Theory of the incommensurate-to-commensurate transition in long-period superlattices of A_3B-type alloys

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A Ginzburg-Landau theory, in which a normal phase and an order parameter are, respectively, the $L1_2$ structure and the charge-density wave, is proposed to explain features of the incommensurate to $M=2$ commensurate transition in long-period superlattices of A_3B-type alloys. Predicted features are found to be consistent with those obtained experimentally.
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Long-period superlattices (LPSL's) have been found in A_3B-type alloys with the $L1_2$ structure, such as Ag-Mg and Au-Zn.[1,2] As is known, LPSL's are composed of the periodic antiphase domains and their periods are expressed by the number M of unit cells involved in one antiphase boundary. Sato and Toth[2] experimentally found that the period is determined by the size of the Fermi surface along the $\langle 110 \rangle$ directions, where the surface has flat portions. This seems to suggest that the LPSL is due to the appearance of charge-density waves (CDW's), although the CDW state in the three-dimensional system has not been accepted. Note that the striped-type superstructure in the γ-brass alloys has been recently pointed out to be regarded as a CDW state in the three-dimensional system.[4]

The period determined by the size of the Fermi surface is generally incommensurate. According to the McMillan theory[5] on transition-metal dichalcogenides, the phase of the purely incommensurate wave at lower temperatures is effectively modulated by waves derived from higher-order harmonics via the umklapp process. The phase modulation leads to a discommensurate structure which consists of the in-phase and phase-slip regions. The phase-slip region is called the discommensuration. On the other hand, the $\langle 2^j1 \rangle$-type and $\langle 2^j3 \rangle$-type structures have been found in the LPSL in the vicinity of $M=2$ in the A_3B-type alloys such as Ag-Mg and Au-Zn.[6−8] A unit cell of the $\langle 2^j1 \rangle$-type structure is, for instance, characterized by j antiphase domains with $M=2$ and one domain with $M=1$. The $\langle 2^j1 \rangle$-type and $\langle 2^j3 \rangle$-type structures can be regarded as incommensurate structures, although de Fontaine and Kulik[9] pointed out that both are commensurate structures. Because the $M=2$ domain region is a commensurate region, the $M=1$ domain should be the discommensuration in the $\langle 2^j1 \rangle$-type structure. However, this has not been confirmed theoretically and is just a supposition.

The incommensurate-to-commensurate transition in the LPSL—that is, the transition from the $\langle 2^j1 \rangle$-type structure to the $M=2$ commensurate structure—has been found in the Ag-Mg alloys.[10] The *in situ* observation of the transition was then carried out in order to examine the details of the transition. Characteristic patterns consisting of four $M=1$ domains play an important role in the transition. In the incommensurate phase, further, the period was found to approach $M=2$ with decreasing temperatures.

In this paper we present a theory to explain features of the incommensurate-to-commensurate transition in terms of the Ginzburg-Landau theory with CDW's as an order parameter, which is analogous to that of McMillan for the dichalcogenides.[5] The present work is, in particular, focused on the one-dimensional LPSL's in the vicinity of $M=2$ in the A_3B-type alloys, where the incommensurate-to-commensurate transition was observed in the Ag-Mg alloys.

Although LPSL's appear from a disordered phase upon cooling, the normal phase is not the disordered phase, but the ordered phase; that is, the $L1_2$-ordered structure in the A_3B-type alloys. The transition from the disordered phase to the LPSL phase actually involves two processes. One is the ordering process from the disordered structure to the $L1_2$-ordered structure, and the other is the introduction of the periodic array of the antiphase boundaries in the ordered structure. The latter is assumed to be due to the appearance of the CDW's in the present theory. From this viewpoint, the transition should be a two-step transition: the disordered phase→the $L1_2$-ordered phase→the LPSL upon cooling. Kikuchi and Sato[11] examined the disordered-to-ordered transition on the basis of the cluster-variation method in the tetrahedron approximation. They found that the transition is of first order and is suppressed largely with respect to temperature because of the frustration in the $L1_2$-ordered structure. This means that the transition temperature can be lowered below that between the ordered and LPSL phases. Because of the experimental fact that LPSL's appear directly from the disordered phase, this possibility must be realized. The free-energy curve of the disordered

phase should be intersected by that of the LPSL, as will be shown in Fig. 2. In the present case, therefore, it is assumed that the normal phase is the $L1_2$-ordered phase and transforms into the LPSL upon cooling, due to the formation of the CDW's.

The electronic charge density of an LPSL is written as $\rho(\mathbf{r})=\rho_0(\mathbf{r})[1+\eta(\mathbf{r})]$, where $\rho_0(\mathbf{r})$ is the charge density of the normal $L1_2$-ordered structure and $\eta(\mathbf{r})$ is a real order parameter due to the formation of the CDW's. The real order parameter is expressed as a real part of the complex order parameter $\Psi(\mathbf{r})$, and $\Psi(\mathbf{r})$ includes the contribution of higher-order harmonics. Note that wave vectors of the complex order parameter for the first-order wave are nesting vectors. The vectors actually deviate from those determined by the size of the Fermi surface as a result of the phase modulation by waves related to the higher-order harmonics through the umklapp process.

When one-dimensional LPSL's are formed along the [010] direction, nesting vectors in the A_3B-type alloys are understood to be $\mathbf{Q}_1=(1, 1+\Delta_0, 0)$, $\mathbf{Q}_2=(-1, 1+\Delta_0, 0)$, $\mathbf{Q}_3=(0, 1, +\Delta_0, 1)$, and $\mathbf{Q}_4=(0, 1+\Delta_0, -1)$, on the basis of the relation between the Fermi surface and the Brillouin zones of the A_3B-type alloys where Δ_0 represents a deviation of the first-order diffraction spots from 1 1 0–type ordered spots along the [010] direction and is equal to $1/2M$. The complex order parameter for the first-order wave is then calculated as a sum of four plane waves with the wave vectors $\mathbf{Q}_1$, $\mathbf{Q}_2$, $\mathbf{Q}_3$, and $\mathbf{Q}_4$, respectively, and is given as $\psi_0=\Phi_0\exp[i(1+\Delta_0)\mathbf{G}_{\langle 010\rangle}\cdot\mathbf{r}]$, where Φ_0 is a complex amplitude of the first-order wave and G_m a reciprocal-lattice vector of the $L1_2$-ordered structure. Note that the complex amplitude includes the periodicity along the [100] and [001] directions perpendicular to the modulation direction, and the periods of both directions coincide with those of the normal structure. Because of this, we neglect the position dependence of Φ_0 in the present calculation for convenience. Moreover, odd-order harmonics are observed around $1\frac{5}{4}0$–type positions in electron-diffraction patterns,[6] as schematically shown in Fig. 1. These positions correspond to that of $M=2$. The complex order parameter including the higher-order harmonics can be expressed as

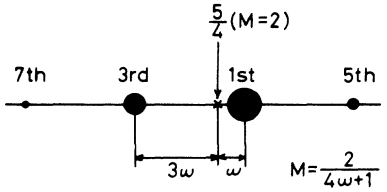

FIG. 1. Schematic representation of odd-order harmonics around the first-order spot in the case of $1.5\leq M_0\leq 3.0$. The distance between the first-order spot and the $\frac{5}{4}$ position is defined to be ω. The period M is related to ω in the relation of $M=2/(4\omega+1)$.

$$\Psi(\mathbf{r})=\sum_j \psi_j=\sum_j \Phi_j \exp[iq_j\mathbf{G}_{\langle 010\rangle}\cdot\mathbf{r}] , \tag{1}$$

where $q_j=1+\Delta_j=\frac{5}{4}+(4j+1)\omega$, as understood from Fig. 1, and values of j for the first-, third-, fifth-, and seventh-order harmonics are 0, -1, 1, and -2, respectively. Note that the complex order parameter given by Eq. (1) can be used for the LPSL with $1.5\cong M\cong 3.0$. A difference between two cases of $1.5\cong M<2.0$ and $2.0<M\cong 3.0$ is only a sign of ω.

In the present theory we adopt the following Ginzburg-Landau free energy,

$$F=\int d\mathbf{r}\{K|(\nabla-i\bar{q}_0\mathbf{G}_{\langle 010\rangle})\Psi(\mathbf{r})|^2 +a[\eta(\mathbf{r})]^2+b[\eta(\mathbf{r})]^3+c[\eta(\mathbf{r})]^4\} , \tag{2}$$

where $\bar{q}_0=1+1/2M_0$, and M_0 is a period determined by the size of the Fermi surface. Because of the invariance of the free energy with respect to the translation symmetry of the normal $L1_2$-ordered structure, the coefficients are given as, for instance, $c=c_0+\sum_m c_m\exp(-i\mathbf{G}_m\cdot\mathbf{r})$. The temperature dependence is assumed to be $a_0=a'(T-T_0)$. By substituting Eq. (1) into (2), the free energy becomes, in a general form,

$$F=\sum_j\sum_{j'}K\Phi_j\Phi_{j'}(q_j-\bar{q}_0)(q_{j'}-\bar{q}_0)\mathbf{G}^2_{\langle 010\rangle}\delta(q_j-q_{j'})+\tfrac{1}{4}\sum_j\sum_{j'}a\Phi_j\Phi_{j'}\delta(q_j+q_{j'})+\tfrac{1}{8}\sum_j\sum_{j'}\sum_{j''}b\Phi_j\Phi_{j'}\Phi_{j''}\delta(q_j+q_{j'}+q_{j''}) +\tfrac{1}{16}\sum_j\sum_{j'}\sum_{j''}\sum_{j'''}c\Phi_j\Phi_{j'}\Phi_{j''}\Phi_{j'''}\delta(q_j+q_{j'}+q_{j''}+q_{j'''}) , \tag{3}$$

where $\delta(q_j)=1$ for $q_j\mathbf{G}_{\langle 010\rangle}=\mathbf{0}$ or $\mathbf{G}_m$, and $\delta(q_j)=0$ otherwise. In Eq. (3), the coefficients are treated as follows; for instance, $c=c_0$ for $(q_j+q_{j'}+q_{j''}+q_{j'''})\mathbf{G}_{\langle 010\rangle}=\mathbf{0}$ and $c=c_m$ for $(q_j+q_{j'}+q_{j''}+q_{j'''})\mathbf{G}_{\langle 010\rangle}=\mathbf{G}_m$. Moreover, Eq. (1) can be changed into

$$\Psi(\mathbf{r})=A\exp[i(\tfrac{5}{4}\mathbf{G}_{\langle 010\rangle}\cdot\mathbf{r}+\theta)] , \tag{4}$$

where an amplitude and a phase are, respectively, given as $A=[a(\mathbf{r})^2+b(\mathbf{r})^2]^{1/2}$ and $\theta=\tan^{-1}[b(\mathbf{r})/a(\mathbf{r})]$ by using

$$a(\mathbf{r})=\sum_j \Phi_j\cos(4j+1)\omega\mathbf{G}_{\langle 010\rangle}\cdot\mathbf{r}$$

and

$$b(\mathbf{r})=\sum_j \Phi_j\sin(4j+1)\omega\mathbf{G}_{\langle 010\rangle}\cdot\mathbf{r} .$$

Hence, the phase and amplitude modulations can be obtained as the position dependence of A and θ, which are calculated from the amplitudes obtained by minimizing the free energy.

In the Ag-Mg alloys that the present theory can be applied to, the first-, third-, fifth-, and seventh-order spots are clearly observed in electron-diffraction patterns.[6] Because of this, the free energy for the four waves are used in order to calculate some physical properties in the

incommensurate-to-commensurate transition. First of all, the complex amplitude is written as $\Phi_j=\phi_j \exp(i\alpha_j)$, where ϕ_j and α_j are, respectively, a real amplitude and a phase of the complex amplitude. The real amplitude is also assumed to be positive. When it is assumed that $\alpha_0=\alpha_{-2}=0$ and $\alpha_{-1}=\alpha_1=\pi$, $\alpha_0=\alpha_{-2}=0$ and $\alpha_{-1}=\alpha_1=\pi$ the free energy for the four waves can be then written as

$$F_I=\sum_j K_j'\phi_j^2+\sum_j C_1\phi_j^4+\sum_j\sum_{k\,(\neq j)} 4C_1\phi_j^2\phi_k^2-C_2(\phi_0^3\phi_{-1}+3\phi_0\phi_{-1}^2\phi_1+3\phi_0^2\phi_1\phi_{-2}+3\phi_{-1}\phi_1^2\phi_{-2})$$
$$+C_3(\phi_0^2\phi_{-1}\phi_1+\phi_0\phi_{-1}^2\phi_{-2}+2\phi_0\phi_{-1}\phi_1\phi_{-2}) \tag{5}$$

with the help of new coefficients C_m instead of c_m, where $K_j'=K_0(q_j-\bar{q}_0)^2G_{\langle 010\rangle}^2+\frac{1}{2}a'(T-T_0')$, $T_0'=T_0-(a_1/a')$. The summation $\sum_j$ is made for $j=-2$, -1, 0, and 1. Both ϕ_j and M were determined by minimizing the above free energy with respect to ϕ_j and M, and the calculation was carried out by the iteration method. Moreover, the commensurate structure in the present case is the LPSL with the $M=2$. From Eq. (3) a free energy of the $M=2$ commensurate structure becomes

$$F_C=K_c'\phi_c^2+(C_1-\tfrac{1}{4}C_2)\phi_c^4 , \tag{6}$$

where $K_c'=K_0(\frac{1}{4}-1/2M_0)^2G_{\langle 010\rangle}^2+\frac{1}{2}a'(T-T_0')$, and ϕ_c is a real amplitude of the $M=2$ commensurate wave.

Figure 2 shows the free-energy curves of both incommensurate and $M=2$ commensurate structures plotted against temperature for $M_0=1.80$, respectively. The predicted curve of the disordered structure is also depicted. The calculation was made by using the parameters $a'=T_0'=1.0$, $K_0G_{\langle 010\rangle}^2=20.0$, $C_1=0.112$, $C_2=0.122$, and $C_3=0.350$. In Fig. 2 the free-energy curve of the incommensurate (IC) structure intersects that of the commensurate one at $T_{IC}=0.73$. This means that the incommensurate-to-commensurate transition occurs at this temperature for $M_0=1.80$. It should be remarked that the curve of the incommensurate structure should be intersected by that of the disordered one on the basis of the experimental fact, as described earlier. In the figure the intersecting temperature T_{DL}; that is, the transition temperature for the disordered to LPSL transition, is assumed to be $T=0.9$, although there is no physical reason for this assumption.

The amplitude and phase modulations at the transition temperature of the incommensurate-to-commensurate transition for $M_0=1.80$ in the case of $1.5\leq M<2.0$ are shown in Fig. 3. Note that features shown here are essentially the same as those in $2.0<M\leq 3.0$. The phase-versus-position curve consists of the constant-phase and phase-slip regions. From Eq. (4) the constant-phase and phase-slip regions are, respectively, understood to be the $M=2$ commensurate region and the discommensuration. The magnitude of the phase slip across the discommensuration is found to be $2\pi/4$. In the present case the phase slip of $2\pi/4$ leads to the introduction of the $M=1$ domain in $1.5\leq M<2.0$ and the $M=3$ domain in $2.0<M\leq 3.0$. Hence, the $\langle 2^j1\rangle$-type and $\langle 2^j3\rangle$-type structures are expected on the basis of the present theory. In addition, the characteristic pattern consisting of four discommensuration lines is expected because of $(2\pi/4)\times 4=2\pi$. As described earlier, these structures and the pattern have been actually observed in the Ag-Mg and Au-Zn alloys.[6-8] Furthermore, the amplitude is found to have a minimum at the discommensuration.

Figure 4 shows the temperature dependence of the period for various M_0, which were calculated by using the same parameters as those in Figs. 2 and 4. When the temperature is lowered, the period tends to approach

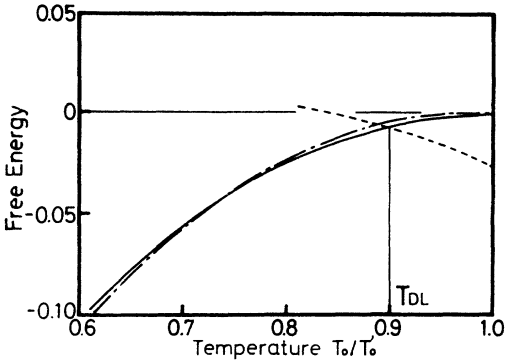

FIG. 2. Free-energy curves of the incommensurate and $M=2$ commensurate phases, as a function of temperature for $M_0=1.80$. The solid and dotted-dashed lines denote curves of the incommensurate and commensurate phases, respectively. The curve of the disordered phase is also shown by the dashed line. Both the free energy and temperature are normalized with respect to T_0', and are thus dimensionless.

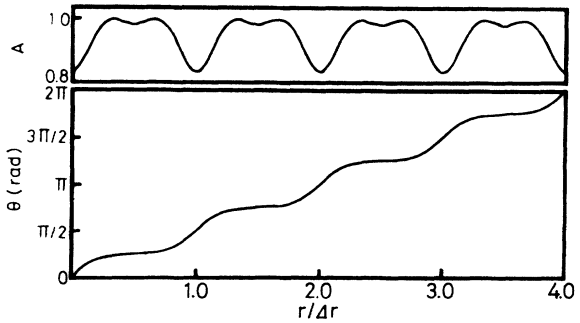

FIG. 3. Calculated amplitude and phase as a function of position at $T=0.73$ for $M_0=1.80$. The amplitude A and the position r are normalized with respect to the maximum of A and the distance between two neighboring discommensurations, Δr, respectively, and are thus dimensionless.

$M=2$. The degree of the change in period is more remarkable in M_0 closer to $M_0=2$. Further, the incommensurate-to-commensurate transition is reproduced for $M_0=1.80$ and 2.20.

As pointed out by de Fontaine and Kulik[9] in the application of the ANNNI model to the LPSL's, the period of the $\langle 2^j1\rangle$-type and $\langle 2^j3\rangle$-type structures can be written as $M=V/W$, where V and W are prime numbers, and are strictly commensurate. In our theory, the commensurate structure should satisfy the condition $vq_0\mathbf{G}_{\langle 010\rangle}=w\mathbf{G}_{\langle 010\rangle}$ (v and w are integers). From $q_0=1+1/2M$, M is derived as $v/2(w-v)$, which coincides with the definition of the commensurate structure mentioned above. Hence, the lock-in term originating from $\delta(vq_0)=1$ appears in the vth-order term. Because the present free energy has terms up to fourth order and the value of v is greater than 5, the lock-in term cannot be taken into account. This means that the $\langle 2^j1\rangle$-type and $\langle 2^j3\rangle$-type structures are regarded as the incommensurate structure. It should be noticed that our treatment is never inappropriate, because the higher-order lock-in term makes only a very small contribution to the free energy. The most important advantage in the present theory is that we are able to understand features of these structures, such as the temperature dependence of the period, and the discommensurate structure. In fact, the present theory can explain the features found experimentally in the A_3B-type alloys, except for the discontinuous change in period, which results from the transition between $\langle 2^j1\rangle$-type structures.

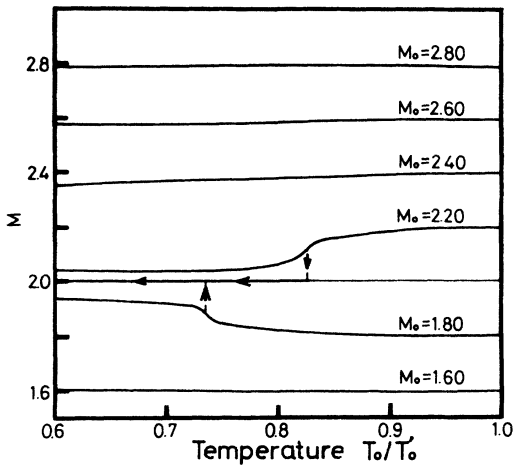

FIG. 4. Calculated period as a function of temperature for various M_0. For $M_0=1.80$ and 2.20, the actual period jumps from the incommensurate value to $M=2.0$ upon cooling, as shown by arrows.

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