A Note on Orderings in Ferromagnetic Binary Alloys*)

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A general formulation is given in treating an interrelationship between magnetic and atomic orderings in ferromagnetic binary alloys. The nature of the order parameter is re-examined reflecting recent development in statistical mechanics. On the basis of the general formulation the usual molecular field approach to binary alloys is reconsidered. The critical slowing down is also discussed.

§ 1. Introduction

The random magnet implies essentially a frozen distribution of magnetic atoms quenched by sudden cooling from a high temperature. The frozen randomness therefore would be rearranged ultimately to be a real thermal equilibrium distribution of atoms even if a particular treatment is not processed to the alloy. In usual cases however the relaxation time for rearrangement is inhibitably so long that the annealed alloy has been studied separately from the quenched one. Since few has been known about the mechanism of annealing so far, we would like to consider a reasonable model in which a proper interaction is considered between atoms, in order to study the magnetic property of the annealed alloy. The atomic ordering is known to give a considerable effect on the magnetic property of alloys; the magnetic ordering seems to oppose the process of the atomic ordering.1)–4) Therefore it is essential to develop a self-consistent theory in which both ordering processes are considered simultaneously. This kind of problem has a long history.5) An additional physical insight has been obtained in our previous work,6) too, which clarified further the interrelationship between two ordering processes. Though we believe the simple molecular field approximation introduced in these previous papers worked well in explaining the overall property of phase transitions in alloys, we would like to make sure of it in a somewhat different way; reexamination of the order parameters used there and the usual mean field approach to this kind of problem. In § 2 the general theory is formulated and resulted in a closed set of simultaneous equations in the averaged quantity. In § 3 the mean field theory is developed on the basis of the general formulation after reconsidering the choice of

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order parameters. In § 4 numerical results are discussed, relating with the new choice of order parameters. The mutual dependence of order parameters is selectively discussed, avoiding the exhausting display of the variety of behavior in the model.

§ 2. Formulation

In order to understand the essence of the interrelationship between the processes of atomic and magnetic orderings in ferromagnetic alloys, the simplest model (a diluted magnet with spin one-half) is considered as a proper example in this paper. The field-induced transition will not be treated.

In order to fix our model concrete, let us define the Hamiltonian:

$$\mathcal{H} = \mathcal{H}^N + \mathcal{H}^L,$$

(2.1)

where $\mathcal{H}^N$ stands for the Ising-type interaction between nearest-neighbor magnetic spins, i.e.,

$$\mathcal{H}^N = -\sum_{ij} J(ij) S_i^x S_j^x x_i^x x_j^x - H \sum_i S_i^z x_i^N.$$

(2.2)

$\mathcal{H}^L$ represents the order-disorder interaction of atoms due to the interatomic coupling:

$$\mathcal{H}^L = \frac{1}{2} \sum_{i,j} V^{ij} x_i^j x_j^i.$$

(2.3)

Here the interaction $V$ is assumed to be effective only between nearest-neighbor atoms. The letter $M(V)$ on $x$ is used to identify a magnetic (nonmagnetic) atom. The occupation operator $x_i^j$ has a character of projection,

$$x_i^j x_i^k = x_i^j \delta_{jk},$$

(2.4)

which is assured of by the definition that $x_i^j = 1$ if a $\lambda$-type of atom is at site $i$ and $x_i^j = 0$ otherwise. Here it is noted that the magnetic part of the Hamiltonian $\mathcal{H}^N$ already includes, the coupling between magnetic and atomic orderings due to its four-body character. The spatial sublattices are assumed to be of the nearest-neighbor and of interpenetrating each other, the $\alpha$- and the $\beta$-sublattices. Introducing a new operator by the definition that

$$\sigma_i^j = (x_i^N - x_i^F)/2,$$

(2.5)

which is regarded as the z-component of a pseudo-spin of magnitude 1/2, the coupling constant of the quadratic term in $\sigma^z$ becomes

$$V(\alpha\beta) = V^{NN} + V^{yy} - 2V^{xy},$$

(2.6)

which is also significant only between nearest neighbors. Also an operator $\bar{S}^z (\equiv S^z = S(\sigma^z + 1/2))$ is introduced hereafter in order to clarify the discussion below.
Now three kinds of Green functions are used in the following:

\[ \tilde{G}_{tt'}(E) = \langle \tilde{S}_t^+ ; S_{t'}^- \rangle, \quad (2.7a) \]
\[ G_{tt'}(E) = \langle S_t^+ ; S_{t'}^- \rangle, \quad (2.7b) \]
\[ g_{tt'}(E) = \langle \sigma_t^+ ; \sigma_{t'}^- \rangle, \quad (2.7c) \]

where the standard notation is used. Then the hierarchy of the Green function’s equations \( (I_t = [S_t^+, S_t^-]) \)

\[ (E - H) \tilde{G}_{tt'}(E) = \delta_{tt'} \langle I_t \rangle + 2 \sum \mu J_{\mu t} \tilde{S}_t^\mu \langle S_{t'}^\mu ; S_{t'}^- \rangle, \]
\[ (E - H) \langle \tilde{S}_t^\mu S_{t'}^+ ; S_{t'}^- \rangle = \delta_{tt'} \langle S_t^\mu I_t \rangle + 2 \sum \mu J_{\mu t} \tilde{S}_t^\mu \langle S_{t'}^\mu S_{t'}^+ ; S_{t'}^- \rangle \quad (2.8) \]

is solved formally in the form

\[ \tilde{G}_{tt'}(E) = \delta_{tt'} \langle I_t \rangle / (E - \tilde{E}_t) \rangle, \quad (2.9) \]

where the effective ‘Zeeman field’ operator \( \tilde{E}_t \) is given by

\[ \tilde{E}_t = H + 2 \sum \mu J_{\mu t} \tilde{S}_t^\mu. \quad (2.10) \]

In the same way we have

\[ G_{tt'}(E) = \tilde{G}_{tt'}(E) - \frac{1}{E} \delta_{tt'} \{ \langle I_t \rangle - \langle [S_t^+, S_t^-] \rangle \} \quad (2.11) \]

and

\[ g_{tt'}(E) = \delta_{tt'} \langle [\sigma_t^+, \sigma_{t'}^-] \rangle / (E - \tilde{E}_t) \rangle, \quad (2.12) \]

where

\[ \tilde{E}_t = \rho - \sum \xi \langle \xi^\xi \rangle \sigma_t^+ + \tilde{E}_t S_t^\xi. \quad (2.13) \]

\( \xi \) denotes \( \alpha \) or \( \beta \) sites while \( \xi \) indicates its counterpart. \( \rho \) is an effective field due to chemical potential of atoms. The sum rule as to spin magnitude gives us three equations:

\[ M_t = \langle \tilde{S}_t^\xi \rangle = \langle x_t^\xi \rangle / 2 - \langle S_t^- \tilde{S}_t^+ \rangle, \quad (2.14a) \]
\[ m_t = \langle S_t^\xi \rangle = 1/2 - \langle S_t^- S_t^+ \rangle, \quad (2.14b) \]
\[ \langle \sigma_t^\xi \rangle = 1/2 - \langle \sigma_t^- \sigma_t^+ \rangle, \quad (2.14c) \]

where correlation functions on the right-hand side are related with Green functions \( \tilde{G}, G \) and \( g \) by means of the spectrum theorem. These equations \((2.9) \sim (2.14)\) then construct a closed set of equations to be solved simultaneously. Until this stage calculation is exactly performed. In this paper, however, an approximate procedure will be introduced, in the next section, to get quantitative results from this formulation, because some difficulty is already pointed out in treating this kind of Green functions.
§ 3. Mean field theory

Self-consistent equations

When two mutually independent, Ising models are considered on the same lattice, two order parameters are, at least, necessary to describe phase transition in the systems. If a four-body interaction between these systems is switched on, there could be one more order parameter in the coupled system. This idea is already developed in the Ashkin-Teller-Potts model.\(^8\) In addition, even in the molecular field approximation the same-site correlation cannot be separated into a product of the averages. Reflecting the present model, it is natural to adopt three order parameters, \(M_t\), \(m_t\) and \(\langle \sigma_t \rangle\). Now in calculating the right-hand side of Green functions \(\hat{G}\), \(G\) and \(g\), all correlations appeared there are approximated by products of \(M\), \(m\) and \(\langle \sigma \rangle\). Then by virtue of the spectrum theorem Eq. (2.14) is reduced to

\[
M_t = \frac{1}{2} \langle x_t^a \rangle \tanh (E_t/2k_BT),
\]

(3.1a)

\[
E_t = \langle \hat{E}_t \rangle = H + 2zJM_t,
\]

(3.1b)

\[
m_t = \langle \langle \sigma_t \rangle e^{\hat{E}_t} \rangle / (e^{\hat{E}_t} + 1), \quad (k_BT = \beta^{-1})
\]

(3.2a)

\[
e_t = \rho - \varepsilon \langle \sigma_t \rangle + E_t m_t,
\]

(3.2b)

\[
2L = \langle \sigma_a^* \rangle - \langle \sigma_b^* \rangle - \langle x_a^a \rangle - \langle x_b^b \rangle
\]

\[
= (1 + 4L^* - (2p-1)^2) \tanh (A/2k_BT),
\]

(3.3a)

\[
A = 2\varepsilon VL + H(m_a - m_b) + 2\varepsilon J(M_a m_a - M_b m_b),
\]

(3.3b)

and by denoting concentration of the magnetic atom as \(p\),

\[
2p = \langle x_a^a \rangle + \langle x_b^b \rangle.
\]

(3.4)

These equations are now the final expressions to be solved simultaneously. The new parameter \(L\) is a more suitable order parameter to express the lattice ordering than \(\langle \sigma_t \rangle\) themselves because the difference of occupation number of atoms on two sublattices should vanish above the lattice ordering temperature. The average occupation of the magnetic atom is given by

\[
\langle x_t^a \rangle = p + L(\delta_{ta} - \delta_{tb}).
\]

(3.5)

Magnetic Susceptibility

From Eq. (3.1) the uniform and staggered susceptibilities are found to be

\[
\chi_a = \frac{\partial}{\partial H} \{M_a + M_b\} \simeq \frac{C_a}{T - T_{cm}},
\]

(3.6a)

\[
\chi_a = \frac{\partial}{\partial H} \{M_a - M_b\} \simeq \frac{C_a}{T - T_{cm}},
\]

(3.6b)
where poles of both susceptibilities have the same value

$$T_{CM} = (zJ/2)\sqrt{p^2 - L^*},$$  \hspace{1cm} (3.7a)

$$C_v = (p + \sqrt{p^2 - L^*}), \hspace{1cm} C_v = L/4,$$  \hspace{1cm} (3.7b)

at which the magnetic transition is second order. The lattice ordering necessarily reduces the magnetic ordering temperature as is seen in (3.7). \( T_{CM} \) tends to zero with increasing \( L \) and the real magnetic transition is inhibited over the range \( p < 0.5 \) because there is no self-consistent solution in the set of equations. While \( M_f \) is the observable quantity, \( m_t \) has no direct physical meaning here. In general \( \langle S_i^t \rangle \) never equals to the product \( \langle S_i^r \rangle \langle x_i^k \rangle \), which is also shown numerically in the next section. \( m_t \) has also a vertical tangent at the temperature where the magnetic transition occurs, and does not become zero above the temperature but takes a finite value \( (p-1)/2 \) even in the high temperature limit.

**Lattice Ordering**

The transition temperature is given by

$$T_{CL} = p(1-p) [zV - 4zJL \lim_{L \to 0} \{ (M_\alpha m_\beta - M_\beta m_\alpha) / L \}],$$  \hspace{1cm} (3.8)

while our previous result is\(^5\)

$$T_{CL} \text{(old)} = p(1-p) (zV - 4zJLm_\alpha m_\beta)$$  \hspace{1cm} (3.9)

in the present notation. In \( T_{CL} \text{(old)} \) the magnetic ordering is apparently opposing the lattice ordering \( (V \text{ is assumed positive}) \) while it is not self-evident in \( T_{CL} \) at a glance.

**§ 4. Discussion**

Through all the computations given below, the sign of lattice coupling \( V(\alpha,\beta) \) is taken to be positive; the state that magnetic atoms locate at one of the sublattices, say the \( \alpha \)-lattice, is favourable with the lowering the lattice ordering energy of the alloy. The negative sign of \( V \) will be considered separately. We would attempt here not to exhaust the variety of combination of parameters \( J, T \) and \( p \), but rather to figure out the essential feature of mutual dependence on two ordering processes. Figure 1 shows their typical behavior.\(^5\) While \( T_{CL} \) is lower than \( T_{CM} \) in Figs. 1(a) and 1(b), the lattice ordering is developed before the magnetic transitions occur in Figs. 1(c) and 1(d). The sublattice magnetizations behave separately as soon as the lattice ordering grows at a certain temperature, above which both magnetizations go as the usual Brillouin function gives. A particular concern should be put in Fig. 2; no magnetic transition occurs below the concentration \( p < 0.5 \) as was stated below (3.7). The three-dimensional figures, Figs. 3(a) and 3(b), correspond to Figs. 1(a) and 1(d). They show how the equilibrium curve of ordering parameters behaves with temperature. In Fig. 3(a) the
Fig. 1. Magnetizations of sublattices, $M_α$ and $M_β$, and the lattice polarization $L$ for $V/J = 2.0$ and zero magnetic field. All temperatures are measured in terms of the normalized temperature $T_{c1}$. The magnetic concentration varies from 0.9 to 0.6 as figures run a, b, c and d. The value of $V$ is chosen as large as the lattice ordering completes at 0K in spite of the magnetic coupling.

Fig. 2. The polarized state with no magnetic transition for $V/J = 2.0$. The magnetic concentration is 0.4, which does not satisfy Eqs. (3.1) ~ (3.3).

Fig. 3. Three-dimensional description of equilibrium order parameters. Figures a and b are plotted from Figs. 1(a) and 1(b), which correspond to cases $T_{c1} > T_{c2}$ and $T_{c1} < T_{c2}$, respectively.
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Fig. 4. Phase diagram of the present model. Region I: no magnetization and no lattice polarization. Region II: magnetic ordering phase with no lattice ordering. Region III: lattice ordering phase with no magnetization. Region IV: Coexistence region of magnetizations and the lattice ordering. The solid line turns at a point X, below whose concentration no magnetic transition exists; non-trivial solution for magnetisation exists only above the concentration 0.5(=p) while the solution M=0 (no magnetisation) is a meaningful one in Eqs. (3-1)~(3-3) below 0.5 (=p).

Fig. 5. The difference between \( \langle S_i^x x_i^y \rangle \) and \( \langle S_i^y x_i^y \rangle \) is shown for the cases of Fig. 1.

line of order parameter goes apart from the T-M plane at \( T_{CL} \), with \( dL/dT \) \( (T=T_{CL}) = \infty \), as the temperature is lowered. In Fig. 3(b) the lattice ordering parameter terminates at \( T_{CM} \), below which the equilibrium curve goes into a mixed state, with \( dM/dT \) \( (T=T_{CM}) = \infty \). These behaviors are summarized in Fig. 4 where five dash-dotted lines named a, b, c, d and e correspond to four sections of Fig. 1 and Fig. 2, respectively. Figure 5 shows the difference between \( \langle S_i^x x_i^y \rangle \) (=\( \langle S_i^y x_i^y \rangle \)) in the present theory. It may give us a reasonable base of our choice of the order parameters. From these computations we found that the lattice ordering was hindered by the magnetic ordering while the magnetic Curie temperature was lowered by the existence of lattice ordering.\(^{3}\sim^{3}\) These results tell us the mutual dependence on two ordering processes.

As far as the dynamical property of the model is concerned, the magnetic ordering and lattice ordering inevitably couple with each other in their motions. However since the time scale for two relaxing mechanisms should be considerably
different, it is reasonable to treat two processes separately in dynamics. When the Glauber model is used to discuss these behaviors, the relaxation time of the magnetization is found to be, with some approximation,

$$\tau^{-1} \propto (1 - T_{CN}/T),$$  \hspace{1cm} (4.1)

with

$$T_{CN} = 0.5zJ\sqrt{\rho^2 - L^2(t)},$$  \hspace{1cm} (4.2)

above the magnetic transition temperature. This means the critical slowing down is seen near $T_{CN}$ which is time-dependent even if it is very weak compared with the magnetic behavior. Therefore as far as the critical slowing down, temperature dependence of the relaxation time, is concerned, there cannot be seen in most cases the difference between the annealed and the quenched magnets.

The points we wish to emphasize in this paper are the following: Firstly the closed set of equations is obtained for the ferromagnetic binary alloy, which enables us to step up the order of approximation. Secondly, from the statistical mechanical point of view we have insisted on necessity of the particular care in choosing the order parameter in the present model. Finally, the usual molecular field theory is enough to clarify the interrelationship between two ordering processes, though they may not be reliable in detail. In the physical aspect the present results may be essentially valid in the wider range of concentration of magnetic atoms except near the percolation concentration. The more satisfactory approximation to Eq. (2.9) will be a future task.

References

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