Ground state of a FCC binary alloy with one magnetic component

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ABSTRACT. The states of minimal energy at $T = 0$ K are calculated for a fcc binary alloy with one magnetic component of spin 1/2 and with zero applied magnetic field. Chemical and magnetic interactions between pairs of nearest neighbor atoms are incorporated. The chemical and magnetic interactions represented, respectively, by V and J, are considered constant and concentration independent parameters. Eight possible ordered structures are found for this alloy. Depending on the values of V and J there are five combinations of mixtures of these structures.

RESUMEN. Se calculan los estados de energía mínima a $T = 0$ K para una aleación binaria fcc con una componente magnética de espín 1/2 y sin campo magnético aplicado. En el cálculo se toman en cuenta interacciones químicas y magnéticas entre pares de átomos primeros vecinos. Las interacciones químicas y magnéticas representadas, respectivamente, por V y J, se consideran parámetros constantes independientes de la concentración. Se encuentran ocho estructuras ordenadas posibles. Hay cinco combinaciones de mezclas de estas estructuras, dependiendo de los valores de V y J.

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1. INTRODUCTION

Experimental studies of alloy phase diagrams are very difficult. Consequently, well characterized systems are scarce, and it is common that an alloy has different experimental versions for its phase diagram. This is true even for the binary systems. For that reason, theoretical studies are very important in order to complete, understand, and unify experimental data. The usual practice in a theoretical treatment is to consider an alloy as an Ising model [1]. There is no exact solution for the Ising model in three dimensions, therefore numerical or approximated methods such as Monte Carlo simulation,

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Bragg-Williams approximation or the Cluster Variation Method are commonly used in the solution of this problem.

Before calculating a phase diagram, it is convenient to know the phases or states that may be present according to the concentration and values of the interatomic interactions. In order to achieve that purpose, the states at $T = 0$ K are calculated considering the interatomic interactions as parameters. These states are named ground states. Generally the alloy assumes those states at finite temperatures. When the ground states are found, we know what interatomic interaction values to use in order to study the desired phases. The ground states determination is considered, by itself, as a separate problem from that of the phase diagram calculation.

If an alloy is formed by different species of atoms $A, B, C, \ldots$, the ground states are the configurations that the atoms can take in the lattice in order to minimize the internal energy E. Therefore, given the concentration of atoms and the interatomic interactions, we want to find out the configurations that minimize the energy. Commonly, the methods for minimizing E are based on linear programming techniques, because E can be expressed as a linear function of several variables. However, these techniques can differ in the literature, depending on the authors.

To the best of our knowledge, there are calculations of ground states in ternary alloys only for the linear chain [2] and the triangular lattice [3]. Excluding these two cases, ground states calculations in the literature are for substitutional binary alloys. A pioneering work was that of Kanamori [4], who calculated the ground states for the magnetization process of a Ising spins system in the fcc and bcc lattices. He took into account interactions between pairs of nearest and next nearest neighbor atoms. This problem is equivalent to that of the calculations of ground states for a non-magnetic binary alloy, because the Ising model is isomorphic to a binary alloy [1]. Kanamori's work was complete: he found out the ground states for the whole range of interactions and concentrations. After that, Allen and Cahn [5], using a different technique, also found the ground states for fcc and bcc lattices, with interactions between pairs of nearest and next nearest neighbor atoms. They also solved the problem in a entirely manner, except for a small domain of the interaction values in the fcc lattice.

Ground states calculations have been done incorporating interactions between pairs up to fifth neighbors [6,7], although in an incomplete way. There are also ground states studies using many-body interactions [8,9]. Ground states calculations include different kinds of lattices [2–24], using either pair or many-body interactions. However, all calculations consider the interatomic interactions as concentration independent parameters.

For magnetic alloys, there are two previous ground states studies. First, Sánchez and Lin [21] carried out a calculation for a fcc binary alloy with two magnetic components. They took into account chemical and magnetic interactions between pairs of first neighbors, but they only considered stoichiometric concentrations. After that, Contreras-Solorio *et al.* [24] found the ground states for a bcc binary alloy with one magnetic component. They incorporated chemical and magnetic interactions up to second neighbors. The analysis was done for the whole range of interactions and concentrations.

In this work, we perform a study of the ground states for a fcc binary alloy with one magnetic component and no applied magnetic field. We take into account chemical and

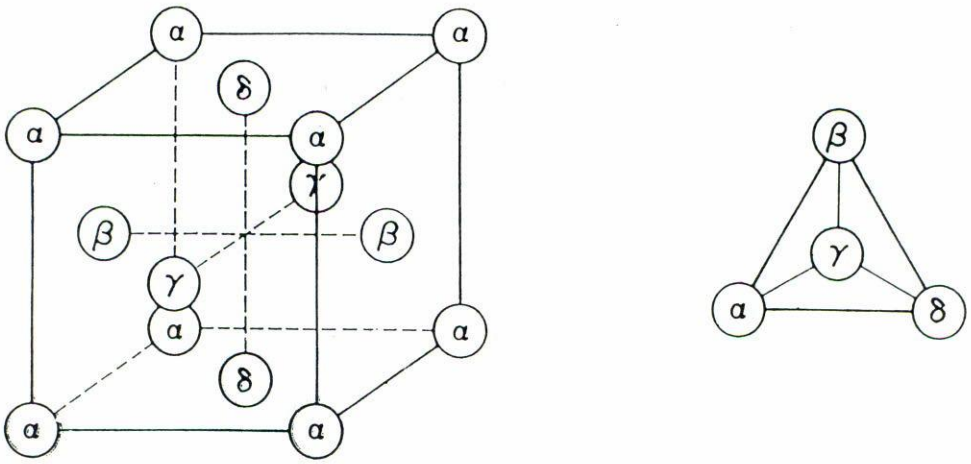

FIGURE 1. a) the four interpenetrating sublattices of fcc lattice, b) tetrahedron including the four sublattices.

magnetic interactions between first neighbors. The ground states for the whole range of concentrations and interactions are found.

2. MODEL

We consider a binary alloy with components A and B. The magnetic atom with spin 1/2 is A, and we designate $A\uparrow$ and $A\downarrow$ the two spin directions. The alloy energy E is approximated by a sum of interaction energies between pairs of nearest neighbor atoms. If there is no external magnetic field the energy can be written as

$$E = -\tfrac{1}{2}N_{AB}V - J\left(N_{A\uparrow A\uparrow} - N_{A\uparrow A\downarrow}\right), \tag{1}$$

where V and J are, respectively, the chemical and magnetic interactions, and N_{ij} is the number of pairs formed by first neighbor atoms of i and j species. The effective interaction V is defined in terms of the chemical interactions V_{ij} between i and j species as

$$V = V_{AA} + V_{BB} - 2V_{AB}, \tag{2}$$

where $J > 0$ favors parallel alignment of neighbor spins, while $V > 0$ favors formation of pairs A–B. In this model, the interactions V and J are considered as concentration independent parameters.

We can pose the ground states problem as follows: How to find the phases or structures at $T = 0$ K for given V, J and the concentration in the fcc lattice? We approach to this problem using the formalism of Allen and Cahn [4]. In order to express the structures that can be built in the fcc lattice taking into account interatomic interactions between nearest neighbors, we divide the lattice into four interpenetrating simple cubic sublattices (Fig. 1a). Incorporating only chemical interactions, according to the configurations of A

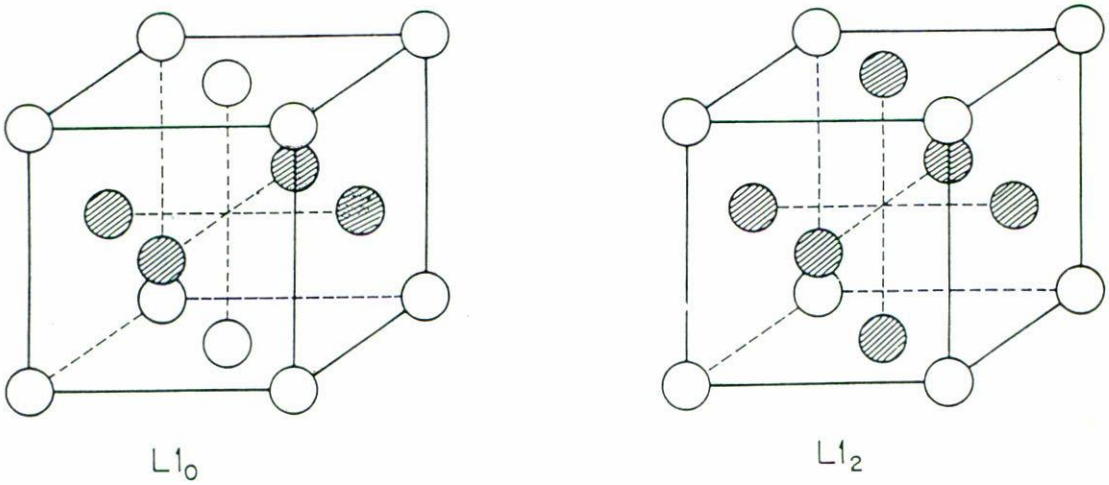

FIGURE 2. $L1_0$ and $L1_2$ structures.

TABLE I. The nine configurations for the tetrahedron, the assignment of the Xr variables, and the kinds of chemical structures. The energy per site and the stability range of J are shown for the eight possible ordered structures.

X_r	configuration	chemical structure	E/N	stability range in J
X_1	$A\uparrow A\uparrow A\uparrow A\uparrow$	$A1$	$-6J$	$J > 0$
X_2	$A\uparrow A\uparrow A\uparrow A\downarrow$	$A1$		forbidden
X_3	$A\uparrow A\uparrow A\downarrow A\downarrow$	$A1$	$2J$	$J < 0$
X_4	$A\uparrow A\uparrow A\uparrow B$	$L1_2$	$-\frac{3}{2}V - 3J$	$J > 0$
X_5	$A\uparrow A\uparrow A\downarrow B$	$L1_2$	$-\frac{3}{2}V + J$	$J < 0$
X_6	$A\uparrow A\uparrow BB$	$L1_0$	$-2V - J$	$J > 0$
X_7	$A\uparrow A\downarrow BB$	$L1_0$	$-2V + J$	$J < 0$
X_8	$A\uparrow BBB$	$L1_2$	$-\frac{3}{2}V$	$-\infty < J < \infty$
X_9	$BBBB$	$A1$	0	$-\infty < J < \infty$

and B atoms, we can obtain ordered structures at stoichiometries A ($A1$), A_3B ($L1_2$), AB ($L1_0$), AB_3 ($L1_2$), and B ($A1$). We have inserted between parentheses the strukturbericht notation for cristalographic structures. $L1_0$ and $L1_2$ structures are shown in Fig. 2. When magnetic interaction between A atoms is considered, the preceding structures can adopt ferromagnetic or antiferromagnetic order.

We choose in the fcc lattice a cluster of points which contains pairs of nearest neighbors. This cluster is a tetrahedron, the vertices of which include points of the four sublattices (Fig. 1b). Next, we look for all the possible configurations of the atoms $A\uparrow$, $A\downarrow$, and B in the tetrahedron. Each tetrahedron site can be occupied in three ways, so, the total number of configurations is 81. Considering the tetrahedron symmetry, this number is reduced to nine. Table I shows the nine configurations and their chemical structure.

Each configuration represents an ordered structure that the alloy may take at stoichiometric concentrations. A variable X_r ($r = 1, \ldots, 9$) is assigned to each configuration.

This variable is the fraction of tetrahedrons in the r configuration. The assignment of variables is given in Table I. The tetrahedrons in the lattice may take any of the nine configurations, thus the variables satisfy the relationship

$$\sum_{r=1}^{9} X_r = 1. \tag{3}$$

In addition, if c_r is the concentration of B atoms in the r configuration, and c the total concentration of B, we have

$$\sum_{r=1}^{9} c_r X_r = c. \tag{4}$$

The number of pairs N_{ij} in (1) can be related to the X_r by the relationship

$$\frac{\text{number of nearest neighbor pairs in the lattice}}{\text{number of nearest neighbor } i\text{–}j \text{ pairs in the lattice}} = \frac{\text{number of pairs in the tetrahedron}}{\text{average number of first neighbor } i\text{–}j \text{ pairs in the nine configurations}}.$$

This relationship can be stated mathematically as

$$\frac{\frac{ZN}{2}}{N_{ij}} = \frac{6}{\sum_{r=1}^{9} N_{ij}^{(r)} X_r}, \tag{5}$$

where $N_{ij}^{(r)}$ is the number of pairs of i–j atoms in the r configuration, and Z is the coordination number.

Using (5) and (1), for the fcc lattice we get

$$E = -\frac{1}{2} N \sum_{r=1}^{9} \left[V N_{AB}^{(r)} + 2J \left(N_{A\uparrow A\uparrow}^{(r)} - N_{A\uparrow A\downarrow}^{(r)} \right) \right] X_r. \tag{6}$$

The problem is to find the X_r fractions which minimize E as a function of V, J and c. The energy function (6) is linear in X_r and subject to the constraints (3) and (4). In addition, we have the constraint $0 \leq X_r \leq 1$. This is a typical linear programming problem. The solution method is developed in the next section.

3. PROCEDURE

To find out the ground states in all concentration range, E in (6) is minimized incorporating the constraints (3) and (4). However, before trying to solve the problem, it is convenient to take a look at the nine structures, since maybe not all of them are possible

for the alloy. This is solved minimizing E at fixed stoichiometric concentrations $c = 0, 1/4, 1/2, 3/4$ and 1, without incorporating the constraint given by (4). This procedure gives the range of J values in which the possible configurations are stable.

We will illustrate the procedure at $c = 0$. For this composition, which corresponds to pure A, the alloy may be in any of the ordered states corresponding to X_1, X_2 or X_3. Taking into account only these configurations, the energy is given by

$$E = -2N(3JX_1 - JX_3), \tag{7}$$

with the constraint (3) for X_1, X_2, and X_3. The procedure followed in linear programming is to eliminate one variable using (3), in order to leave the energy as a function of the two remaining variables. E is a minimum when the coefficients of these two X's are positive. This condition gives the range of J values. The value of E is given by requiring that the two X's be zero. For instance, by eliminating X_1 we get

$$E = 2N(3JX_2 + 4JX_3 - 3J). \tag{8}$$

The coefficients of X_2 and X_3 must be positive to get a minimum in E. This condition gives $J > 0$, so that this is the stability range for the structure represented by X_1. The minimum occurs when $E = -6NJ$, $X_2 = X_3 = 0$, and $X_1 = 1$. The previous solution tell us that the whole alloy is in the ordered structure X_1, with energy given by $E = -6NJ$. For X_2, following the same procedure, from the condition that the coefficients of X_1 and X_3 are positive, it is obtained that $J > 0$ and $J < 0$ simultaneously. This inconsistency means that the configuration X_2 is forbidden. The above procedure is also applied to X_3 when $c = 0$, and also to configurations with stoichiometries $c = 1/4, 1/2, 3/4$, or 1.

Next, the ground states are investigated minimizing E at arbitrary concentrations. Now the two constraints given by (3) and (4) are taken into account, and a process similar to that described for stoichiometric concentrations is followed. We use the two constraints to eliminate two of the nine Xr and to obtain an expression for E in terms of the remaining seven. The coefficients of this seven variables must be positive for E to be a minimum. This condition leads to a homogeneous system of seven inequalities in two unknowns: V and J. The solution of the system gives the values of V and J for which the mixture of structures represented by the two X's exists. The minimum value for E is obtained by making the remaining seven variables equal to zero. The use of the constraint $0 \leq X_r \leq 1$ gives the concentration range for the existence of the considered mixture of the two X's.

As an example, let us apply to the pair X_4, X_6 the process outlined above. Using (3) and (4) we get

$$\begin{aligned} X_4 &= 2 - 4c - 2X_1 - 2X_2 - 2X_3 - X_5 + X_8 + 2X_9, \\ X_6 &= -1 + 4c + X_1 + X_2 + X_3 - X_7 - 2X_8 - 3X_9. \end{aligned} \tag{9}$$

Substituting (9) in (6), the expression for E becomes

$$\begin{aligned} E = N\big[&(V - J)X_1 + (V + 5J)X_2 + (V + 7J)X_3 + 4JX_5 + 2JX_7 \\ &+ (V - J)X_8 + (V - J)X_9 - V - 5J - 2Vc + 8Jc\big]. \end{aligned} \tag{10}$$

From the condition that the coefficients of the seven X's are positive for E to be a minimum, a system of seven inequalities is obtained, and its solution is

$$\begin{aligned} V - J &> 0, \\ J &> 0. \end{aligned} \tag{11}$$

The above result gives the range of interactions for which the mixture of structures X_4, X_6 is a ground state. Setting the seven X's equal to zero in Eq. (10), we get the energy of the mixture:

$$E = N[-V - 5J - c(2V - 8J)]. \tag{12}$$

According to (9) the fractions of tetrahedrons in configurations X_4 or X_6 in the alloy are

$$\begin{aligned} X_4 &= 2 - 4c, \\ X_6 &= -1 + 4c. \end{aligned} \tag{13}$$

From the constraint that the X's lie between 0 and 1 it follows that

$$\tfrac{1}{4} \leq c \leq \tfrac{1}{2}. \tag{14}$$

For the stoichiometric concentration $c = 1/4$ or $c = 1/2$, the alloy is in the ordered phase represented, respectively, by X_4 or X_6.

Taking the results obtained at stoichiometric concentrations as a guide, the above process was repeated for each pair of Xr the J values of which are in the same range of stability.

4. RESULTS

From the analysis for stoichiometric concentrations, it is found that the structure represented by X_2 is not stable at zero applied magnetic field. Therefore, the number of possible ordered states of the alloy is reduced to eight. These allowed structures are shown in Table I. They can be built using the four interpenetrating sublattices of Fig. 1a. For pure A there are two possible states represented by the ferromagnetic phase X_1 or the antiferromagnetic structure X_3. For the stoichiometry A_3B ($L1_2$) there are two states represented by the ferromagnetic order X_4 or the antiferromagnetic one X_5. The ferromagnetic phase X_6 or the antiferromagnetic phase X_7 can be present at stoichiometry AB ($L1_0$). For the stoichiometry AB_3 ($L1_2$) only the paramagnetic structure represented by X_8 is present. Finally, for pure B the state is the structure $A1$ symbolized by X_9.

The energies of the eight possible ordered structures are shown in Table I; with the table also appear the J values for which the magnetic structures are stable. Before presenting our results, the ground states obtained incorporating only the chemical interaction V between pairs of nearest neighbor atoms are shown in Fig. 3. In this diagram, for $V > 0$

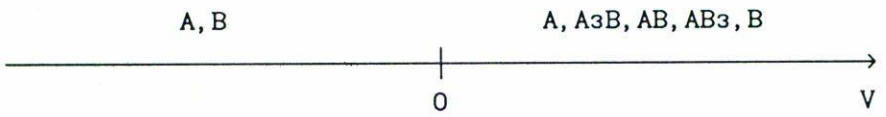

FIGURE 3. Ground state diagram for a non-magnetic fcc binary alloy taking into account only nearest neighbor interactions (Ref. [7]).

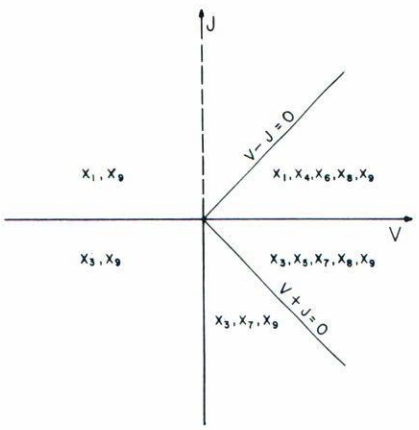

FIGURE 4. Ground state diagram in the $V - J$ plane for a fcc binary alloy with one magnetic component.

there is a sequence of ordered states A, A_3B, AB, AB_3 and B at stoichiometric concentrations. For intermediate concentrations, the ground state is given by a mixture of the two neighboring structures. For $V < 0$ the alloy is segregating: the ground state is a mixture of the two pure components A and B for the whole range of concentration. To show in only one diagram our results for the magnetic alloy, a three-dimensional space with axis V, J, and c is necessary. As an alternative, we prefer to present the values of V and J in a more practical way, using a cartesian plot V–J in Fig. 4. The concentration dependence of the ground states appears separately in Table II.

At stoichiometric concentrations the alloy is found in a perfectly ordered state given by any of the eight possible structures. The diagram of ground states of Fig. 4 is divided in five sections. We associate with each section a precise sequence of ordered structures X_r when the concentration c of B atoms increases and has stoichiometric values. For

TABLE II. Concentration ranges under which mixtures of two configurations X_r can exist as alloy ground states. Values for the fractions X_r in the mixtures are also shown as a function of the concentration c.

range	pairs	values
$[0, 0.25]$	X_1, X_4	$X_1, X_3 = 1 - 4c$
	X_3, X_5	$X_4, X_5 = 4c$
$[0.25, 0.5]$	X_4, X_6	$X_4, X_5 = 2 - 4c$
	X_5, X_7	$X_6, X_7 = -1 + 4c$
$[0.5, 0.75]$	X_6, X_8	$X_6, X_7 = 3 - 4c$
	X_7, X_8	$X_8 = -2 + 4c$
$[0.75, 1]$	X_8, X_9	$X_8 = 4 - 4c$
		$X_9 = -3 + 4c$
$[0, 0.5]$	X_3, X_7	$X_3 = 1 - 2c$
		$X_7 = 2c$
$[0.5, 1]$	X_7, X_9	$X_7 = 2 - 2c$
		$X_9 = -1 + 2c$
$[0, 1]$	X_1, X_9	$X_1, X_3 = 1 - c$
	X_3, X_9	$X_9 = c$

intermediate concentrations between stoichiometric values, the ground state is a mixture of the two neighboring ordered structures. Table II indicates the ranges of concentration for which the mixtures can exist as ground states. This table also shows the values the fractions X_r take as a function of c. The energy of the ground state given by a mixture of two X_r is obtained by adding the energies of Table I times the corresponding fractions of Table II. This energy can also be obtained by the process outlined in Sect. 3.

Comparing Fig. 4 with Fig. 3 we notice that considering magnetic interaction, the sequence of states with chemical structure A, AB, B for $V + J < 0$, $V > 0$ (the section X_3, X_7, X_9 in Fig. 4) can exist as a ground state. This sequence is not present in the diagram of ground states of Fig. 3 with only chemical interaction.

5. CONCLUSIONS

Using a model of chemical and magnetic interactions between pairs of nearest neighbor atoms, we have determined the ground states of a fcc binary alloy with one magnetic component for the whole range of concentration and interactions. The energy minimization was carried out using linear programming by the Allen and Cahn's method. For zero external magnetic field the analysis reveals eight possible structures which present chemical order and ferro and antiferromagnetic order. There are five different combinations for mixtures of these structures according to the V and J values. Special attention is paid to the fact that one of the five combinations is the sequence of structures A, AB, B. This

sequence does not exist for the ground states of a fcc binary alloy taking into account only chemical interactions between nearest neighbors.

The Ising model used in the calculations is simple, because it incorporates interatomic interactions only between nearest neighbors. Moreover, it does not take into account that V and J may be concentration dependent. However, the structures observed in coherent fcc binary systems with one magnetic component (such as Co-Pt and Ni-Pt [25]), are found among the calculated ground states, which indicates that nearest neighbor interactions are strongly dominant.

REFERENCES

1. Ziman, *Models of disorder*, Cambridge University Press (1982), Sect. 1.5
2. J. Kanamori, *Prog. Theor. Phys.* **35** (1966) 16.
3. M.J. Richards and J.W. Cahn, *Acta Metall.* **19** (1971) 1236.
4. S.M. Allen and J.W. Cahn, *Acta Metall.* **20** (1972) 423.
5. S. Katsura and A. Narita, *Prog. Theor.* **50** (1973) 1426 and 1750.
6. S.M. Allen and J.W. Cahn, *Scripta Metall.* **7** (1973) 1261.
7. A. Narita and S. Katsura, *Prog. Theor. Phys.* **52** (1974) 1448.
8. T. Morita, *J. Phys. A: Math., Nucl. Gen.* **7** (1974) 289.
9. T. Morita, *J. Phys. A: Math., Nucl. Gen.* **7** (1974) 1613.
10. M. Kaburagi and J. Kanamori, *Prog. Theor. Phys.* **54** (1975) 30.
11. T. Kudo and S. Katsura, *Prog. Theor. Phys.* **56** (1976) 435.
12. J. Kanamori and Y. Kakehashi, *J. de Physique* **38** (1977) C7-274.
13. M. Kaburagi, *J. Phys. Soc. Jap.* **44** (1978) 54 and 394.
14. T. Moriya and H. Ino, *J. Phys. Soc. Jap.* **46** (1979) 1776.
15. J.W. Cahn and R. Kikuchi, *Acta Metall.* **27** (1979) 1329.
16. J.M. Sánchez and D. de Fontaine, *Structure and Bonding in Crystals*, Vol. II, Academic Press, New York (1981) p. 117.
17. Roberto Osorio de Cerqueira, Ph. D. Thesis, University of California, Berkeley (1982).
18. J. Kanamori and M. Kaburagi, *J. Phys. Soc. Jap.* **52** (1983) 4184.
19. A. Finel and F. Ducastelle, *Mat. Res. Soc. Symp. Proc.* **21** (1984) 293.
20. J.M. Sánchez and C.H. Lin, *Phys. Rev.* **B30** (1984) 1448.
21. J. Kanamori, *J. Phys. Soc. Jap.* **53** (1984) 250.
22. U. Brandt and J. Stolze, *Z. Phys.* **B64** (1986) 481.
23. A. Finel, Ph. D. Thesis, Universitè Pierre et Marie Curie, Paris (1987).
24. D.A. Contreras-Solorio, F. Mejía-Lira, J.L. Morán-López, and J.M. Sánchez, *Phys. Rev.* **B38** (1988) 4955.
25. M.C. Cadeville and J.L. Morán-López, *Phys. Rev.* **153** (1987) 331.