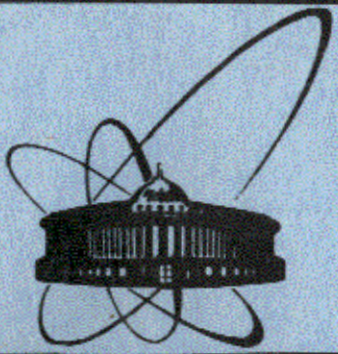

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# STRUCTURAL GLASS IN SOLID SOLUTIONS WITH COMPETING INTERACTIONS

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1. The active research of spin glasses in recent years has stimulated the study of analogous phenomena in nonmagnetic systems where similar states in structurally frustrated systems have been called structural glass. Solid solutions seem to be suitable for the study of the peculiarities of the structural glass phase [1]. This follows from recent experiments on salts $Rb_{1-x}(NH_4)_x H_2PO_4$ which are solid solutions of order-disorder ferroelectrics and antiferroelectrics [1-3]. In the present paper we investigate the conditions for the existence of the structural glass phase in a model of a displacive-type solid solution with competing interactions. This model corresponds to mixed perovskites, e.g., to $Sr_{1-x} Ba_x TiO_3$.

2. Let us consider the following model Hamiltonian of a structurally unstable solid solution [4], which we write in the form

$$H = \sum_i \left( \frac{P_i^2}{2m_i} - \frac{A_i}{2} \phi_i^2 + \frac{B_i}{4} \phi_i^4 \right) + \frac{1}{4} \sum_{ij} C_{ij} (\phi_i - \phi_j)^2 , \qquad (1)$$

where $\phi_i$ is the displacement of the i-th atom of mass $m_i$ (effectively characterizing the unit cell of the lattice), which is situated in a one-particle double-well potential, and $p_i$ is the conjugate momentum. The parameters of the Hamiltonian are random quantities. The coupling constants $C_{ij}$ may be positive or negative in dependence on the kind of the atoms (the distribution of which is statistically homogeneous according to our assumption) at sites $R_i$ and $R_j$ as well as on the interaction radius $|R_i - R_j|$. If we write the displacements $\phi_i$ as a sum of equilibrium positions $\eta_i = \langle \phi_i \rangle$ and fluctuations $u_i(t)$: $\phi_i(t) = \eta_i + u_i(t)$, and perform the thermodynamic average of the equation of motion: $d/dt \langle p_i(t) \rangle = 0$, we get the following equation for the equilibrium positions

$$(-A_i + 3B_i \langle u_i^2 \rangle + C_{oi}) \eta_i + B_i \eta_i^3 = \sum_{ij} C_{ij} \eta_j , \qquad (2)$$

where $C_{oi} = \sum_k C_{ik}$. Eq. (2) has been obtained by neglecting the anharmonic term $\langle u_i^3 \rangle$, i.e., by applying the first-order self-consistent phonon approximation. Because of the stochastic nature of the Hamiltonian (1) the solutions $\eta_i$ of Eq. (2) are inhomogeneous. Analogously to spin glasses we introduce the

following two order parameters for the description of the structural glass phase: $\bar{\eta}_i$ and $\overline{\eta_i^2}$, where the bars denote a configurational avarage. The equation for the order parameter $\bar{\eta}_i$ is obtained after averaging of linearized eq. (2) in the virtual crystal approximation (VCA)

$$(-\bar{A}_i + 3\bar{B}_i \langle\overline{u_i^2}\rangle + \bar{C}_{0i})\,\bar{\eta}_j = \sum_j \bar{C}_{ij}\,\bar{\eta}_j \,. \qquad (3)$$

This equation allows an estimation of the critical value of the fluctuations $\langle\overline{u_i^2}\rangle_c$ at which the transition from the paraphase, where $\eta_i = 0$, to a long-range ordered modulated phase, where $\bar{\eta}_i \sim \cos q_0 R_i$, takes place. The value of the wave vector $q_0$ is determined by the maximum of the Fourier transform of the averaged coupling constants $\bar{C}_{ij}$, ($\max \bar{C}_q = \bar{C}_{q_0}$), and characterized this phase: it may be incommensurate or commensurate (the ferrophase for $q_0 = 0$ and the antiferrophase for $q_0 = q_{BZ}$). To simplify matter we assume that the averaged fluctuations $\langle\overline{u_i^2}\rangle$ are approximately homogeneous. Then, the Fourier transformation of Eq. (3) yields

$$3\bar{B}_i \langle\overline{u_i^2}\rangle_c = \bar{A}_i + \bar{C}_{q_0} - \bar{C}_{q=0} \,. \qquad (4)$$

For an estimation of the value of the fluctuations $\langle\overline{u_i^2}\rangle_g$, at which the transition to the glass phase with $\bar{\eta}_i = 0$ and $\overline{\eta_i^2} \neq 0$ takes place, we apply a similar method as has been used in the mean field theory of spin glasses /5/. Squaring the linearized Eq. (2) and performing the configurational average in the sense of the VCA with approximation $\overline{\eta_j \eta_k} = \overline{\eta_j^2}\,\delta_{jk}$ we obtain equation like Eq. (3) which gives us:

$$3\bar{B}_i^2 \langle\overline{u_i^2}\rangle_g = \overline{B_i (A_i - C_{0i})} + \{\overline{B_i (A_i - C_{0i})}^2 + \bar{B}_i^2 [\overline{C_i^2} - \overline{(C_{0i} - A_i)^2}]\}^{1/2} , \qquad (5)$$

where $C_{2i}^2 = \sum_k C_{ik}^2$ .

The fluctuations may be found from the fluctuation-dissipation theorem. The calculation of the susceptibility of the system (1) in VCA yields

$$\langle\overline{u_i^2}\rangle = \frac{1}{2\bar{m}_i N} \sum_q \frac{1}{\omega_q} \coth \frac{\omega_q}{2T} \,, \qquad (6)$$

where $\omega_q$ is the phonon frequency given by

$$\bar{m}_i \omega_q^2 = -\bar{A}_i + 3\bar{B}_i (\langle\overline{u_i^2}\rangle + \overline{\eta_i^2}) + \bar{C}_{q=0} - \bar{C}_q \,. \qquad (7)$$

The system of equations (4)–(7) determines the temperature $T_{q_0}$ of the transition to a phase modulated with the wave vector $q_0$ and the temperature $T_g$ of the transition to the glass phase.



3. Now let us apply the derived estimations to a binary alloy where the sites of the model (1) are randomly occupied by atoms of kind A or B. In this case we get

$$\bar{C}_{ij} = x_A^2 C_{ij}^{AA} + 2x_A x_B C_{ij}^{AB} + x_B^2 C_{ij}^{BB} \,, \quad \bar{m}_i = x_A m_A + x_B m_B \,,$$

and analogous equations for $\bar{A}_i$ and $\bar{B}_i$, where $x_A, x_B$ are the concentrations of the components. The component A shows a ferrodistortive transition ($\max C_q^{AA} = C_{q=0}^{AA} = C_0^{AA}$) and the component B an antiferrodistortive one ($\max C_q^{BB} = C_{q_{BZ}}^{BB}$). For the calculation of the sum in Eq. (6) we suppose a simple cubic lattice and approximate the phonon spectrum by a Debye one. The temperatures $T_{q_0}$ and $T_g$ calculated from eqs. (4)–(7) are plotted in Fig. 1. They give an estimation of the transition temperatures to the ferrodistortive (F), antiferrodistortive (AF) and structural glass phase (SG), respectively. The parameters have been chosen as follows: $A_B = -0.2\,A_A$, $B_B = B_A$, $m_B = m_A$, $C_0^{AA}/A_A = 1.1$, $C_0^{AB} = -0.6\,C_0^{AA}$, $C_0^{BB} = -1.2\,C_0^{AA}$ and $\lambda_A = 10^{-3}$ (the parameter $\lambda_A = \hbar (A_A/m_A)^{1/2} / (A_A^2/B_A)$ characterizes the strength of the quantum fluctuations, see ref. /4/).

Numerical calculations show that the structural glass phase may be found only for special relations of the parameters of the Hamiltonian (1). In Fig. 2 we have shown the range of existence of the glass phase for varying parameters $\gamma = A_B/A_A$ and $f_0 = C_0^{AA}/A_A$ and for other fixed parameters of the above example.

For a short discussion of the static susceptibility behaviour we consider the special case $A_i = A$, $B_i = B$. Considering the stability of F- and SG-phase in the classic limit $T \gg \omega_D$, where $\langle\overline{u_i^2}\rangle = (T/\bar{m}_i N) \sum_q \omega_q^{-2}$ we obtain $\overline{\eta_i^2} = (T_g - T)$ with $T_g = T_0 [1 - \bar{C}_{0i}/A + [\overline{C_{2i}^2} - (\overline{C_{0i}^2} - \overline{C_{0i}}^2)]^{1/2}/A]$, where $T_0$ denotes the transition temperature to the ferrodistortive phase. An estimation of the susceptibility for $T \leq T_g$ yields $\chi \sim [T_g - T_0 + a(T_g - T)]^{-1}$ and exhibits a usual for spin glasses cusp at $T_g$.

As a result, in the present model for binary solid solutions with competing ferro- and antiferrodistortive interaction the appearance of a glass phase is possible but at special relations between model parameters. The observation of a similar phase diagram, as has been shown in Fig. 1, may be expected, e.g., in the solid solution $(Sr, Ba)\,Ti\,O_3$ for which the transitions to the F- and AF-phase have been measured /6/. In this connection the experimental investigations of these mixed crystals, as have been performed for the compounds $(Rb, NH_4)\,H_2PO_4$ /1-3/, would be very interesting.

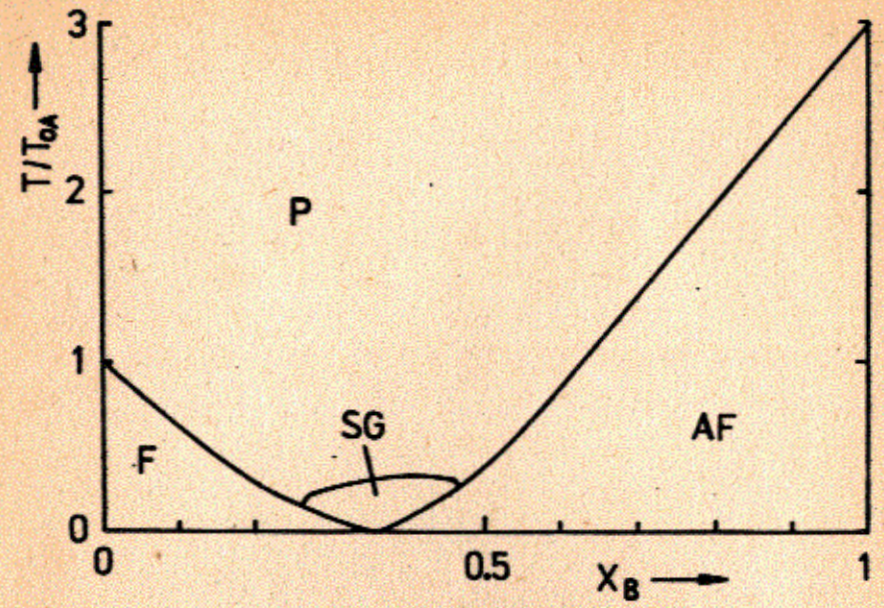


Fig.1. Phase diagram of a model of displacive type binary solid solution with competing interactions.

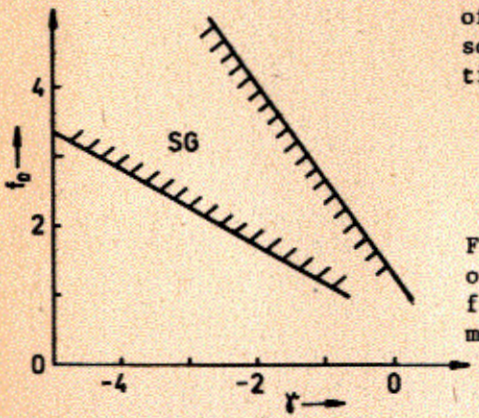


Fig.2. Region of the existence of the structural glass phase for varied parameters of the model.

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Структурное стекло в твердых растворах с конкурирующим взаимодействием

Исследуются фазовые переходы в модели структурно-неустойчивых твердых растворов типа смещения с конкурирующими ферро- и антиферродисторсионным взаимодействиями и показана возможность появления фазы типа спинового стекла.

Работа выполнена в Лаборатории теоретической физики ОИЯИ.

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Structural Glass in Solid Solutions with Competing Interactions

Phase transitions in the model of displacive-type structurally-unstable solid solutions with competing ferro- and antiferrodistortive interactions are investigated and the possibility of the appearance of spin glass-like phase is shown.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

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