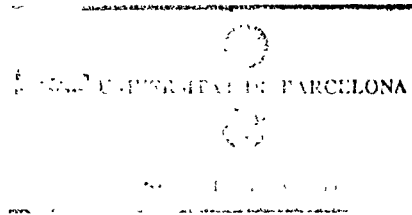


**SIMULACIO MONTE CARLO DE SISTEMES  
AMB ACOBLAMENT DE GRAUS DE LLIBERTAT.**



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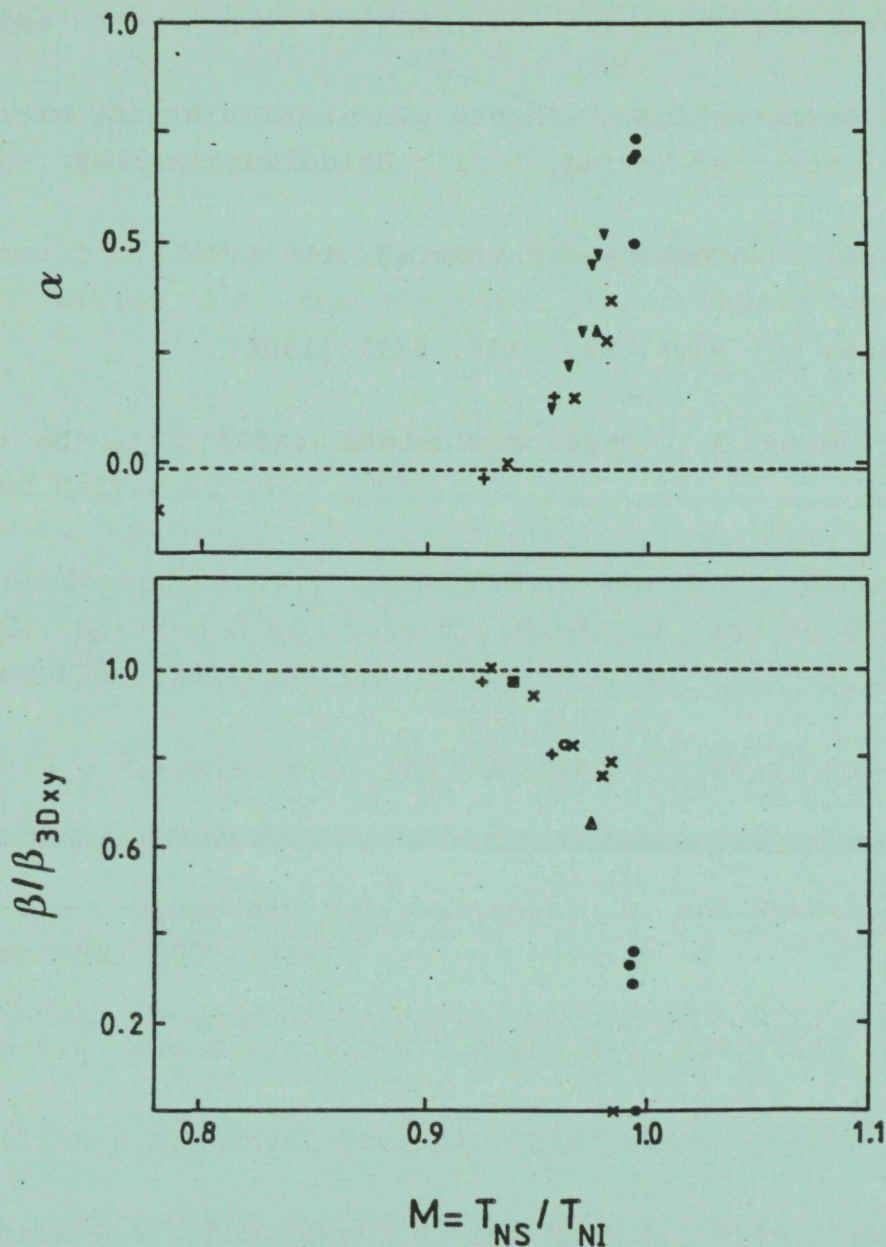


Fig. 1. Values of the  $\alpha$  and  $\beta$  critical exponents of the Smectic-Nematic phase transition for several liquid crystals and liquid crystal mixtures found in the literature (some  $\beta$  exponents are calculated using relations between critical exponents). The values are plotted versus the Mc Millan parameter defined in the text. The values of  $\beta$  are normalized with respect to the value of the 3 dimensional XY model, that is supposed to belong to the same universality class: (X) nS5 [3], (■) CBOOA [2,4], (+) 40.8-40.7 [2,4], (●) 9CB-10CB [3], (▼) 40.8-60.8 [7], (○) 8OCB [2,4], (Δ) 8CB [2].

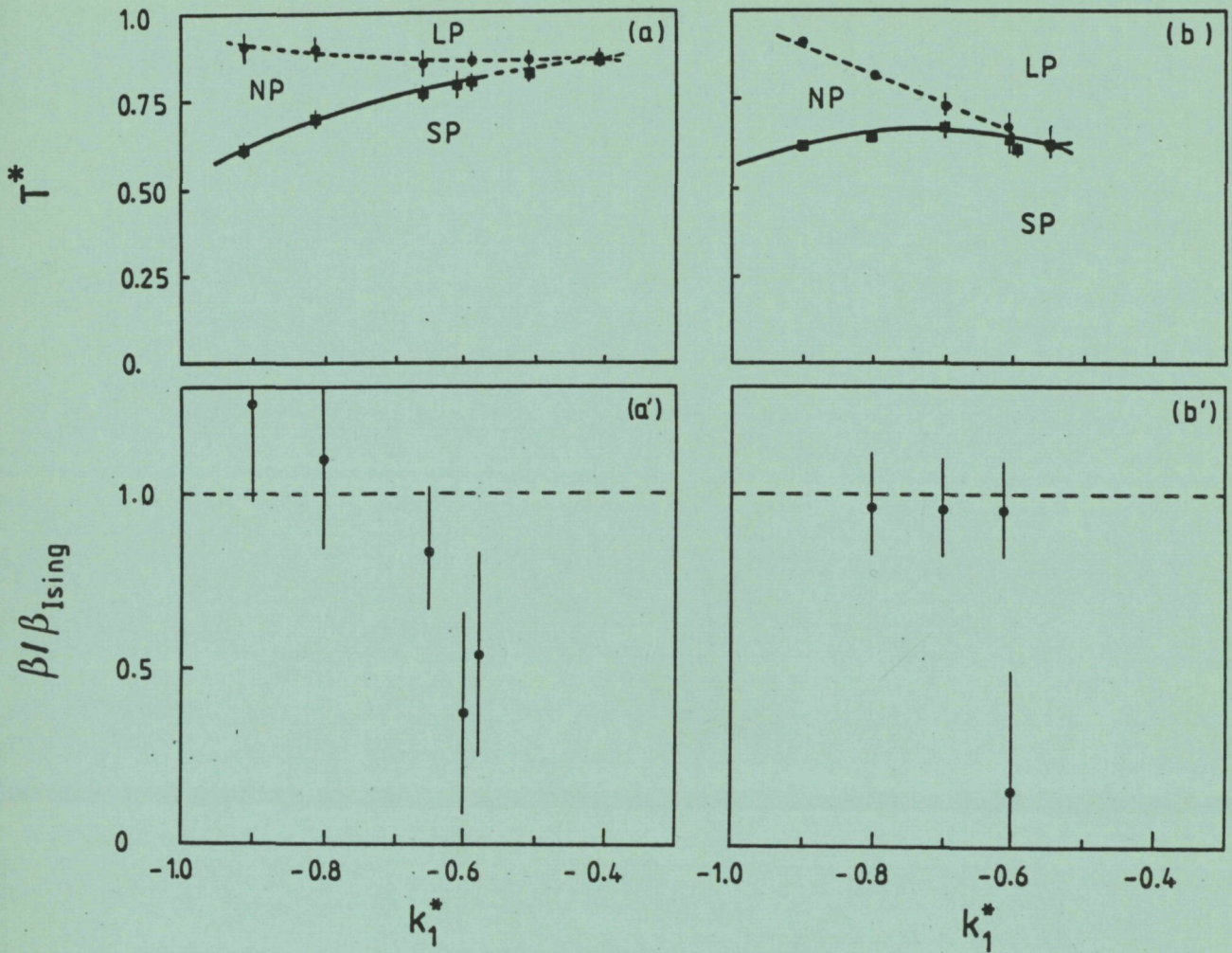


Fig. 2. Results obtained by Monte Carlo simulation of the model described in the text. The upper figures are sections of the phase diagram. (a) corresponds to the case  $K_2^* = -0.9$  and  $K_1^*$  variable, while (b) corresponds to the case  $K_1^* = K_2^*$ . Different phases are observed: Liquid Phase (LP), Nematic Phase (NP) and Solid Phase (SP). Continuous and discontinuous lines represent second and first order phase transitions respectively. The lower figures show the corresponding  $\beta$  exponents (normalized with respect to the value corresponding to the Ising model).



## 5 APLICACIO A TRANSICIONS ESTRUCTURALS I ORDRE-DESORDRE.

L'objectiu d'aquesta part del treball és explicar diferents fenòmens que apareixen en l'estudi de les transicions de fase estructurals que sofreixen alguns aliatges metàl·lics com el Cu-Zn, el Cu-Zn-Al, etc.

Aquests sistemes experimenten a una temperatura  $M_s$  ("Martensite start"), una transició estructural no difusiva (de tipus martensític) entre una fase de baixa temperatura molt compacta (tipus FCC, 2H etc..) i una fase d'alta temperatura menys compacta però més simètrica (tipus BCC). El mecanisme d'aquesta transició és una distorsió que afecta col·lectivament als graus de llibertat posicional de cada nus de la xarxa. La transició pot induir-se no únicament per efecte d'un canvi de temperatura sinó també per efecte d'un esforç aplicat externament.

A part d'aquesta transformació de la simetria de la xarxa cristal·lina, aquests aliatges experimenten a temperatures més altes, transicions de tipus difusiu que afecten el seu ordre configuracional, és a dir la distribució dels diferents tipus d'àtoms sobre els diferents nusos de la xarxa. Per exemple en la xarxa BCC es poden presentar fases tipus  $A_2$ ,  $B_2$ ,  $DO_3$  o  $L2_1$ .

Els dos tipus de graus de llibertat (configuracionals i posicionals) corresponen de fet a dues escales temporals del moviment dels àtoms, tal i com hem explicat al punt 1.1.2. En condicions d'equilibri no interactuen entre ells ja que a les temperatures corresponents a la transició ordre desordre la xarxa es manté BCC estable i durant la transició estructural la temperatura és suficientment baixa per impedir tota difusió. Ara bé, tal i com s'ha explicat al punt 1.3.3, mitjançant variacions molt ràpides de temperatura es pot realitzar la transformació estructural amb diferents tipus d'ordre configuracional. Això dona lloc a que es produeixin fenòmens d'acoblament tals com variacions

en la temperatura de transició o en el comportament de les propietats termodinàmiques.

Aquests sistemes han estat molt estudiats, a causa de la gran importància metal·lúrgica que tenen: la transformació martensítica que presenten els dona propietats de memòria de forma. La temperatura de la transició estructural pot ésser controlada externament mitjançant tractaments metal·lúrgics, la qual cosa els fa molt interessants per aplicacions en enginyeria.

Existeixen molts resultats experimentals, encara que alguns són de poca utilitat física a conseqüència que s'han realitzat sense un control prou rigorós d'efectes tals com la presència d'impureses, l'aparició d'altres fases, etc.. Un article de recopilació recent que intenta ordenar aquests resultats és [Ahlers M. 1986]. D'entre les tècniques que s'han utilitzat destaquen resultats de calorimetria [Ortin J. i Planes A. 1988], mesura de constants elàstiques [Verlinden B. i Delaey L. 1988], raigs X [Suzuki T., Fujii Y. i Nagasawa A. 1990] i mesura d'emissió acústica [Mañosa LL. et al. 1990], i atenuació ultrasonora [Szente J. i Trivisonno J. 1988].

Sobre l'aspecte teòric i deixant de banda treballs d'aplicació, una bona introducció es pot trobar a la tesi doctoral de [Castán T. 1987]. Models basats en teories de Landau inhomogènies [Cao W., Krumhansl J.A. i Gooding R.J. 1990] permeten reproduir algunes temperatures de transició i alguns paràmetres d'ordre.

L'objectiu final per a la resolució d'aquest problema de d'acoblament seria elaborar un model microscòpic complet que inclogués tant els efectes configuracionals com estructurals. Això però és difícil, a causa de que no es coneix molt bé quin tipus de potencial d'interacció dona lloc al mecanisme físic que produeix la transició estructural i per tant no existeixen models microscòpics adequats per aquesta. Si es coneix, en canvi, que la transició està relacionada amb una variació anòmala de les constants elàstiques d'aquest material amb la temperatura que produeix un estovament parcial en algunes direccions de la xarxa, la qual cosa afavoreix



la transició. Els canvis en l'ordre configuracional provoquen modificacions en les constants elàstiques del sistema que repercuteixen en canvis en la transició estructural.

Els nostres estudis s'han centrat doncs en simular per tècniques de Monte Carlo o resoldre per camp mitjà el problema de la ordenació dels àtoms a alta temperatura en estructures A<sub>2</sub>B<sub>2</sub> i DO<sub>3</sub> en el si d'una xarxa BCC i després utilitzar estudis microscòpics existents a la literatura per veure com l'ordre configuracional afecta les constants elàstiques del material.

Mitjançant simulació de Monte Carlo s'han obtingut configuracions corresponents a l'estat d'ordre atòmic d'un aliatge binari A-B en una xarxa BCC amb interacció a primers i segons veïns i diferents concentracions  $x = N_A / (N_A + N_B)$ . El diagrama de fases s'ha obtingut en un ampli rang de temperatures T i per a diferents valors del paràmetre del model W que relaciona les interaccions a primers i segons veïns, i per concentracions properes a 0.75. L'acord amb resultats teòrics aproximats [Bell J.M. 1987] és força bo. A part de l'evolució de l'energia i els paràmetres d'ordre de llarg abast s'ha calculat també la dependència dels paràmetres d'ordre de curt abast (parelles de primers i segons veïns de tipus AA, AB i BB) en funció de la temperatura T<sub>q</sub>.

Aquesta informació, juntament amb un model pel càlcul de les constants elàstiques [Castán T. i Planes A. 1988] permet de calcular la dependència de les constants elàstiques del material amb l'ordre configuracional i preveure quin serà l'efecte de refredaments ràpids des de diferents temperatures T<sub>q</sub> sobre els valors de les constants elàstiques més rellevants per a la transició estructural: C<sub>44</sub> i C'. La principal conclusió és que la constant elàstica C', que depèn bàsicament del nombre de parelles a primers i segons veïns de tipus AB, es veu fortament afectada per T<sub>q</sub> sempre que els refredaments es facin des de la fase ordenada DO<sub>3</sub> i, en canvi, és menys sensible en el cas en que T<sub>q</sub> es situï per sobre de la temperatura d'aparició de la fase DO<sub>3</sub>. Aquest resultat explica de forma semi-quantitativa perquè experimentalment es troba

que la temperatura a la qual s'esdevé la transició estructural varia fortament quan es fan refredaments des de temperatures per sota la temperatura de transició DO<sub>3</sub>-B2.

A través de les constants elàstiques i mitjançant un model similar al suggerit per [Friedel J. 1974] es pot justificar el fet experimental que la variació de l'AS (en la transició estructural) amb l'estat d'ordre configuracional és molt petita o nul·la.

Aquest resultat és important quan es compara amb un estudi general de tipus Landau per l'acoblament entre transicions de primer ordre (pe. estructurals) i ordre-desordre. Mitjançant una energia lliure amb dos paràmetres d'ordre, es comprova com una condició necessària perquè l'AS en la transició de primer ordre sigui independent de l'ordre atòmic, és que el terme d'acoblament sigui quadràtic en el paràmetre d'ordre estructural i independent de la temperatura. Aquests resultats també es poden comparar amb d'altres casos d'acoblament, com per exemple el cas d'un aliatge binari amb variables de tipus Potts.

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# Elastic constants of BCC binary alloys near the $A_3B$ composition and their relation to martensitic transitions

**Abstract.** The present work deals with the analysis of the atomic-order dependence of the elastic constants of a BCC binary alloy near the  $A_3B$  composition. We assume that each atom interacts with nearest and next-nearest neighbours through a pairwise interatomic potential. The configurational phase diagram of the system has been obtained from Monte Carlo simulation of a lattice model for such an alloy system. The  $DO_3$ , B2 and A2 phases are found to be stable for appropriate values of the interaction parameters.

The elastic constants of partially ordered configurations are calculated at  $T = 0$  K, after quenches from different temperatures  $T_q$  ranging over the stability regions of the three phases. The results are compared with experimental data corresponding to the Cu-Zn-Al shape memory alloy and their relevance in connection with the martensitic transformation is discussed.

## 1. Introduction

Elastic constants of solids are intrinsically related to lattice stability. They depend on composition and temperature (Born and Huang 1956). In the case of metallic alloys undergoing an order-disorder transition, the elastic constants exhibit an additional dependence on the configurational ordering state which, in turn, depends on temperature. This extra contribution is revealed experimentally by an anomalous behaviour of the elastic constants around the order-disorder transition point (MacManus 1969).

Theoretical expressions of isothermal elastic constants involve ensemble averages of functions of particle coordinates and of interparticle potential energies (Squire *et al* 1969). Their calculation, which is believed to be a hard task, can be done by using Monte Carlo (Ray 1988, Castán *et al* 1989) or molecular dynamics (Ray 1988) techniques.

Here we deal with BCC alloy systems which exhibit, from low to high temperatures,  $DO_3$ , B2 and A2 ordered structures. Examples are the  $Fe_3Al$ ,  $Cu_3Al$  and  $Fe_3Pt$  binary alloys, and the Cu-Zn-Al or the Cu-Ni-Al ternary alloys. Some of these alloys ( $Fe_3Pt$  (ordered), Cu-Zn-Al and Cu-Ni-Al) are found to be shape memory alloys (SMA). From a practical point of view, these materials are of great importance because of their very interesting thermomechanical properties (shape memory effect, pseudoelasticity, high damping capacity) which are intimately related to the martensitic phase transition (MPT) that they undergo at low temperatures (Delaey *et al* 1974). Such a transition is a displacive first-order transition from a BCC to a close-packed structure, mainly described by a shear deformation on the  $\{110\}$  planes along the  $\langle 1\bar{1}0 \rangle$  directions. Close to the MPT point ( $M_s$ ),

the shear elastic modulus  $C' = \frac{1}{2}(C_{11} - C_{12})$  presents an 'abnormal' behaviour (Guéniñ and Gobin 1982): (i) its value is small (in relation to the other relevant elastic constants of a cubic lattice), and (ii) decreases with decreasing temperature. Zener (1947) first predicted that the large elastic anisotropy due to the small value of  $C'$  stabilises the  $\beta$ -phase at high temperature by a large vibrational entropy, but the stability against a  $\{110\}\langle 1\bar{1}0\rangle$  shear is reduced at low temperature. This favours the MPT. The Zener picture has been recently confirmed from first-principles calculations for the (BCC) Zr system (Ye *et al* 1987) and in the case of Cu-Zn and Cu-Zn-Al alloys from the analysis of measurements giving the resolved shear stress to induce the transformation as a function of temperature (Romero and Ahlers 1989). In spite of these results, the experimental studies clearly show that these transitions are not soft-mode transitions. It has then been proposed (Lindgård and Mouritsen 1986) that the transition is rather a consequence of the anharmonic interaction between the homogeneous strain associated with  $C'$  and an inhomogeneous modulation. In the same framework, the martensitic transitions of Li (Gooding and Krumhansl 1988) and  $\text{Ni}_x\text{Al}_{1-x}$  (Gooding and Krumhansl 1989) have recently been studied with encouraging results.

The fact that  $C'$  depends on the atomic ordering state of the system makes this last quantity relevant in relation to the characterisation of the MPT. This idea is supported by both theory (Viñals *et al* 1984) and experiments (Rapacioli and Ahlers 1979) and gives rise to a dependence of  $M_s$  on the state of order of the system. In addition, it is known that the amount of order present in the system can be drastically changed by means of fast quenches (Planes *et al* 1981).

Very recently (Castán and Planes 1988), a Monte Carlo study of the relationship between  $C'$  and the state of order, described in terms of suitable order parameters, has been carried out for the (BCC)  $\beta$ -CuZn SMA. In order to eliminate the contribution arising from thermal effects, the equilibrium atomic-order configuration at a temperature  $T_q$  was suddenly quenched to  $T = 0$  K. Then the elastic constants can be simply calculated in terms of the interaction potential energies.

In the present work we focus our attention on the BCC binary alloy  $\text{A}_x\text{B}_{1-x}$  close to the  $\text{A}_3\text{B}$  composition ( $x \approx 0.75$ ). We use an Ising-type model to describe the state of order of the system with interactions up to next-nearest neighbours. The calculation of the phase diagram allows the establishment of the stability range of the  $\text{DO}_3$ , B2 and A2 phases we are interested in. Following standard procedures, we assume pairwise additive potentials for nearest and next-nearest neighbours and analyse the dependence of the elastic constants on the configurational ordering state in the  $\text{DO}_3$  and B2 regions. We find that the qualitative behaviour is independent of particular details of the potential. These results are discussed in relation to experimental data corresponding to the martensitic transformation of Cu-Zn-Al SMA.

## 2. Theoretical considerations

### 2.1. The model

In this section we briefly summarise the main features of the model used to describe the state of order of the BCC alloy  $\text{A}_x\text{B}_{1-x}$  when  $x$  is close to the stoichiometric composition ( $x \approx 0.75$ ).

Consider a binary alloy with the following configurational Hamiltonian:

$$H = \sum_{\mu=1}^2 (N_{AA}^{(\mu)} \Phi_{AA}(r_{\mu}) + N_{BB}^{(\mu)} \Phi_{BB}(r_{\mu}) + N_{AB}^{(\mu)} \Phi_{AB}(r_{\mu})). \quad (1)$$

$N_{\alpha\beta}^{(\mu)}$  ( $\alpha, \beta = A, B$ ) is the number of  $\mu$ -neighbour  $\alpha\beta$  pairs and  $\Phi_{\alpha\beta}(r_{\mu})$  its corresponding interaction potential energy when they are separated by a distance  $r_{\mu}$ . We now introduce pseudo-spin variables (Gunton and Droz 1983)  $\sigma_i$ , which take the value 1 (-1) when the lattice site  $i$  is occupied by an atom A (B). Using spin language, the Hamiltonian (1) takes the form

$$H = J_1 \sum_{\langle ij \rangle_{NN}} \sigma_i \sigma_j + J_2 \sum_{\langle ij \rangle_{NNN}} \sigma_i \sigma_j + H_0(x). \quad (2)$$

The first sum refers to nearest neighbours (NN) and the second to next-nearest neighbour (NNN) pairs.  $J_1$  and  $J_2$  are the ordering energies for NN and NNN respectively, which have the form

$$J_k = \frac{1}{4} (\Phi_{AA}(r_k) + \Phi_{BB}(r_k) - 2\Phi_{AB}(r_k)) \quad k = 1, 2. \quad (3)$$

$x$  is the A-component atom fraction. Since  $N_A$  and  $N_B$  are respectively the numbers of atoms A and B,  $x = N_A/N$ , with  $N = N_A + N_B$  being the total number of particles. The term  $H_0(x)$  can be written as

$$H_0(x) = N[(2x - 1)h + h_0] \quad (4)$$

where

$$h = +2(\Phi_{AA}(r_1) - \Phi_{BB}(r_1)) + \frac{3}{2}(\Phi_{AA}(r_2) - \Phi_{BB}(r_2)) \quad (5a)$$

and  $h_0$  is a constant given by

$$h_0 = (\Phi_{AA}(r_1) + \Phi_{BB}(r_1) + 2\Phi_{AB}(r_1)) + \frac{3}{4}(\Phi_{AA}(r_2) + \Phi_{BB}(r_2) + 2\Phi_{AB}(r_2)). \quad (5b)$$

Now we define the following dimensionless quantities:

$$E = (H - H_0(x))/J_1 = H/J_1 - (2x - 1)Nh/J_1 - Nh_0/J_1 \quad (6)$$

$$W = J_2/J_1. \quad (7)$$

Finally we get

$$E = \sum_{\langle ij \rangle_{NN}} \sigma_i \sigma_j + W \sum_{\langle ij \rangle_{NNN}} \sigma_i \sigma_j. \quad (8)$$

## 2.2. Relation to the elastic constants

We introduce the effect of ordering by assuming that  $N_{AB}^{(1)}$  and  $N_{AB}^{(2)}$  are the mean values of these quantities in equilibrium at temperature  $T_q$ . The procedure simulates measurements of elastic constants after ideally fast quenches from  $T_q$  to temperatures  $T_f$ —low enough to neglect the role of thermal fluctuations. We have taken in all cases  $T_f = 0$  K (Castán and Planes 1988).

Assuming pairwise additive central forces and interaction up to NNN, the elastic constants of a BCC binary crystal can be written, at  $T = 0$  K, as (Castán and Planes 1988)

$$VC_{11} = A_{11} - \frac{1}{32} N_{AB}^{(1)} \bar{\Phi}_f^{(1)} - \frac{1}{8} N_{AB}^{(2)} \bar{\Phi}_f^{(2)} \quad (9a)$$

$$VC_{44} = VC_{12} = A - \frac{1}{32} N_{AB}^{(1)} \bar{\Phi}_f^{(1)} \quad (9b)$$

$$VC' = A' - \frac{1}{12} N_{AB}^{(2)} \bar{\Phi}_f^{(2)} \quad (9c)$$

where  $V$  is the volume of the system. The terms  $A_{11}$ ,  $A$  and  $A'$  are given by the expressions

$$A_{11} = N_A(\bar{\Phi}_{AA}^{(1)}/4 + \bar{\Phi}_{AA}^{(2)}) + N_B(\bar{\Phi}_{BB}^{(1)}/4 + \bar{\Phi}_{BB}^{(2)}) \quad (10a)$$

$$A = (N_A \bar{\Phi}_{AA}^{(1)} + N_B \bar{\Phi}_{BB}^{(1)})/4 \quad (10b)$$

$$A' = (N_A \bar{\Phi}_{AA}^{(2)} + N_B \bar{\Phi}_{BB}^{(2)})/2 \quad (10c)$$

and

$$\bar{\Phi}_{\alpha\beta}^{(\mu)} = 4(d^2\Phi_{\alpha\beta}(r)/d(r^2)^2)_{r=r_\mu^0} \quad (11a)$$

$$\bar{\Phi}_J^{(\mu)} = \bar{\Phi}_{AA}^{(\mu)} + \bar{\Phi}_{BB}^{(\mu)} - 2\bar{\Phi}_{AB}^{(\mu)} \quad \mu = 1, 2. \quad (11b)$$

In (11a), the derivatives are calculated at  $r_\mu^0$ , which is the equilibrium distance between  $\mu$ -neighbour pairs. A direct look at expression (9) shows that, in this approximation,  $C_{11}$  depends on both  $N_{AB}^{(1)}$  and  $N_{AB}^{(2)}$ , whereas  $C_{44}$  and  $C'$  only depend on  $N_{AB}^{(1)}$  and  $N_{AB}^{(2)}$  respectively. We expect a NN and NNN approximation, which in turn ensures the mechanical stability of the BCC lattice (Milstein 1970) to be good enough to reveal the main effects associated with B2 and DO<sub>3</sub> orderings. Concerning the centrality of the potential, it is believed to be a poor approximation for BCC metal systems. In particular, Monte Carlo simulations of elastic constants at finite temperature (Castán *et al* 1989) show that a central potential cannot simultaneously reproduce the behaviour of all the elastic constants. Nevertheless, we expect this approximation to be good enough to analyse the effect of atomic ordering on the elastic constants after quenches to very low temperature. Also, eventual changes of the lattice parameter with atomic order should be considered. Available experimental data corresponding to the Cu<sub>3</sub>Au (FCC) system indicate that changes of the lattice parameter with atomic order are very small (Roy *et al* 1974). Unfortunately, to our knowledge, no similar study has been done for the systems we are dealing with. However, experimental results show that the lattice parameter of  $\beta$ -CuZn presents only slight changes with composition (the lattice parameter changes by approximately 0.06% per 1% change in composition, Massalski and King 1961). Consequently the variation of the elastic constants with  $T_q$  are given by

$$V \delta C_{11}/\delta T_q = -\frac{1}{32}\bar{\Phi}_J^{(1)} \delta N_{AB}^{(1)}/\delta T_q - \frac{1}{8}\bar{\Phi}_J^{(2)} \delta N_{AB}^{(2)}/\delta T_q \quad (12a)$$

$$V \delta C_{44}/\delta T_q = -\frac{1}{32}\bar{\Phi}_J^{(1)} \delta N_{AB}^{(1)}/\delta T_q \quad (12b)$$

$$V \delta C'/\delta T_q = -\frac{1}{12}\bar{\Phi}_J^{(2)} \delta N_{AB}^{(2)}/\delta T_q. \quad (12c)$$

That is, with  $\bar{\Phi}_J^{(\mu)}$  ( $\mu = 1, 2$ ) fixed, the behaviour of  $C_{11}$ ,  $C_{44}$  and  $C'$  with  $T_q$  will be mainly controlled by the variation of  $N_{AB}^{(1)}$  and  $N_{AB}^{(2)}$  with  $T_q$ .

In alloy systems undergoing an MPT, it has been found that the MPT temperature changes after a quench from  $T_q$ . It has been justified that this change  $\delta M_s$  is, to a first approximation, proportional to the corresponding change in  $C'$  (Nakanishi *et al* 1968, Planes *et al* 1985)). That is,

$$\delta M_s = -K\delta C' \quad (13)$$

$K$  is a positive constant related to the slope of the temperature variation of  $C'(T)$  ( $K^{-1} = dC'/dT$ ) close to but above  $M_s$ . For a given alloy,  $K$  is independent of temperature (Guénin *et al* 1977). If one additionally assumes  $K$  independent of the state of order, the results are consistent with experimental data (Castán and Planes 1989). Then,

$$\delta M_s/\delta T_q = -K \delta C'/\delta T_q. \quad (14)$$



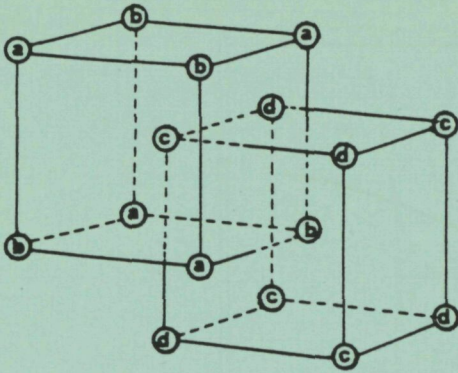


Figure 1. Sublattice structure of the BCC lattice

Let us specify that in the experimental procedure, the  $T_q$ -quenches are performed, to a final temperature  $T_f$  very close to but above  $M_s$ . Immediately afterwards, one continues decreasing the temperature and the MPT starts. Because of the diffusionless nature of the MPT, the state of order frozen at  $T_f$  will be preserved during the transformation. In addition,  $M_s$  is usually low enough to neglect thermal fluctuations. Hence, it can be assumed that the change in  $C'$  after the quench from  $T_q$  may be identified with the change obtained from equation (12). All these considerations enable us to write

$$\delta M_s / \delta T_q = (K \bar{\Phi}^{(2)} / 12 V) \delta N_{AB}^{(2)} / \delta T_q. \quad (15)$$

This expression tells us that changes in  $M_s$  with  $T_q$  depend on the interaction potential through  $\bar{\Phi}^{(2)}$  and on the way  $N_{AB}^{(2)}$  varies with the temperature  $T_q$ . Notice, however, that the role of the interaction potential is, in this approximation, limited to a coefficient in the linear relation between the  $T_q$ -variations of  $M_s$  and  $N_{AB}^{(2)}$  and that (15) no longer implies any necessary reference to particular fine details of the interaction potential. The comparison between experimental  $M_s$ -behaviour and Monte Carlo calculations of  $N_{AB}^{(2)}$ , both as function of  $T_q$ , will give us information about the validity of these statements.

### 3. Results and discussion

In this section we present the Monte Carlo results corresponding to the equilibrium order behaviour of the alloy  $A_x B_{1-x}$  ( $x \approx 0.75$ ) described by the model (8), using appropriate interaction parameters. The ground state of the system has been analysed by Richards and Cahn (1971). A wide variety of phases can appear depending on the values of  $x$  and  $W$ . Particularly for  $x = 0.75$  and  $\frac{2}{3} > W > 0$ , the ground state is  $DO_3$ , and for  $x \neq 0.75$  but close to it, the ground state can show a mixture of the stoichiometric phases  $DO_3$  and B2 or a gradual change in the occupancy of some of the sites due to the large degeneracy.

Calculations have been carried out following standard Monte Carlo techniques (Binder 1984). The system is a BCC lattice with  $N = N_A + N_B = 2(8)^3$  particles obeying periodic boundary conditions. The volume of the system,  $V = (8a)^3$ , and the temperature remain fixed in each simulation. Starting from an initial random configuration, the system relaxes to the equilibrium state by means of a two-sites spin-exchange excitation mechanism.

In order to characterise the state of order of the system, let us define the following order parameters:

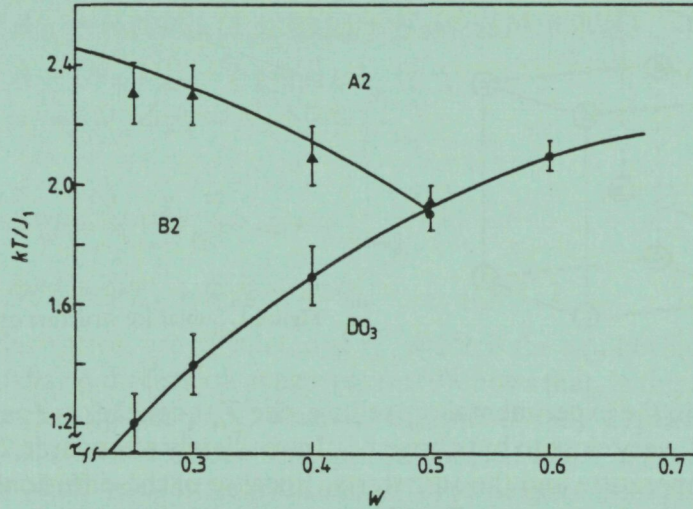


Figure 2. Phase diagram, for  $x = 0.75$ , showing the stability region of the A2, B2 and  $\text{DO}_3$  phases obtained from Monte Carlo simulations.

$$m_\mu = 4 \left( \sum_{i \in \mu} \sigma_i \right) / N \quad (16)$$

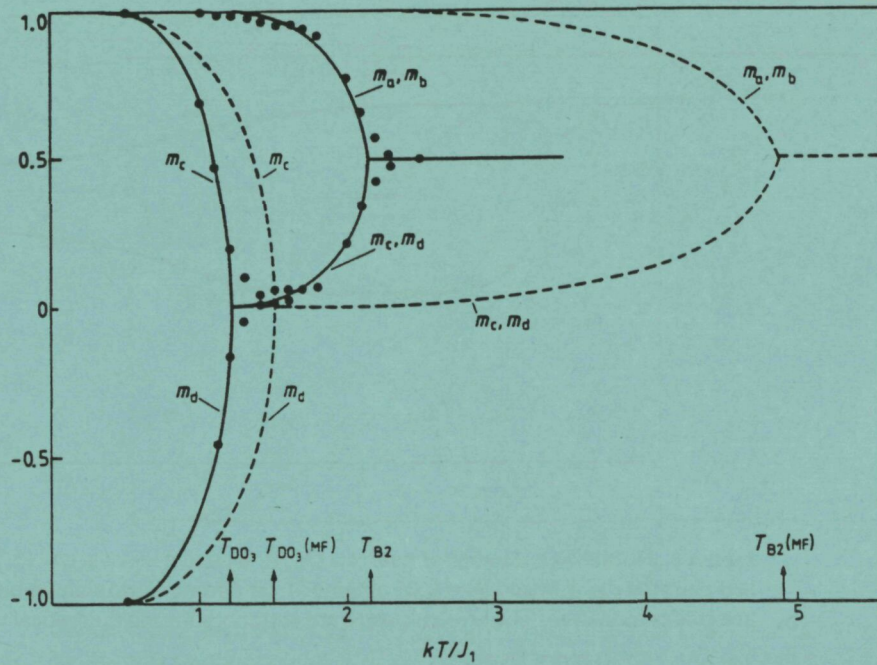
where  $\mu = (a, b, c, d)$  means the four equivalent sublattices usually defined to subdivide the BCC lattice (see figure 1).

In figure 2 we present the phase diagram for the stoichiometric composition ( $x = 0.75$ ) within the range of interaction parameters  $0 < W < \frac{2}{3}$ . This is in agreement with previous Monte Carlo calculations (Dünweg and Binder 1987) and theoretical results (Bell 1987). One observes that when  $W < 0.50$ , the system passes through all three phases,  $\text{DO}_3$ , B2 and A2, when one moves along the temperature axis. For  $W > 0.50$ , the B2 phase does not appear and only the  $\text{DO}_3$  and A2 phases are present.

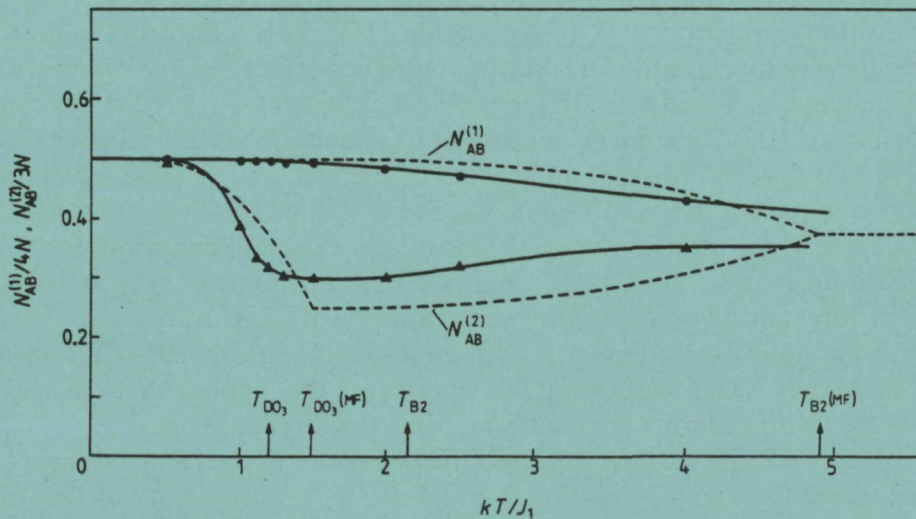
To exemplify the procedure used to calculate the phase diagram, we show in figure 3 the behaviour of the order parameters (16) as a function of temperature for a value of the interaction parameter  $W = 0.25$ . In the same figure we have plotted both the Monte Carlo result and the mean-field calculation (Dünweg and Binder 1987). Near the transition points, finite-size effects cause the round shape exhibited by the order parameters, and introduce a quite important uncertainty in the determination of such points as  $T_{\text{B2}}$  and  $T_{\text{DO}_3}$ . We chose  $W = 0.25$  to separate  $T_{\text{B2}}$  and  $T_{\text{DO}_3}$  in order to reveal the distinct effects of both transition points on the different properties of the system. In what follows we restrict ourselves to this value. Nevertheless, the same qualitative results are obtained with different values of  $W$ . In particular, we have also studied the cases  $W = 0.20$ ,  $0.30$  and  $0.40$ .

Figure 4 illustrates the temperature evolution of  $N_{\text{AB}}^{(1)}$  and  $N_{\text{AB}}^{(2)}$ , when  $x = 0.75$ , calculated using Monte Carlo and mean-field techniques. One observes that both methods give the same qualitative behaviour for  $N_{\text{AB}}^{(1)}$  and  $N_{\text{AB}}^{(2)}$  across the range of temperatures. This is an unexpected result considering the disagreement between the values obtained from both techniques for the long-range order parameters (as displayed in figure 3). It means that mean-field calculations can provide quite good qualitative information about the variation of  $N_{\text{AB}}^{(1)}$  and  $N_{\text{AB}}^{(2)}$  with temperature. Consequently, this approximation, provided no more exact theories are available, is good enough to obtain qualitative information about the change of elastic constants with ordering.

In studying figure 4, one observes that  $N_{\text{AB}}^{(1)}$  keeps nearly constant inside the  $\text{DO}_3$  phase, whereas it shows a smooth decreasing in the B2 and A2 regions. Contrarily,



**Figure 3.** Long-range order parameters  $m_\mu$  as a function of temperature for  $x = 0.75$  and  $W = 0.25$ . The full circles correspond to Monte Carlo results and the full curves are just guides to the eye. Notice that near the transition temperatures, Monte Carlo results exhibit tails due to finite-size effects. The broken curves correspond to the mean-field solution. The arrows indicate the positions of transition temperatures from Monte Carlo ( $T_{DO_3}$ ,  $T_{B_2}$ ) and mean-field ( $T_{DO_3(MF)}$ ,  $T_{B_2(MF)}$ ) approximations.



**Figure 4.** Normalised number of nearest- ( $N_{AB}^{(1)}$ ) and next-nearest- ( $N_{AB}^{(2)}$ ) neighbour AB pairs for  $x = 0.75$  and  $W = 0.25$  and different values of temperature  $T_q$ .  $\bullet$ :  $N_{AB}^{(1)}$ ;  $\blacktriangle$ :  $N_{AB}^{(2)}$  obtained from Monte Carlo simulations. The full curves are just guides to the eye. The broken curves are the mean-field solutions.

$N_{AB}^{(2)}$  displays a remarkable decrease in the  $DO_3$  region, remains almost constant in the  $B_2$  phase, and slowly increases in the  $A_2$  region.

We have also performed Monte Carlo studies slightly below ( $x = 0.70$ ) the stoichiometric composition. At low temperatures, complications arise from the high

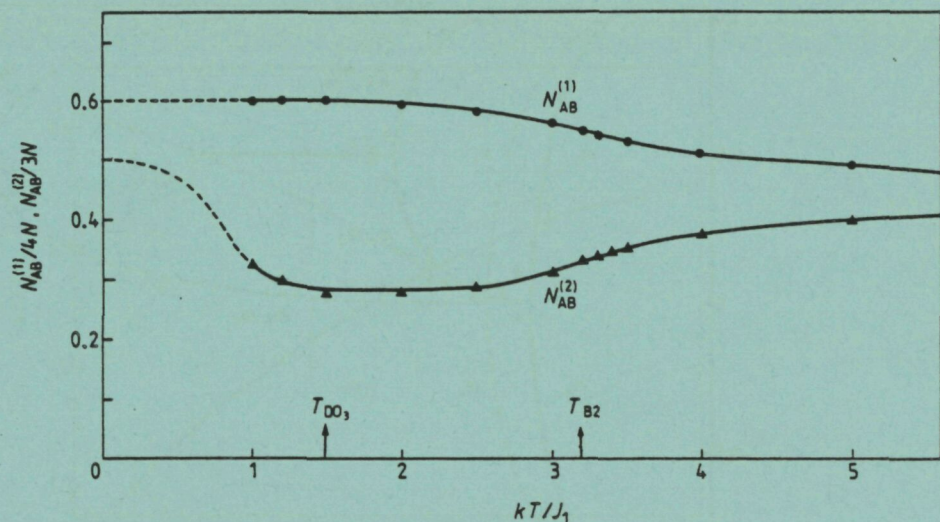


Figure 5. Normalised number of nearest- ( $N_{AB}^{(1)}$ : ●) and next-nearest- ( $N_{AB}^{(2)}$ : ▲) neighbour AB pairs for  $x = 0.70$  and  $W = 0.25$  obtained from Monte Carlo simulations. The full curves are guides to the eye. The broken curves are extrapolations to theoretical values at  $T = 0$  K.

degeneracy of the ground state which prevents the system from reaching the proper equilibrium state in a reasonable time. The behaviour obtained for both  $N_{AB}^{(1)}$  and  $N_{AB}^{(2)}$  (figure 5) is similar to the one obtained in the stoichiometric case.

From these results we argue that the temperature behaviour of properties depending on  $N_{AB}^{(1)}$  and  $N_{AB}^{(2)}$  will be mainly distorted near the  $T_{DO_3}$  ordering transition. In particular, taking into account equation (12), after quenches from  $T_q$  to very low temperatures, this effect should be found in the elastic constants  $C_{11}$ ,  $C_{44}$ , and  $C'$  as well as in the martensitic transition temperature  $M_s$  (see equation (15)). It is interesting to note that from our results we expect, in the  $DO_3$  region, more important relative changes with ordering in  $C'$  than in  $C_{44}$ . When considering the elastic constant  $C_{11}$ , predictions cannot be done in such a straightforward way because of its simultaneous dependence on both  $N_{AB}^{(1)}$  and  $N_{AB}^{(2)}$ . To proceed further, an analysis of the sign and relative magnitude of  $\bar{\Phi}^{(1)}$  and  $\bar{\Phi}^{(2)}$  is required. In the B2 region,  $C_{44}$  and  $C'$  exhibit relative variations with ordering of the same order of magnitude. As before, the expected behaviour for  $C_{11}$  needs a more elaborate analysis. In certain cases, the terms depending on  $N_{AB}^{(1)}$  and  $N_{AB}^{(2)}$  could balance each other and give rise to a very weak variation of  $C_{11}$  with ordering. This is in agreement with previous experimental results corresponding to the B2-A2 transition in Cu-Zn (MacManus 1969). Following our arguments this implies that changes of elastic anisotropy with ordering are mainly associated with changes in  $C'$ .

Very recently we have analysed the behaviour of the resolved shear stress to induce the martensitic transformation in two Cu-Zn-Al alloys as a function of quenching  $T_q$  temperatures (Planes *et al* 1989). Such an alloy can be viewed, to ordering effects, as a binary alloy. This is because ordering energies for the CuAl pairs are about 1.5 times greater than for CuZn pairs, but around 20 times greater than for ZnAl pairs (Ahlens 1986, Castán and Planes 1989). By using the Clausius-Clapeyron equation, it is possible to obtain the corresponding shift of the  $M_s$  temperature,  $\Delta M_s$ , after quenches from the temperature  $T_q$ . It has been obtained that the equilibrium state at  $T_q$  can be frozen-in at low temperature by fast quenches if  $T_q < 600$  K. For temperatures above this, reordering takes place to a significant degree during the quench due to a large vacancy concentration in the system.