

01 Jan 1975

Analogy Between Spinodal Decomposition And Martensitic Transformation

Tetsuro Suzuki

Missouri University of Science and Technology

Manfred Wuttig

Missouri University of Science and Technology

Follow this and additional works at: https://scholarsmine.mst.edu/phys_facwork

 Part of the [Metallurgy Commons](#), and the [Physics Commons](#)

Recommended Citation

T. Suzuki and M. Wuttig, "Analogy Between Spinodal Decomposition And Martensitic Transformation," *Acta Metallurgica*, vol. 23, no. 9, pp. 1069 - 1076, Elsevier, Jan 1975.

The definitive version is available at [https://doi.org/10.1016/0001-6160\(75\)90111-X](https://doi.org/10.1016/0001-6160(75)90111-X)

This Article - Journal is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Physics Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.

ANALOGY BETWEEN SPINODAL DECOMPOSITION AND MARTENSITIC TRANSFORMATION*

TETSURO SUZUKI† and M. WUTTIG‡§

The translation of the theory developed for the spinodal decomposition of a supercooled alloy to the language appropriate for the martensitic transformation is carried out. In the spinodal theory, the stability of the alloy with respect to the composition fluctuation is examined, while in the present theory the stability of the crystal with respect to the shear displacement fluctuation, the transverse phonon, is studied. The analogy to the spinodal theory requires the revival of the strain gradient energy term or the couple stress term, the presence of which has been a subject of controversies for a long time since Laval.

A simple model lattice with the bond bending and stretching interaction is constructed as an instrument to study numerically the stability of the lattice with respect to the shear displacement fluctuation. The results of the numerical investigation indicate that the simultaneous presence of the anharmonic strain energy term and the strain gradient energy term is required to trigger the martensitic transformation.

ANALOGIES ENTRE LA DECOMPOSITION SPINODALE ET LA TRANSFORMATION MARTENSITIQUE

On a traduit la théorie de la décomposition spinodale d'un alliage surfondu en des termes adaptés à la transformation martensitique. Dans la théorie de la décomposition spinodale, on étudie la stabilité de l'alliage par rapport aux fluctuations de composition, alors que dans cette théorie, on étudie la stabilité du cristal par rapport aux fluctuations de la cission, c'est à dire aux phonons transverses. L'analogie avec la théorie de la décomposition spinodale implique que l'on reprenne en compte le terme du gradient de déformation ou de la contrainte couplée dans l'énergie, terme dont la présence avait fait l'objet de nombreuses controverses depuis Laval.

On construit un modèle simple de réseau avec des liaisons de flexion et de tension pour étudier numériquement la stabilité du réseau par rapport aux fluctuations de cission. Les résultats des calculs numériques montrent que la présence simultanée dans l'énergie des termes de déformation anharmonique et de gradient de déformation est nécessaire pour déclencher la transformation martensitique.

ANALOGIE ZWISCHEN SPINODALER ENTMISCHUNG UND MARTENSITISCHER UMWANDLUNG

Die für die spinodale Entmischung unterkühlter Legierungen entwickelte Theorie wird auf die martensitische Umwandlung übertragen. In der Spinodalentheorie wird die Stabilität der Legierung in Bezug auf Kompositionsfluktuationen untersucht; in der vorliegenden Theorie wird dagegen die Stabilität des Kristalls in Bezug auf die Scherungsfluktuationen, nämlich die transversalen Phononen, betrachtet. Die Analogie zur spinodalen Theorie erfordert die Wiederbelebung des Energieterms des Dehnungsgradienten oder Paarspannungsterms, dessen Existenz seit Laval Gegenstand von Kontroversen ist.

Es wird ein einfaches Modellgitter mit Biege- und Dehnungswechselwirkung konstruiert, um die Stabilität des Gitters in Bezug auf die Scherungsfluktuationen numerisch untersuchen zu können. Die Ergebnisse der numerischen Untersuchung zeigen, daß die gleichzeitige Gegenwart des anharmonischen Dehnungsenergieterms und des Energieterms des Dehnungsgradienten erforderlich ist, um die martensitische Umwandlung auszulösen.

1. INTRODUCTION

The purpose of the present paper is to present the translation of the theory developed for the spinodal decomposition of a supercooled alloy to the language appropriate for the martensitic transformation. The theory developed by Hillert⁽¹⁾ and Cahn⁽²⁾ aims at establishing a relationship between the two modes of the decomposition process of binary alloy, i.e. the fluctuation mechanism and the nucleation and growth mechanism. The present model is based on the analogy between the spinodal decomposition and the martensitic transformation and is developed to serve the same purpose for the relationship between the two mechanisms of the martensitic transformation, i.e. the

soft phonon mechanism⁽³⁻⁶⁾ and the nucleation and growth mechanism.⁽⁷⁾

As shown by the work of Hillert and Cahn, the spinodal decomposition can be understood as the phenomenon associated with the instability of composition fluctuation in supercooled alloys. The martensitic transformation can be described as the phenomenon associated with the instability of the parent lattice with respect to a finite deformation in supercooled metals and alloys. In this paper, the authors wish to draw attention to the close analogy between the spinodal decomposition and a certain feature of the martensitic transformation. The qualification 'a certain feature' has to come in because of the following situation. The treatment of the spinodal decomposition by Hillert and Cahn is essentially macroscopic in the sense that the free energy density is defined in terms of the thermodynamical variables, the local concentration of the component and its gradient, without reference to the

* Received May 4, 1974; revised February 14, 1975.

† Department of Physics, Yokohama City University, Yokohama 236, Japan.

‡ Department of Metallurgical Engineering, University of Missouri at Rolla, Rolla, Missouri 65401, U.S.A.

§ Supported by the American Iron and Steel Institute, Project No. 62-261.

atomic structure of the alloy. If we wish to develop a close analogy between the spinodal decomposition and the martensitic transformation, we have to restrict our discussion to the features of the martensitic transformation which can be defined by a macroscopic quantity, i.e. the deformation parameter which describes the deformation of the unit cell. In short, the present treatment is limited to the examination of the stability of the acoustic branches of the phonons.

2. ANALOGY BETWEEN SPINODAL DECOMPOSITION AND MARTENSITIC TRANSFORMATION

2.1 Deformation parameter

In this section, a parameter ε , which describes the progress of the deformation process of the parent phase during the martensitic transformation, is defined. The Kurdjumov-Sachs⁽⁸⁾ or Nishiyama⁽⁹⁾ relationship between the lattice vectors $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ of the martensitic phase and the lattice vectors $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ of the parent phase suggests the linear transformation T ,

$$\mathbf{b}_i = T\mathbf{a}_i \quad (i = 1, 2, 3), \quad (1)$$

between $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ and $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$. This transformation becomes unique if the assumption of the smallest distortion proposed by Jaswon and Wheeler⁽¹⁰⁾ is made. They show that the linear transformation thus determined is very favourable in explaining the observed habit plane in iron-carbon alloys. More elaborate and accurate procedures to determine the linear transformation are described by Wayman,⁽¹¹⁾ Christian⁽¹²⁾ and others. It is assumed here that the linear transformation T is already given by one of these procedures.

We now introduce a scalar parameter describing the progress of the transformation process as follows:

$$\mathbf{b}_i' = \mathbf{a}_i + \varepsilon(T\mathbf{a}_i - \mathbf{a}_i) \quad (i = 1, 2, 3). \quad (2)$$

When $\varepsilon = 0$, the three vectors $\mathbf{b}_1', \mathbf{b}_2', \mathbf{b}_3'$ represent the original undeformed unit cell. When $\varepsilon = 1$, these three vectors represent the unit cell of the martensitic phase. It should be noted that there is no *a priori* reason that the intermediate phase described by $\mathbf{b}_1', \mathbf{b}_2', \mathbf{b}_3'$ of equation (2) should give the actual crystal structure during the transformation process. For example, the martensitic transformation of sodium starts as a pure shear deformation in the (110) plane in the [110] direction of the body centered cubic phase.⁽¹³⁾ The linear transformation as defined by equation (1) does not represent this shear deformation. It is thus necessary to take into account the functional dependence of T on ε

$$\mathbf{b}_i'(\varepsilon) = \mathbf{a}_i + \varepsilon\{T(\varepsilon)\mathbf{a}_i - \mathbf{a}_i\} \quad (i = 1, 2, 3). \quad (3)$$

In the limit of $\varepsilon = 1$, $T(\varepsilon)$ should be equal to T in equation (1). On the other hand, in the limit of $\varepsilon = 0$, $T(\varepsilon)$ should represent the pure shear deformation in the (110) plane in the [110] direction for the martensitic transformation in sodium. Theoretical investigations of the functional dependence of $T(\varepsilon)$ on ε may be carried out by finding the minimum free energy path between the parent and martensitic phases. In this paper, $T(\varepsilon)$ is assumed to be known at least in the limit of $\varepsilon = 0$. Then, the Gibbs free energy per unit undeformed volume of the crystal $g(\varepsilon)$ can be written down for the hypothetical uniform deformation, which is specified by the parameter ε as follows:

$$g(\varepsilon) = C_2\varepsilon^2 + C_3\varepsilon^3 + C_4\varepsilon^4 + \dots \quad (4)$$

As the parameter ε specifies the uniform deformation of the crystal, the expansion coefficients C_2, C_3 and C_4 are given in terms of the linear combination of the second order elastic constants, second and third order elastic constants, and second, third and fourth order elastic constants, respectively. The free energy density $g(\varepsilon)$ given by equation (4) should have two minima, one corresponding to the undeformed lattice ($\varepsilon = 0$, parent lattice) and another one corresponding to the deformed lattice ($\varepsilon = 1$, martensitic lattice). The latter minimum should be deeper than the former at the starting temperature of the martensitic transformation M_s .

2.2 Expression for free energy

The free energy G of a system which undergoes the phase transition is expanded in terms of a proper order parameter η , in the vicinity of the transition point, as follows:⁽¹⁴⁾

$$G = A\eta^2 + B\eta^3 + C\eta^4 + \dots \quad (5)$$

where the expansion coefficients A, B and C are functions of the thermodynamical variables such as pressure and temperature. However, in the vicinity of the transition point, the variation of A is most important in determining the overall characteristics of the dependence of the free energy G . Assuming B and C remain constant, the variation of G against the order parameter η is plotted in Fig. 1. If the cubic coefficient B is zero, the value of the order parameter which corresponds to the minimum of the free energy G will change continuously, as the sign of A changes from plus to minus, as shown in Fig. 1(a). If the coefficient B is not zero, the free energy G possesses two minima and the discontinuous transition from one value of the order parameter ($\eta = 0$) to another ($\eta = \eta_1$) occurs at a certain value of the thermodynamical variables, as shown in Fig. 1(b). The

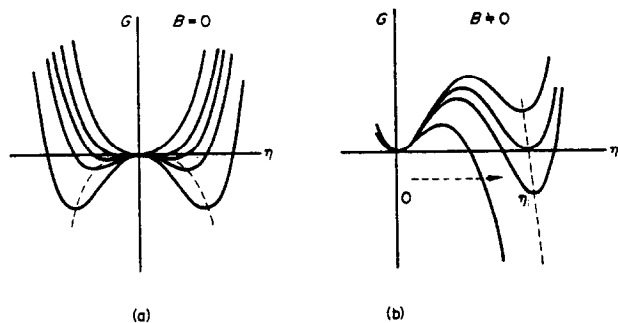


FIG. 1. The free energy G as a function of the order parameter is shown for different values of the second order expansion coefficient A , keeping B and C constant. (a) In the second order phase transformation ($B = 0$), the value of the order parameter η , which corresponds to the minimum of the free energy G , changes continuously with the decrease of A . (b) In the first order phase transformation ($B \neq 0$), it jumps over discontinuously from one value ($\eta = 0$) to a finite value ($\eta = \eta_1$).

coexistence of two different phases, the transformed phase ($\eta = \eta_1$) and the untransformed phase ($\eta = 0$), is another important characteristic of the first order phase transition. The first order transition is characterized by (1) the discontinuity of the change of the value of the order parameter (and 2) the non-uniformity of the progress of the transition process in the system

An expression which explicitly takes into account the dependence of the order parameter on the position has already been developed by Cahn, in his systematic study of the spinodal decomposition of a binary alloy. Here, the relevant order parameter is the composition c of the alloy. Cahn⁽²⁾ writes down the Helmholtz free energy of an alloy in terms of the Helmholtz free energy per unit volume $f(c)$ and of the term $\chi(\nabla c)^2$, which expresses the incipient surface energy due to the introduction of the composition fluctuation, as follows:

$$F = \int [f(c) + \chi(\nabla c)^2] dV. \quad (6)$$

The free energy G of a system which undergoes the first order phase transition is expected to be described by an analogous expression,

$$G = \int [g(\eta) + \gamma(\nabla \eta)^2] dV \quad (7)$$

instead of equation (5), which is valid only for the second order phase transition ($B = 0$). Here, $g(\eta)$ is the density of the free energy instead of the total free energy of the system.

We seek to find out the literal translation of the above expression equation (6) applicable to the martensitic transformation or the proper interpreta-

tion of the general expression equation (7) suitable to the martensitic transformation. The translation of the composition c to the deformation parameter ϵ looks self-evident. The Gibbs free energy per unit volume of the undeformed crystal is already given by equation (4) in terms of the elastic constants and the deformation parameter ϵ . Then, we are confronted with the problem of finding the meaning of the term which is given in terms of the gradient of the deformation or strain parameter. The standard elasticity theory does not include the strain gradient energy term, although the presence of such term has been a subject of controversies for a long time since Laval⁽¹⁵⁾ brought up the issue in 1951. Truesdell⁽¹⁶⁾ has insisted that there is no rational reason to reject the presence of such a term, which implies the presence of the couple stress besides the ordinary stress in the crystal. The importance of such a term in the problems of the molecular crystal and of the crystal surface was pointed out by Krumhansl,⁽¹⁷⁾ Toupin and Gazis,⁽¹⁸⁾ respectively.

In the martensitic transformation, which accompany the appreciable deformation of the unit cell of the crystal, the transformation process is known to proceed with the propagation of the distinct interface between the deformed (martensitic) phase and the undeformed (parent) phase. Accordingly, the introduction of the incipient surface energy seems to be permissible and at the same time mandatory. Thus, the literal translation of equation (6) or (7) to the expression applicable for the total Gibbs free energy G of the crystal, which will undergo the martensitic transformation, may be given as follows:

$$G = \int [g(\epsilon) + \gamma(\nabla \epsilon)^2] dV \quad (8)$$

where $g(\epsilon)$ is already given by equation (4).

3. MODEL

3.1 A model lattice with strain gradient energy

A model of the bond stretching and bond bending used by Krumhansl⁽¹⁷⁾ for a molecular crystal is adopted here for the study of the martensitic transformation, because this model seems to be the simplest possible model which provides an expression for the free energy containing the usual strain energy term as well as the strain gradient energy term.

The atoms in this model crystal are considered to have two kinds of interactions with their neighbors, one being the interaction dependent solely on the distance between them (bond stretching interaction), and the other one the interaction dependent solely

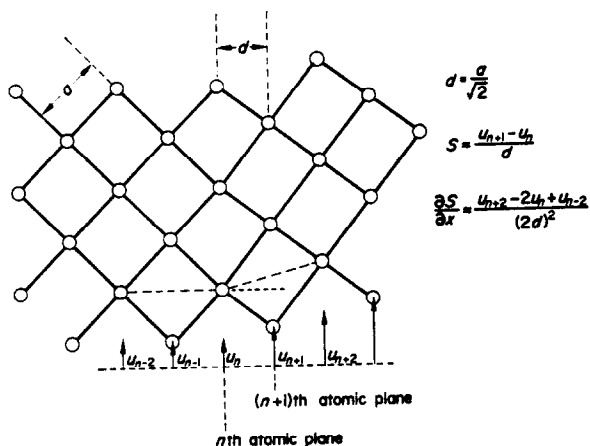


FIG. 2. A simple atomic model of the crystal, in which atoms have two kinds of interactions: (1) the bond stretching interaction with the nearest neighbors and (2) the bond bending interaction with the next nearest neighbors. The martensitic transformation in this model crystal is accomplished by a planar shear deformation.

on the angle between two bonds connecting opposite neighbors of a particular atom (bond bending interaction). It is assumed that the two body interaction (bond stretching interaction) with nearest neighbors in the model crystal represents the strong interaction between neighboring atomic cores in metals and the three body interaction (bond bending interaction) with next nearest neighbors represents the non-central interaction in metals. The atoms are arranged in a simple cubic lattice with the lattice parameter a as depicted in Fig. 2. The increase of the interaction energy is calculated for the planar shear deformation as indicated by the arrows in Fig. 2.

The increase of the sum of the two body interaction energy of an atom in the n th atomic plane with its nearest neighbor atoms in the $(n + 1)$ th atomic plane is expanded in terms of the shear displacements

$$V_n^{(2)} = \frac{p}{2} (u_{n+1} - u_n)^2 + \frac{b}{3} (u_{n+1} - u_n)^3 + \frac{c}{4} (u_{n+1} - u_n)^4, \quad (9)$$

where p , b and c represent harmonic, third order and fourth order anharmonic force constants, respectively. The leading term in the increase of the three body interaction energy of the same atom with its two next nearest neighbors is given by

$$V_n^{(3)} = \frac{q}{2} (u_{n+2} + u_{n-2} - 2u_n)^2, \quad (10)$$

where q represents a force constant associated with the bond bending interaction between next nearest

neighbors. Equations (9) and (10) yield the total increase of the energy V of the crystal due to the planar shear deformation,

$$V = \sum_n (V_n^{(2)} + V_n^{(3)}), \quad (11)$$

where the summation is carried over all atoms in the unit undeformed volume. When the deformation is very gradual, i.e. in the limit of the long wave-length, the differences of the displacement in equations (9) and (10) can be approximated in terms of the strain and its gradient as follows:

$$\begin{aligned} u_{n+1} - u_n &\simeq \frac{\partial u}{\partial x} d + \frac{1}{2} \frac{\partial^2 u}{\partial x^2} d^2 + \dots \\ &= Sd + \frac{1}{2} \frac{\partial S}{\partial x} d^2 + \dots, \end{aligned} \quad (12)$$

$$\begin{aligned} u_{n+2} + u_{n-2} - 2u_n &\simeq 4 \frac{\partial^2 u}{\partial x^2} d^2 + \dots \\ &= 4 \frac{\partial S}{\partial x} d^2. \end{aligned} \quad (13)$$

Here, d represents the distance between the neighboring atomic planes, i.e. $d = a/\sqrt{2}$. Hence, in the long wave-length limit, equation (11) reduces to

$$\begin{aligned} V &\simeq \int \left(\frac{p}{2d} \cdot S^2 + \frac{b}{3} \cdot S^3 + \frac{c}{4} \cdot S^4 \right. \\ &\quad \left. + \frac{d}{2} \left(\frac{p}{4} + 16q \right) \left(\frac{\partial S}{\partial x} \right)^2 \right) dV. \end{aligned} \quad (14)$$

It is assumed here that the dependence of the increase of the Gibbs free energy of the model crystal due to shear deformation on the temperature can be incorporated by supposing a proper temperature dependence of the force constants p , b , c and q , a simplified quasi-harmonic approximation.⁽¹⁹⁾ Then, it can be seen that the expression for the interaction energy of the atomic model given by equation (11) is formally equal to the expression for the free energy given by equation (8) derived from the analogy with the spinodal decomposition in the limit of long wave-length. As it is understood that the martensitic transformation in the model crystal is accomplished by a planar shear deformation depicted in Fig. 2, the strain S in equation (14) is proportional to the deformation parameter ϵ in equation (8). For the choice of parameters $b/p = 2.5$ and $c/p = 1.0$, the free energy of this model crystal has two minima, one corresponding to the undeformed state and the other corresponding to the deformed (martensitic) state.

3.2 Stability with respect to displacement fluctuations

The stability of the model crystal described in the previous section† is studied numerically with respect to the fluctuation of the displacement of various wave-length in the same way as in the discussions of the spinodal decomposition by Cahn. The fluctuation of the shear displacement in the present model is expressed by a normal mode transverse wave

$$u_n = A \sin(\omega t - knd). \quad (15)$$

The equation of motion for the transverse vibration of an atom in the n th atomic plane in Fig. 2 is given by:

$$\begin{aligned} m \frac{\partial^2 u_n}{\partial t^2} &= p(u_{n+1} - 2u_n + u_{n-1}) \\ &\times \left[1 + \frac{b}{p}(u_{n+1} - u_{n-1}) + \frac{c}{p}\{(u_{n+1} - u_n)^2 \right. \\ &\left. + (u_{n+1} - u_n)(u_n - u_{n-1}) + (u_n - u_{n-1})^2\} \right] \\ &- q(u_{n+4} - 4u_{n+2} + 6u_n - 4u_{n-2} + u_{n-4}), \quad (16) \end{aligned}$$

where m is the mass of an atom in the model crystal. Inserting the displacement given by equation (15) into (16) and neglecting the anharmonic term, we obtain the relationship between the frequency and the wave-vector of the phonon

$$m\omega^2 = 4p \sin^2 \frac{k \cdot d}{2} + 16q \sin^4 k \cdot d. \quad (17)$$

This expression gives the phonon dispersion curve for the small amplitude transverse vibration in the model crystal depicted in Fig. 2.‡ The small amplitude dispersion relationship of equation (17) is plotted in Fig. 3 for the values of the ratio q/p used in the numerical investigation of the following section. As far as ω in Fig. 3 is real, the model crystal is stable with respect to small amplitude vibrations. The

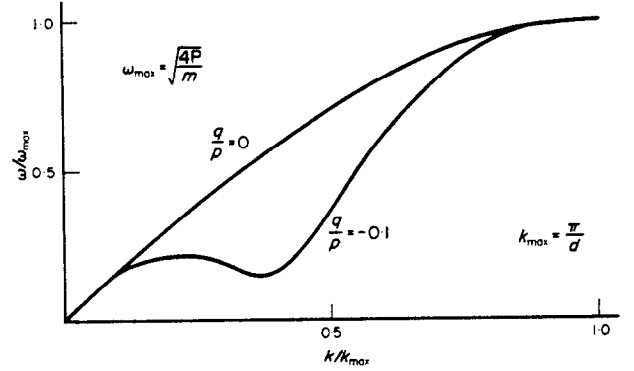


FIG. 3. The small amplitude dispersion relationship for the transverse phonons in the model crystal shown in Fig. 2 is shown for the values of the ratio q/p used in the numerical investigation shown in Fig. 4.

condition that the right hand side of equation (17) is positive can be interpreted as the martensitic equivalent of the stability criterion of a binary alloy, which is given by:

$$\frac{\partial^2 f}{\partial c^2} + 2\chi k^2 > 0 \quad (18)$$

for the small amplitude composition fluctuation

$$c - c_0 = A \cos kx. \quad (19)$$

However, the assumption of the small amplitude is not necessarily adequate for the displacement fluctuation in the lattices. The average kinetic energy of the lattice vibration associated with a normal mode of the lattice vibration given by equation (15) is estimated by:

$$\sum_{n=1}^N \frac{1}{2} m \cdot \overline{\dot{u}_n^2} = \frac{1}{2} m \cdot A^2 \cdot \omega^2 \cdot N. \quad (20)$$

Here, N is the number of atoms involved in the normal mode vibration. Because the average kinetic energy of an oscillator is equal to the total energy of an oscillator, which is given by the Bose-Einstein statistics,

$$\frac{1}{2} m \cdot A^2 \cdot \omega^2 \cdot N = \frac{\hbar\omega}{2} \cdot \frac{1}{\exp(\hbar\omega/kT) - 1}. \quad (21)$$

Especially for the lower frequency mode, it can be assumed that $\hbar\omega \ll kT$. With this approximation, the amplitude of a normal mode is estimated as

$$A = \left(\frac{2kT}{m \cdot \omega^2 \cdot N} \right)^{1/2}. \quad (22)$$

It is seen here that the amplitude of a normal mode of the lattice vibration is proportional to the inverse square root of the number of atoms N involved in the normal mode. Accordingly, the amplitude of the

† In the more realistic model for the martensitic transformation than the present one, the deformation parameter c should depend on a planar shear as well as dilatational deformation parameters. At the same time, equation (16) should also include the anharmonic coupling term between the shear deformation and dilatational deformations. The present model represented by equation (16) as it stands is only the simplest one to study the significance of the simultaneous presence of the anharmonic strain energy and the strain gradient energy.

‡ The phonon dispersion curve in Fig. 3 is for the shear wave propagating in the [110] direction of the model crystal in Fig. 2. For the shear wave in other directions of propagation, the dip in the dispersion curve due to negative value of q appears in a different area of the Brillouin zone. However, the dip always appears in some area away from the center of the Brillouin zone ($k = 0$), because the strain gradient energy comes in only when there is a non-uniformity ($k \neq 0$) of the strain.

normal mode which extends throughout the entire crystal is appreciably smaller compared with that of the localized normal mode of the same frequency. The spatial extent of some of normal modes in the actual crystal is inevitably confined because of the presence of various kinds of lattice defects, such as crystal surfaces, grain boundaries, dislocations and various point defects.

The amplitude of the normal mode for $N = 10^{22}$ and $\omega = 2\pi \times 10^6/\text{sec}$ is estimated to be the order of 10^{-14} cm at room temperature. If N is limited to 10^{10} due to the presence of some defects, the amplitude will be enhanced to 10^{-8} cm for the same angular frequency of the normal mode. Hence, it is expected that the amplitude of normal mode vibration is not uniform throughout the crystal, but is enhanced near the defects in the crystal. This expectation seems to be supported, at least for crystal surfaces, by the results of experimental⁽²⁰⁾ and theoretical⁽²¹⁾ investigations. Accordingly, the stability of the lattice must be studied with respect to the finite amplitude vibration, retaining the third and fourth order anharmonic terms in equation (16). The study of the stability of the lattice with respect to a special finite amplitude vibration as to produce omega phase has recently been carried out by Cook.^(22,23)

3.3 Triggering of martensitic transformation

The temporal evolution of the initially sinusoidal lattice vibration in the model lattice specified by equation (16) is studied numerically by use of an integration subroutine program for simultaneous differential equations available by the code RKGNI at the Tokyo University Computer Center. Although the details of the computation will be published elsewhere, the relevant results of the computation are summarized in Fig. 4. In each map in Fig. 4, the horizontal direction corresponds to the coordinates of atoms, i.e. the atomic plane numbers in Fig. 2, while the vertical direction indicates the shear displacement of atoms in each atomic plane. The computation is carried out for the model lattice consisting of 63 atomic planes with the periodic boundary condition. Accordingly, the atom at the left end of each map in Fig. 4 is actually the same atom at the right end of the map. The amplitude used in the computational results shown in Fig. 4 corresponds to the maximum displacement equal to two interatomic spacings. The time separation between the consecutive maps corresponds approximately to 1.3×10^{-12} sec.

The role of the anharmonic strain energy term in breaking up a sinusoidal wave form is clearly seen in Fig. 4(b). But it does not trigger the martensitic

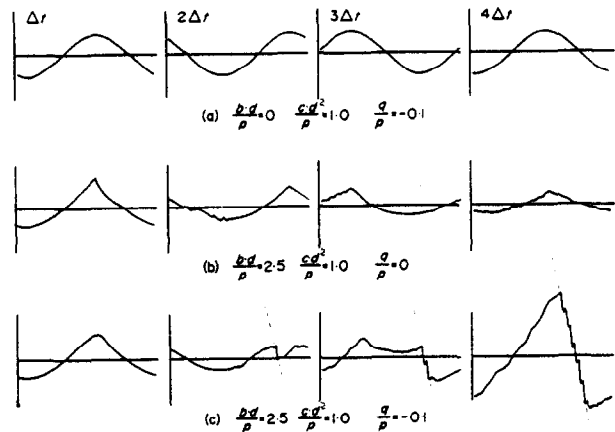


FIG. 4. The evolution of the initially sinusoidal lattice wave is shown for (a) a dispersive ($q/p = -0.1$) nearly harmonic ($b/p = 0$) lattice, (b) a weakly dispersive ($q/p = 0$) anharmonic ($b/p = 2.5$) lattice and (c) a dispersive ($q/p = -0.1$) anharmonic ($b/p = 2.5$) lattice. The time separation between consecutive maps is $\Delta t = 1.3 \times 10^{-12}$ sec.

transformation. On the other hand, Fig. 4(a) shows that the contribution from the strain gradient energy term without the third order anharmonic strain energy term does not induce any appreciable change in the initial sinusoidal wave form. Figure 4(c) shows that the triggering of the martensitic transformation is possible only when the anharmonic strain energy term and the strain gradient energy term are simultaneously present. Because the martensitic transformation in the present model is assumed to be accomplished through a finite simple shear deformation, the group of atoms displaced along the tilted line in Fig. 4(c) represents an embryo of the martensitic phase.

Furthermore, with a half of the amplitude used in the computation shown in Fig. 4, no evolution of the wave form into the martensitic embryo is observed for the same values of the anharmonic and strain gradient energy terms as in Fig. 4(c) during the time interval up to ten times of that shown in the same figure. This indicates that the triggering mechanism is critically dependent on the amplitude of the normal mode vibration, which is expected to be dependent on the distribution of defects in the crystal as discussed in the previous section. Thus, it is proposed that the 'heterogeneous' nucleation of the martensite is correlated with the non-uniformity of the atomic vibration amplitude in the crystal.

4. DISCUSSION

By means of the computational study of the lattice model, it has been shown that the simultaneous presence of the two energy terms, the anharmonic strain energy⁽²⁴⁾ and the strain gradient energy,⁽²⁵⁾

which have already been discussed separately by different authors, is essential in providing the triggering mechanism for the martensitic transformation. While the presence of the anharmonicity can be understood as the inherent nature of the atomic binding interaction,^(26,27) the presence of the strain gradient energy term is inferred from the analogy with the spinodal decomposition in the present paper. The experimental data, which suggest the presence of the strain gradient energy term, are discussed in the followings.

The presence of the strain gradient energy introduces an anomaly in the small amplitude phonon dispersion curve of the model lattice as shown in Fig. 3. The group led by Yamada⁽²⁸⁾ has studied, by means of the neutron inelastic scattering, the dispersion relationship of the transverse phonon propagating in [110] direction with the polarization direction [1 $\bar{1}$ 0] in a single crystal of CuAuZn₂ alloy, which is known to transform martensitically near 270 K. Their data show a small but distinct dip qualitatively similar to that shown in Fig. 3 at 298 K.

Another interesting observation results from the features of the phonon dispersion curve of Zn at room temperature measured by Maliszewski *et al.*⁽²⁹⁾ Although Zn does not transform martensitically, it is known that it has tendency to deform plastically by twinning besides by dislocation slip mechanism. As known, the twinning can be considered as a special martensitic transformation to a crystallographically equivalent structure under the influence of an applied stress. The dispersion curve of the transverse phonon propagating in the [01 $\bar{1}$ 0] direction with the polarization perpendicular to the basal plane shows an appreciable dip for the wave-vector $0.11 \times 10^8/\text{cm}$.

In contrast to these observation of the anomaly in the phonon dispersion curves, Dolling *et al.*⁽³⁰⁾ have observed neither any anomaly nor any anomalous temperature dependence in the phonon dispersion curve obtained from the neutron inelastic scattering from sodium single crystals, down to M_s . Here, it is to be noted that the sound velocity estimated by extrapolating the neutron data to the small wave-vector region agrees within 2% with the velocity obtained directly from the ultrasonic pulse echo method on sodium single crystals by Diederich and Trivisonno,⁽³¹⁾ except for the shear wave propagating in [110] direction with the polarization [1 $\bar{1}$ 0] direction. The velocity of this shear wave obtained directly from the ultrasonic experiment is approximately 10% less than the one estimated from the neutron data.

In a similar vein, Hallman and Brockhouse⁽³²⁾ have not observed any anomalous temperature dependence

in the phonon dispersion curve obtained from the neutron inelastic scattering of a Fe-Ni 30% alloy single crystal. However, Salama and Alers⁽³³⁾ have observed a remarkable decrease of the ultrasonic velocity of a shear wave propagating [110] direction with polarization [1 $\bar{1}$ 0] direction with the decrease of the temperature.

It is proposed here that these inconsistencies between the neutron data (large k) and the ultrasonic data (small k) of a shear wave can be understood as the indirect indication of the presence of the anomalous dispersion in the intermediate wave-vector region which has not yet directly investigated either by the neutron or ultrasonic experiment. On the other hand, the anomalous dispersion is predicted in the large wave-vector region by the atomic bond model for the strain gradient energy used in the numerical investigation of the present paper. For the crystal which shows the anomalous phonon dispersion in the intermediate wave-vector region, the atomic bond model used in the present study should be understood as an instrument to recognize the significance of the simultaneous presence of the strain gradient energy and the anharmonic strain energy in triggering the martensitic transformation, while the physical origin of the strain gradient energy term is still left for further investigation.

ACKNOWLEDGEMENT

The authors would like to express their deep appreciation for the financial support from the University of Missouri and from the Yokohama City University, which provided them with the opportunity to work together during the summer of 1973.

REFERENCES

1. M. HILLERT, *Acta Met.* **9**, 525 (1961).
2. J. W. CAHN, *Acta Met.* **9**, 795 (1961).
3. P. A. FLEURY, J. F. SCOTT and J. M. WORLOCK, *Phys. Rev. Lett.* **21**, 16 (1968).
4. E. PYTTE, *Phys. Rev.* **187**, 1077 (1969).
5. D. DE FONTAINE, *Acta Met.* **18**, 275 (1970).
6. D. DE FONTAINE, N. E. PATON and J. C. WILLIAMS, *Acta Met.* **19**, 1153 (1971).
7. L. KAUFMAN and M. COHEN, Thermodynamics and kinetic of martensitic transformation, *Progress in Metal Physics*, Vol. 7, p. 165. Pergamon Press, Oxford (1968).
8. G. KUBDJUMOV and G. SACHS, *Z. Phys.* **64**, 325 (1930).
9. Z. NISHIYAMA, *Sci. Rept. Tohoku University* **23**, 638 (1934-35).
10. M. A. JASWON and J. A. WHEELER, *Acta Crystallogr.* **1**, 216 (1948).
11. C. M. WAXMAN, *Introduction to the Crystallography of the Martensitic Transformations*. Macmillan, New York (1964).
12. J. W. CHRISTIAN, *The Theory of Transformation in Metals and Alloys*. Pergamon Press, Oxford (1965).
13. C. ZENER, *Elasticity and Anelasticity*. University of Chicago Press (1948).
14. L. D. LANDAU and E. M. LIFSHITZ, *Statistical Physics*. Pergamon Press, Oxford (1948).
15. J. LAVAL, *C. r. Acad. Sci., Paris* **232**, 1947 (1951).

16. C. TRUESDELL and R. TOUPIN, *The Classical Field Theories*. Springer, New York (1960).
17. J. A. KRUMHANSL, *J. Phys. Chem. Solids*, Supplement 1, 627 (1965).
18. R. A. TOUPIN and D. C. GAZIS, *J. Phys. Chem. Solids*, Suppl. 1, 597 (1965).
19. G. LEIBFRIED and W. LUDWIG, *Solid State Physics*, Vol. 12, p. 275. Academic Press, New York (1961).
20. A. Ü. MACRAE and L. H. GERMER, *Phys. Rev. Lett.* **8**, 489 (1962).
21. B. C. CLARK, R. HERMAN and R. F. WALLIS, *Phys. Rev.* **139**, A860 (1965).
22. H. E. COOK, *Acta Met.* **21**, 1445 (1973).
23. H. E. COOK, *Acta Met.* **22**, 239 (1974).
24. P. C. CLAPP, *Phys. Status Solidi* (B)**57**, 561 (1973).
25. H. E. COOK and D. DE FONTAINE, *Acta Met.* **17**, 915 (1969).
26. Y. HIKI and A. V. GRANATO, *Phys. Rev.* **144**, 411 (1966).
27. T. SUZUKI, A. V. GRANATO and J. F. THOMAS, JR., *Phys. Rev.* **175** (1968).
28. Y. YAMADA, A. MORI, J. D. AXE and G. SHIRANE, Bull. Japanese Phys. Soc., 1973 Fall Meeting, *Solid St. Phys.* (A), 167 (1973).
29. E. MALISZEWSKI, J. ROSOŁOWSKI, D. SLEDZIEWSKA and A. CZACHOR, *J. Phys. Chem. Solids*, Suppl. 1, 33 (1965).
30. G. DOLLING, B. M. POWELL and P. MARTEL, *Can. J. Phys.* **46**, 1727 (1968).
31. M. E. DIEDERICH and J. TRIVISONNO, *J. Phys. Chem. Solids* **27**, 637 (1966).
32. E. D. HALLMAN and B. N. BROCKHOUSE, *Can. J. Phys.* **47**, 1115 (1969).
33. K. SALAMA and G. A. ALERS, *J. appl. Phys.* **39**, 4357 (1968).