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Elastic constants of bcc shape-memory binary alloys: Effect of the configurational ordering

T. Castán and A. Planes

Departament d'Estructura i Constituents de la Matèria, Facultat de Física,
Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

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The relationship between the elastic shear modulus $C'=\frac{1}{2}(C_{11}-C_{12})$ and the atomic order state in a shape-memory binary alloy A_xB_{1-x} above its martensitic transition temperature is analyzed. We first present a simple method to evaluate the elastic constants in binary alloys, assuming the atoms interact via a two-body Morse potential. For CuZn and AgZn alloys, the potential parameters corresponding to the different A-A, B-B, and A-B pairs are determined from experimental data of the elastic constant C' for different alloy compositions. We next calculate C' at 0 K as a function of the ordering state. To do this, we use atomic configurations obtained with a Monte Carlo simulation of the Ising model for a bcc binary alloy, at each temperature T_i. We obtain a linear relationship between C' and the short-range-order parameter η. We also show that the deviations from the linear behavior observed when C' is represented against the square of the long-rang-order parameter $\langle S\rangle$ come mainly from the critical behavior of the system near the order-disorder temperature T_c.

I. INTRODUCTION

A wide variety of noble-metal-based alloy systems (e.g., CuZn, AgZn, AuCd, . . .) undergo, at low temperatures, a structural phase transition mainly described by a shear deformation from a bcc to a close-packed structure. This transition, called martensitic (MT), is responsible for the pseudoelasticity and the shape-memory effects observed in these alloys.[1] Above the MT temperature (MS), these alloy systems exhibit atomic order of the $B2$, $DO3$, or $L21$ type, and undergo an order-disorder transition at a temperature T_c normally much higher than MS and dependent on the composition of the alloy. Important features of shape-memory alloys are the low (but finite) value of the elastic constant $C'=(C_{11}-C_{12})/2$, which measures the resistance against a $\{110\}\langle 1\bar{1}0\rangle$ shear, and its "abnormal" behavior with temperature: C' decreases with decreasing temperature as MS is approached.[2] This fact has led several authors to suggest that the MT is driven by a local elastic instability and that the behavior of C' near MS plays a very important role in determining the properties of the transition.[3,4]

In addition, the atomic order in the alloy has a strong influence on the properties of the MT. In this sense, it is experimentally known that the state of atomic order, established by annealing at a particular temperature T_i and retained by a quench to lower temperatures, can substantially modify quantities such as temperature MS and enthalpy change of the MT.[5,6]

In the frame of a mean-field theory, the natural way to introduce the effect of the long-range atomic order on the characteristics of the MT is through the elastic constants of the system, and particularly through the shear modulus C'.[7,8] Such a model includes a linear coupling between C' and the square of the long-range atomic order parameter $\langle S\rangle$, and gives the shift in the MT temperature and in the enthalpy change of the transformation as functions of this parameter $\langle S\rangle$. The validity of this result has only been indirectly justified from the correlation observed between the changes in the MT temperature and the relative changes of C' during the isothermal ordering process that follows a quench from T_i to temperatures T_f above MS.[9]

The significance of the results obtained from a mean-field approximation is not definitive, however, and one would like to perform a more exact kind of calculation. In this sense, we have computed the elastic shear contant C' of bcc binary alloys with different degrees of atomic order using simulated ordered or partially ordered structures. These structures have been obtained at different temperatures T_i (above and below T_c) by a Monte Carlo simulation of an appropriate Ising model for binary alloys. In every case C' has been calculated at $T=0$ K. The procedure simulates measurements of C' after ideally fast quenches from T_i to temperatures T_f, low enough to neglect the role of thermal fluctuations ($T_f \ll T_c$). In such a situation the atoms of the system are restricted to be at the sites of a bcc lattice. It is assumed that they interact with their next (NN) and next-nearest neighbors (NNN) through a pairwise Morse potential. This empirical interatomic potential has proven to be successful in many different solid-state studies.[10]

The paper is organized as follows: In Sec. II we present the mathematical formulation of the problem and obtain the expressions of the elastic constants in terms of the interatomic potential. The parameters of the potential corresponding to the A-A, B-B, and A-B interactions, for CuZn and AgZn alloys, are obtained in Sec. III from available experimental data giving C' as a function of the alloy composition. In Sec. IV we describe the Ising model of a binary alloy and the Monte Carlo simulation procedure used to obtain the atomic configurations. For each configuration we calculate C' and analyze its dependence on atomic order. The analysis provides the limits of validity of the linear relation between C' and $\langle S\rangle^2$, a result of the mean-field model.

II. MORSE INTERATOMIC POTENTIAL: STABILITY CONDITIONS AND ELASTIC CONSTANTS FOR bcc BINARY ALLOYS

Let us suppose that $\varphi(r^{mn})$ is the interatomic potential energy of two atoms (m and n) separated a distance r^{mn}. Assuming interaction only to NN and NNN, the bound energy of the crystal per unit volume is given by

$$E=V^{-1}\sum_{m,n}\varphi(r^{mn}) \tag{1}$$

where the sum is taken over all the lattice atoms (m) and over its nearest and next-nearest neighbors (n). V is the volume of the system.

Consider now the system homogeneously deformed. For small displacements of the atoms about their equilibrium positions, a Taylor expansion of Eq. (1) yields[11]

$$E=A+A_{ij}\epsilon_{ij}+\tfrac{1}{2}C_{ijkl}\epsilon_{ij}\epsilon_{kl}+\cdots \tag{2}$$

with

$$A=V^{-1}\sum_{m,n}[\varphi(r_0^{mn})] , \tag{3a}$$

$$A_{ij}=V^{-1}\sum_{m,n}\left[\frac{\partial\varphi(r^{mn})}{\partial r_j^{mn}}\right]_0 r_{0i}^{mn} , \tag{3b}$$

$$C_{ijkl}=V^{-1}\sum_{m,n}\left[\frac{\partial^2\varphi(r^{mn})}{\partial r_j^{mn}\partial r_l^{mn}}\right]_0 r_{0i}^{mn}r_{0k}^{mn} . \tag{3c}$$

Here r_j^{mn} is a Cartesian component of $\mathbf{r}^{mn}$, and $\mathbf{r}_0^{mn}$ is the undeformed value of $\mathbf{r}^{mn}$. The derivatives of the potential energy are evaluated at the undeformed lattice positions, and summation by repeated indexes is implied. ϵ_{ij} are the components of the strain tensor defined in the usual form[12] and C_{ijkl} are directly the components of the elastic constant tensor if the external pressure is zero and the effect of temperature is negligible. In such a case $A_{ij}=0$ is the equilibrium condition. For crystals with a cubic symmetry, there are only three independent components of the elastic constant tensor: C_{11}, C_{12}, and C_{44} using Voigt notation ($xx\rightarrow1$, $yy\rightarrow2$, $zz\rightarrow3$, $yz\rightarrow4$, $xz\rightarrow5$, $xy\rightarrow6$). For central forces, in addition, the Cauchy conditions yield $C_{12}=C_{44}$. Consequently there are only two independent components, which may be written as

$$C_{11}=4V^{-1}\sum_{m,n}\left[\frac{\partial^2\varphi(r^{mn})}{\partial[(r^{mn})^2]}\right](r_{0x}^{mn})^4 , \tag{4a}$$

$$C_{12}=C_{44}=4V^{-1}\sum_{m,n}\left[\frac{\partial z\varphi(r^{mn})}{\partial[(r^{mn})^2]}\right](r_{0x}^{mn})^2(r_{0y}^{mn})^2 . \tag{4b}$$

Born and Huang[13,14] have investigated the conditions under which a crystal lattice is thermodynamically stable. A necessary condition is the mechanical stability of the crystal with respect to arbitrary (small) homogeneous deformations. In the case of crystals with cubic symmetry and interactions given by central forces this condition may be expressed simply as

$$C_{11}/C_{12}>1 , \quad C_{12}>0 . \tag{5}$$

Suppose now that the interaction potential energy is given by a Morse potential function:

$$\varphi(r)=D\{\exp[-2\alpha(r-r_0)]-2\exp[-\alpha(r-r_0)]\} \tag{6}$$

where α and D are positive constants with dimensions of reciprocal distance and energy, respectively. This function has its minimum at $r=r_0$ and $\varphi(r_0)=-D$. In order to obtain the stability criteria solely in terms of the dimensionless parameter (αa) (a being the lattice parameter of a bcc structure) we define

$$\rho^{mn}=\frac{r^{mn}}{a} \tag{7a}$$

and

$$P=D\exp(2\alpha r_0) , \tag{7b}$$

$$Q=2D\exp(\alpha r_0) . \tag{7c}$$

Now

$$\varphi(\rho^{mn})=P\exp[-2(\alpha a)\rho^{mn}]-Q\exp[-(\alpha a)\rho^{mn}] . \tag{8}$$

With the Morse potential energy the elastic constants [(4a) and (4b)] may be written as

$$C_{11}=V^{-1}\sum_{m=1}^{N}\sum_{n=1}^{z(m)}\left\{P\left[\left[\frac{2\alpha a}{\rho^{mn}}\right]^2+\frac{\alpha a}{(\rho^{mn})^3}\right]e^{-2(\alpha a)\rho^{mn}}-Q\left[\left[\frac{\alpha a}{\rho^{mn}}\right]^2+\frac{\alpha a}{(\rho^{mn})^3}\right]e^{-(\alpha a)\rho^{mn}}\right\}(\rho_x^{mn})^4 , \tag{9a}$$

$$C_{12}=V^{-1}\sum_{m=1}^{N}\sum_{n=1}^{z(m)}\left\{P\left[\left[\frac{2\alpha a}{\rho^{mn}}\right]^2+\frac{\alpha a}{(\rho^{mn})^3}\right]e^{-2(\alpha a)\rho^{mn}}-Q\left[\left[\frac{\alpha a}{\rho^{mn}}\right]^2+\frac{\alpha a}{(\rho^{mn})^3}\right]e^{-(\alpha a)\rho^{mn}}\right\}(\rho_x^{mn})^2(\rho_y^{mn})^2 , \tag{9b}$$

and the equilibrium condition is given by

$$e^{\alpha r_0}=\frac{2\sum_{m=1}^{N}\sum_{n=1}^{z(m)}\frac{\alpha a}{\rho^{mn}}e^{-(\alpha a)\rho^{mn}}(\rho_x^{mn})^2}{\sum_{m=1}^{N}\sum_{n=1}^{z(m)}\frac{2\alpha a}{\rho^{mn}}e^{-2(\alpha a)\rho^{mn}}(\rho_x^{mn})^2} , \tag{10}$$

where $Z(m)$ is the specific number of neighbors considered. For a bcc system $Z=14$ (eight NN and six NNN) is sufficient to obtain mechanical stability. The Born stability criteria (5) are satisfied for $\alpha a<(\alpha a)^*=5.8$ (see Fig. 1). In a previous work, Milstein[15] found $(\alpha a)^*=4.8$ but the difference arises from the

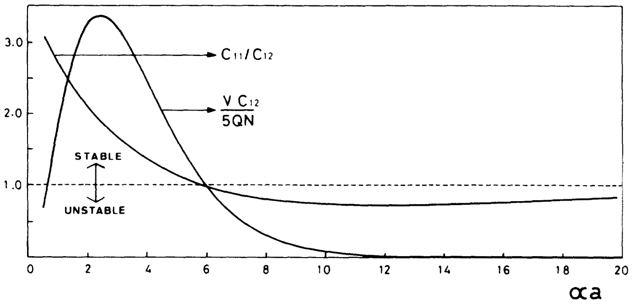

FIG. 1. Ratio of elastic constants C_{11}/C_{12} and C_{12} (in reduced units) vs the dimensionless parameter (αa). The Born stability criteria are satisfied for values of (αa) less than 5.8.

periodic boundary conditions considered in our calculations.

III. APPLICATION TO bcc BINARY ALLOYS

In the case of an A_xB_{1-x} binary alloy system the equations (4a) and (4b) can be rewritten in the form

$$C_{11}=V^{-1}(N_{AA}^{(1)}\tilde{\varphi}_{AA}^{(1)}+N_{BB}^{(1)}\tilde{\varphi}_{BB}^{(1)}+N_{AB}^{(1)}\tilde{\varphi}_{AB}^{(1)})(r_{0x}^{(1)})^4$$
$$+(3V)^{-1}(N_{AA}^{(2)}\tilde{\varphi}_{AA}^{(2)}+N_{BB}^{(2)}\tilde{\varphi}_{BB}^{(2)}+N_{AB}^{(2)}\tilde{\varphi}_{AB}^{(2)})$$
$$\times(r_{0x}^{(2)})^2(r_{0y}^{(1)})^2\ , \tag{11a}$$

$$C_{12}=V^{-1}(N_{AA}^{(1)}\tilde{\varphi}_{AA}^{(1)}+N_{BB}^{(1)}\tilde{\varphi}_{BB}^{(1)}+N_{AB}^{(1)}\tilde{\varphi}_{AB}^{(1)})$$
$$\times(r_{0x}^{(1)})^2(r_{0y}^{(1)})^2 \tag{11b}$$

with

$$\tilde{\varphi}_{ij}^{(1)}=4\left[\frac{\partial^2\varphi_{ij}(r)}{\partial(r^2)^2}\right]_{r=r_0^{(1)}}\ ,$$
$$\tilde{\varphi}_{ij}^{(2)}=4\left[\frac{\partial^2\varphi_{ij}(r)}{\partial(r^2)^2}\right]_{r=r_0^{(2)}}\ . \tag{12}$$

$\varphi_{ij}(r)$ is the interaction potential energy for atom pairs i and j. $N_{ij}^{(1)}$ and $N_{ij}^{(2)}$ are the number of next- and next-nearest-neighbor ij pairs, respectively. For a bcc structure $r_0^{(1)}=\sqrt{3}/2$ and $r_0^{(2)}=1$ (in units of a). Let us focus our attention on the relevant elastic constant $C'=(C_{11}-C_{12})/2$, given by

$$C'=(6V)^{-1}(N_{AA}^{(2)}\tilde{\varphi}_{AA}^{(2)}+N_{BB}^{(2)}\tilde{\varphi}_{BB}^{(2)}+N_{AB}^{(2)}\tilde{\varphi}_{AB}^{(2)})\ . \tag{13}$$

Taking into account that

$$N_{AA}^{(2)}=3N_A-\tfrac{1}{2}N_{AB}^{(2)}\ ,$$
$$N_{BB}^{(2)}=3N_B-\tfrac{1}{2}N_{AB}^{(2)}\ , \tag{14}$$

we obtain

$$C'=(6V)^{-1}[3(N_A\tilde{\varphi}_{AA}^{(2)}+N_B\tilde{\varphi}_{BB}^{(2)})-\tfrac{1}{2}N_{AB}^{(2)}\tilde{\varphi}_J^{(2)}] \tag{15}$$

where

$$\tilde{\varphi}_J^{(2)}=\tilde{\varphi}_{AA}^{(2)}+\tilde{\varphi}_{BB}^{(2)}-2\tilde{\varphi}_{AB}^{(2)} \tag{16}$$

and N_A, N_B are the number of atoms A and B, respectively.

For completely ordered configurations, Eq. (15) as a function of the concentration x reads

$$\frac{2VC'}{N}=x\tilde{\varphi}_{AA}^{(2)}+(1-x)\tilde{\varphi}_{BB}^{(2)}-(1-x)(2x-1)\tilde{\varphi}_J^{(2)} \tag{17}$$

when $x\geq 0.50$, and

$$\frac{2VC'}{N}=x\tilde{\varphi}_{AA}^{(2)}+(1-x)\tilde{\varphi}_{BB}^{(2)}-x(1-2x)\tilde{\varphi}_J^{(2)} \tag{18}$$

when $x\leq 0.50$.

The parameters of the Morse potential for the AA, BB, and AB interactions must be determined from experimental data. We use C' values of AgZn and CuZn alloys, measured at room temperature for different compositions in the range $0.45<x<0.55$ and $0.55>x>0.50$, respectively.[16] The qualitative observable behavior around $x=0.50$ is determined by

$$\frac{\partial C'}{\partial x}>0 \quad \text{if } x>0.50\ ,$$
$$\frac{\partial C'}{\partial x}<0 \quad \text{if } x<0.50\ . \tag{19}$$

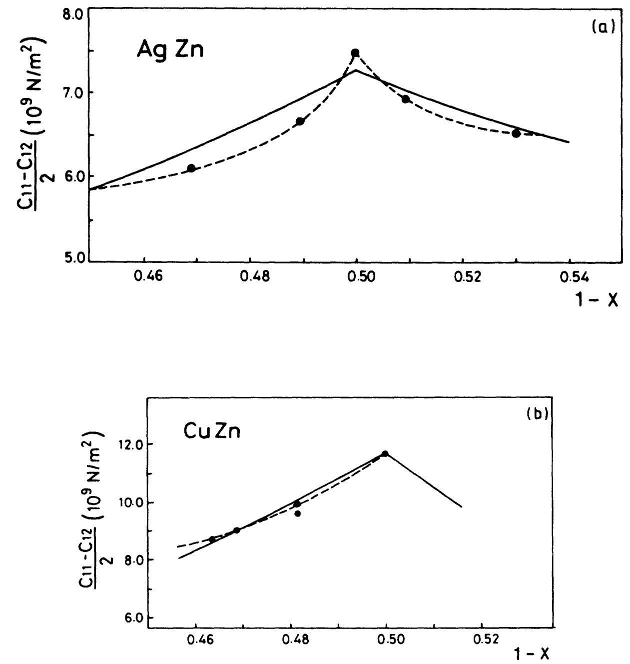

FIG. 2. (a) Composition dependence of C' in AgZn alloy at 0 K. Solid line is our result whereas points indicate experimental data values. Dotted line corresponds to an empirical behavior proposed by Verlinden and Delaey (Ref. 25). (b) Composition dependence of C' in CuZn alloy at 0 K. Solid line is our result whereas points indicate experimental data values. Dotted line is the empirical behavior proposed by Verlinden and Delaey (Ref. 25).

Imposing this behavior on the analytical expressions of C' (17) and (18) we obtain that $\tilde{\varphi}\,^{(2)}_{AA}$ and $\tilde{\varphi}\,^{(2)}_{BB}$ must have the same sign and $\tilde{\varphi}\,^{(2)}_{AB}$ the opposite one. On the other hand, the stability conditions (5) near $x=0.50$ require that $\tilde{\varphi}\,^{(2)}_{AA}>0$ and $\tilde{\varphi}\,^{(2)}_{BB}>0$ which implies that $\tilde{\varphi}\,^{(2)}_{AB}<0$.

A fit of the functions (17) and (18) to the experimental data of CuZn and AgZn alloys [see Figs. 2(a) and 2(b)], gives the parameters of the Morse interactions summarized in Tables I(a) and I(b). An analysis of the sensitivity of $C'(x)$ to these parameters shows that the calculated value of $C'(x)$ does not change significantly with $(a\alpha)_{ij}$ parameters (at least around $x=0.50$) for fixed values of the parameters listed in Table I(b). Finally, Figs. 3(a) and 3(b) show the Morse interatomic potentials for the different atom pairs corresponding to CuZn and AgZn alloys, in units of $Q_{\text{Cu-Cu}}$, and $Q_{\text{Ag-Ag}}$, respectively [(7c)]. $Q_{\text{Cu-Cu}}$ (or $Q_{\text{Ag-Ag}}$) may be obtained from the Debye temperature using the expressions of $\Theta_0^{T\to 0}$ as a function of the elastic constants.[17] Taking $a=2.94$ Å and $\Theta_0^{T\to 0}=288$ K (Ref. 18) for the CuZn alloy we have obtained $Q_{\text{Cu-Cu}}=8.2\times 10^{-19}$ J. This value is consistent with the value obtained from Monte Carlo simulations of C' at finite temperature.[19] In addition, the evaluated potentials yield the sign of the NN ordering energy $[=2\varphi_{AB}(r_0^{(1)})-\varphi_{11}(r_0^{(1)})-\varphi_{BB}(r_0^{(1)})<0]$ according to the tendency to ordering exhibited by these systems.

IV. ELASTIC CONSTANTS AND ATOMIC ORDER

A. Monte Carlo simulations of partially ordered configurations

Using a Monte Carlo simulation of an Ising model for a binary alloy[20] we have obtained the equilibrium atomic configurations at different temperatures T_i for a fixed composition. The Monte Carlo calculations have been carried out following the standard procedure originated by Metropolis *et al.*[21]

The system is a bcc lattice with $N=N_A+N_B=(8)^3\times 2$ particles, obeying periodic boundary conditions. The volume $(8)^3$ and the temperature T_i remain fixed in each simulation. The Hamiltonian of the system reads

$$H=-J\sum_{i,j}\sigma_i\sigma_j-h\sum_i\sigma_i\ ,\quad J<0 \tag{20}$$

where the first summation gives all nearest-neighbor pairs ij in the lattice. $\sigma_i=1$ if the site i is occupied by a constituent of type A and $\sigma_i=-1$ if the constituent is of type B. J is a negative parameter giving the ordering energy for NN. The equilibrium state of this system includes long and short ordering modes.

Starting from an initial random configuration, the system moves through the phase space with a transition probability corresponding to a "spin-exchange" operation, i.e., following a Kawasaki's dynamics.[22] The averages are based on samples ranging from 15 000 to 30 000 configurations. The first configurations are omitted since they show nonequilibrium effects and slow the convergence of the averages.

In order to define the long-range atomic order parameter $\langle S\rangle$, the bcc lattice is divided into two interpenetrating simple-cubic sublattices a and b. $\langle S\rangle$ is given by

$$\langle s\rangle=\left\langle\frac{1}{N}\sum_{i=1}^{N}(-1)^j\sigma_i\right\rangle \tag{21}$$

where $j=0$ if i is a site of the a sublattice, and $j=1$ if i is

TABLE I. Parameters of the Morse potential for A-A, B-B, and A-B interactions obtained from experimental data for CuZn and AgZn alloy systems.

(a)

Interaction	$a\alpha$	P/Q	αr_0
A-A	1.865	2.760	1.708
B-B	2.840	6.630	2.585
A-B	6.545	171.232	5.836

(b)

Alloy AB	$Q_{B\text{-}B}/Q_{A\text{-}A}$	$Q_{A\text{-}B}/Q_{A\text{-}A}$
CuZn	0.3597	131.9205
AgZn	2.6358	67.3614

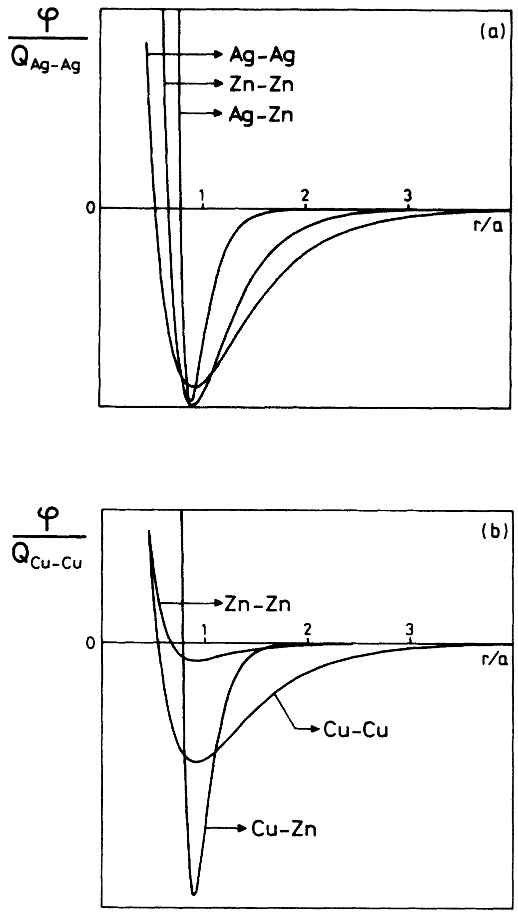

FIG. 3. (a) Interatomic potentials (in reduced units) for the different pairs of AgZn. (b) Interatomic potentials (in reduced units) for the different pairs of CuZn.

a site of the b sublattice. The bracket represents statistical averages. The short-range order parameter η is defined by

$$\eta=\frac{-\langle H\rangle/J}{2zNx_Ax_B}=\frac{1}{4x_Ax_B}\left[\frac{2N_{AB}^{(1)}}{zN/2}-1\right] \tag{22}$$

where z is the coordination number for NN pairs, and $N_{AB}^{(1)}$ the number of A-B NN pairs.

In Figs. 4(a) and 4(b), respectively, we show $\langle S\rangle$ and η as functions of (T/T_c) for four alloy systems with different compositions ($x=0.50$, 0.55, 0.61, and 0.65). T_c is the critical order-disorder temperature. For $x=0.50$ we obtain—in Ising-model units—$T_c\simeq 6.3J/k_B$ in agreement with previous Monte Carlo results.[23] Experimentally $T_c=735$ K,[24] and then $J/k_B=115$ K. This value is one order of magnitude lower than is obtained from the potential evaluated in Sec. III. This contrariety, probably due to the fact that we have only considered elastic constant data in the evaluation potential parameters, does not prevent us from performing our initial proposition.

B. Influence of atomic order on the shear modulus C'

Suppose now the binary alloy A_xB_{1-x} at a temperature T_i with an atomic order configuration described by a long-range-order parameter $\langle S\rangle$ and by a short-range-order parameter η, both obtained from the numerical simulations explained above. Just after a quench from T_i to T_f ($\ll T_c$) the system retains the atomic configuration it had at T_i. It is interesting to evaluate the functional dependence of C' with $\langle S\rangle$ and η under these conditions. We would like to remark that the two problems involved, ordering and elastic constants, are dealt with independently; that is, we assume that the calculation of elastic constants can be performed on ordered structures obtained by a model without connection with elastic properties. This point is important since it assures that we have not imposed any correlation between both issues, which in fact could exist in real systems.

To do this, the different sampled configurations considered in the calculation of statistical averages (i.e., in the evaluation of $\langle S\rangle$ and η) are frozen at a temperature $T_f\ll T_c$. To simplify the calculations it is assumed that the effect of thermal fluctuations on the elastic constants is irrelevant at T_f, and $T_f=0$ K can be assumed. For each atomic order state, C' is obtained now as an average of the C' values calculated for each microstate (using periodic boundary conditions and the interatomic Morse potential obtained previously for the different atom pairs). This calculation is performed by accounting for, in every microscopic situation, the number of atomic pairs ij ($i,j=A,B$) (NNN).

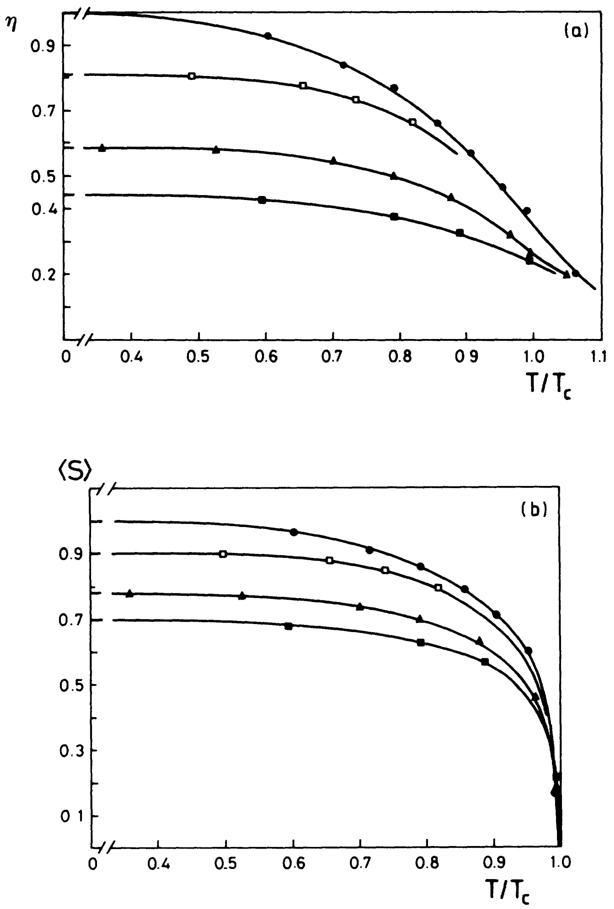

FIG. 4. (a) Monte Carlo results for the short-range-order parameter vs reduced temperature for A_xB_{1-x} binary systems, with $x=0.50$ (●), $x=0.55$ (□), $x=0.61$ (▲), and $X=0.65$ (■). (b) Monte Carlo results for the long-range-order parameter vs reduced temperature for A_xB_{1-x} binary systems, with $x=0.50$ (●), $x=0.55$ (□), $x=0.61$ (▲), and $X=0.65$ (■).

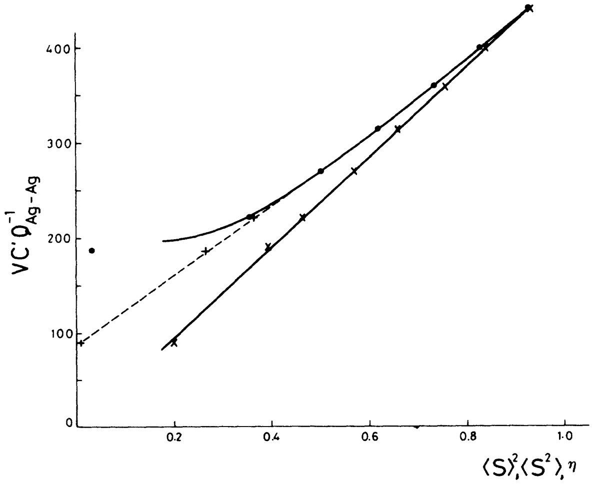

FIG. 5. Calculated value of C' (in reduced units) for $Ag_{0.5}Zn_{0.5}$ alloy at $T_f=0$ K, after quenches from different T_i vs the short-range-order parameter (solid line on x), the square of the long-range-order parameter $\langle S\rangle^2$ (solid line on ●) and the $\langle S^2\rangle$ (dashed line on x).

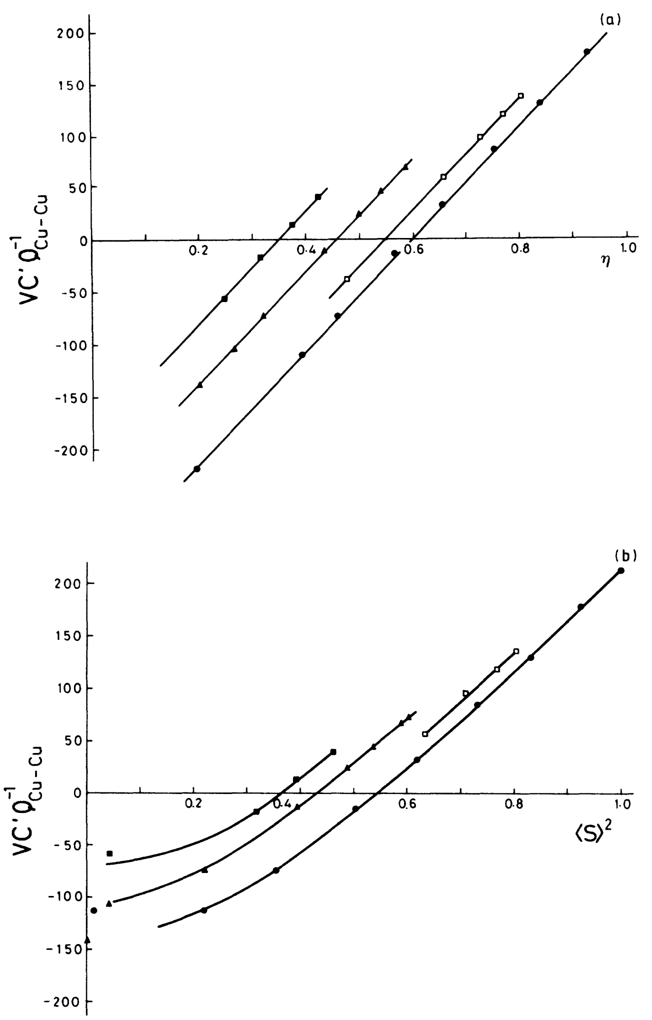

FIG. 6. (a) Calculated value of C' (in reduced units) for Cu_xZn_{1-x} alloy at $T_f = 0$ K, after quenches from different T_i vs the short-range-order parameter for $x = 0.50$ (●), $x = 0.55$ (□), $x = 0.61$ (▲), and $x = 0.65$ (■). (b) Calculated value of C' (in reduced units) for Cu_xZn_{1-x} alloy at $T_f = 0$ K, after quenches from different T_i vs the square of the long-range-order parameter for $x = 0.50$ (●), $x = 0.55$ (□), $x = 0.61$ (▲), and $x = 0.65$ (■).

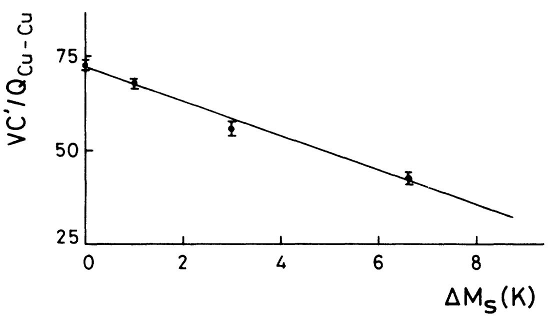

FIG. 7. C' (in units of $Q_{Cu\text{-}Cu}/V$) has been represented vs the experimental shift of the MT temperature (MS) for Cu_xZn_{1-x} ($x = 0.61$) alloy after quenches from different T_i temperatures.

V. RESULTS AND DISCUSSION

In this section we present the results obtained for CuZn and AgZn alloy systems. In Fig. 5 we have plotted C' as a function of $\langle S \rangle^2$, $\langle S^2 \rangle$, and η for the $Ag_{0.5}Zn_{0.5}$ alloy. We observe an almost perfectly linear behavior of C' with η. When C' is represented against $\langle S \rangle^2$, however, we observe deviations from the linear behavior for $\langle S \rangle$ sufficiently small, i.e., for T_i close enough to T_c. In this case the deviations from the linear behavior are evident for quenches from $T_i/T_c \sim 0.93$. When C' is represented against $\langle S^2 \rangle$ the deviations become much smaller, even for configurations quenched from a temperature T_i very close to T_c (Fig. 5). These results are evidence that the nonlinearities arise mainly from the critical behavior of the system near T_c, i.e., from the divergency of $(\langle S^2 \rangle - \langle S \rangle^2)$ near the critical point. In Figs. 6(a) and 6(b), respectively, C' is shown against $\langle S \rangle^2$ and η for Cu_xZn_{1-x} with $x = 0.50$, 0.55, 0.61, and 0.65. In all cases we observe, as before, a linear behavior between C' and η, and deviations from this behavior for T_i close to T_c when C' is represented against $\langle S \rangle^2$. In addition, it is worth noting that at least in the range of concentrations analyzed, $\partial C'/\partial \eta$ and $\partial C'/\partial \langle S \rangle^2$ seem to be independent of the alloy composition. On the other hand, we observe that alloys with a low enough degree of configurational order are mechanically unstable, because C' becomes negative at a particular value of $\langle S \rangle$ (or η) depending on x. This fact suggests that sudden changes in the state of atomic order can induce mechanical instabilities in the system. Following these results and in spite of the deviations from the linear behavior, we conclude that the functionality proposed phenomenologically between C' and $\langle S \rangle$ in shape-memory alloys is in agreement with our numerical calculations, at least when T_i is not close to T_c. In Fig. 7 finally we have represented the calculated value of C' at 0 K in differently ordered configurations (in equilibrium at T_i), versus the experimental shift of the MS temperature measured just after quenches from different temperatures T_i ($< T_c$) for a Cu_xZn_{1-x} alloy with $x = 0.61$.[5] We observe a linear relationship between both magnitudes as predicted from mean-field treatments.[7,8] This result provides new evidence to justify that the shift in MS temperature is due to changes in C' arising from the difference in long-range order in the sample.

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