The kinetics of ordering during second-order phase transitions is investigated. It is found that reorganization of the lattice does not occur via uniform relaxation or by a nucleation mechanism, but as a result of a peculiar process of formation of web-like ordered regions and their subsequent swelling. The intermediate stages of this process are investigated and its speed is determined as a function of time and of the characteristic parameters of the problem.

1. GENERAL CONSIDERATIONS

It is well known that in a first-order phase transition the system reorganization proceeds via fluctuating production and subsequent growth of the nuclei of the new phase. In second-order phase transformations the resultant equilibrium state can be attained, generally speaking, by successive transitions through a continuous series of intermediate states, each of which is thermodynamically more favored than the preceding one. This indicates that there is no need for the nucleation mechanism and that there should exist another mechanism for the kinetics of the system reorganization.

On the other hand, the very nature of the ordering process excludes the possibility of spatially homogeneous relaxation, which always takes place when the initial and final states are not separated by singular lines on the phase diagram. This fact in itself hardly calls for special argumentation, but in order to make the considerations that follow clearer we shall discuss this question in somewhat greater detail, choosing, to be specific, the ordering of an alloy (AB) with two equivalent sublattices.

It should be recalled that the energy and probability of each microstate depend only on the short-range order and that all local reorganization processes are therefore connected with just the short-range order relaxation; the occurrence of a long-range order \( \eta \) is due exclusively to entropy considerations, viz. starting with a certain critical value of the short-range order coefficient, the appearance of a superstructure becomes overwhelmingly probable, i.e., the appearance of a preferred filling of each of the equivalent sublattices by atoms of a definite sort.

Indeed, if the short-range coefficient \( x \) is defined in such a way that the energy of a given configuration can be written in the form

\[
E = E_0 + Nvx,
\]

and the number of configurations with short-range order \( x \) and long-range order \( \eta \) is

\[
\text{exp} \left\{ N\Theta(x, \eta) \right\},
\]

then the free energy of the nonequilibrium state \( x, \eta \) is

\[
F = F_0 + N_\eta x - N\Theta(x, \eta), \quad \Theta = kT.
\]

For a given \( x \), the equilibrium (i.e., the overwhelmingly more probable) value \( \bar{\eta}(x) \) does not depend on either the temperature or on the displacement energy \( v \), and is determined only by the parameter \( x \) in accordance with the equation

\[
\frac{\partial \Theta(x, \eta)}{\partial \eta}|_{x=\bar{\eta}} = 0.
\]

The value \( x = x_C \), for which (2) has a nonvanishing root \( \bar{\eta} \), is the critical value of the short-range order. We note, incidently, that the equilibrium value of short-range order \( \bar{x} = \bar{x}(\Theta) \) is determined in turn from the equation

\[
\sigma'(\bar{x}) = \psi(\Theta), \quad \sigma(x) \equiv \sigma(x, \bar{x}(\Theta))
\]

and the character of the thermodynamic singularities at the transition point is thus determined by the behavior of the function \( \sigma(x) \) (i.e., by the logarithm of the number of configurations for a given short-range order \( x \)) near the point \( x_C \).

Thus, for example, the Landau phenomenological theory of second-order phase transitions corresponds in this aspect to assuming that the function

\[ \sigma'(x) = \psi(\Theta), \quad \sigma(x) \equiv \sigma(x, \bar{x}(\Theta)) \]
\( \sigma(x, \eta) \) is analytic in the vicinity of the point \( \eta = 0, x = x_0 \). Yet in the two-dimensional Ising model, the only case that has been accurately calculated, the function \( \sigma(x, \eta) \) has a logarithmic singularity at the point \( \eta = 0 \); the character of the singularity in the three-dimensional case has not yet been explained.

It is quite obvious that in accordance with the symmetry of the problem there are two equivalent possibilities of preferred filling of the sublattices with atoms A and B, corresponding to the values \( \pm \eta \) of the order coefficient. At the initial ordering stage, when essentially the short-range order relaxation has already taken place, the appearance of a structure \( +\eta \) or \( -\eta \) is perfectly accidental and regions with both signs, \( \pm \eta \), should exist at different points at the crystal, thus excluding the mechanism of homogeneous ordering over the entire volume of the crystal.

### 2. Kinetics of Ordering in the Presence of Two Equivalent Structures \((\pm \eta)\)

We shall attempt to trace the kinetics of the reorganization of an initially disordered system (for example, a solution AB), which has been placed, say by hardening, in conditions for which an ordered structure represents equilibrium.

In accordance with the statements made above, the short-range order is essentially relaxed over the entire volume of the crystal within microscopic time (on the order of the time of heterodiffusion over atomic distances). As a result, the ordering of each microscopic infinitesimally small volume element is either \( +\eta \) or \( -\eta \). The kinetics of this first stage is very difficult to describe and its details are apparently quite individualized. From the macroscopic point of view, however, this process occurs instantaneously and is not decisive in the formation of the ordered structure. The "initial" state in the macroscopic picture is, as follows from the foregoing, a state for which each infinitesimal volume element of the crystal can have with equal probability an ordered structure \( +\eta \) or \( -\eta \), and there is no correlation between neighboring elements. Since, however, neighboring elements with identical structures must be regarded as a single ordered domain, it is easy to understand that all of space will consist predominantly of mutually intertwined web-like regions with \( +\eta \) or \( -\eta \); the total volumes of the regions of each type should be equal in the mean.

A two-dimensional model of such a structure is shown for the isotropic case in Fig. 1a. The characteristic linear dimension of this structure (which determines both the average diameter of the "filaments" or "islands" and their curvature) is the average radius of curvature of the boundary between the regions. The radius of spatial correlation \( R \) of the ordered regions is obviously of the same order of magnitude.* It is clear that to be able to speak of ordered regions this characteristic dimension should be considerably greater than atomic; however, in accord with the foregoing, we shall assume that in the macroscopic picture the initial correlation radius \( R \) is equal to zero.

Since the structures \( \pm \eta \) are thermodynamically equivalent, there are no reasons for regions of one type to grow predominantly at the expense of the other. The kinetics of ordering should constitute "swelling" of the web-like regions of both types and an increase in the correlation radius as the boundaries of these regions move in such a way that the total volumes become of equal magnitude. The "moving force" displacing the boundaries and swelling the regions is the surface energy on the interfaces between the regions.

As is well known, the change in thermodynamic potential accompanying the displacement \( \delta n \) of a unit area of phase boundary in the normal direction (in the isotropic case) is

\[
\delta \Phi = (\varphi_2 - \varphi_1) \delta n + \frac{2x}{r} \delta n, \quad \frac{2}{r} = \frac{1}{r_1} + \frac{1}{r_2}. \tag{4}
\]

\( r_1 \) and \( r_2 \) —principal radii of curvature on the boundary; \( \varphi_1 \) and \( \varphi_2 \) —thermodynamic potentials per unit phase volume. In our case there is no volume term \( (\varphi_2 - \varphi_1) \delta n \) and \( \delta \Phi \) is determined by the change in the surface energy

\[
\delta \Phi/\delta n = 2\alpha/r. \tag{5}
\]

Since \( r \gg a \) (a —lattice parameter), the rate of motion of the boundary \( \delta \eta/\delta t \) is proportional in first approximation to \( \delta \Phi/\delta n \sim 1/r^2 \):

\[
\delta \eta/\delta t = -x/r. \tag{6}
\]

To estimate the constant \( \kappa \) it is necessary to take it into account that (5) is the normal force

*We can define the correlation radius \( R \) by means of the probability \( q(\Delta x) = \Delta x/R \) that two points an infinitesimal distance \( \Delta x \) apart have opposite signs of \( \eta \) (i.e., are separated by an interface).
acting on a unit area of the boundary; on the other hand, to move a unit boundary area over an atomic distance in a normal direction it is necessary to perform \( \sim |\eta|/a^2 \) acts of relative transfer of pairs of neighboring atoms \( AB \) on the boundary in a suitable direction (a —lattice parameter, the long-range order coefficient \( \eta \) is defined for the solution \( AB \) in the usual fashion as

\[
\eta = (N_A^I - N_A^II)/N_A;
\]

\( N_A^I \) and \( N_A^II \) are the numbers of \( A \) atoms in each of the equivalent sublattices. Therefore the rate of motion of the boundary is expressed in terms of the diffusion mobility \( u \) of the solid-solution atoms*

\[
\frac{dn}{dt} \sim \frac{a^2}{2|\eta|} u \frac{2a}{r^2}.
\]  \( (7) \)

Comparing (6) and (7) and taking into account the Einstein relation between the mobility and the diffusion coefficient, \( u = D/kT \), we obtain the estimate

\[
x \sim a^2 D/|\eta| kT.
\]

(Here \( D \) —diffusion coefficient connected with the mutual exchange of the neighboring atoms \( AB \)). Finally, the interphase surface tension \( \alpha \) can be expressed in terms of the displacement energy \( v \) (see the first footnote) and the long-range order coefficient \( \eta \) by means of the estimate \( \alpha a^2 \sim v\eta^2 \). This yields ultimately

\[
x \sim D/|\eta| v/ kT.
\]  \( (8) \)

In principle, knowing the initial form of the surface we can determine its time variation from (6).† However, it is in general not necessary to solve so complicated a problem, since we are interested only in averaged characteristics, and primarily the average radius of curvature \(|\tilde{\Gamma}| \sim R\). From dimensionality considerations it is clear that \( \delta n \sim \pm \delta r \) and consequently we can write, in order of magnitude,

\[
\delta r / \delta t = \pm x / r.
\]  \( (9) \)

The minus sign in (8) corresponds to the “erosion” of the convex region (see, for example, Fig. 2a), while the plus sign corresponds to a straightening of the boundary (Fig. 2b). For our purpose there

\* The dependence on \( \eta \) is given in this and following formulas only qualitatively, i.e., only in order of magnitude, for \( \eta < 1 \) and \( \eta \approx 1 \).

† Thus, for example, in the two-dimensional case, if \( y = y(x, t) \) is the equation of the boundary at the instant \( t \) and \( y(x, 0) = y_0(x) \), then the determination of \( y(x, t) \) reduces, in accordance with (7), to a solution of the equation

\[
y_t = w y_{xx} / (t + y_x^2), \quad y|_{t=0} = y_0(x).
\]

is no need for a more detailed study of the character of the deformation of the boundaries; in particular, in the three-dimensional case discontinuities in the “neck” will also fit qualitatively within this scheme.

Accordingly, in the first case \( r^2 = r_0^2 - \kappa t \), i.e., all the “inclusions” with maximum dimensions \( r_0 < \kappa t \) should vanish, with overwhelming probability, after a time \( t \).

In the second case the radius \( r \) increases, \( r^2 = r_0^2 + \kappa t \). In both cases this means that the characteristic dimensions of the remaining regions (correlation radius or average radius of curvature) increase as*

\[
R \approx V^{1/2} (R_0 = 0).
\]  \( (10) \)

A progressive picture of the growth of the regions via straightening of the boundaries and erosion of the “inclusions,” using a two-dimension example, is shown in Fig. 1. When the dimensions of the regions become comparable with the dimensions of a single crystallite, the conditions on the crystallite boundaries may bring about a predominant growth of one of the regions, and this leads in final analysis to a single ordering over the entire crystallite.

It should be pointed out that the initial non-nucleation stage of relaxation of the short-range order (on going through the Curie-point line) can be expected with certainty only when the interval between the initial value of the short-range order \( x_0 \) and the final equilibrium value \( \bar{x}(\theta) \) is not too large, i.e., when the free energy \( F(x) = vz - \theta(x) \) [see (1) and (3)] in this interval is a monotonic function of \( x \); in this case the possibility of transition from \( x_0 \) to \( \bar{x} \) via a continuous series of states is assured (although in principle a transition through a different series of intermediate non-equilibrium states is also possible).

In the case of the nucleation mechanism, the regions grow as \( R \sim t \), since the rate \( \delta n / \delta t \sim \delta \Phi / \delta n \) contains a volume part that is independent of \( r (\varphi_2 - \varphi_1) \) in Eq. (4).

*Relation (10) can be derived from (6) directly by dimensionality considerations; the arguments given above are aimed at explaining the swelling mechanism.
In the case of the two equivalent types of ordering $\pm \eta$, however, even in the presence of a first-order discontinuous transformation, the regional structure described above will arise at a later stage of the process, after all the ordered portions formed as a result of the growth of the nuclei have come in contact. Further increase in the ordered regions will continue as in the case of a second-order transformation, the only difference being that the initial correlation radius $R_0$ is no longer zero but equal to the average distance between nuclei.

The described ordering pattern is, of course, essentially qualitative, primarily because of the oversimplified assumption that the surface tension $\alpha$ and the kinetic coefficient $\kappa$ have no anisotropy.

3. POSSIBILITY OF FORMATION OF A “DOMAIN STRUCTURE” DURING ORDERING

An essentially different situation can arise when the number of thermodynamically equivalent methods of realizing the ordered structure is $p \geq 4$. This is precisely the situation in many antiferromagnets, where $p = 4$ and $p = 6$. In this case the initial relaxation stage does not lead to the formation of intertwined web-like regions, since each small element with ordering $\eta_k$ ($k = 1, \ldots, p$) is surrounded, with high probability, by elements of several different types $\eta_l$. This means that the initial structure of the ordered domain is similar to the structure of a polycrystalline body, and the role of the individual crystal is played by the region with the given type of order $\eta_k$. Figure 3a shows schematically such a two-dimensional structure with $p = 3$ (such a structure occurs in the two-dimensional case even when $p = 3$).

Since each of the structures $\eta_k$ is thermodynamically equivalent, any further relaxation reduces, as before, to a movement of the boundaries, leading to a decrease in the surface energy. This brings about a gradual straightening of the region boundary; however, the junction of three regions and, most important, the junction of four regions presents an essentially different situation. The conditions for the minimum surface energy call for definite angles to arise along the lines of junction and on the junction points. The first condition makes the displacement of the junction lines very difficult once the optimal angles are attained. The second condition makes in fact impossible any displacement of the junction point after the optimal angles on all the junction points have already been attained in a finite macroscopic volume (see Fig. 3b). Such a displacement without an external stimulus calls for fluctuations on a macroscopic scale and has of course a low probability.

This should therefore cause the regions of ordering to acquire a domain structure which is not the most favorable from the thermodynamic point of view but is stable from kinetic considerations. Such a domain structure is not similar to the domain structure of ferromagnets, where the presence of the spontaneous moment and the field associated with it make the domain thermodynamically stable.

A similar situation should obtain in antiferromagnets without weak ferromagnetism, however, in the case of structures with $p = 4$ and $p = 6$ (for example, $\text{UO}_2$ or $\text{MnO}$), and the domain structure of such antiferromagnets should be of kinetic origin. Its annihilation, in accord with the foregoing, can be brought about only by external factors (for example deformation), which make some of the $\eta_k$ structures thermodynamically preferred.

An essential modification in the situation can be brought about by a sharp anisotropy in the rates of the reorganization processes. Thus, for example, the limiting case of lamellar growth should result in so-called crystals of alternating structure, consisting of alternating differently ordered layers. In this case stratified “domain” structure arises even if there are only two ordering possibilities.

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