 \varphi(\bar{r}), \quad (3)$$

where U_0 is the self-energy of SFD, n_0 is the number of nearest neighbours, $\bar{r} = N^{-1/3}$ is the average distance between the SFD and $\varphi(r - r_i)$ is the stress field produced by

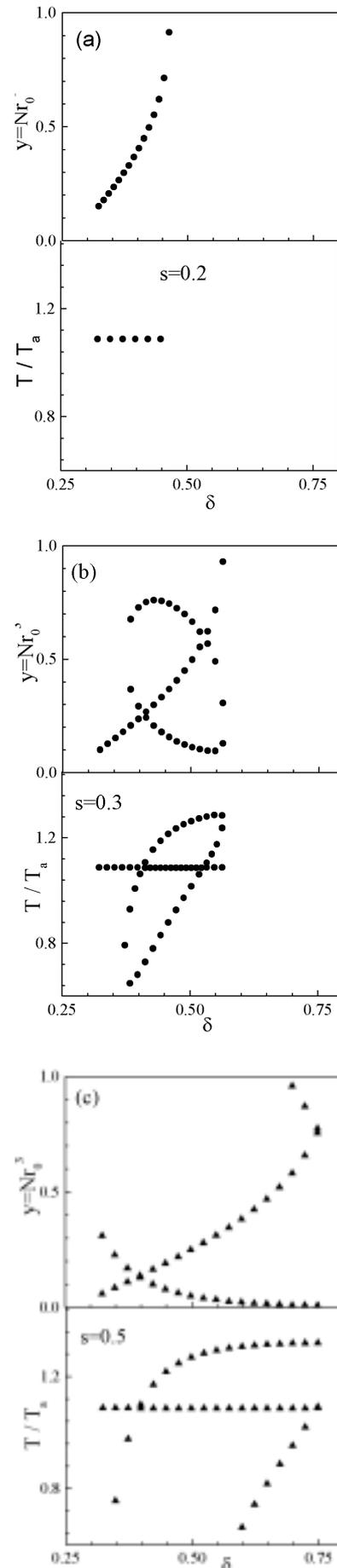


Figure 1. Stable points of Eqs 2 for the different parameter s .

the SFD with the number i . A detailed discussion of the choice of the most adequate model potential $\varphi(r)$ is given in [11]. In the present paper we use the model form

$$\varphi(r) = \varphi_0 \chi(r/r_0) \quad \text{with} \quad \chi(x) = 2x^3 / (1 + x^6), \quad (4)$$

where φ_0 and r_0 are the amplitude and radius of interaction between the SFD, respectively.

Using the autowave variable, the Eq. (3) can be written as

$$U(y) = \Delta(1 + \delta - s\chi(y^{-1/3})), \quad (5)$$

where we introduce the characteristic parameter of the SFD, whose influence we are going to investigate in this paper, namely $\delta = (U_0 - \Delta)/\Delta$ and $s = \varphi_0 n_0 / \Delta$. The value of δ settles the difference between the activation energies for the single act of the SFD creation and the SFD annihilation and, hence, it characterises the efficiency of the SFD creation. The parameter s controls the intensity of the interaction between the SFD and, hence, the amplitude of non linearity of Eqs. (2).

Results

We have analysed the stable points of Eqs. (2). The possible structure of the autowave solution depends strongly on the parameters of the deformation field. If the value s is small (weak interaction of the SFD, $r_0 \approx a$), the Eqs. (2) have only one stable point (Fig. 1 a). It corresponds to a "soft" SSA scenario. The initial sample contents no structural forming defects and has a uniform structure. The efficiency of the SFD creation is small and the self-sustaining wave of amorphization can not exist in such a system.

The increasing of the interaction intensity leads to the appearance of the second and third roots of the system (Figs. 1 b and c). In this case a phase transition wave with constant velocity can spread into the excited state. It corresponds to a sort of a jump between the stable points. According to the basic assumptions of the model, the biggest root y_{max} should be associated with the amorphous state having a coherence length $L_{MRO} = r_0 y_{max}^{-1/3}$, see Eq. (1). Then the SSA process follows the "hard" scenario: the initial sample must contain a significant number of defects, corresponding to the root y_1 . Then at the moment of amorphization, the amorphous phase with $L_{MRO} \approx r_0$ develops. Thus, presence of the defect regions in an initial crystal becomes the necessary condition for the SSA onset. It coincides

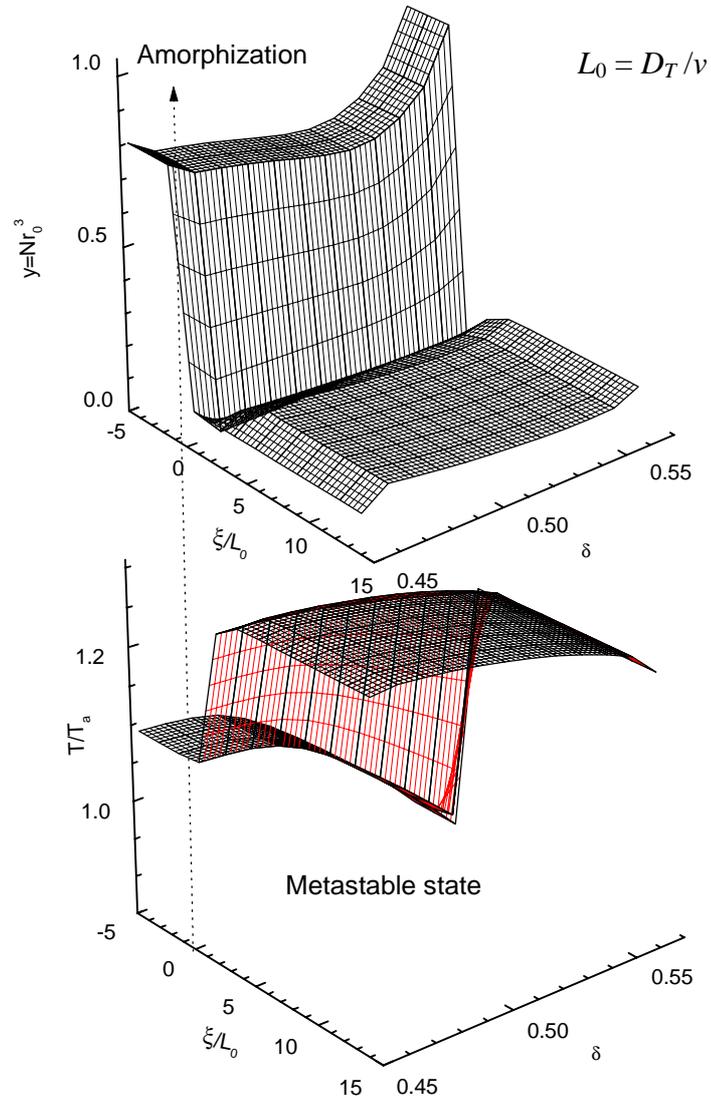


Figure 2. Autowave solution for the temperature and concentration profiles.

well with the results obtained by molecular dynamics calculations [9] and with experimental data [18]. A further increasing of the parameter s induces the growth of $y_3 = y_{max}$ and as a result the characteristic correlation length of the amorphous matrix, L_{MRO} is reduced (Fig. 1 c).

Typical results for the concentration and temperature profiles are given in Fig. 2. Interestingly, the change of the parameter δ alters the stationary asymptotic for $\xi \rightarrow \pm\infty$. As can be expected, its growth limits the creation of a new defect and the stable roots are diminished (Fig. 2). This result supports the proposition that the SSA is essentially a dynamical process. It is worth to note that in the non-uniform case $y(t=0) = y(r)$ the hard scenario leads to a bistability of the phase transition and the other stable autowave solution in the form of an impulse can spread into the sample. As a result, the sample will in general be a mixture of the amorphous and crystalline phases. This is precisely the situation observed in SSA of gallium antimonide [19].

As a summary, we have proposed the model of solid state amorphization (SSA), which is alternative to the semiempirical and first-principal models based on the general approach to the non-equilibrium phase transition developed before. The model allows taking into account the physical mechanisms of the SSA process and analysing the influence of different parameters of the deformation field created by non-homogeneties of the system. Unfortunately, the required experimental information about these parameters is almost missing, therefore we can only estimate the possible values of the microscopic characteristics of the SSA, which may lead to the observed values of the macroscopic parameters of SSA process. Nevertheless even this qualitative approach predicts the existence of the SSA several scenario and allows to calculate characteristics of the amorphous phase structure.

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References

1. M. Seyffert, A. Siber, and P. Ziemann, Phys. Rev. Lett. **67**, 3792 (1991).
2. H. J. Fecht, Z. Fu, and W. L. Johnson, Phys. Rev. Lett. **64**, 1753 (1990).
3. E. G. Ponyatovsky and O. I. Barcalov, Mater. Sci. Rep. **8**, 147 (1992).
4. V. V. Brazhkin, A. G. Lyapin, S. V. Popova and R. N. Voloshin, JETP Lett. **56**, 152 (1992); Phys. Rev. B **51**, 7549 (1995).
5. O. Mishima, L. D. Calvert and E. Whalley, Nature **310**, 393 (1984).
6. A. G. Lyapin and V. V. Brazhkin, Phys. Rev. B **54**, 12036 (1996).
7. C. Massobrio and V. Pontikis, Phys. Rev. B **45** 2484 (1992).
8. J. Wang, J. Li, S. Yip, S. R. Phillpot and D. Wolf, Phys. Rev. B **52**, 12627 (1995).
9. L. J. Lewis and R. M. Nieminen, Phys. Rev. B **54**, 1459 (1996).
10. M. O. Ruault, J. Chaumont and H. Bernas, Nucl. Instrum. Methods **209/210**, 351 (1983).
11. S. V. Demishev, T. V. Ischenko and F. V. Pirogov, Phys. Solid State **37**, 331 (1995).
12. M. Suzuki, Yu. Masaki and A. Kitagawa, Phys. Rev. B **53**, 3124 (1996).
13. C. A. Volkert, J. Appl. Phys. **70**, 3521 (1991).
14. S. V. Demishev, T. V. Ischenko and S. J. Blundell, J. Phys.: Cond. Matt. **7**, 9173 (1995).
15. T.V. Ischenko and S.V. Demishev, Mater. Sci. Forum **294-296**, 481 (1999).
16. S. V. Demishev, T. V. Ischenko and S. J. Blundell, J. Phys.: Cond. Matt. **9**, 9199 (1997).
17. P. Kringho, A. N. Larsen and S. Yu. Shirayev, Phys. Rev. Lett. **76**, 3372 (1996).
18. H. Hsieh and S. Yip, Phys. Rev. B **39**, 7476 (1989).
19. S. V. Demishev, Yu. V. Kosichkin, D. G. Lunts, A. G. Lyapin, N. E. Sluchanko and M. S. Sharanbeyan, Sov. Phys. JETP **73**, 394 (1991).