First-Principles Investigation of L1₀-Disorder Phase Equilibrium in Fe–Pt System

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First-principles study is attempted to investigate L1₀-disorder phase equilibrium in Fe–Pt system. The present study consists of electronic structure total energy calculations by FLAPW for the ground state and statistical mechanics calculations by Cluster Variation Method for finite temperatures. It is revealed that the magnetism plays a crucial role in the phase stability. The spin polarized FLAPW calculation confirms that the most stable magnetic state for FePt₃ (L1₂) is *anti-ferro*, and the incorporation of anti-ferro magnetic state is critical to reproduce the experimental L1₀-disorder transition temperature. Thermal vibration effects considered based on Debye-Gruneisen model further improve the calculated transition temperature.

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1. Introduction

Recently, L1₀ ordered phase of Fe–Pt system has been attracting broad attentions for its significantly high magnetic anisotropy with tetragonal c-axis as the easy direction of magnetization. When such a peculiar magnetic feature is realized in fine particles and thin layers, developments of new functional materials for high density magnetic recording media can be expected. Also, from the kinetics point of view, the diffusion properties of an L1₀ ordered phase is quite unique. The distinctive preferential sites for each atomic species result in a low symmetric structure, which causes peculiar atomistic diffusion paths. Hence, atomistic investigation on the structural and thermodynamic properties of the L1₀ ordered phase in Fe–Pt system is in high demand.

In the previous studies,^{1,2)} we conducted systematic first-principles studies on the ground state properties and phase equilibria at finite temperatures for Fe–Pd system which is also a candidate alloy system for magnetic media. And it was demonstrated that the FLAPW electronic structure total energy calculations reproduce the global feature of the phase diagram when magnetic state of the system is properly taken into account. Furthermore, experimental L1₀-disorder transition temperature was reproduced with high accuracy.

In fact, both Pt and Pd belong to the same column of the periodic table, and when these elements are alloyed with Fe, various similarities are observed in the phase diagrams. Among them are the appearances of L1₀ ordered phase in the middle of the concentration and L1₂ ordered phase near FeX₃ stoichiometry (X = Pt or Pd). The major difference, however, is the fact that an additional L1₂ ordered phase is formed near Fe₃Pt stoichiometry for Fe–Pt system, while wide range of phase separation is extended in the Fe-rich portion for Fe–Pd system. This implies that the ordering tendency of the entire system is more enhanced for Fe–Pt system, which is confirmed by the higher transition temperatures of L1₀ and L1₂ (FePt₃) ordered phases in the equilibrium phase diagram.

In the present study, the same calculation procedure

adopted for Fe–Pd system is applied to Fe–Pt system and we attempt the first-principles studies on the phase stability and phase equilibria. The major objective of the present study is placed on the reproduction of experimental L1₀-disorder phase diagram. For this, our main focus is placed on two effects. One is the magnetic states of constituent ordered compounds and the other is the lattice thermal vibration. For the former, FLAPW total energy calculations with spin polarized and non-polarized schemes are attempted, and the effects of *non-magnetic*, *ferro-magnetic* and *anti-ferro-magnetic* states of constituent ordered compounds are investigated. For the latter, Debye-Gruneisen model which was originally applied to metals by Morruzi *et al.*³⁾ and to alloys by Becker *et al.*⁴⁾ is employed to estimate the vibrational free energy, and by combining with Cluster Variation Method⁵⁾ to evaluate the configurational entropy contributions the total free energy of a phase is calculated.

The organization of the present report is as follows. In the next section, we briefly review the theoretical procedure, and in the third section various phase boundaries calculated with/without the effects of magnetic states and lattice thermal vibration are demonstrated and compared.

2. Theoretical Calculation

By following the previous studies,^{2–4)} the free energy of the formation $\Delta F^{(n)}(r, T)$ of a stoichiometric ordered compound and a pure metal n is written as

$$\Delta F^{(n)}(r, T) = \Delta E_{el}^{(n)}(r) + \Delta E_{vib}^{(n)}(r, T) - T \cdot \Delta S_{vib}^{(n)}(r, T), \quad (1)$$

where right hand side is the sum of heats of formation, $\Delta E_{el}^{(n)}(r)$, lattice vibration energy $\Delta E_{vib}^{(n)}(r, T)$, and vibration entropy, $\Delta S_{vib}^{(n)}(r, T)$. Among three terms, the heats of formation is originated from electronic structure and depends only on lattice constant, r , under the assumption that the electronic entropy is negligible. The heats of formation, $\Delta E_{el}^{(n)}(r)$, is evaluated by FLAPW total energy calculation and plays a key

role in the whole calculation procedure. The lattice vibration effects described by the remaining two terms generally depend both on temperature, T , and lattice constant. In order to evaluate these terms, Debye-Grüneisen model which is the quasi-harmonic approximation is employed. Within this model, both $\Delta E_{vib}^{(n)}(r, T)$ and $\Delta S_{vib}^{(n)}(r, T)$ can be evaluated from the heats of formation, $\Delta E_{el}^{(n)}(r)$, as will be shown latter. FLAPW electronic structure calculation, therefore, is supposed to fully provide the free energy of formation with respect to an appropriate standard state.

The particular phases n we studied are five kinds of *fcc* based structure, Fe ($n = 1$), Fe₃Pt ($n = 2$) with L1₂, FePt ($n = 3$) with L1₀, FePt₃ ($n = 4$) with L1₂ and Pt ($n = 5$). In view of the fact that the most stable phase of Fe at the ground state is not *fcc* but *bcc*, an additional calculation is performed on *bcc*-Fe to define the standard state.

According to the Cluster Expansion Method,⁶⁾ the obtained free energy of formation of each phase n can be related to effective cluster interaction energy, $v_m(r, T)$, of a cluster m through

$$\Delta F^{(n)}(r, T) = \sum_{m=0} v_m(r, T) \cdot \xi_m^n \quad (2)$$

where ξ_m^n is the correlation function which spans the orthonormal basis in the thermodynamic configuration space⁷⁾ and is defined as the ensemble average of spin operator, $\sigma(p)$, which takes either +1 or -1 depending upon Fe or Pt located at a lattice point p , and represents the atomic arrangement on the cluster m in the phase n . With five kinds of *fcc*-based structure described above, a set of five simultaneous equations obtained from eq. (2) can be re-written by vector-matrix notation in which $\{\xi_m^n\}$ forms 5×5 matrix. Since the details of the matrix elements have been amply demonstrated in the previous publications^{1,2,8-13)} we do not duplicate here. But, it is worth repeating that the correlation matrix $\{\xi_m^n\}$ is regular for the choice of the five *fcc*-based phases with four nearest neighbor (n.n.) m -point clusters, a point cluster for $m = 1$, n.n. pair cluster for $m = 2$, n.n. triangle cluster for $m = 3$ and n.n. tetrahedron cluster for $m = 4$ in addition to a null cluster designated by $m = 0$. The regular matrix assures the existence of an inverse matrix and the eq. (2) is inverted to yield the

effective cluster interaction energies as,

$$v_m(r, T) = \sum_{n=1}^5 \{\xi_m^n\}^{-1} \cdot \Delta F^{(n)}(r, T). \quad (3)$$

It is realized that the vibrational contribution is effectively renormalized into the temperature dependent effective cluster interaction energies, $v_m(r, T)$, derived in this manner.

With these effective cluster interaction energies, the internal energy of a phase which is characterized by a lattice constant r and a set of correlation function $\{\xi_m\}$ can be written as

$$\Delta F_0(r, T) = \sum_{m=0}^4 v_m(r, T) \cdot \xi_m. \quad (4)$$

In this equation, in addition to an averaged vibrational energy contribution carried by $v_m(r, T)$, the correlation function, ξ_m , describes the configurational excitation at finite temperatures when this is employed as a variational parameter in the free energy. Hence, eq. (4) is regarded as the effective internal energy in which vibrational energies are renormalized. By adding configurational entropy term, the free energy of a phase of interest is finally written as

$$\Delta F = \Delta F_0 - T \cdot \Delta S_{Conf}. \quad (5)$$

Among various theoretical models to approximate configurational entropy, ΔS_{Conf} , one of the most efficient and reliable tools is the Cluster Variation Method (hereafter abbreviated as CVM). The approximate nature of the CVM is characterized by the largest cluster, which is termed *basic cluster*, of which cluster correlations are explicitly considered. The larger the basic cluster is, the more accuracy is generally expected. But the number of variables increases rapidly with the size of the basic cluster and the numerical procedure is seriously hampered. The actual calculation is, therefore, determined by the economy of the calculation and the accuracy demanded. In the conventional practice of the CVM for *fcc*-based system, tetrahedron approximation¹⁴⁾ has been employed in which the nearest neighbor tetrahedron cluster is taken as the basic cluster. For the L1₀ ordered phase, which is the main concern of the present study, the entropy formula is given¹⁴⁾ as

$$\Delta S_{Conf} = k_B \cdot \ln \frac{\left\{ \prod_{i,j} (N y_{ij}^{\alpha\alpha})! \right\} \left\{ \prod_{i,j} (N y_{ij}^{\alpha\beta})! \right\}^4 \left\{ \prod_{i,j} (N y_{ij}^{\beta\beta})! \right\} N!}{\left\{ \prod_i (N x_i^\alpha)! \right\}^{5/2} \left\{ \prod_i (N x_i^\beta)! \right\}^{5/2} \left\{ \prod_{i,j,k,l} (N w_{ijkl}^{\alpha\alpha\beta\beta})! \right\}^2}, \quad (6)$$

where α and β specify the sub-lattice of the L1₀ ordered phase, $i, j, \dots$ indicate either Fe or Pt, and x_i^α , $y_{ij}^{\alpha\beta}$ and $w_{ijkl}^{\alpha\alpha\beta\beta}$ are cluster probabilities of finding atomic arrangement specified by subscript(s) on a sub-cluster specified by superscript(s) on a point, pair and tetrahedron cluster, respectively.

The CVM formula reflects the symmetry of the phase, and for the disordered phase the distinction of the sub-lattice vanishes and the entropy formula is simplified.

By substituting eqs. (4) and (6) into eq. (5), a final form of the free energy of an L1₀ ordered phase is obtained as

$$\Delta F = \sum_{m=0}^4 v_m(r, T) \cdot \xi_m - k_B \cdot T \cdot \ln \frac{\left\{ \prod_{i,j} (N y_{ij}^{\alpha\alpha})! \right\} \left\{ \prod_{i,j} (N y_{ij}^{\alpha\beta})! \right\}^4 \left\{ \prod_{i,j} (N y_{ij}^{\beta\beta})! \right\} N!}{\left\{ \prod_i (N x_i^\alpha)! \right\}^{5/2} \left\{ \prod_i (N x_i^\beta)! \right\}^{5/2} \left\{ \prod_{i,j,k,l} (N w_{ijkl}^{\alpha\alpha\beta\beta})! \right\}^2}. \quad (7)$$

In eq. (7), the cluster probabilities, $x_i^\alpha, x_i^\beta, y_{ij}^{\alpha\alpha}, \dots, w_{ijkl}^{\alpha\alpha\beta\beta}$, are not mutually independent but interrelated each other through normalization and geometrical conditions.¹⁴⁾ While a set of correlation function $\{\xi_m\}$ forms an independent set of configuration variables. It is readily shown^{15,16)} that cluster probabilities, $\{x_i^\alpha, x_i^\beta, y_{ij}^{\alpha\alpha}, \dots, w_{ijkl}^{\alpha\alpha\beta\beta}\}$, and correlation functions, $\{\xi_m\}$, are related by linear transformation. Hence, eq. (7) can be symbolically written as $\Delta F(v_m(r), T, \{\xi_m\}) = \Delta F(r, T, \{\xi_m\})$ which is to be minimized to determine an equilibrium state. The actual operation of the minimization can be performed by imposing the Legendre transformation on $\Delta F(r, T, \{\xi_m\})$ with respect to the point correlation function, ξ_1 , which yields the grand potential as follows,

$$\Delta\Omega = \Delta F - \mu_{eff} \cdot \xi_1, \quad (8)$$

where μ_{eff} is the effective chemical potential defined as the difference of chemical potential of Fe and Pt and is the conjugate variable of point correlation function, ξ_1 . Hence, the grand potential is symbolically written as $\Delta\Omega(r, T, \mu_{eff}, \{\xi_{i \neq 1}\})$ and the equilibrium state is obtained by

$$\left. \frac{\partial \Delta\Omega}{\partial \{\xi_i\}} \right|_{T, \mu_{eff}, \{\xi_{j \neq 1}\}, r} = 0 \quad (9)$$

and

$$\left. \frac{\partial \Delta\Omega}{\partial r} \right|_{T, \mu_{eff}, \{\xi_{i \neq 1}\}} = 0. \quad (10)$$

With minimized grand potentials, it is readily shown¹⁴⁾ that two phase equilibria of disorder and L1₀ ordered phases can be determined by $\Delta\Omega^{dis} = \Delta\Omega^{L10}$, which indicates that the conventional common tangent construction on Helmholtz potentials can be replaced by equality of grand potentials.

3. Results and Discussion

3.1 Ground state analysis

As was described in the previous section, one of the key procedures of the present first-principles study is to calculate the total energy $E_{\text{Fe}_{4-n}\text{Pt}_n}(r)$ for $\text{Fe}_{4-n}\text{Pt}_n$ with $n = 0, 1, 2, 3$ and 4 at the ground state. For this, FLAPW electronic structure calculation¹⁷⁾ is performed with spin polarized and non-polarized techniques within the generalized gradient approximation (GGA).¹⁸⁾ With total energies $E_{\text{Fe}_{4-n}\text{Pt}_n}$, the heats of formation, $\Delta E_{el}^{(n)}$ is obtained as,

$$\Delta E_{el}^{(n)}(r) = E_{\text{Fe}_{4-n}\text{Pt}_n}(r) - \frac{4-n}{4} E_{\text{Fe}_4}^{bcc}(r_{bcc}) - \frac{n}{4} E_{\text{Pt}_4}(r_4), \quad (11)$$

where r_4 and r_{bcc} are the equilibrium lattice constants at which the total energies E_{Pt_4} and $E_{\text{Fe}_4}^{bcc}$ for Pt_4 and $bcc\text{-Fe}_4$ with *ferro* magnetic state, respectively, take minimum values. The above

operation defines the *segregation limit* at the ground state. The resultant $\Delta E_{el}^{(n)}$ is fitted into the Lennard-Jones type potential expressed as,

$$\Delta E_{el}^{(n)}(r) = \frac{a_n}{r^7} - \frac{b_n}{r^{3.5}} + c_n \quad (12)$$

and the resultant fitting parameters, a_n, b_n and c_n obtained by spin polarized calculations are tabulated in Table 1. It is noted that, since our main interest is *fcc*-based phases, *fcc* structure is meant for Fe throughout this study unless “*bcc*” is specified.

The results of calculated $\Delta E_{el}^{(n)}(r)$ are shown in Figs. 1(a) and 1(b) for spin non-polarized and spin polarized calculations, respectively. The energy reference state in both figures is the segregation limit which is defined as the concentration average of total energies of *bcc*-Fe (*ferro*) and Pt since the most stable ground state is *bcc*-Fe (*ferro*). Note that the calculated lattice constant of *bcc*-Fe is 5.36 (a.u.) which is quite small as compared with those of the other *fcc*-based phases. In order to facilitate comparison of all the phases, we converted this value to a *fcc-equivalent* keeping the same atomic volume.

One can see that for non-polarized calculations (Fig. 1(a)), $\Delta E_{el}^{(n)}(r)$ of all the ordered phases, which are in non-magnetic state, are positive, implying the destabilization and none of them can be expected to appear. This is in serious contradiction with the equilibrium phase diagram¹⁹⁾ in which, as mentioned previously, three ordered phases appear. While for the spin-polarized calculation (Fig. 1(b)) in which *ferro* or *anti-ferro* magnetic configurations are assumed, all the three ordered phases have negative heats of formation, indicating the stabilization. Note that the broken line of FePt_3 is the result of *ferro* while the solid line is that of *anti-ferro* magnetic state. Hence, these results clearly indicate the importance of the magnetism on the phase stability of the system.

According to the previous experimental result,²⁰⁾ it has been reported that the most stable magnetic state of FePt_3 (L1₂) phase is not *ferro* but *anti-ferro* (hereafter abbreviated as *af*) of which magnetic spin configuration is demonstrated in Fig. 2. In Fig. 1(b), one confirms that the heats of formation of *af*- FePt_3 is lower than that of *ferro*- FePt_3 . Although

Table 1 Lennard-Jones type potential parameters in eq. (12) for six phases obtained by spin polarized calculations. For FePt_3 , *fm* and *af* imply *ferro* magnetic state and *anti-ferro* magnetic state, respectively.

	a	b	c
Fe	1.9914	5.4245	0.3792
Fe_3Pt	3.3541	7.173	0.3816
FePt	5.1795	10.264	0.4917
FePt_3 (<i>fm</i>)	7.0272	12.721	0.5669
FePt_3 (<i>af</i>)	7.1982	13.097	0.5814
Pt	9.1405	15.900	0.6915

Fig. 1 Heats of formation (binding energy), $\Delta E_{el}^{(n)}(r)$, of Fe, Fe₃Pt, FePt, FePt₃ and Pt obtained by spin non-polarized calculations as a function of lattice constant (Fig. 1(a)) and by spin polarized calculation (Fig. 1(b)). In Fig. 1(b), for FePt₃, broken line indicates *ferro* magnetic state while the solid one indicates the *anti-ferro* magnetic state. The segregation limit is defined as the concentration average of total energies of *bcc*-Fe (*ferro*) and Pt.

Fig. 2 Spin configuration of the *anti-ferro* magnetic FePt₃. An open circle indicates Pt atom, while a dark solid circle and a light solid circle indicate Fe atom with up and down spins, respectively.

the energy difference is not so significant, the effects on the phase diagram is not negligible and this point is discussed in the latter section. The Lennard-Jones fitting parameters for *af*-FePt₃ are also listed in Table 1.

3.2 Thermal and structural properties

Following the previous studies,²⁻⁴⁾ the heats of formation, $\Delta E_{el}^{(n)}$, obtained by FLAPW total energy calculations for each phase n is employed to derive Bulk modulus, Debye temperature and Gruneisen constant. In particular, the Debye temperature is important to estimate the vibrational energy and entropy as will be discussed in the next section. Note, in the following of this section, the superscript n is omitted without the loss of generality.

The calculated heats of formation, ΔE_{el} , is fitted into the following four-parameter Morse potential,

$$\Delta E_{el}(r) = A - 2 \cdot D \cdot \exp(-\lambda \cdot (r - r_{min})) + D \cdot \exp(-2\lambda(r - r_{min})), \quad (13)$$

where A , D , λ and r_{min} are fitting parameters. The derived parameters are listed in Table 2. Note that r_{min} is the equilibrium Wigner-Seitz radius (r_{ws}) at which the heats of formation takes minimum value, $(\Delta E_{el})_{min}$, and r_{min} is related to equilibrium lattice constant, a_{min} , through

$$r_{min} = \left(\frac{3}{16\pi} \right)^{1/3} \cdot a_{min}. \quad (14)$$

With these fitting parameters, Bulk Modulus B , Debye temperature Θ_D and Gruneisen constant γ_0 are derived as

$$B(r_{min}) = -\frac{D \cdot x_0^2 \cdot \lambda^3}{6\pi \cdot \ln x_0} \quad (15)$$

$$(\Theta_D)_0 = 41.63 \left[\frac{r_{min} \cdot B}{M} \right]^{1/2} \quad (16)$$

and

$$\gamma_0 = \frac{\lambda \cdot r_{min}}{2} \quad (17)$$

where x_0 is defined as $x_0 = \exp(-\lambda \cdot r_{min})$, M the molecular weight which is, in the present calculation, the average value of atomic weight of constituent elements as listed in the right column of Table 2. The obtained B , Θ_D and γ_0 are tabulated in Table 3 together with the ones derived by Murnaghan's²¹⁾ prescription and available experimental data from literature.²²⁾ One confirms that the agreement is reasonable. The experimental data of Gruneisen constant to be compared with the present results are not available. However, it is generally accepted that the Gruneisen constant falls between 1.0 and 3.0 for most solids, and the present results also satisfy this general trend.

3.3 Phase diagram

In order to obtain vibrational energy and entropy contributions in eq. (1) Debye-Gruneisen prescription²⁻⁴⁾ is employed and each term is written as,

$$\Delta E_{vib}^{(n)}(r, T) = \frac{9}{8} k_B \cdot \Theta_D^{(n)} + 3k_B \cdot T \cdot D \left(\frac{\Theta_D^{(n)}}{T} \right) \quad (18)$$

Table 2 Morse potential parameters in eq. (13) for five phases obtained based on spin polarized calculations. FePt₃ is in *anti-ferro* magnetic state.

	A	D	$(\Delta E_{el})_{min} = A - D$	λ	a_{min}	r_{WS} W-S rad.	M Mol mass
Fe	0.25038	0.25051	-0.00013	1.6590	6.5946	2.57714	55.85
Fe ₃ Pt	0.20937	0.21871	-0.00941	1.7019	7.0537	2.75656	90.64
FePt	0.24801	0.26966	-0.02160	1.7143	7.2071	2.81651	125.4
FePt ₃	0.31094	0.32523	-0.01430	1.6446	7.3899	2.88794	160.2
Pt	0.37943	0.37932	0.00011	1.6171	7.4868	2.92581	195.0

Table 3 Comparisons of present results of Bulk modulus (B) and Debye temperature $(\Theta_D)_0$ with the ones obtained by Murnaghan's equation of state and experimental data cited from Kittel.²²⁾ Gruneisen constant of each phase is listed in the right column.

	B ($\times 10^2$ MPa)			$(\Theta_D)_0$ (K)			γ_0
	Morse-fitting	Murnaghan-fitting	Exp. ²²⁾	Morse-fitting	Murnaghan-fitting	Exp. ²²⁾	
Fe	2087.87	1988.3	1683	408.62	398.40	470	2.138
Fe ₃ Pt	1793.96	1701.8		307.50	299.49		2.346
FePt	2195.85	2037.5		292.33	281.62		2.414
FePt ₃	2377.08	2323.2		272.50	269.41		2.375
Pt	2645.67	2569.0	2783	262.29	259.81	230	2.366

and

$$\Delta S_{vib}^{(n)}(r, T) = 3k_B \cdot \left[\frac{4}{3} D \left(\frac{\Theta_D^{(n)}}{T} \right) - \ln \left\{ 1 - \exp \left(-\frac{\Theta_D^{(n)}}{T} \right) \right\} \right] \quad (19)$$

where $\Theta_D^{(n)}$ is the Debye temperature which is obtained by eq. (16), $D(x)$ the Debye function and k_B is the Boltzman constant and the first term of the vibrational energy represents the *zero point energy*. Hence, all the necessary terms in eq. (1) are fixed now and the phase diagram is calculated based on the equality of the grand potential as mentioned in the previous section. One thing to be noticed is the fact that the segregation limit depends on temperature through the temperature dependencies of $F_{Fe}(r_{Fe}^*, T^*)$ and $F_{Pt}(r_{Pt}^*, T^*)$ where $r_{Fe}^*(r_{Pt}^*)$ is the equilibrium lattice constant of Fe (Pt) at temperature T^* at which F_{Fe} (F_{Pt}) attains minimum value.

Shown in Fig. 3 are the three phase boundaries of L1₀-disorder obtained in the present study. The broken lines and dot-broken lines are derived without incorporating thermal vibration effects. Then, eq. (1) is reduced to $\Delta F^{(n)}(r, T) = \Delta E_{el}^{(n)}(r)$ and the temperature dependency is neglected from effective cluster interaction energies given by eq. (3), which further reduces the effective internal energy ΔF_0 to an ordinary internal energy. Among these two phase boundaries, the broken boundaries are obtained by employing *ferro*-FePt₃ for $\Delta E_{el}^{(3)}(r)$, while the dot-broken boundaries are obtained with *af*-FePt₃. The transition temperature obtained by these calculations are 2100 K and 1900 K at 1:1 stoichiometric composition, respectively, while the experimental one is ~ 1600 K.¹⁹⁾

Two points should be addressed. One is that the magnetic state of the L1₂ ordered phase at 1:3 affects the stability of the L1₀ ordered phase at 1:1. This is because the change in $\Delta E^{(3)}(r)$ is transmitted to the free energy of L1₀ ordered phase through the internal energy contribution, ΔE , since the

Fig. 3 Disorder-L1₀ phase boundaries. Broken lines are obtained with ΔE_{FePt_3} in the *ferro* magnetic state, while dot-broken lines are calculated with ΔE_{FePt_3} in the *anti-ferro* magnetic state. In both calculations, the thermal lattice vibration effects are neglected. Solid lines are derived with ΔE_{FePt_3} in the *anti-ferro* magnetic state and thermal vibration effects are considered.

internal energy without lattice vibration effects can be deduced from eqs. (1)–(3) as

$$\Delta E(r) = \sum_{m=0}^4 \left\{ \sum_{n=1}^5 \{\xi_n^m\}^{-1} \cdot \Delta E_{el}^{(n)}(r) \right\} \cdot \xi_n. \quad (20)$$

The second point is the fact that the employment of $\Delta E^{(3)}(r)$ with more stable *anti-ferro* magnetic ordered phase result in lower transition temperature *i.e.* less stabilization of an ordered phase. This is because the order-disorder transition temperature is determined not only by the stability of a single phase but by the relative stability of two competing phases. The incorporation of more stable *af*-FePt₃ is considered to enhance the stability of a solid solution.

The overestimated transition temperatures obtained above are improved by the incorporation of the thermal vibration effects as are shown by the solid lines in Fig. 3. In fact, the

transition temperature is 1610 K which is in closed agreement with the experimental transition temperature cited above. The origin of this improvement can be explained in the following manner.

The rigid lattice at the ground state, of which internal energy is employed to calculate the two phase boundaries mentioned above, is frustrated in two senses. One is the neglect of local lattice distortion effect. This effect is crucial for an alloy such as Cu–Au which consists of species with a large difference in atomic size. And an arrangement of these species on a rigid lattice induces extra energy in the system. The explicit incorporation of local relaxation effect, however, is anticipated to alter the symmetry of the lattice from one point to another and the conventional CVM is not rationalized. The difficulty may be resolved by employing so called continuous CVM^{23,24)} which allows the atomic displacement around a rigid Bravais lattice point. Unfortunately, however, this new scheme of the CVM is still at its beginning stage and no attempts have been made for applying it to a realistic alloy system.

The second kind of the frustration of the rigid lattice at the ground state is due to the neglect of lattice softening associated with lattice thermal vibrations. In fact, atoms in different size can be accommodated with less expenditure of energy on the softened lattice than on the stiffed lattice at the ground state, even if the local distortion is not explicitly considered. The present calculation with thermal vibration effects takes this into account and is regarded as a precursor to a fully relaxed calculation.

Recalling that the L1₀-disorder transition is of the first order, the ordered atomic arrangement is well maintained up to the transition temperature. For such an ordered phase, two kinds of species in different size can be well accommodated and the frustration is less emphasized for a disordered solid. Hence, the lattice softening introduced by thermal vibration effects enhances the stability of disordered phase more than the L1₀ ordered phase, resulting in the lower transition temperature.

According to recent experiment,²⁵⁾ the congruent composition corresponding to the highest transition temperature is shifting slightly towards the Pt-rich side. Yet, the present calculation places it almost exactly at 1:1 stoichiometric composition. The elucidation of this point is remaining subject for the future investigation.

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REFERENCES

- 1) Y. Chen, T. Atago and T. Mohri: *J. Phys. Condensed Matter*. **14** (2002) 1903–1913.
- 2) T. Mohri, Y. Chen and T. Atago: under review.
- 3) V. Moruzzi, J. F. Janak and K. Schwarz: *Phys. Rev.* **B37** (1988) 790–799.
- 4) J. D. Becker, J. M. Sanchez and J. K. Tien: *Proc. MRS in Boston* (1990).
- 5) R. Kikuchi: *Phys. Rev.* **81** (1951) 998–1003.
- 6) J. W. Connolly and A. R. Williams: *Phys. Rev.* **B27** (1983) 5169–5172.
- 7) J. M. Sanchez, F. Ducastelle and D. Gratias: *Physica (Utrecht)* **128A** (1984) 334–350.
- 8) T. Mohri, K. Koyanagi, T. Ito and K. Watanabe: *Jpn. J. Appl. Phys.* **28** (1989) 1312–1319.
- 9) T. Mohri, S. Takizawa and K. Terakura: *Mater. Trans., JIM* **31** (1990), 315–316.
- 10) T. Mohri, K. Terakura, S. Takizawa and J. M. Sanchez: *Acta Metal.* **39** (1991) 493–501.
- 11) T. Mohri, K. Nakamura and T. Ito: *J. Appl. Phys.* **70** (1991) 1320–1330.
- 12) K. Nakamura and T. Mohri: *Modelling and Simul. Mater. Sci. Eng.* **1** (1993) 143–150.
- 13) T. Mohri: *Prog. Theoret. Phys. Suppl.* **115** (1994) 147–164.
- 14) R. Kikuchi: *J. Chem. Phys.* **60** (1974) 1071–1080.
- 15) J. M. Sanchez and D. de Fontaine: *Phys. Rev.* **B17** (1978) 2926–2936.
- 16) T. Mohri, J. M. Sanchez and D. de Fontaine: *Acta Metal.* **33** (1985) 1171–1185.
- 17) H. J. F. Jansen and A. J. Freeman: *Phys. Rev.* **B30** (1984) 561–569.
- 18) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais: *Phys. Rev.* **B46** (1992) 6671–6687.
- 19) in *Binary Phase Diagrams*, ed. by Thaddeus B. Massalski: (ASM 1986) 1093.
- 20) G. E. Bacon and J. Crangle: *Proc. Royal Soc. London* **272** (1963) 387–405.
- 21) F. D. Murnaghan: *Proc. Natl. Acad. Sci. USA* **30** (1944) 244.
- 22) C. Kittel: *Introduction to Solid State Physics (6th edition)*, (John Wiley & Sons Inc., 1986).
- 23) K. Masuda-Jindo and R. Kikuchi: *Comp. Mater. Sci.* **14** (1999) 295–310.
- 24) H. Uzawa and T. Mohri: *Mater. Trans.* **42** (2001) 1866–1869.
- 25) A. Kushida, Y. Nose, K. Tanaka and H. Numakura: personal communication to authors.