Elastic constants of the β-Cu-Zn alloy system: A Monte Carlo study

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Monte Carlo calculations of the isothermal elastic constants of the β-Cu_xZn_{1-x} alloy system as a function of the composition have been carried out. We assume the atoms interact via a two-body Morse potential function and use numerical values for the potential parameters evaluated taking into account experimental data. We find a quite good agreement between our results and the expected experimental behavior.

I. INTRODUCTION

Elastic constants in solid systems provide valuable mechanical and dynamical information about crystal behavior and lattice stability. In addition, the comparison of experimentally measured and theoretically calculated elastic constants is an important tool for testing microscopic interaction potentials such as those used in simulation studies.

Reviews on computer studies of elastic constants can be found in Refs. 1–3 (Monte Carlo method) and Refs. 4–7 (molecular dynamics). There is no consensus on which technique requires a larger amount of computer time.[8] In a very recent review[7] Ray suggests that both techniques require approximately the same amount of computer time for the same accuracy.

The calculation of elastic constants by computer simulation techniques has been mainly restricted to one-component systems that in most cases exhibit a fcc crystal structure. The aim of this paper is to calculate, by using the Monte Carlo method, the second-order elastic constants of the β-Cu_xZn_{1-x} binary system, at room temperature (T_r) and as a function of the composition (x). This system is known to undergo a lattice instability (martensitic transformation) at temperatures which depend both on the composition x and on the long-range order.[4] The determination of a suitable potential which reproduces the macroscopic elastic data is a first step in a more microscopic study of the kinetics of the transformation and its dependence on composition and long-range order. We note that β-Cu_xZn_{1-x} exhibits a B_2 structure below a certain temperature T_c ($\gg T_r$) and that we need three (Cu-Cu, Zn-Zn, and Cu-Zn) different interaction potentials. We follow the conventional procedure that pairwise additive potentials are sufficient to describe the behavior of the alloy.

For the present investigation we will use the Morse potential function, which is a central pairwise potential, extensively used in solid-state studies[10–11] and in particular in the analysis of elastic properties.[12] The different Morse potential parameters for the system under study were obtained in a previous work,[13] where experimental elastic-constant data were considered and the lattice was required to be stable in terms of Born stability criteria.[14]

Using these Morse potential parameters and standard Monte Carlo techniques,[15] we have calculated the C_{11}, C_{44}, and $C'=(C_{11}-C_{12})/2$ isothermal elastic constants. Numerical results are compared to available experimental data[16] corresponding to β-CuZn system. Considering the simplicity of the potential model, the agreement obtained seems to be quite appealing.

II. NUMERICAL PROCEDURE

The isothermal elastic constants involve ensemble averages of functions of particle coordinates and interparticle potential energies, which can be evaluated conveniently by using Monte Carlo simulations.[17] The corresponding formulas are available in the literature.[2] The simulations proceeds in the following way. A system of N particles ($N=N_{Cu}+N_{Zn}=128$) is placed inside a computational cell of volume V ($V=4a\times 2$, where a is the lattice parameter), with periodic boundary conditions. The system is also assumed to be in thermal equilibrium at a temperature $T=297$ K. Starting from an initial random configuration, the following sequence of configurations is generated by choosing a particular atom at random and giving it a small random displacement of magnitude smaller than Δ. The displacement is accepted if it lowers the energy or if it raises it with a probability given by the Boltzmann factor. This choice ensures that we sample the equilibrium probability distribution function. The magnitude of Δ depends on temperature and it is chosen such that the average acceptance ratio in each Monte Carlo step is close to 50%.[15,17] The Monte Carlo step is our unit of time defined as a total of N attempts to change the value of the particle coordinates of a randomly chosen lattice site. The Hamiltonian of the system is given by

$$H=\sum_{i,j}\phi_{ij}(r)\ . \tag{1}$$

TABLE I. Parameters of the Morse potential function for Cu-Cu, Zn-Zn, and Cu-Zn interactions. P and Q are expressed in units of $Q_{\text{Cu-Cu}}$.

	αa	αr_0	$P(Q_{\text{Cu-Cu}})$	$Q(Q_{\text{Cu-Cu}})$
Cu-Cu	1.865	1.708	2.760	1.000
Zn-Zn	2.840	2.585	2.385	0.360
Cu-Zn	6.545	5.836	22 589	131.9

The summation symbol denotes sum over all distinct pairs of particles which are nearest and next-nearest neighbors, which can be either Cu-Cu, Zn-Zn, or Cu-Zn pairs. φ_{ij} is the usual Morse potential function which expresses the potential energy between two atoms separated by a distance r as

$$\varphi(r)=Pe^{-2\alpha r}-Qe^{-\alpha r} \tag{2}$$

with

$$P=De^{2\alpha r_0}, \tag{3a}$$

$$Q=2De^{\alpha r_0}. \tag{3b}$$

This function has a minimum at $r=r_0$. D and α are positive constants with energy and inverse of distance dimensions, respectively. For (3) we use the numerical values evaluated in Ref. 13 and tabulated in Table I. Such parameters were obtained by fitting the analytical expressions of the elastic constants at $T=0$ K to the available experimental data[16] (at T_r temperature). With the present simulations we want to know if these potential parameters keep the system mechanically stable when the temperature is raised (at least until T_r).

We assume that at temperature T_r the system shows its maximum configurational ordering. Experimentally, this is consistent with the weak change in the elastic constants during a reordering processes,[18] and also with the high value of T_c as compared to T_r.[13]

We have averaged the different quantities which we have calculated over 150 000–200 000 uncorrelated configurations omitting the first 20 000. They are affected by nonequilibrium effects as the initial configuration relaxes to equilibrium. Although the averages have been performed on subgroups of 200 000 effective configurations, and due to the fact that the acceptance rate is 50% (we chose the Δ parameter in this way), we used a double number of real configurations.

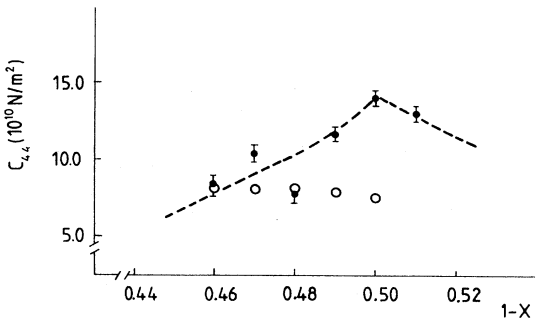

FIG. 2. Composition dependence of calculated (●) and experimental (○) C_{44} values in Cu-Zn alloy at room temperature. Dashed line is only a guide for the eye.

We would like to remark on the non-close-packed character of the bcc structure, for which entropic contributions play a very important role in determining thermodynamical stability.[19] In spite of this fact, which can amplify the fluctuations, the final averaged values of the elastic constants, determined within an error of 8–12 %, follow quite well the expected experimental behavior.

III. RESULTS AND DISCUSSION

We present in Figs. 1, 2, and 3 the results obtained for the elastic constants C_{11}, C_{44}, and $C'=(C_{11}-C_{12})/2$ for our model β-Cu_xZn_{1-x}, when the molar fraction of Zn $(1-x)$, ranges between 0.46 and 0.51. We also show in these figures experimental data for the same elastic constants.[16] We observe quite good agreement in C_{11} and C', whereas the values obtained for C_{44} markedly deviate from the experimental data. The discrepancy can be due to the noncentrality of the model potential as well as to the procedure by which the parameters of the various interparticle potentials were evaluated.[13] In that evalua-

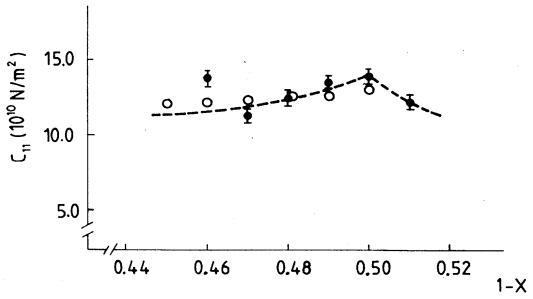

FIG. 1. Composition dependence of calculated (●) and experimental (○) C_{11} values in Cu-Zn alloy at room temperature. Dashed line is only a guide for the eye.

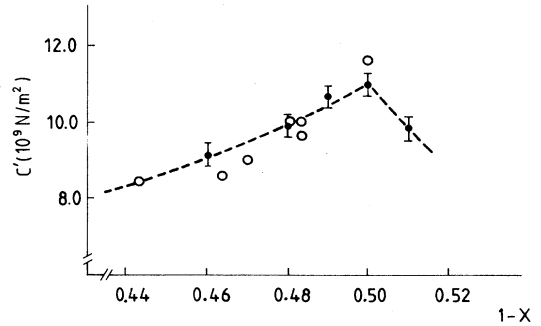

FIG. 3. Composition dependence of calculated (●) and experimental (○) C' values in Cu-Zn alloy at room temperature. Dashed line is only a guide for the eye.

tion, except for $Q_{\text{Cu-Cu}}=2D_{\text{Cu-Cu}}\exp[(\alpha r_0)_{\text{Cu-Cu}}]$ [Eq. (3b)], all the parameters were obtained by considering experimental elastic-constant data but paying special attention to the behavior of C' because of its special relevance in shape-memory alloys,[20] such as β-CuZn. By rescaling C' given by a Monte Carlo simulation to the experimental data, one can evaluate $Q_{\text{Cu-Cu}}=8.2\times10^{-19}$ J. We obtain a better agreement in the value of C_{44} if $Q_{\text{Cu-Cu}}=4.2\times10^{-19}$ J. As we mentioned in Ref. 13, $Q_{\text{Cu-Cu}}$ can also be obtained from the theoretical expression for the Debye temperature as a function of the elastic constants when $T\rightarrow0$.[21] This calculation yields $Q_{\text{Cu-Cu}}=5.7\times10^{-19}$ J which is intermediate between the two values given above.

In spite of the discrepancies observed in the behavior of C_{44}, we suggest that our results are encouraging even using such a simple model potential to describe the alloy. Our numerical results on the elastic properties of the binary system are in reasonable agreement with experimental data. Nevertheless, it is clear that a more sophisticated (noncentral) potential is required. Consequently, future efforts will be concentrated on more realistic potentials and range of interactions.

Finally, let us conclude saying that the present study reveals that simple pairwise potentials can be used to study the elastic properties of systems that exhibit ordered structures such as binary alloys. Particularly interesting are the shape-memory alloys because of the thermomechanical properties[22] related with the martensitic transformation that are undergone at very low temperatures. Recently, the constant-pressure molecular-dynamics technique has been successfully applied to the study of structural phase transitions.[23] In this sense, a very interesting work could be to study structural elastic instabilities in shape-memory alloys by using Monte Carlo methods at constant pressure.

[1]E. R. Cowley, Phys. Rev. B **28**, 3160 (1983).
[2]D. R. Squire, A. C. Holt, and W. G. Hoover, Physica (Utrecht) **42**, 388 (1969).
[3]M. L. Klein and R. D. Murphy, Phys. Rev. B **6**, 2433 (1972).
[4]J. R. Ray, M. C. Moody, and A. Rahman, Phys. Rev. B **32**, 733 (1985).
[5]M. Parrinello and A. Rahman, J. Chem. Phys. **76**, 2662 (1982).
[6]J. R. Ray, M. C. Moody, and A. Rahman, Phys. Rev. B **33**, 895 (1986).
[7]J. R. Ray, Comput. Phys. Rep. **58**, 110 (1988).
[8]M. Sprik, R. W. Impey, and M. Klein, Phys. Rev. B **29**, 4368 (1984).
[9]J. Viñals, V. Torra, A. Planes, and J. L. Macqueron, Philos. Mag. A **50**, 653 (1984).
[10]S. K. Das, D. Roy, and S. Sengupta, J. Phys. F **7**, 5 (1977).
[11]D. Roy, A. Hanna, and S. Sengupta, J. Phys. F **2**, 1092 (1972).
[12]F. Milstein, Phys. Rev. B **2**, 512 (1970).
[13]T. Castán and A. Planes, Phys. Rev. B **38**, 7959 (1988).
[14]M. Born and H. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1956).
[15]K. Binder, in *Monte Carlo Methods in Statistical Physics*, edited by K. Binder (Springer-Verlag, Berlin, 1979).
[16]Y. Murakami and S. Kachi, Jpn. J. Appl. Phys. **13**, 1728 (1974).
[17]F. F. Abraham, Adv. Phys. **35**, 1 (1986).
[18]A. Planes, G. Guénin, and J. L. Macqueron, J. Phys. F **15**, 1203 (1985).
[19]J. Friedel, J. Phys. (Paris) Lett. **34**, L59 (1974).
[20]G. Guénin and P. F. Gobin, J. Phys. (Paris) Colloq. **43**, C4-57 (1982); Metall. Trans. A **13**, 1127 (1982).
[21]J. De Launay, J. Chem. Phys. **22**, 1673 (1973).
[22]L. Delaey, R. V. Krishnan, H. Tas, and H. Warlimont, Mater. Sci. **9**, 1521 (1974).
[23]L. J. Lewis and M. L. Klein, Phys. Rev. Lett. **57**, 2698 (1986).