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Close packing of atoms, geometric frustrations and the formation of heterogeneous states in crystals

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Abstract. To describe the structural peculiarities in inhomogeneous media caused by a tendency towards close packing of atoms, a formalism based on the use of Riemann geometry methods (which, recently, were successfully applied in a description of the structures of quasicrystals and glasses) is developed. On the basis of this formalism we find, in particular, the criterion of stability for precipitates of the Frank–Kasper phases in metallic systems. The nature of the ‘rhenium effect’ in W–Re alloys is discussed.

Recently, interest has been growing in the role of crystallogometrical factors in determining the structure of condensed matter—in particular, in those cases which are connected with the close packing of atoms [1]. This is a whole class of metallic systems, including quasicrystals, metallic glasses [1], small metallic clusters [2], and Frank–Kasper (FK) phases [3], whose structures are probably determined by a tendency towards close packing of ionic spheres with different radii. Note that the requirements of the closest local packing may contradict the existence of long-range crystal order. This essentially distinguishes the real three-dimensional case from the two-dimensional one, where (in the case of spheres of equal radii) the triangle lattice has the closest packing both for the whole space and for each of its parts, i.e. both globally and locally [4]. The classical problem of the distribution of spheres in three-dimensional space with the closest packing has not yet been solved rigorously (it is a part of the 18th Gilbert problem). However, it is known that spheres may be packed locally with higher density than in fcc, hcp, and other close-packed lattices [4]. Therefore the situation of geometric frustrations arises when the structural optimum from the point of view of the local surroundings cannot be optimum globally. The concept of frustrations appeared to be useful in particular when considering the structure of disordered systems [1, 5].

The cause of the existence of the geometric frustrations is that the *Euclidean* space cannot be occupied completely by regular tetrahedra (the regular tetrahedron is the structural unit providing the closest packing of four atom groups). An elegant technique has been proposed in reference [6] for constructing the structures of FK phases where the latter are obtained starting from the closest packing of tetrahedrons in *Riemannian* space, by introducing the net of structural disclinations (SD) ‘decurving’ the space and then filling the Euclidean space with the structure units that have arisen. Here we use a similar approach to analyse the problem of the formation of a heterogeneous state (HS) in metallic alloys. Such a state is now a subject of great interest to researchers in the field of materials science. From

the experimental point of view, it is characterized by the peculiar diffuse x-ray scattering corresponding in real space to the presence of relatively small clusters containing only hundreds or even tens of atoms [7]. Examples include the so-called athermic ω -phase in some Ti- and Zr-based alloys [8] and in $\text{Cr}_{1-x}\text{Al}_x$ [9], the σ -phase in $\text{Fe}_{1-x}\text{Cr}_x$ [10], and precipitates of W_3Re phase with A15 structure in $\text{W}_{1-x}\text{Re}_x$ [11]. Recent investigations of $\text{Ti}_{1-x}\text{Fe}_x$ alloys by means of the Mössbauer effect [12] have demonstrated the geometric frustrations, i.e. differences between the type of short-range order in the local surroundings of Fe nuclei and the type of long-range order in the crystal as a whole. A hypothesis has been proposed in reference [13] concerning the existence of small icosahedral clusters in these alloys.

Generally speaking, the structure of crystal phases is determined by a number of factors. Among them, apart from the tendency towards close packing, the spatial orientation of covalent bonds, peculiarities of the electronic structure near the Fermi surface, etc, are the most frequently discussed. Therefore one may expect that the nature of HS may be different for different systems. In particular, Krivoglaz [7] stressed the role of peculiar features of the shape of the Fermi surface in the formation of HS in Ti- and Zr-based alloys. However, this mechanism can hardly be universal, since in all of the systems with HS the electron mean free path is short, and therefore the alloy smearing of the Fermi surface is essential.

The alternative mechanism proposed in the present work is based on considerations of the closest packing of atoms for small atomic groups, and geometric frustrations connected with them. As will be shown below, they may lead to the formation of HS with a characteristic scale of the order of a few interatomic distances. The model proposed is rather rough, and claims to describe only some of the main features of the phenomenon. Nevertheless it serves to stress, in our opinion, the peculiar role of a factor which is important for many real systems but which was not taken into account in previous work.

Consider precipitates of A15 phase in a bcc host (e.g. of W_3Re phase in the solid solution $\text{W}_{1-x}\text{Re}_x$ [11]) as an example of a heterogeneous state of the type under consideration, because A15 structure is the simplest and most well-known example of a FK phase [1]. It contains eight atoms per cell, two of them having icosahedral coordination and six of them being surrounded by polyhedra with 14 vertices [6]. The latter may be obtained from the regular icosahedron by introducing an edge disclination with the axis passing through its centre and the Frank vector $-\pi/5$. Using such a procedure, it was shown in reference [6] that the net of SD for A15 structure consists of three mutually orthogonal sets of equidistant parallel disclinations with their period equal to the lattice constant a . Other FK phases differ from A15 structure only in the geometry of the SD net.

To investigate the stability of HS, one needs to generalize the approach [6]. With this aim, we use the basic relation between the curvature tensor R_{ijkl} and the disclination density tensor $\theta_{ij}^{(c)}$ [14]:

$$R_{ijkl} = -\epsilon_{ijp}\epsilon_{klq}\theta_{pq}^{(c)} \quad (1)$$

where ϵ_{ijp} is the unit antisymmetric tensor. It is worthwhile to note that, strictly speaking, this relation can be exactly satisfied only in 2D space. In 3D case this is only an approximation—but a rather good one, as was shown in [6]. In the light of equation (1), the space curvature providing the ideal tetrahedral packing is created, in the approach of [1, 6], by introducing partial edge disclinations with the value of Frank vector (angular deficit) $\Omega = 7^\circ 20'$, which compensates for the deficiency of the dihedral angles in the packing of five tetrahedra around the common edge [15]. To construct FK phases it is necessary to ‘decurve’ the space by introducing SD with the average density $\bar{\theta}_{ij}^{SD} = -\theta_{ij}^{(c)}$ where the bar means the average over the volume containing a large enough number of cells. Thus, in

contrast with the approach of reference [6], where SD were introduced in *curved* space, we introduce *two* sets of disclinations in *Euclidean* space, with the mean total density tensor equal to zero. At the same time, local variation of the curvature of the lattice (i.e. the deviation of the *local* disclination density tensor from zero) is possible, and is connected with the elastic distortions of the bonds. The corresponding stresses are similar to those which have been discussed in reference [5] for glasses.

Apart from the energy of elastic distortions, an electronic ('chemical') contribution to the energy describing the tendency towards the closest packing of atoms also exists. If in some places the density of SD differs from the mean density in the FK phase, and, therefore, according to (1) the lattice appears to be locally curved, the local values of the packing density are higher or lower than in the FK phase.

In the framework of the approach under consideration, the energy of the FK phase counted from the energy of the 'host' phase with $\theta = 0$ may be written as

$$E = \int d\mathbf{r} f[\theta_{ij}(\mathbf{r})] + E_{el} \quad (2)$$

where f is the density of 'chemical' energy, depending on the degree of the atomic packing which is connected with the disclination density tensor θ_{ij} , and E_{el} is the elastic energy. As usual [16], the latter may be represented in linear elasticity theory in the following form:

$$E_{el} = \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \eta^{\nu\rho}(\mathbf{r}) H_{\nu\rho\kappa\tau}(\mathbf{r} - \mathbf{r}') \eta^{\kappa\tau}(\mathbf{r}') \quad (3)$$

where $H_{\nu\rho\kappa\tau}$ is the Green tensor for internal stresses, and $\eta_{\nu\rho}$ is the incompatibility tensor describing the density of sources of internal stresses. According to [14], it is defined as

$$\eta^{\nu\rho} = -\frac{1}{2} (\epsilon_{\rho pq} \alpha_{\nu q, p} + \theta_{\nu\rho} + \epsilon_{\nu pq} \alpha_{\rho q, p} + \theta_{\rho\nu}) \quad (4)$$

where $\alpha_{\nu\rho}$ is the dislocation density tensor. Separating the singular part of the Green tensor, we may represent the energy E_{el} as the sum $E_{el} = E_{el}^{(0)} + E_{el}^{(1)}$ of the energy of the distortions in the disclination cores $E_{el}^{(0)}$ and the energy of the elastic deformations outside the cores $E_{el}^{(1)}$.

In the absence of dislocations, one has $\eta_{\nu\rho} = -(1/2)(\theta_{\nu\rho} + \theta_{\rho\nu})$. For a single disclination with the Frank vector $(0, 0, \Omega)$, the tensor $\eta_{\nu\rho} = -\theta_{\nu\rho}$ has only one non-zero component [14]:

$$\eta^{33} = -\Omega \delta(\rho) \quad (5)$$

where $\rho = (x, y)$. In the case of a set of edge disclinations considered here, the tensor θ_{ij} according to (5) may be characterized by the only scalar parameter $\theta = \text{Tr} \theta_{ij}$, which is equal to the mean value of the z -component of the Frank vector at a given point. It is proportional to the scalar curvature R_{ijij} (see (1)). For the geometry given, the energy of disclination cores (per unit length) may be represented as

$$\frac{E_{el}^{(0)}}{L} = e_0 \int d^2\rho \theta^2(\rho) \quad (6)$$

where e_0 is the energy of the core of the disclination with the unit Frank vector defined by the relation $e_0 \delta(\rho) = \frac{1}{2} H_{3333}(0)$. Note that, for the elastic continuum, $e_0 = 0$, and to describe the core energy correctly it is necessary to use the quasicontinuum model [16].

It is common practice in materials science to treat an inhomogeneous state mainly as a multiphase state with the coexistence of regions with different crystal structures, each of which may be stable in principle over the whole space. In this case, the inhomogeneity

may be described in terms of elastic distortions due to the conjugation of crystal lattices on the boundary between the precipitate and the host. To calculate the distortions, the Eshelby model [17] is usually used, their energy appearing to be proportional to the volume of the precipitate. It is a consequence of this fact that, in the Eshelby model, the deformation $\varepsilon_{ij}^{(0)}$ connected with the phase transition is constant inside the precipitate. Then, according to Eshelby, the deformation $\varepsilon_{ij}^{(0)}$ may be simulated by a system of dislocation loops on the boundary of the precipitate. Since the energy of each loop is proportional to its radius R (equal to the precipitate radius) and the number of loops is proportional to R^2 , their total energy turns out to be proportional to R^3 . In our model the precipitate has a type of short-range order (e.g. icosahedral) which cannot correspond to long-range order for any bulk crystal (periodic) phase. Therefore, in contrast with the Eshelby model, the deformation appears to be inhomogeneous not only outside the precipitate but also inside it. It will be shown below that, as a result, the elastic energy of the precipitate grows with the increase of R faster than R^3 , and, therefore, the stabilization of HS is possible.

The real form of the function $f(\theta)$ in (2) is unknown. In accordance with our choice of the zero point for the energy, we have for the host phase ($\theta = 0$) $f(0) = 0$, and the minimum of $f(\theta)$ lies at the value $\theta = \theta_0$ corresponding to the closest tetrahedral packing in the Riemannian space [2]. We suppose for simplicity that

$$f = \alpha(\theta - 2\theta_0)\theta \quad (0 < \theta < \theta_0)$$

where the parameter $\alpha > 0$ depends on the explicit form of the interatomic interactions. Generally speaking, the function f may also contain terms proportional to $(\nabla\theta)^2$, but in the framework of the variational approach used below (see (8)) they do not alter the results.

To demonstrate the possibility of the formation of a heterogeneous state, we use the direct variational approach, and explicitly construct the distribution $\theta(r) \neq \text{constant}$, leading to a lower value of the total energy than that of the homogeneous state. The problem may be solved in the simplest way for the cylindrical precipitate of the close-packed phase. Let Oz be the axis and R the radius of the precipitate; then the axes of all of the disclinations are parallel to Oz , and $\theta = \theta(\rho)$ where $\rho = \sqrt{x^2 + y^2}$.

Since it is obvious that the discontinuities on the boundary between the host and the precipitate are energetically unfavourable, we restrict ourselves to the case of their coherent conjugation when the discontinuities are absent. In this case, the disclinations cannot be abrupt at the boundary, and should form loops with external segments in the host. In contrast with the homogeneous A15 phase, the ‘polarized’ distribution of disclinations is typical in our case—that is, the uniform distribution of positive partial disclinations inside the precipitate and a ‘cloud’ of negative disclinations outside it. From topological considerations (the vanishing of the total Frank vector), one has

$$\int d^2\rho \theta(\rho) = 0. \quad (7)$$

To evaluate the minimum of the energy (2), we use the trial function

$$\theta(\rho) = \begin{cases} \theta_1 & \rho < R \\ \frac{-\theta_1 R^2}{2R\Delta + \Delta^2} & R < \rho < R + \Delta \\ 0 & \rho > R + \Delta \end{cases} \quad (8)$$

answering the requirement (7) automatically. Using the discontinuous trial function for the disclination density does not lead to any difficulties, since the energy of interaction of two disclinations vanishes when the distance between them tends to zero, and, therefore, the

detailed shape of the interface between the core and the cloud is not too important. The value Δ describes the thickness of the ‘cloud’ and should be found from the solution of the variational problem. In the model under consideration, the energy of elastic distortions concentrated in the disclination cores in the cloud would play the role of a surface energy. However, due to condition (7), the total number of disclinations in the cloud is equal to that in the precipitate itself, and is proportional to its volume (in the 2D case, $\sim R^2$). Therefore, in contrast with the Eshelby model case, it is impossible to separate explicitly the bulk and surface parts in the precipitate energy.

We use for $H_{3333}(\rho - \rho') = H(\rho - \rho')$ the known expression [16]

$$H(r) = -\frac{2\mu}{1-\nu} \frac{\rho^2}{8\pi} \left[1 - \ln \frac{\rho}{R_c} \right] + C \quad (9)$$

corresponding to the continuum approximation in the elastically isotropic model, where μ is the shear modulus, ν is the Poisson ratio, R_c is the cut-off radius, of the order of the size of a crystal, and C is a constant which does not contribute to the energy $E_{el}^{(1)}$ for a given geometry (the total Frank vector equals zero). To describe the energy of disclination cores $E_{el}^{(0)}$ correctly, one should use the quasicontinuum approximation [16]

$$C = -\frac{\mu}{2\pi(1-\nu)k_d^2} [1 + 2\gamma \ln k_d R_c]$$

where k_d is the Debye wave vector, and γ is a parameter depending on the explicit form of the phonon dispersion curves in the model.

Then the elastic energy (3) per unit length of the precipitate does not depend on the cut-off radius R_c , and has the form

$$\frac{E_{el}^{(1)}}{L} = \theta_1^2 \frac{\mu a^4}{1-\nu} \tilde{\psi}(R, \Delta) \quad (10)$$

where

$$\tilde{\psi}(R, \Delta) = \frac{R^4(\Delta + R)^2}{192a^4\Delta^2(\Delta + 2R)^2} \left[\Delta(5\Delta^3 + 20\Delta^2R + 26\Delta R^2 + 12R^3) - 12R^2(\Delta + R)^2 \ln\left(\frac{\Delta + R}{R}\right) \right].$$

Minimizing the function $\tilde{\psi}(R, \Delta)$ with respect to Δ gives the dependence of the cloud thickness $\Delta = \Delta(R)$. As a result, the total energy may be represented in the following form:

$$\frac{E}{L} = \pi R^2 \alpha p (\theta_1 - 2\tilde{\theta}_0) \theta_1 + \theta_1^2 \frac{\mu a^4}{1-\nu} \psi(R) \quad (11)$$

where $\psi(R) = \tilde{\psi}(R, \Delta(R))$, and $\tilde{\theta}_0 = \theta_0/p$, $p = 1 + 2e_0/\alpha$. The minimum of energy (11) corresponds to the disclination density

$$\theta_1 = \frac{\tilde{\theta}_0}{1 + \psi(R)/\kappa R^2} \quad (12)$$

where the precipitate radius R is found from the equation

$$R \frac{d\psi(R)}{dR} = 2(2\psi(R) + \kappa R^2). \quad (13)$$

Here

$$\kappa = \frac{\delta f (1-\nu)\pi p}{\mu a^4 \theta_0^2} \quad (14)$$

and the value $\delta f = \alpha \theta_0^2$ describes the chemical energy gain (per unit volume) for the ideal tetrahedral packing.

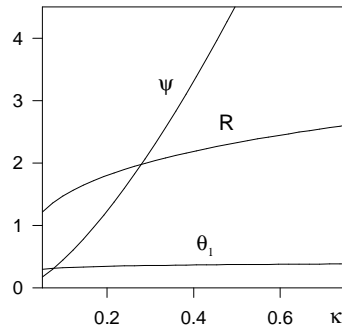


Figure 1. The dependence of the equilibrium values of the precipitate radius R (in units of a), the disclination density θ_1 (in units of $\bar{\theta}_0$), and the value of the elastic change energy ψ in equation (11) on the parameter κ defined by equation (14).

As follows from equation (13), the precipitate radius R depends on the parameter κ characterizing the ratio of the chemical contribution to the elastic one. According to (14), its value varies from 0.1 to 1 for $\delta f \approx 0.01$ – 0.1 eV per atom. Direct calculations show that, in all of these limits of the variation of κ , the function $\psi(R)$ is almost constant for $R < 2a$ and increases sharply for $R > 3a$. On these grounds, the equilibrium value of R grows slowly with the increase of κ (see figure 1). For $\kappa < 0.1$, the continuum approach under consideration does not hold, because $R < a$. For this range of values of κ , the disclination density θ_1 determined by equation (12) is less than the minimal possible value corresponding to one disclination with the value of the Frank vector of $7^\circ 20'$ per precipitate.

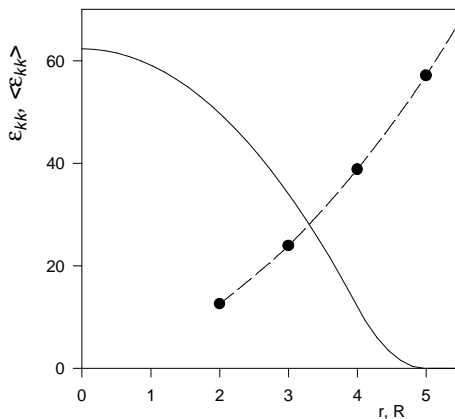


Figure 2. The distribution of the dilatation ϵ_{kk} in the precipitate (solid line) on the polar coordinate r ($R = 4$, $\Delta = 1$), and the dependence of the average dilatation $\langle \epsilon_{kk} \rangle$ on the precipitate radius R (dashed line) in units of $\theta_1(1 - 2\nu)/(2\pi(1 - \nu))$.

The spatial distribution of the dilatation obtained by numerical integration is shown in figure 2. It can be seen that the internal part of the precipitate is expanded, and the dilatation ϵ_{ll} vanishes sharply at the boundary. The mean value in the precipitate $\langle \epsilon_{ll} \rangle$ increases approximately linearly with the precipitate radius. This demonstrates the

qualitative difference between the model under consideration and the Eshelby model. Since the average deformation increases with the increase of R , the elastic energy grows faster than R^2 in the 2D case (or than R^3 for spherical precipitates).

Putting the equilibrium values of θ_1 and R in equation (11), one obtains the expressions for the energy change at the formation of the precipitate:

$$\frac{E}{L} = -\delta f \pi R^2 \frac{\theta_1}{\theta_0} = -\frac{\theta_0 \theta_1^2}{\theta_0 - \theta_1} \frac{\mu a^4 \psi(R)}{1 - \nu} < 0. \quad (15)$$

Thus, in the model under consideration, the precipitates are stable, and the heterogeneous state has lower energy than the host lattice. According to the dependence of θ_1 on R , its value (12), generally speaking, does not coincide with any of the values which correspond to homogeneous FK phases.

Thus, we have shown that for certain ratios between ‘chemical’ and elastic properties of the media ($\kappa \geq 0.1$) the heterogeneous state may be energetically favourable, owing to the crystallogometrical factors (the tendency towards the closest local packing). It is worthwhile to stress again the most important features of this state in the framework of the model under consideration:

- (i) the sizes of the precipitates are of the order of few lattice constants;
- (ii) the structure of the precipitates is distorted in comparison with the structures of FK phases in an infinite crystal;
- (iii) the precipitates are surrounded by a cloud of the distorted host lattice, with a thickness of the order of the sizes of the precipitates.

The existence of this cloud has an obvious sense: since it is impossible to fill the whole space with regular tetrahedra, an attempt to realize such a filling locally in some part of the space results inevitably in the appearance of voids at the boundary. Introducing the external segments of disclination loops leads to the elimination of these voids, and coherent conjugation of the precipitate with the host surroundings.

In the specific case where the host phase is bcc, a sharp increase of the solubility of light interstitial impurities is one of the characteristic features of the mechanism of the formation of HS under consideration. It is connected with the presence of large tetrahedral voids in close-packed structures and their absence in a bcc lattice. This feature, together with the change of the type of short-range order and the appearance of elastic distortions, can help in the identification of this kind of HS experimentally.

The results obtained here may explain some important features of the so-called ‘rhenium effect’ (the improvement of the ductility of W and Mo upon doping with Re). According to reference [11], the increase of the solubility of interstitial impurities connected with the appearance of the precipitates of the FK phases—in particular, W_3Re —is the key feature in this phenomenon. The results presented here allow us, on the one hand, to understand the causes of the appearance of the precipitates, and, on the other hand, to identify the specific mechanism of their influence on the solubility of interstitial impurities. Indeed, considerable dilatation in the cloud surrounding the precipitate may lead to the substantial energy gain at the transfer of the interstitial atom from the host to the shell. This may prevent the appearance of the carbide precipitates or impurity segregation at the intergrain boundaries.

Note in conclusion that the transition from the two-dimensional case considered here to the three-dimensional one is not trivial, since, in ‘dressing’ the spherical precipitate with the cloud of compensated defects, we cannot restrict ourselves to disclinations only, and it is necessary to introduce the density of disclination loops as an additional variable. However, the results presented here seem to be sufficient for demonstrating the instability of the homogeneous state under certain conditions.

Finally, it is worthwhile to note that the present work shows the interconnection of some specific facts known in materials science with non-trivial properties of three-dimensional space, and, therefore, demonstrates the general physical meaning of these facts.

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