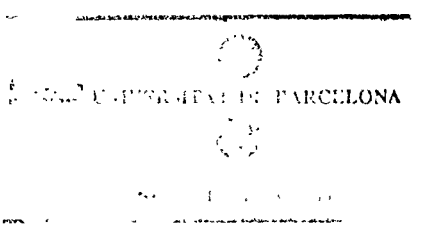
SIMULACIO MONTE CARLO DE SISTEMES AMB ACOBLAMENT DE GRAUS DE LLIBERTAT.



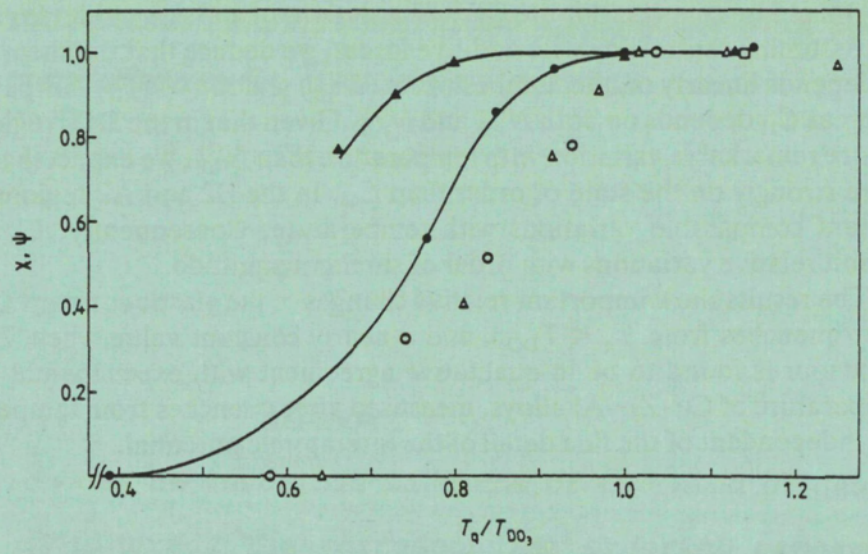


Figure 6. Representation of $\chi = (N_{AB}^{(2)}(T_q) - N_{AB}^{(2)}(0))/(N_{AB}^{(2)}(T_{DO_3}) - N_{AB}^{(2)}(0))$ as a function of the reduced temperature T_q/T_{DO_3} for the system with $x = 0.70$ (▲) and $x = 0.75$ (●). The behaviour of χ with T_q is compared with experimental values of $\psi = (M_s(T_q) - M_s^*)/(M_s(T_{DO_3}) - M_s^*)$ corresponding to two Cu–Zn–Al alloys with Cu atomic fractions of 0.619 (○) and 0.633 (△).

For the two alloys considered here, the composition is: 61.96 at.% Cu; 28.09 at.% Zn for alloy A, and 63.37 at.% Cu; 25.26 at.% Zn for alloy B. The corresponding order–disorder temperatures are: $T_{DO_3} = 460$ K and $T_{B2} = 825$ K for alloy A, and $T_{DO_3} = 500$ K and $T_{B2} = 825$ K for alloy B. Following the previous argument, the DO_3–B2 transition should then be suppressed by fast quenches from temperatures above 500 K. Consequently, the effect of the B2 ordering alone on the M_s temperature can be analysed after quenches from T_q temperatures ranging between 500 and 600 K. In figure 6 we have plotted $(N_{AB}^{(2)}(T_q) - N_{AB}^{(2)}(T_q = 0\,\text{K}))/(N_{AB}^{(2)}(T_q = T_{DO_3}) - N_{AB}^{(2)}(T_q = 0\,\text{K}))$ as a function of T_q/T_{DO_3} obtained from Monte Carlo simulations for the alloy A_xB_{1-x}, with $x = 0.70$ and 0.75. This quantity is compared with experimental values of $(M_s(T_q) - M_s^*)/(M_s(T_{DO_3}) - M_s^*)$ as a function of T_q/T_{DO_3} corresponding to the Cu–Zn–Al alloys considered. M_s^* is the MPT temperature measured after air cooling from $T_q = 1093$ K and aging at room temperature. After this temperature treatment the degree of atomic order is very close to the maximum at room temperature. Indeed, we note that the two curves show the same qualitative behaviour. Up to T_{DO_3}, M_s decreases as T_q increases and remains practically constant for T_q above this temperature. This is the expected behaviour in view of equation (15) and the behaviour of $N_{AB}^{(2)}$ with temperature (figure 5). In addition, it is interesting to note that this decrease of both M_s and $N_{AB}^{(2)}$ after quenches from T_q temperatures in the DO_3 region enables us (taking into account equation (14)) to conclude that C' increases in this region. This result means that for the class of alloy considered here, the term $\tilde{\Phi}^{(2)} > 0$.

4. Conclusions

We have studied the atomic order dependence of elastic constants of BCC binary alloys near the A_3B composition. The elastic constants are obtained at $T = 0$ K for frozen-in configurations quenched from different temperatures T_q across the stability regions of

the three phases DO_3, B2 and A2. At each temperature T_q, the equilibrium configuration is obtained by means of Monte Carlo simulations of an Ising model for such an alloy.

Assuming central pairwise additive forces, we deduce that the shear moduli C_{44} and C' depends linearly on the number of NN ($N_{AB}^{(1)}$) and NNN ($N_{AB}^{(2)}$) AB pairs respectively, whereas C_{11} depends on both $N_{AB}^{(1)}$ and $N_{AB}^{(2)}$. Given that in the DO_3 region $N_{AB}^{(2)}$ exhibits a more remarkable variation with temperature than $N_{AB}^{(1)}$, we expect that C' will depend more strongly on the state of order than C_{44}. In the B2 and A2 regions $N_{AB}^{(1)}$ and $N_{AB}^{(2)}$ present comparable variations with temperature. Consequently, C' and C_{44} should exhibit relative variations with order of similar magnitude.

The results show important relative changes of the elastic constant C' with ordering after quenches from $T_q < T_{DO_3}$, and a nearly constant value when $T_q > T_{DO_3}$. This behaviour is found to be in qualitative agreement with experimental data on the M_s temperature of Cu–Zn–Al alloys, measured after quenches from temperatures T_q, and it is independent of the fine detail of the interatomic potential.

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DIFFUSIONLESS FIRST ORDER PHASE TRANSITIONS IN SYSTEMS WITH FROZEN CONFIGURATIONAL DEGREES OF FREEDOM

ABSTRACT

Systems which can be described in terms of two kind of degrees of freedom are considered. The corresponding ordering modes may, under certain conditions, be coupled one to the other. We suppose that the primary ordering mode gives rise to a diffusionless first-order phase-transition. The change of its thermodynamic properties as 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 the 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 the martensitic type in a binary alloy are,as a function of atomic order, studied. Because of the directional character of the martensitic transition mechanism, we obtain that the entropy dependence on atomic order is very small.

Both models are contrasted. Comparisons with experimental results are in quite good agreement with theoretical predictions.

1.- 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 [4,5].

We consider the case of systems with two relevant kinds of internal degrees of freedom, respectively 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 during the last 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 one to the other [8].

In this paper we consider that both phase transitions take place at very separated temperatures. The properties of the phase transition associated to the primary ordering mode are then studied assuming the secondary ordering mode can be externally controlled. The experimental realization of this situation is for instance

observed in metallic alloys undergoing an order-disorder transition and 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 the different kind 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 quench to 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 in two particular cases. Firstly we consider a three-state Potts model in a cubic lattice with two kind 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.

Secondly 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 theoretical as well as from experimental point of view. Based on the displacive character of the transition, it was suggested [11]

that the entropy change is independent of the ordering state. In addition, experiments seems to confirm this idea. Here we reformulate the problem in a more general context and discuss the results in the light of those obtained in the Potts model system for which the transition is simple and well understood. We find that, in general, the displacive character of the first-order phase 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. We finally compare the theoretical predictions with available experimental results.

2.- GENERAL CONSIDERATIONS

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

$$\Delta F = 0 = \Delta E - T_0 \Delta S \qquad (1)$$

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 equation (1) we have assumed that the volume change at the phase transition is negligible. In what follows we denote H-phase and L-phase respectively the high (stable for $T > T_0$) and low (stable for $T < T_0$) temperature phases and restrict ourselves to difussionless 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 $\sigma = (\sigma_1, \sigma_2, \ldots . \sigma_N)$ 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 $T_c << T_0$, the application of an external magnetic field provokes a change in the internal state of the system. In a substitutional alloy, if $T_c >> T_0$, 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 σ

to $\sigma+\delta\sigma$. Then the transition temperature changes from T_0 to $T_0+\delta T_0$ which is a solution of the equation:

$$\delta(\Delta E) - T_0\,\delta(\Delta S) - \Delta S\,\delta T_0 = 0 \qquad (2)$$

equivalent to :

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

where $\delta(\Delta E) = \Delta E(\sigma+\delta\sigma) - \Delta E(\sigma)$ and $\delta(\Delta S) = \Delta S(\sigma+\delta\sigma) - \Delta S(\sigma)$. In the particular case $\delta(\Delta S)=0$, then :

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

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

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

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

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

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

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

$$\Delta S = -\left[\left(\frac{\partial f}{\partial T}\right)_{\bar\eta} - \left(\frac{\partial f}{\partial T}\right)_{\bar\eta_0}\right] = -a_1(\bar\eta^2-\bar\eta_0^2) - K\frac{\partial\psi_{12}(\xi,T)}{\partial T}(\bar\eta^x-\bar\eta_0^x) \qquad (7)$$

$\bar\eta - \bar\eta_0$ is the jump of the order parameter at the first-order transition point. $\bar\eta$ and $\bar\eta_0$ are solutions of the equations:

$$2a_1(T-T_{c1})(\overline{\eta}-\overline{\eta_0}) + \left[\left(\frac{\partial\psi_1}{\partial\eta}\right)_{\overline{\eta}} - \left(\frac{\partial\psi_1}{\partial\eta}\right)_{\overline{\eta_0}}\right] + Kx\psi_{12}(\xi,T)(\overline{\eta}^{x-1}-\overline{\eta_0}^{x-1}) = 0 \quad (8a)$$

$$a_1(T-T_{c1})(\overline{\eta}^2-\overline{\eta_0}^2) + \left[\psi_1(\overline{\eta})-\psi_1(\overline{\eta_0})\right] + Kx\psi_{12}(\xi,T)(\overline{\eta}^{x}-\overline{\eta_0}^{x}) = 0 \quad (8b)$$

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 equation (8a) by $(\bar{\eta} + \bar{\eta}_0)$, equation (8b) by (-2) and taking into account equation (7), one obtains that only when $x = 2$ and ψ_{12} does not show and explicit dependence on temperature, ΔS is independent of ξ. This kind of coupling is merely energetic and its effect is only to induce a shift on the transition temperature.

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

Let us consider a d-dimensional lattice with N sites and z nearest-neighbours per site. On each site i = 1,.....,N, we define two variables. A spin-like variable σ_i which takes value +1(-1) when the site i is occupied by an atom A(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:

$$H = \sum_{i,j}^{n.n.} \delta(S_i - S_j) \{ J_{AA}\delta(\sigma_i - 1)\delta(\sigma_j - 1) + J_{AB}\delta(\sigma_i + 1)\delta(\sigma_j - 1) + J_{AB}\delta(\sigma_i - 1)\delta(\sigma_j + 1) + J_{BB}\delta(\sigma_i + 1)\delta(\sigma_j + 1) \} \quad (9)$$

Where the summation extends over all nearest-neighbour (n.n) pairs. δ is the Kronecker delta 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 $N_A/N = 1/2$, being N_A ($N_B=N-N_A$) the number of A atoms. Given that N_A is constant, we have the following conservation condition:

$$\sum_{i=1}^{N} \sigma_i = 0 \quad (10)$$

Let be $J_{AB} < J_{AA} \approx J_{BB}$ 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 b.c.c. lattices apply to this case with z = 4, 6 and 8 respectively. This ground state is six-fold degenerated and its energy is $E_0 = J_{AB}\ z\ N/2$.

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 Potts state S (1,2 or 3).

In mean-field approximation the hamiltonian can be written as:

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

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, except constants, as:

$$S=k_B\ T\left(\ln(W_A^{+})+\ln(W_A^{-})+\ln(W_B^{+})+\ln(W_B^{-})\right) \quad (12)$$

where k_B is the Boltzmann constant and:

$$W_\sigma^\pm = \frac{\frac{N}{2}!}{N_{\sigma 1}^\pm ! \, (N_{\sigma 2}^\pm !)^2} \qquad (13)$$

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

$$m_\sigma^\pm = \frac{N_{\sigma 1}^\pm - N_{\sigma 2}}{N_{\sigma 1}^\pm + 2N_{\sigma 2}^\pm} \qquad (14)$$

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 to be externally controlled. This parameter is the one that would depend on the quenching conditions. It is defined as:

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

$m_p = 0$ 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 $J_{AA} = J_{BB} = -J \cdot J_0$ with $J_{AB} = -J_0$. $J(<1)$ is a parameter and J_0 is a positive number that will be taken as unit of

energy. With these definitions, the mean-field free-energy per particle (in z J_0 units) can be written as:

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

where $T^* = k_BT / zJ_0$ and:

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

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

$$m_A^+=m_B^-=m_0 \quad , \quad m_A^-=m_B^+=m_1 \qquad (17)$$

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

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

$$J(1+m_p)\,m_0+(1-m_p)\,m_1 = 2\;T^*\ln\left(\frac{1+2m_1}{1-m_1}\right) \qquad (19)$$

We can now analyze some simple solutions:

i) Totally disordered alloy ($m_p = 0$) with $J = 0$: In this case the solution of equations (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 $T^*_l = 1/6$, 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 $\Delta S = 0.23105$.

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 respectively associated to the order parameters m_0 and m_1. 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 two 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. Fig 1 shows the phase transition line for different values of J. In order to characterize better the transition is also useful to study ΔS which is shown in Figure 2, for J=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 point. Fig.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.

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