Phenomenological Theory of Phase Change from FCC to FCT in the Indium Alloy

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In-Tl alloy transforms from *fcc* to *fcc* when the Tl composition becomes lower than about 23 at%. In the In-Hg and the In-Pb alloys, *fcc*, *fcc*($c/a > 1$) and *fcc*($c/a < 1$) phases appear and the axial ratio (c/a) is dependent on the electron atom ratio. These phase changes in the indium alloys are treated by the phenomenological theory based on the Landau's theory of phase transition, by assuming that the elastic constant $(C_{11} - C_{12})/2$ of the *fcc* phase is directly proportional to composition m and becomes zero at $m = m_0$. As a result, composition dependences of the axial ratio (c/a) and $(C_{11} - C_{12})/2$ in both *fcc* and *fcc* phases are well explained phenomenologically.

(Received May 7, 1974)

I. Introduction

Indium alloys such as In-Tl and In-Pb transforms from *fcc* to *fcc* dependent on composition^{(1)~(4)}. For example, in the In-Tl alloy the *fcc* phase appears in an composition range higher than 23 at%Tl at room temperature⁽¹⁾. As an interesting problem, the axial ratio (c/a) of the indium alloys containing solute atoms such as Cd, Hg, Sn and Pb has been found to change depending on the electron atom ratio (e/a) of the alloy^{(2)~(4)}. As shown in Fig. 1, the *fcc*($c/a > 1$) phase appears in a region of $e/a = 2.935 \sim 3.12$ and the *fcc*($c/a < 1$) phase in a region of $e/a = 3.14 \sim 3.31$.

Yonemitsu et al.⁽⁴⁾⁽⁵⁾ have shown that the decrease of Fermi energy due to tetragonal distortion is the origin of phase transition in the indium alloy. Anderson et al.⁽⁶⁾ have explained the cubic-tetragonal transition in alloys by applying Landau's theory of phase transition⁽⁷⁾. However, detailed analysis has not been reported in their paper⁽⁶⁾. Therefore, in this paper, phase changes from *fcc* to *fcc* and from *fcc*($c/a > 1$) to *fcc*($c/a < 1$) are analyzed phenomenologically according to the suggestion given by Anderson et al.⁽⁶⁾ Here in this paper, following notation is used for simplicity: $\alpha = \text{fcc}$ phase ($e/a < 2.935$), $\alpha_1 = \text{fcc}(c/a > 1)$ phase, $\alpha_2 = \text{fcc}(c/a < 1)$ phase and $\alpha' = \text{fcc}$ phase ($e/a > 3.310$).

Fig. 1 Axial ratio (c/a) of the indium alloy containing Cd, Hg, Pb and Sn metals as a function of electron atom ratio ($n = e/a$) at room temperature^{(2)~(4)}.

II. Phenomenological Consideration

1. Phase transition in the In-Tl alloy

Indium alloy transforms from *fcc*($m3m$) to *fcc*($4/mmm$) with a very small change in volume. Strain of the unit cell due to this phase transition is represented by using ϵ_{xx} , ϵ_{yy} and ϵ_{zz} as strain components:

$$u_1 = \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz} = 0, u_2 = (2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy})/\sqrt{3} \text{ and } u_3 = \epsilon_{xx} - \epsilon_{yy}. \quad (1)$$

Gibbs free energy of an alloy is shown by a function of u_2 and u_3 according to the suggestion given by Anderson et al.⁽⁶⁾:

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$$F = F_0 + \frac{1}{2}B(u_2^2 + u_3^2) + \frac{1}{3}p(u_2^3 - 3u_3^2)u_2 + \frac{1}{4}q(u_2^4 + u_3^4) + \frac{1}{2}qu_2^2u_3^2. \quad (2)$$

Here, F_0 is an energy at $u_2 = u_3 = 0$, p is a negative constant and q is a positive constant. For the appearance of phase transition, coefficient B of the second order term in eq. (2) should become zero at a composition m_0 , judging from Landau's theory of transition⁽⁷⁾:

$$B = (C_{11} - C_{12})/2 = \beta(m - m_0). \quad (3)$$

Here, $\beta = dB/dm$, β and m_0 are positive constants and m is a mole fraction of Tl atom. From eqs. (2) and (3), the free energy of an alloy can be given as a function of u_2 and u_3 at each composition m . Equilibrium condition is given by $\partial F/\partial u_2 = \partial F/\partial u_3 = 0$ as follows:

$$Bu_2 + pu_2^2 - pu_3^2 + qu_3^2 + qu_2u_3^2 = 0, \quad (4)$$

$$Bu_3 - 2pu_2u_3 + qu_3^3 + qu_2^2u_3 = 0. \quad (5)$$

Values of u_2 and u_3 in an equilibrium state are given by eqs. (4) and (5) as follows:

(i) When m is higher than m_t (transition point), $u_2 = u_3 = 0$. This gives a *fcc* lattice. And when m is lower than m_t , the following values are obtained:

(ii) $u_3 = 0$ and $u_2 \neq 0$. This gives a *fct* lattice having the c axis along the z direction.

(iii) $u_3 = -\sqrt{3}u_2$. This gives a *fct* lattice having the c axis along the x direction.

(iv) $u_3 = \sqrt{3}u_2$. This gives a *fct* lattice having the c axis along the y direction. As a result of this phase change, three *fct* lattices having the c axis along the x or y or z direction are formed. In this paper, only the composition dependence of axial ratio (c/a) is discussed and the analysis is conducted only for the case (ii), $u_3 = 0$ and $u_2 \neq 0$. For simplicity, if u_2 is designated by u , the free energy of eq. (2) will be given by

$$F = F_0 + \frac{1}{2}Bu^2 + \frac{1}{3}pu^3 + \frac{1}{4}qu^4. \quad (2')$$

Values of u in the *fct* phase is indicated by u_s and calculated from eqs. (1) and (4) as follows:

$$u_s = 2(c/a - 1)/\sqrt{3} = (-p + \sqrt{p^2 - 4Bq})/2q. \quad (6)$$

From eqs. (3) and (6), composition dependence of u_s can be obtained. Transition point m_t is given as follows:

$$m_t = m_0 + 2p^2/9q\beta. \quad (7)$$

Elastic constant of the *fct* phase can be given by

the following equation:

$$B_{fct} = |\partial^2 F/\partial u^2|_{u=u_s} = B + 2pu_s + 3qu_s^2. \quad (8)$$

2. α - α_1 - α_2 - α' transition in In-Hg and In-Pb alloys

In the indium alloy free energy changes as a function of electron concentration $n = e/a$. There appear the α phase in a range of electron atom ratio $n < n_t (= 2.935)$, the α_1 phase at $n_t < n < n_c (= 3.317)$, α_2 phase at $n_c < n < n'_t (= 3.310)$, and the α' phase at $n'_t < n$ ⁽²⁾⁻⁽⁴⁾. For the appearance of α - α_1 transition, coefficient B of the second order term of eq. (2') should be dependent on n and becomes zero at $n = n_0$:

$$B = (C_{11} - C_{12})/2 = \beta(n - n_0), \quad (9)$$

and for the α' - α_2 transition, B of the α' phase should also be dependent on n :

$$B = (C_{11} - C_{12})/2 = \beta'(n - n'_0). \quad (9')$$

Here, $\beta < 0$ and $\beta' > 0$. n_0 and n'_0 are positive constants. At $n = n_c$, α_1 and α_2 phases coexist. Therefore, coefficient p of the third order term of free energy in eq. (2') should become zero at $n = n_c$, and it should be dependent on n for the appearance of α_1 - α_2 transition:

$$p = \delta(n_c - n)^r, \text{ in } \alpha_1 \text{ phase } (n < n_c), \quad (10)$$

$$p = \delta'(n - n_c)^r, \text{ in } \alpha_2 \text{ phase } (n > n_c). \quad (10')$$

Here, δ is a negative constant, r and δ' are positive constants. As a result, $p < 0$ in the α_1 phase and $u_s > 0$, and $p > 0$ and $u_s < 0$ in the α_2 phase. By using eqs. (9)~(10'), the free energy of eq. (2') in the indium alloy is shown schematically in Fig. 2 as a function of u in each concentration range. This diagram can qualitatively

Fig. 2 Schematic diagram of the free energy of indium alloy as a function of u in each range of electron concentration n : (a) $n > n_t$, (b) $n = n_t$, (c) $n_t < n < n_c$, (d) $n = n_c$, (e) $n_c < n < n'_t$, (f) $n = n'_t$ and (g) $n > n'_t$.

explain the appearance of $\alpha-\alpha_1-\alpha_2-\alpha'$ transition in the indium alloy. Values of u_s at the α_1 and α_2 phases are given by:

$$u_s = (-p + \sqrt{p^2 - 4Bq})/2q \text{ in } \alpha_1 \text{ phase,} \quad (6)$$

$$u_s = (-p - \sqrt{p^2 - 4Bq})/2q \text{ in } \alpha_2 \text{ phase.} \quad (6')$$

III. Comparison with Experiment

1. Phase change in In-Tl alloy

In-Tl alloy transforms from *fcc* to *fct* when m becomes lower than $m_t = 0.225$ at a temperature 300 K⁽¹⁾. Composition dependences of u_s and $(C_{11} - C_{12})/2$ are calculated from eqs. (3), (6) and (8) by using the following parameters: $m_0 = 0.207$, $\beta = 4.00 \times 10^{10}$ dyn/cm² mol, $q = 2.08 \times 10^{12}$ dyn/cm² and $p/2q = -0.02$. Calculated results, shown in Figs. 3 and 4, are in good agreement with the experiment⁽¹⁾⁽⁸⁾⁽⁹⁾. Therefore, the present theory can well explain the phase change in In-Tl alloy. In-Tl alloy transforms also from *fcc* to *fct* martensitically as the temperature is lowered. This martensitic transformation has been analyzed phenomenologically in a previous paper by assuming that $(C_{11} - C_{12})/2$ is dependent on temperature⁽¹⁰⁾. Accordingly, this is not described in this paper.

2. Phase change in In-Hg and In-Pb alloys

In the α , α_1 , α_2 and α' phases, values of $u_s = 2(c/a - 1)/\sqrt{3}$ and elastic constant

Fig. 3 Comparison of the calculated value of $u_s = 2(c/a - 1)/\sqrt{3}$ with the experiment⁽¹⁾ in the $\text{In}_{1-m}\text{Tl}_m$ alloy at a temperature 300K.

$(C_{11} - C_{12})/2$ are calculated from eqs. (6), (6'), (8) and (9)~(10') by using the following parameters: $q = 0.92 \times 10^{12}$ dyn/cm² and $r = 0.9$ in all composition. $\beta = -2.0 \times 10^{11}$ dyn/cm² n ($n = e/a$), and $\beta' = 5.0 \times 10^{10}$ dyn/cm² n . $\delta/2q = -0.146$ and $\delta'/2q = 0.294$. $n_0 = 2.94$ and $n'_0 = 3.27$. Leigh⁽¹¹⁾ has also shown that β is about -2.5×10^{11} dyn/cm² n at Al metal (*fcc*, $n = 3.0$). In this paper, $\beta = -2.0 \times 10^{11}$ dyn/cm² n is assumed for the α phase. Figure 5 represents a n dependence of $B = (C_{11} - C_{12})/2$ calculated for the α , α_1 , α_2 and α' phases of the indium alloy. Dotted line in Fig. 5 indicates an assumed

Fig. 4 Comparison of the calculated value of $B = (C_{11} - C_{12})/2$ with the experiment⁽⁸⁾⁽⁹⁾⁽¹⁵⁾ in both *fcc* and *fct* phases of the $\text{In}_{1-m}\text{Tl}_m$ alloy at 300K.

Fig. 5 Comparison of the calculated value of $B = (C_{11} - C_{12})/2$ with the experiment⁽⁹⁾⁽¹²⁾⁽¹³⁾ in *fcc* and *fct* phases of In-Hg and In-Pb alloys as a function of electron atom ratio at room temperature.

value of B in the hypothetical *fcc* phase at $n=2.935\sim 3.310$ and the minimum of B near $n=3.03$ is expected from the values of β and β' in eqs. (9) and (9'). Calculated result of B is fairly consistent with the experimental values⁽¹²⁾⁽¹³⁾ of In ($n=3.0$) and Pb ($n=4.0$) metals. In the *fct* phase, the maximum of B is expected at $n=3.03$ in the present calculation. Figure 6 represents the calculated result of the n dependence of $u_s=2(c/a-1)/\sqrt{3}$, compared with the experiment⁽²⁾⁽⁴⁾. In the α_2 phase ($n=3.137\sim 3.310$), calculated value of u_s is in good agreement with the experiment. In the α_1 phase ($n=2.935\sim 3.317$), this agreement is not so complete; this may come from the assumption that the parameters such as δ and q are independent on n . Leigh⁽¹¹⁾ has shown theoretically that the n dependence of $(C_{11}-C_{12})/2$ in the α phase is not linear. Also in this paper, the n dependence of $(C_{11}-C_{12})/2$ near $n=3.03$ is assumed to be shown by a curved line as shown in Fig. 5. However, the agreement between the calculated and experimental values of u_s is not so good in the α_1 phase. Therefore, the problem is considered to be more complicated especially in the α_1 phase and requires some theoretical treatment based on the electronic theory using pseudopotential⁽¹⁴⁾.

IV. Discussion

Phase change in the indium alloy is found to be well explained by the phenomenological theory based on Landau's theory of phase transition. Elastic constant B of the *fcc* phase changes as a function of composition and becomes negative in a composition region where the *fct* phase appears. The phenomenon shown by eqs. (3), (9) and (9') is called lattice softening. Gunton et al.⁽¹⁵⁾ has also shown that the lattice softening due to the existence of the soft acoustic phonon mode is the origin of phase transition in the indium alloy. In the In-Hg and In-Pb alloys, the elastic constant in the *fcc* phase is expected to become minimum near $n=3.03$, where the gain of Fermi energy due to tetragonal distortion is expected to become maximum. Yonemitsu et al.⁽⁴⁾⁽⁵⁾⁽¹⁴⁾ have shown theoretically that the phase change in the indium alloy occurs by the gain of Fermi

Fig. 6 Comparison of the calculated value of $u_s=2(c/a-1)/\sqrt{3}$ with the experiment^{(2)~(4)} in In-Hg and In-Pb alloys as a function of electron atom ratio at room temperature.

energy due to tetragonal distortion and that the axial ratio is dependent on electron concentration. Because this gain of Fermi energy can be shown as a function of c/a ⁽⁵⁾, the present theory that represents the free energy as a function of u is considered to be a good approximation for the analysis of phase transition.

Leigh⁽¹¹⁾ has shown theoretically that in Al alloy elastic constant $(C_{11}-C_{12})/2$ decreases with the increase in electron concentration n by a contribution of the overlapped electrons at the 2nd zone. Accordingly, the *fcc* alloy near $n=2.9$ is considered to have a tendency of becoming unstable with increase in n . However, when n increases still more, the number of the overlapped electrons at the 2nd and 3rd zones increases, and as a result, the gain of Fermi energy due to tetragonal distortion becomes smaller as reported by Yonemitsu⁽⁵⁾. Therefore, the *fcc* structure becomes stable again in the large region of n . In the indium alloy, the number of the overlapped electrons is dependent on both axial ratio (i.e. strain, u_s) and electron concentration⁽⁵⁾. Therefore, strong electron phonon interaction is expected in the indium alloy. This may be an origin of lattice softening in the indium alloy. The result given in this paper should be analyzed further according to the electronic theory using pseudopotential. This is an interesting problem as the subject of study in the future.

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Appendix

It is well known that the elastic free energy is shown as a function of strain components by using 2nd and 3rd order elastic constants as follows⁽¹⁶⁾:

$$F = F_0 + \frac{1}{2}C_{11}(\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_3^2) + C_{12}(\varepsilon_1\varepsilon_2 + \varepsilon_2\varepsilon_3 + \varepsilon_3\varepsilon_1) + \frac{1}{6}C_{111}(\varepsilon_1^3 + \varepsilon_2^3 + \varepsilon_3^3) + \frac{1}{2}C_{112} \times [\varepsilon_1^2(\varepsilon_2 + \varepsilon_3) + \varepsilon_2^2(\varepsilon_3 + \varepsilon_1) + \varepsilon_3^2(\varepsilon_1 + \varepsilon_2)] + C_{123}\varepsilon_1\varepsilon_2\varepsilon_3 + \dots, \quad (\text{A1})$$

where $\varepsilon_1 = \varepsilon_{xx}$, $\varepsilon_2 = \varepsilon_{yy}$, $\varepsilon_3 = \varepsilon_{zz}$, and in the present *fcc-fct* transition $\varepsilon_{yz} = \varepsilon_{zx} = \varepsilon_{xy} = 0$ is assumed. By comparing eq. (2) with eq. (A1), the following relation is obtained:

$$B = (C_{11} - C_{12})/2, \quad (\text{A2})$$

$$16p/3\sqrt{3} = C_{111} = C_{123} = -2C_{112}. \quad (\text{A3})$$

This means that the anharmonicity (i.e. 3rd order elastic constants) of the alloy has an important effect on the phase transition. Relation among the 3rd order elastic constants shown in eq. (A3) has not been observed in such metals as Cu and Al⁽¹⁶⁾ and is considered to be peculiar to the indium alloy having *fcc-fct* transition. Effect of anharmonicity on the phase transition is now under investigation.