PHYSICAL REVIEW B VOLUME 44, NUMBER 13 1 OCTOBER 1991-I

Diffusionless first-order phase transitions in systems with frozen configurational degrees of freedom

Antoni Planes, Eduard Vives, and Teresa Castán
Departament d'Estructura i Constituents de la Materia, Facultat de Física, Universitat de Barcelona,
Diagonal 647, 08028 Barcelona, Catalonia, Spain

(Received 15 January 1991)

We consider systems that can be described in terms of two kinds of degree of freedom. The corresponding ordering modes may, under certain conditions, be coupled to each other. We may thus assume that the primary ordering mode gives rise to a diffusionless first-order phase transition. The change of its thermodynamic properties as a function of the secondary-ordering-mode state is then analyzed. Two specific examples are discussed. First, we study a three-state Potts model in a binary system. Using mean-field techniques, we obtain the phase diagram and different properties of the system as a function of the distribution of atoms on the different lattice sites. In the second case, the properties of a displacive structural phase transition of martensitic type in a binary alloy are studied as a function of atomic order. Because of the directional character of the martensitic-transition mechanism, we find only a very weak dependence of the entropy on atomic order. Experimental results are found to be in quite good agreement with theoretical predictions.

I. INTRODUCTION

The interplay between different ordering modes can strongly modify the shape of phase diagrams. Typical examples of such a situation are magnetic alloys[1,2] and liquids crystals.[3] In the former case, the presence of magnetism can influence the atomic distribution among the different lattice sites. In the second case, the interplay between translational and rotational ordering modes can even change the order of the smectic-nematic phase transition.[4]

We consider the case of systems with two relevant kinds of internal degrees of freedom, associated with two different ordering modes. Landau theories with two order parameters are the natural way to deal with such problems and they have been investigated for 20 years.[5,6] Different coupling terms between the two order parameters can be included in the expansion of the free energy depending on the symmetry properties of each system.[7] The equilibrium values of the order parameter are then found after minimization of the proposed free-energy functional. Generally speaking, equilibrium coupling effects appear when the phase transitions associated with both ordering modes are close to each other.[8]

In this paper, we assume that these two phase transitions take place at very widely separated temperatures. Properties of the phase transition associated with the primary ordering mode are then studied, assuming that the secondary ordering mode can be externally controlled. An experimental realization of this situation is, for instance, observed in metallic alloys which undergo an order-disorder transition as well as a displacive structural transition at a much lower temperature.[9] In this case, the primary and secondary ordering modes are, respectively, the deformation associated with the displacive transition and the configurational atomic order. The interplay between them comes from the fact that the atomic correlations between different kinds of atoms can modify the characteristics of the displacive transition. The configurational atomic order can be externally controlled in the following way. It is first established by annealing at a temperature T_i and then retained by quenching to a lower temperature T_f, above the structural transition temperature. If T_f is low enough to ensure that no diffusion takes place in the system, by changing T_i in a suitable way, the displacive structural transition can then be studied in systems with different internal states.[10,11]

We focus our attention on two particular cases. First, we consider a three-state Potts model on a cubic lattice with two kinds of atoms, A and B. The mean-field approximation allows us to study how the first-order transition, associated with the Potts variables, is modified when the distribution of atoms over the lattice sites is externally changed. The goal is then to obtain a complete mean-field solution of the problem.

Second, we consider, from a more phenomenological point of view, the case of bcc alloys undergoing a structural transition of the martensitic type. This problem has already been considered from a theoretical as well as from an experimental point of view. On the basis of the displacive character of the transition, it was suggested[11] that the entropy change is independent of the ordering state. In addition, experiments seem to confirm this idea. Here we reformulate the problem in a more general context and discuss the results in the light of those obtained from the Potts model system for which the transition is simple and well understood. We find that, in general, the displacive character of the transition is not a definitive condition for the entropy change to be independent on the internal state of the system. Symmetry conditions play an important role as well and have to be considered in the discussion. The main reason for the entropy change to be, in the case of martensitic transitions, nearly independent of the ordering state is the large elastic anisotropy. Finally we compare the theoretical predictions with available experimental results.

II. GENERAL CONSIDERATIONS

The equilibrium condition for a first-order phase transition to occur is given by

$$\Delta F = 0 = \Delta E - T_0 \Delta S \ , \tag{1}$$

where ΔF, ΔE, and ΔS are, respectively, the free energy, energy, and entropy changes at the phase transition and T_0 is the equilibrium transition temperature. In writing Eq. (1) we have assumed that the volume change at the phase transition is negligible. In what follows we denote the H and L phases, respectively, as the high (stable for $T > T_0$) and low (stable for $T < T_0$) temperature phases and restrict ourselves to diffusionless first-order transitions.

For a system of N atoms, we assume that the state of the system, associated with externally controlled degrees of freedom, can be characterized by a state vector $\boldsymbol{\sigma} = (\sigma_1, \sigma_2, \ldots, \sigma_N)$, where σ_i describes the internal state of the atom i. σ_i can be, for example, a magnetic or an occupation variable. In these two cases, the internal state is the magnetic or the atomic configurational order state.

Associated with this internal state, we assume that the system presents, at a certain temperature T_c far from T_0, a secondary phase transition. In a magnetic system, if $T_c \ll T_0$, the application of an external magnetic field provokes a change in the internal state of the system. In a substitutional alloy, if $T_c \gg T_0$, and T_0 is low enough, the internal state can be changed by means of a fast quench as explained in the Introduction.

Suppose we now change the internal state of our system from $\boldsymbol{\sigma}$ to $\boldsymbol{\sigma} + \delta\boldsymbol{\sigma}$. Then the transition temperature changes from T_0 to $T_0 + \delta T_0$, which, for a small $\delta\Delta S$, is a solution of the equation

$$\delta(\Delta E) - T_0 \delta(\Delta S) - \Delta S \delta T_0 = 0 \tag{2}$$

equivalent to

$$\frac{\delta(\Delta E)}{\Delta E} - \frac{\delta(\Delta S)}{\Delta S} = \frac{\delta T_0}{T_0} \ , \tag{3}$$

where $\delta(\Delta E) = \Delta E(\boldsymbol{\sigma} + \delta\boldsymbol{\sigma}) - \Delta E(\boldsymbol{\sigma})$ and

$$\delta(\Delta S) = \Delta S(\boldsymbol{\sigma} + \delta\boldsymbol{\sigma}) - \Delta S(\boldsymbol{\sigma}) \ .$$

In the particular case $\delta(\Delta S) = 0$, then

$$\delta T_0 = T_0 \frac{\delta(\Delta E)}{\Delta E} = \frac{\delta(\Delta E)}{\Delta S} \ . \tag{4}$$

Let us consider that both ordering modes can be described by scalar magnitudes, and define η and ξ as the primary and secondary order parameters, respectively. The free-energy density f of the system can be written as

$$f = f_1(\eta, T) + f_2(\xi, T) + f_{12}(\eta, \xi, T) \ , \tag{5}$$

where f_1 gives rise to a first-order transition associated with η. In Landau theory, f is, in the absence of external fields, usually written as

$$\begin{aligned} f = {} & a_1(T - T_{c1})\eta^2 + \psi_1(\eta) + a_2(T - T_{c2})\xi^2 \\ & + \psi_2(\xi) + k\eta^x \psi_{12}(\xi, T) \ , \end{aligned} \tag{6}$$

where the integer x and the functions ψ_1, ψ_2, and ψ_{12} depend on the symmetry properties of the system.

Suppose now that ξ remains constant, ΔS is then given by

$$\begin{aligned} \Delta S &= -\left[\left. \frac{\partial f}{\partial T} \right|_{\bar{\eta}} - \left. \frac{\partial f}{\partial T} \right|_{\bar{\eta}_0} \right] \\ &= -a_1(\bar{\eta}^2 - \bar{\eta}_0^2) - K \frac{\partial \psi_{12}(\xi, T)}{\partial T} (\bar{\eta}^x - \bar{\eta}_0^x) \ . \end{aligned} \tag{7}$$

$\bar{\eta} - \bar{\eta}_0$ is the discontinuity of the order parameter at the first-order transition point. $\bar{\eta}$ and $\bar{\eta}_0$ are solutions of the equations

$$\begin{aligned} 2a_1(T - T_{c1})(\bar{\eta} - \bar{\eta}_0) + \left[\left. \frac{\partial \psi_1}{\partial \eta} \right|_{\bar{\eta}} - \left. \frac{\partial \psi_1}{\partial \eta} \right|_{\bar{\eta}_0} \right] & \\ + Kx\psi_{12}(\xi, T)(\bar{\eta}^{x-1} - \bar{\eta}_0^{x-1}) = 0 \ , & \end{aligned} \tag{8a}$$

$$\begin{aligned} a_1(T - T_{c1})(\bar{\eta}^2 - \bar{\eta}_0^2) + [\psi_1(\bar{\eta}) - \psi_1(\overline{\eta_0})] & \\ + K\psi_{12}(\xi, T)(\bar{\eta}^x - \bar{\eta}_0^x) = 0 \ . & \end{aligned} \tag{8b}$$

The first equation comes from the minimization condition $\partial f / \partial \eta = 0$, and the second from the condition $\Delta f = 0$ that determines the position of the equilibrium first-order transition. Multiplying Eq. (8a) by $(\bar{\eta} + \bar{\eta}_0)$, Eq. (8b) by (-2), and taking into account Eq. (7), one obtains that, only when $x = 2$ and ψ_{12} does not show an explicit dependence on temperature, is ΔS independent of ξ. This kind of coupling is merely energetic and its effect is to induce a shift on the transition temperature only.

III. EXAMPLE: BINARY ALLOY WITH THREE-STATE POTTS MODEL VARIABLES

Let us consider a d-dimensional lattice with N sites and z nearest neighbors per site. On each site $i = 1, 2, \ldots, N$, we define two variables: a spinlike variable σ_i which takes value $+1$ (-1) when the site i is occupied by an atom A (atom B) and a three-state Potts variable $S_i = (1, 2, 3)$ which describes the state of the particle sitting on the site i.

We then consider the following Hamiltonian:

$$\begin{aligned} H = \sum_{i,j}^{\mathrm{NN}} \delta(S_i - S_j)[& J_{AA}\delta(\sigma_i - 1)\delta(\sigma_j - 1) \\ & + J_{AA}\delta(\sigma_i + 1)\delta(\sigma_j - 1) \\ & + J_{AB}\delta(\sigma_i - 1)\delta(\sigma_j + 1) \\ & + J_{BB}\delta(\sigma_i + 1)\delta(\sigma_i + 1)] \ , \end{aligned} \tag{9}$$

where the summation extends over all nearest-neighbor (NN) pairs. δ is the Kronecker δ function [$\delta(0) = 1$, or 0 otherwise), and the different pair interactions are J_{AA}, J_{AB}, and J_{BB}.

In the present work we restrict ourselves to the case of stoichiometric composition $N_A / N = \frac{1}{2}$, N_A

($N_B = N - N_A$) being the number of A atoms. Given that N_A is constant, we have the following conservation condition:

$$\sum_{i=1}^{N} \sigma_i = 0 \ . \tag{10}$$

Let $J_{AB} \ll J_{AA} \approx J_{BB}$ and further assume that the geometry of the lattice is such that the ground state of the system is formed by two equivalent sublattices, called + and −, occupied by A and B atoms, respectively, and with all the particles in the same Potts state. The square, cubic, and bcc lattices apply to this case with $z=4$, 6, and 8, respectively. This ground state is sixfold degenerate and its energy is $E_0 = J_{AB} zN/2$.

We now introduce the occupation numbers $N_{\sigma s}^{+}$ and $N_{\sigma s}^{-}$ defined as the number of particles in sublattice + (−) of kind σ (A or B) in the Potts state S (1,2, or 3).

In the mean-field (MF) approximation, the Hamiltonian can be written as

$$H_{\mathrm{MF}} = \left[2\frac{z}{N} \right] \sum_{k=1}^{3} [J_{AA} N_{Ak}^{+} N_{Ak}^{-} + J_{AB}(N_{Ak}^{+} N_{Bk}^{-} + N_{Bk}^{+} N_{Ak}^{-}) + J_{BB} N_{Bk}^{+} N_{Bk}^{-}] \ . \tag{11}$$

Let us choose one of the six ground states as the starting point of our mean-field analysis. For instance, the configuration with $N_{A1}^{+} = N/2$, $N_{B1}^{-} = N/2$, and all the other occupation numbers equal to zero. Using symmetry considerations we can write $N_{A2}^{+} = N_{A3}^{+}$, $N_{B2}^{+} = N_{B3}^{+}$, $N_{A2}^{-} = N_{A3}^{-}$, and $N_{B2}^{-} = N_{B3}^{-}$. This is equivalent to restrict the study to only one branch in the full order-parameter space.[12,13]

Provided that the configurational degrees of freedom (σ) are frozen, the entropy of the system can be written, up to constants, as

$$S = k_B T[\ln(W_A^{+}) + \ln(W_A^{-}) + \ln(W_B^{+}) + \ln(W_B^{-})] \ , \tag{12}$$

where k_B is the Boltzmann constant and

$$W_\sigma^{\pm} = \frac{(N/2)!}{N_{\sigma 1}^{\pm}!(N_{\sigma 2}^{\pm}!)^2} \ . \tag{13}$$

Let us now define the following four order parameters corresponding to the Potts variables:

$$m_\sigma^{\pm} = \frac{N_{\sigma 1}^{\pm} - N_{\sigma 2}}{N_{\sigma 1}^{\pm} + 2N_{\sigma 2}^{\pm}} \ . \tag{14}$$

The total number of A and B particles is constant and equal to $N/2$. Therefore, we can define a unique quantity m_p that controls the amount of A and B atoms in each sublattice and that we consider can be externally controlled. This parameter is the one that would depend on the quenching conditions. It is defined as

$$m_p = \frac{4(N_{A1}^{+} + 2N_{A2}^{+})}{N} - 1 \ . \tag{15}$$

$m_p = 0$ corresponds to the case in which the A and B atoms are randomly distributed on the lattice sites. The case $m_p = 1$ means that the A and B atoms are perfectly arranged in the + and − sublattices, respectively.

In order to simplify the solution of the problem, let us consider only the case $J_{AA} = J_{BB} = -JJ_0$ with $J_{AB} = -J_0$. J (<1) is a parameter and J_0 is a positive unit of energy. With these definitions, the mean-field free energy per particle (in zJ_0 units) can be written as

$$f = -\tfrac{1}{24}[J(1+2m_A^{+} m_A^{-})(1+m_p)(1-m_p) + (1+2m_A^{+} m_B^{-})(1+m_p)^2 + (1+2m_B^{+} m_A^{-})(1-m_p)^2 + J(1+2m_B^{+} m_B^{-})(1+m_p)(1-m_p)] + \left[\frac{T^*}{4} \right] \{(1+m_p)[\mathcal{L}(m_A^{+}) + \mathcal{L}(m_B^{-})] + (1-m_p)[\mathcal{L}(m_A^{-}) + \mathcal{L}(m_B^{+})]\} \ , \tag{16a}$$

where $T^* = k_B T/zJ_0$ and

$$\mathcal{L}(m) = \tfrac{1}{3}(1+2m)\ln[\tfrac{1}{3}(1+2m)] + \tfrac{2}{3}(1-m)\ln[\tfrac{1}{3}(1-m)] \ . \tag{16b}$$

A minimization with respect to the four order parameters, defined in (14), yields

$$m_A^{+} = m_B^{-} = m_0, \quad m_A^{-} = m_B^{+} = m_1 \ . \tag{17}$$

m_0 (m_1) is the order parameter which informs us about the Potts order of the rich (poor) component. The temperature dependence of m_0 and m_1 is given by

$$J(1-m_p)m_1 + (1+m_p)m_0 = 2T^* \ln\left[\frac{1+2m_0}{1-m_0} \right] , \tag{18}$$

$$J(1+m_p)m_0 + (1-m_p)m_1 = 2T^* \ln\left[\frac{1+2m_1}{1-m_1} \right] . \tag{19}$$

We can now analyze some simple solutions:

(i) Totally disordered alloy ($m_p = 0$) with $J=0$. In this case the solution of Eqs. (18) and (19) gives $m_0 = m_1 = m$. The system shows a Potts-like first-order phase transition. The low-temperature limit of the coexistence region is $T_l^* = \frac{1}{6}$, while the upper one is $T_u^* = 0.1821$. A careful study of the stability of these solutions gives an equilibrium transition temperature of $T_e^* = 0.1803$, with an entropy change of $\Delta S = 0.231\,05$.

(ii) $1 > m_p > 0$ and $J=0$. The case of $J=0$ is, actually, a very particular case because the Potts transition splits off in two decoupled first-order transitions, associated to

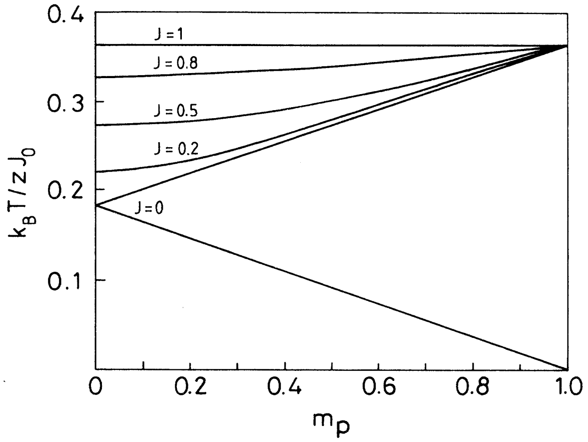

FIG. 1. Phase diagram showing the transition temperature lines for $J=0$, 0.2, 0.5, 0.8, and 1 as a function of the configurational order parameter m_p. Note the splitting off in two phase transitions when $J=0$, as explained in the text.

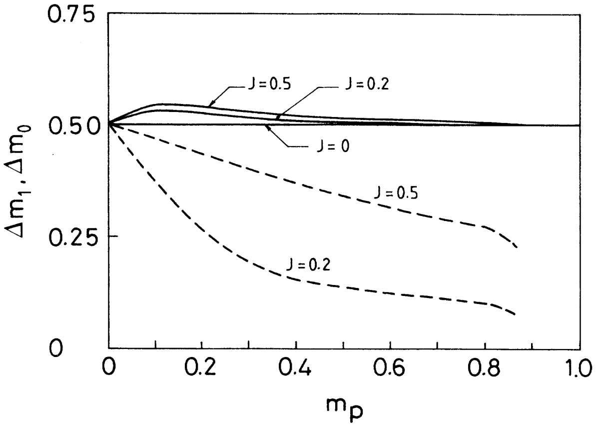

FIG. 3. Discontinuity of the order parameters at the transition point vs m_p in the case $J=0.2$ and 0.5. Solid lines correspond to Δm_1 and dashed lines to Δm_0. The solid line at $\Delta m=0.5$ corresponds to the case $J=0$ ($\Delta m_1=\Delta m_0=\Delta m$).

the order parameters m_0 and m_1, respectively. The reason is the lack of interaction between the AA and BB pairs.

(iii) $m_p=1$, $J=0$. In the limiting case of $m_p=1$, the order parameter m_1 becomes meaningless because, in the fully configurational ordered case, there are no misplaced atoms on the sublattices. The m_0 order parameter suffers a first-order phase transition similar to the one described in (i) but including a factor of 2 in the temperature scale ($T_e^*=0.3607$).

(iv) In the case of $1>J>0$ ($J>1$ is not considered because we are only studying the case of small J_{AA} and J_{BB}) the two order parameters are always coupled, and a unique first-order phase transition occurs. Figure 1 shows the phase-transition line for different values of J. In order to better characterize the transition it is also useful to study the behavior of ΔS which is shown in Fig. 2 for $J=0.1$, 0.2, 0.5, and 1. It is interesting to notice that, as a consequence of the frozen configurational order (controlled by m_p), a minimum on ΔS appears. Only in the trivial limit $J=1$, where the distinction between A and B atoms vanishes, there is no influence of the configurational order on the phase-transition properties. Figure 3 shows the values of the jump in the order parameters at the transition point. The continuous line corresponds to m_0 and the dashed line to m_1.

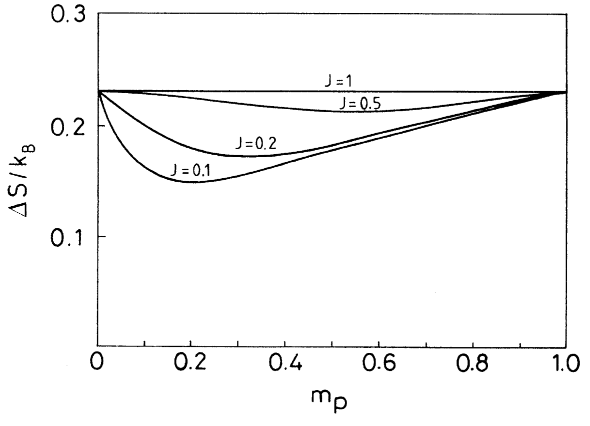

FIG. 2. ΔS values for $J=0.1$, 0.2, 0.5, and 1 as a function of m_p.

In this example of diffusionless first-order transition, the entropy change ΔS shows a dependence on the internal ordering state. This dependence is nonmonotonic and exhibits a minimum at a given value of m_p which, in turn, depends on the interaction.

IV. APPLICATION TO A DISPLACIVE PHASE TRANSITION IN A BINARY ALLOY

Let us consider a binary alloy that undergoes, at T_0, a structural first-order phase transition (SPT) and an order-disorder transition (ODT) at $T_c>T_0$. This system is exemplified by a bcc A_xB_{1-x} binary alloy which shows at low (or relatively low) temperatures a martensitic transition (MT) and well above an ODT. Specific examples are the β-Cu-Zn and the β-Cu-Al alloys.[9]

Let $\mathbf{x}_i$ ($i=1,2,\ldots,N$) be the positional coordinates of the particles in the lattice. The structural first-order phase transition will be, conversely to the Potts model described in Sec. III, associated to continuous degrees of freedom. We also need a set of variables $\sigma=\{\sigma_1,\sigma_2,\ldots,\sigma_N\}$ in order to describe the atom distribution over the different lattice sites. σ_i takes the value 1 (-1) when site i is occupied by an atom A (B).

We assume that the value of σ can be changed by quenching from T_i to a low enough temperature T_f as explained before. The state obtained in this way will be a long-lived metastable state which does not change, at least at the usual experimental time scales.

A. Calculation of $\delta\Delta E$

The Hamiltonian for this system can be written as

$$\begin{aligned}H=\sum_{\langle ij\rangle}\{&\varepsilon_{AA}(x_{ij})\delta(\sigma_i-1)\delta(\sigma_j-1)\\&+\varepsilon_{AB}(x_{ij})[\delta(\sigma_i+1)\delta(\sigma_j-1)\\&+\delta(\sigma_i-1)\delta(\sigma_j+1)]\\&+\varepsilon_{BB}(x_{ij})\delta(\sigma_i+1)\delta(\sigma_j+1)\}\ ,\end{aligned} \tag{20}$$

where the summation extends over all the ij pairs (separated by distances x_{ij}). $\varepsilon_{\alpha\beta}(x)$ $(\alpha,\beta=A,B)$ are the pair-interaction potentials assumed to be central.

Most of the bcc alloys undergoing a MT have a $D0_3$ or a $L2_1$ ordered structure.[9] In order to compare our results with experimental data, we consider a bcc binary alloy which undergoes two order-disorder transitions: a $D0_3$ (or $L2_1$) $\rightarrow B2$ transition at T_{c2} and a $B2\rightarrow A2$ (disordered alloy) transition at $T_{c1}>T_{c2}$ $(\gg T_0)$. For the sake of simplicity we assume that the structure of the L phase is fcc which can be obtained from the bcc H phase through a Bain distortion mechanism[14] (Fig. 4).

We divide the bcc lattice into four sublattices (see Fig. 4). If the fraction of A atoms $x>0.50$, then the $L2_1$ is defined by $P_A^1=P_A^2\neq P_A^3\neq P_A^4\neq P_A^1$, where P_α^i ($\alpha=A,B$ and $i=1,2,3,4$) are the occupation probabilities (directly related to the σ_i variables). The $D0_3$ ordered structure is defined by $P_A^1=P_A^2=P_A^3\neq P_A^4$. Due to the diffusionless character of the MT, the distribution of atoms (occupation probabilities) will be the same in the H phase and in the L phase.

Note that, in the (bcc) H phase, a given atom has $z_1=8$ NN and $z_2=6$ next-nearest neighbors (NNN). The z_1 NN are also NN in the fcc phase, four of the z_2 NNN in the bcc phase transform in NN in the fcc phase and the other two NNN remain NNN in the L phase. For each structure, we extend the summation in (20) to the minimum range to assure its mechanical stability.

In the H phase we consider pairwise interactions up to NNN. The energy of the system in the H phase E_H is

$$E_H=\left[\sum_{\alpha,\beta}N^{(1)}_{\alpha\beta}\varepsilon^{(1)}_{\alpha\beta}+\sum_{\alpha,\beta}N^{(2)}_{\alpha\beta}\varepsilon^{(2)}_{\alpha\beta}\right]\ , \tag{21}$$

while in the fcc phase we consider only interactions up to NN:

$$E_L=\sum_{\alpha,\beta}\hat{N}^{(1)}_{\alpha\beta}\hat{\varepsilon}^{(1)}_{\alpha\beta} \tag{22}$$

where $N^{(i)}_{\alpha\beta}$ $(\hat{N}^{(i)}_{\alpha\beta})$ is the number of ith-neighbor $\alpha\beta$ pairs in the H (L) phase. $\varepsilon^{(i)}_{\alpha\beta}$ $(\hat{\varepsilon}^{(i)}_{\alpha\beta})$ is the interaction energy corresponding to the value of $\varepsilon_{\alpha\beta}(x)$ [in Eq. (20)] at the equilibrium distance between the ith-neighbor pairs in the H (L) phase. In principle, we should consider that the $\varepsilon_{\alpha\beta}$ energies depend on $\boldsymbol{\sigma}$. Nevertheless, we will consider that the Bain distortion associated with the transformation from the H to the L phase does not depend on the frozen internal state of the system. We will return to this point later.

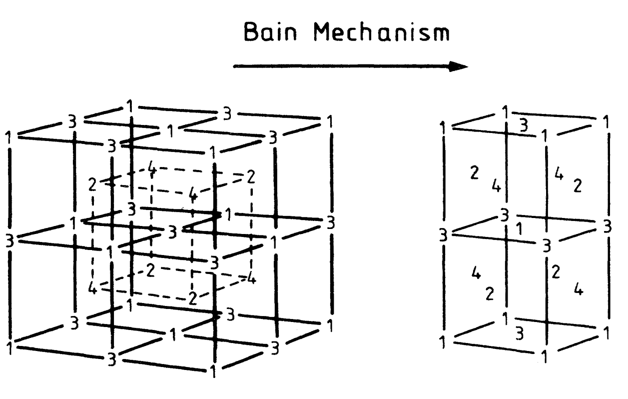

FIG. 4. Schematic sublattice representation for the bcc and fcc structures.

Given that $\boldsymbol{\sigma}$ remains unchanged by the MT, the energy shift $\delta\Delta E$ associated to a change from $\boldsymbol{\sigma}$ to $\boldsymbol{\sigma}'$ is

$$\begin{aligned}\delta\Delta E&=[E_L(\boldsymbol{\sigma}')-E_H(\boldsymbol{\sigma}')]-[E_L(\boldsymbol{\sigma})-E_H(\boldsymbol{\sigma})]\\&=[E_L(\boldsymbol{\sigma}')-E_L(\boldsymbol{\sigma})]-[E_H(\boldsymbol{\sigma}')-E_H(\boldsymbol{\sigma})]\\&=\delta E_L-\delta E_H\ .\end{aligned} \tag{23}$$

Taking into consideration that

$$\hat{N}^{(1)}_{\alpha\beta}=N^{(1)}_{\alpha\beta}+\tfrac{2}{3}N^{(2)}_{\alpha\beta}\ , \tag{24}$$

a straightforward calculation gives

$$\begin{aligned}\delta\Delta E=&(\hat{V}^{(1)}-V^{(1)})\delta N^{(1)}_{AB}\\&+(\tfrac{2}{3}\hat{V}^{(1)}-V^{(2)})\delta N^{(2)}_{AB}\ ,\end{aligned} \tag{25}$$

where

$$V^{(i)}=\varepsilon^{(i)}_{AB}-\tfrac{1}{2}(\varepsilon^{(i)}_{AA}+\varepsilon^{(i)}_{BB})$$

and

$$\hat{V}^{(i)}=\hat{\varepsilon}^{(i)}_{AB}-\tfrac{1}{2}(\hat{\varepsilon}^{(i)}_{AA}+\hat{\varepsilon}^{(i)}_{BB})$$

are the ordering energies in the H and L phases, respectively.

When $T_{c1}>T_{c2}$, even for quenches from temperatures slightly higher than T_{c2}, the number of NN AB pairs remain nearly constant.[15] One can then write

$$\delta\Delta E\cong(\tfrac{2}{3}\hat{V}^{(1)}-V^{(2)})\delta N^{(2)}_{AB}\ . \tag{26}$$

B. Calculation of $\delta\Delta S$

Let us assume that the entropy change for the transition from the H phase to the L phase is given by[16]

$$\Delta S=3Nk_B\ln(w_H/w_L)\ , \tag{27}$$

where w_H and w_L are Einstein frequencies corresponding to the H and L phases, respectively. Equation (27) is appropriated for temperatures above the Einstein temperatures.

The change in the Einstein frequency from the H to the L phase is due to both changes in the geometry and changes in the strength of bonds (interaction energies) between atoms. If C_1 and C_2 represent, respectively, the strength of NN and NNN bonds between atoms. For $C_1 \gg C_2$, then[16]

$$w_H \cong (z_1 C_1 + z_2 C_2)^{1/2} \ . \tag{28}$$

In the hypothesis of central forces, the elastic constants C_{44} and $C' = \frac{1}{2}(C_{11} - C_{12})$ only depend on C_1 and C_2, respectively, in such a way that

$$(C_{11} - C_{12})/C_{44} = 2C_2/C_1 = 2A^{-1} \ , \tag{29}$$

where A is the elastic anisotropy. For the alloys transforming martensitically, A is large (it varies from 10 to 15 in Cu-based alloys) which justifies the assumption that $C_1 \gg C_2$. We now assume that the change in C_1 can be neglected. Considering, as before, only NN interactions in the L phase, we obtain

$$\Delta S = \tfrac{3}{2} N k_B \ln[(z_1 + z_2/A)/\hat{z}_1] \ , \tag{30}$$

where $\hat{z}_1 = 12$ is the number of NN in the fcc phase. Now

$$\begin{aligned} \delta \Delta S &= \Delta S(\sigma') - \Delta S(\sigma) \\ &= \tfrac{3}{2} N k_B \ln\{[1 + \alpha A^{-1}(\sigma')]/[1 + \alpha A^{-1}(\sigma)]\} \ , \end{aligned} \tag{31}$$

where $\alpha = z_2/z_1$. Taking into account that αA^{-1} is small, Eq. (31) can be rewritten as

$$\begin{aligned} \delta \Delta S &= \tfrac{3}{2} N k_B \alpha \left[\frac{1}{A(\sigma')} - \frac{1}{A(\sigma)} \right] \\ &\approx \tfrac{3}{2} N k_B \alpha \left[1 - \frac{\delta C_{44}}{\delta C'} \frac{C'}{C_{44}} \right] \frac{\delta C'}{C_{44}} \ , \end{aligned} \tag{32}$$

where $\delta C' = C'(\sigma') - C'(\sigma)$ and

$$\delta C_{44} = C_{44}(\sigma') - C_{44}(\sigma) \ .$$

In the central-potential approximation, C_{44} only depends on NN, AB pairs.[15] If these kind of pairs is not affected by the quench, then

$$\delta \Delta S \cong \tfrac{3}{2} N k_B \alpha (\delta C'/C_{44}) \ , \tag{33}$$

where $\delta C'$ can be written in terms of $\delta N_{AB}^{(2)}$,[15] resulting that $\delta \Delta S$ is proportional to $\delta N_{AB}^{(2)}$.

It is interesting to notice that, for the kind of alloys considered here, $\delta C'/C_{44} \ll 1$. For example, for the Cu-Zn-Al alloy (studied in Sec. IV C), this ratio can be evaluated using elastic constant values taken from Ref. 17. One then obtains that $\delta \Delta S / \Delta S < 0.01$. Hence, from Eqs. (4) and (26) we obtain

$$\delta T_0 \cong \delta \Delta E / \Delta S \cong (1/\Delta S)/(\tfrac{2}{3}\hat{V}^{(1)} - V^{(2)}) \delta N_{AB}^{(2)} \ , \tag{34}$$

where now ΔS can be taken as constant.

Using standard mean-field theory, one can calculate $\delta N_{AB}^{(2)}$. We define, in terms of the occupation probabilities, the following long-range order parameter (LROP) Σ:

$$\Sigma = (P_A^2 - P_B^2) - (4x - 3) \ . \tag{35}$$

The ordered structure is supposed to be of the $L2_1$ type for $0.5 < x < 0.75$, and of the $D0_3$ type for $x = 0.75$.[15] It is easy to see that

$$\delta N_{AB}^{(2)} = \tfrac{3}{4} N [\Sigma^2 - (4x - 2)^2] \ . \tag{36}$$

Introducing (36) in (34), one gets

$$\delta T_0 \cong (1/\Delta S)(\tfrac{2}{3}\hat{V}^{(1)} - V^{(2)})[\Sigma^2 - (4x - 2)^2] \ . \tag{37}$$

The dependence of δT_0 on Σ^2 has already been predicted in the frame of the Landau theory.[11] Here we obtain (37) from a more microscopic justification.

C. Comparison with experimental results

Given that, to our knowledge, no experimental results are available for binary alloys, we compare our theoretical predictions with data corresponding to the Cu-(Zn-Al) ternary system. Nevertheless, this alloy can be regarded as a binarylike system. This is because the ordering energy for Cu-Al pairs is only around 1.5 times greater than the ordering energy for Cu-Zn pairs but 20 times greater than the corresponding to Zn-Al pairs.[9] We then assume

$$\hat{V}^{(1)} = (x_{\mathrm{Zn}} \hat{V}^{(1)}_{\text{Cu-Zn}} + x_{\mathrm{Al}} \hat{V}^{(1)}_{\text{Cu-Al}})/(1 - x) \ , \tag{38a}$$

$$V^{(2)} = (x_{\mathrm{Zn}} V^{(2)}_{\text{Cu-Zn}} + x_{\mathrm{Al}} V^{(2)}_{\text{Cu-Al}})/(1 - x) \ , \tag{38b}$$

where x_{Zn} and x_{Al} ($1 - x = x_{\mathrm{Zn}} + x_{\mathrm{Al}}$) are the atomic fractions of Zn and Al, respectively, and $V^{(k)}_{\alpha\text{-}\beta}$ ($\hat{V}^{(k)}_{\alpha\text{-}\beta}$) are the ordering energies between the kth α-β pairs in the H (L) phase.

Within the composition of interest, $x \sim 0.65$, the $\mathrm{Cu}_x(\text{Zn-Al})_{1-x}$ shows, at low temperatures, a $L2_1$ structure and a $B2$ structure at higher temperatures. In this case, the ordering energies in the H and L phases have been evaluated for the different atom pairs.[9] For the particular alloy: Cu; 28.09 at. % Zn; 9.95 at. % Al, we obtain (in units of R) $\hat{V}^{(1)} = 863$ K and $V^{(2)} = 610$ K. Taking $\Delta S = -1.30$ J/K mol,[18] Eq. (37) leads to a maximum shift of the transition temperature of $\delta T_{0\max} = -38$ K while the maximum value obtained experimentally is $(\delta T_0)_{\exp} = -62$ K.[19] For the $\mathrm{Cu_3Al}$ alloy, $\hat{V}^{(1)} = 1250$ K and $V^{(2)} = 825$ K, and the maximum shift predicted is $\delta T_{0\max} = 49$ K of opposed sign to the previous case. This result is consistent with experiments carried out on Cu-(Al-Be) with $x = 0.74$ and only a 2 at. % of Be for which a positive shift of T_0 after quench has recently been obtained.[20]

In Fig. 5 we present for Cu; 16 at. % Zn; 16 at. % Al alloy, the measured δT_0 as a function of the relative change $\Delta I/I$ in the x-ray intensity of the (111) superlattice reflections.[21] The 111 superlattice reflections arise from the L_{21} ordering. Measurements correspond to different T_i temperatures. In spite of experimental uncertainties, results show a quite good correlation between ordering and transition temperature shift. However, more accuracy is needed to justify the explicit dependence predicted in Eq. (36). Furthermore, in agreement with our assumption of neglecting contributions coming from

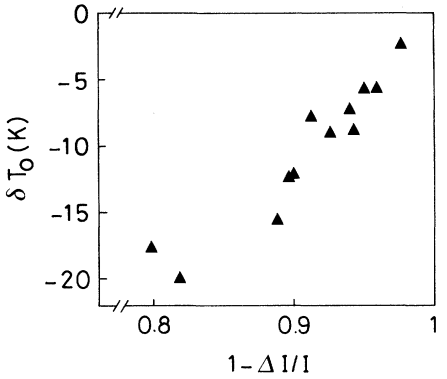

FIG. 5. T_0 as a function of $(1-\Delta I/I)$ for a Cu-16 at. % Zn-16 at. % Al alloy. $\Delta I/I$ is the relative change of the x-ray intensity of the (111) superlattice reflection.

$\delta N_{AB}^{(1)}$, the intensity of the 200 superlattice reflections arising from the $B2$ ordering presents a very small dependence on T_i.[21]

V. DISCUSSION

In this paper we have considered two different examples of systems undergoing a diffusionless first-order phase transition which thermodynamic properties depend on the internal state at which the transition takes place. Associated with the degrees of freedom describing this internal state, the system exhibits a secondary phase transition at a higher temperature, distant from the diffusionless first order or primary phase transition. The internal state can then be changed by means of a fast quench and one can study the coupling effects between the ordering modes associated to both phase transitions.

In the first example, we consider a three-state Potts model in a system with two kinds of particles arranged on a regular lattice. The specification of the particle distribution on the different lattice sites determines the internal state of the system. We find that changes on such an internal state produce a shift in the primary transition temperature which is associated with shifts in both energy and entropy changes. The shift in the entropy change between both high- and low-temperature phases is related to different values of the discontinuity of the Potts order parameter at the first-order transition point. The shift in the energy change is associated with the different distribution of particles which provokes variations in the effective interactions.

In the second example, we analyze a metallic binary alloy which undergoes a displacive transition of martensitic type from a bcc structure to a more compact phase (for instance, a fcc). These systems are characterized by a large elastic anisotropy. This property is intimately related to the directional character of the MT mechanism which is mainly described by a shear deformation associated to the C' elastic constant. This favors that the entropy change between both phases depends only very weakly on the ordering state of the system. When only the $L2_1$ (or DO_3) ordering (associated to NNN pairs) is changed, the shift in the entropy change is proportional to the ratio $\delta C'/\delta C_{44}$ (33), which, in turn, is vanishingly small. In a more general situation, when changes in both NN and NNN pairs are induced, from Eq. (32), we expect that the assertion concerning the weak dependence of the entropy change on the ordering state be right as well. Consequently, the final low-temperature structure is, in this case, independent of the internal state of the system and the corresponding interaction pair energies are now independent on the ordering state. The transition temperature shift is then only associated to a shift in the energy change which, in turn, will depend only on changes of the NNN AB pairs (34).

In terms of a Landau description, a φ-6 free-energy expansion in the primary order parameter (related to the deformation) has been proposed to describe MT.[22] The simplest suitable coupling term is then biquadratic in both order parameters. This coupling gives rise to formally the same results explained above. This Landau model has been previously discussed in the context of the MT.[11] Here we have proceeded further and have shown that the displacive character of the structural transition is not a definitive condition to assure that the shift of the entropy change is zero for different ordering states. Also, the large elastic anisotropy together with symmetry characteristics of the transition mechanism are relevant for this condition to be satisfied.

In the case of the three-state Potts model, the description of the first-order transition needs a cubic term in the Landau free-energy expansion.[13] The coupling with the frozen internal degrees of freedom can be introduced, at least, by means of a cubic-quadratic term in the primary and secondary order parameters, respectively. This minimal model is qualitatively consistent with the mean-field results discussed above.

ACKNOWLEDGMENT

This research was supported by CICyT (Spain) under Project No. MAT890748.

---

[1] M. C. Cadeville and J. L. Morán-López, Phys. Rep. **153**, 331 (1987).
[2] B. Dünweg and K. Binder, Phys. Rev. B **36**, 6935 (1987).
[3] E. Vives and A. Planes, Phys. Rev. A **38**, 5391 (1988).
[4] M. A. Anisimov *et al.*, Phys. Rev. A **41**, 6749 (1990).
[5] Y. Imry, J. Phys. C. **8**, 567 (1975).
[6] S. Watanabe and T. Utsui, Prog. Theor. Phys. **73**, 1305 (1985).
[7] J. C. Tolédano and P. Tolédano, *The Landau Theory of Phase Transitions* (World-Scientific, Singapore, 1987).
[8] E. Vives and A. Planes, Phys. Rev. B **43**, 13 335 (1991).
[9] M. Ahlers, Prog. Mater. Sci. **30**, 135 (1986).
[10] R. Rapacioli and M. Ahlers, Acta Metall. **27**, 777 (1979).

[11]A. Planes, J. Viñals and V. Torra, Philos. Mag. A **48**, 501 (1983); J. Viñals, V. Torra, A. Planes, and J. L. Macqueron *ibid.* **50**, 653 (1984).

[12]S. J. Knak Jensen and O. G. Mouritsen, Phys. Rev. Lett. **43**, 1736 (1979).

[13]J. P. Straley and M. E. Fisher, J. Phys. A **6**, 1310 (1973).

[14]E. C. Bain, Trans AIME **70**, 24 (1924); A. J. Borgers and W. G. Burgers, Acta Mattal. **12**, 255 (1964).

[15]T. Castán, E. Vives, and A. Planes, J. Phys.: Condens. Matter **2**, 1743 (1990).

[16]J. Friedel, J. Phys. Lett. **35**, L59 (1974).

[17]G. Guénin and P. F. Gobin, Metall. Trans. A **13**, 1127 (1982).

[18]A. Planes, J. L. Macqueron, R. Rapacioli, and G. Guénin, Philos. Mag. A **61**, 221 (1990).

[19]A. Planes, R. Romero, and M. Ahlers, Acta Metall. **38**, 757 (1990).

[20]J. L. Macqueron and A. Planes (unpublished).

[21]T. Suzuki, Y. Fujii, and A. Nagasawa, Mater. Sci. Forum **56-58**, 481 (1990).

[22]F. Falk and P. Konopka, J. Phys.: Condens. Matter **2**, 61 (1990).