

Monte Carlo Study of an Ordering Alloy on an fcc Lattice

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We report results of computer simulations of a binary alloy on an fcc lattice, equivalent to an Ising system with a nearest-neighbor antiferromagnetic interaction $J > 0$ and a next-nearest-neighbor ferromagnetic interaction $-\alpha J$, $\alpha > 0$. Our data indicate the existence of a discontinuous change in energy and in sublattice magnetization as a function of temperature, for small α . For $\alpha \geq 0.25$, the transition appears to be continuous, suggesting a tricritical point at some intermediate α .

We investigate the phase diagram of an ordering AB alloy, equivalently an antiferromagnetic Ising spin system in zero magnetic field, described by the Hamiltonian (in spin language)¹⁻³

$$H = J \sum_{nn} \sigma_i \sigma_j - \alpha J \sum_{nnn} \sigma_i \sigma_j, \quad (1)$$

$$J > 0, \quad \alpha \geq 0, \quad \sigma_i = \pm 1,$$

where nn and nnn are nearest neighbor and next nearest neighbor, and the sum goes over the sites of an fcc lattice.

Different approximation schemes give greatly varying results for this system. Thus, for nn interactions, $\alpha = 0$, the mean-field approximation predicts a second-order transition at $T = 4J/k$, the quasicheical approximation predicts a first-order transition at $T \approx 1.46J/k$, while the cluster-variation method of Kikuchi, using tetrahedral clusters, gives a first-order transition^{1,2} at $T \approx 1.89J/k$.

Following the work of Danielian,⁴ Betts and Elliot⁵ obtained the first five terms in a low-temperature expansion of the free energy for $\alpha = 0$. The coefficients in this series (beginning with the third) depend on the structure of the ground state, of which there are infinitely many for $\alpha = 0$, about which the expansion is made. [For $\alpha > 0$, only the six maximally symmetric ground states, two sublattices occupied by an A particle and two by B particles (CuAu structure) survive and the ambiguity in the coefficients is removed.] To take account of this degeneracy, Betts and Elliot averaged over all ground states. Assuming that the system would undergo a second-order transition at some temperature T_c ,

they tried to estimate T_c from the terms in their series. Using different estimation methods they obtain values of kT_c/J in the range 1.6-1.9. Correcting what appears to be an arithmetic error in Ref. 6, we find that the (2, 2) Padé approximant for the specific heat gives $T_c \approx 1.73J/k$ and leads to an energy curve depicted in Fig. 4.

Using the general Landau theory about the transformation of the symmetry-breaking order parameter in a second-order phase transition, Lifshitz concluded^{7,8} that the transition to the CuAu structure should not be second order. A similar question was investigated by Mukamel and Krinsky⁹ by a renormalization-group analysis of the Landau-Ginzburg-Wilson Hamiltonians with appropriate symmetry. They found no stable fixed point, in an ϵ expansion, for systems with this symmetry and suggested, in agreement with Lifshitz's analysis, that the transition ought to be first order. This is consistent with the usual interpretation of experiments on CuAu (Ref. 10) and some other materials (UO_2 and MnO), but is by no means fully established. (It is indeed possible that our Hamiltonian belongs in the same universality class as the Heisenberg model with cubic anisotropy.¹¹)

Computer simulations.—The simulations were carried out by the Monte Carlo method in a cube, with periodic boundary conditions, containing $N = 2048$ sites. Starting with some initial configuration we applied single-flip (Glauber) dynamics to bring the system to and keep it in equilibrium at a specified temperature T . The energy and magnetization of each simple cubic sublattice (there are four) were then averaged over time intervals

of length between 500 and 2500 attempted interchanges per site.

In simulating our system at high temperatures we generally started with a random configuration. However, because of the slowing down of the Glauber kinetics at low temperatures it was not feasible to start with a random configuration to obtain equilibrium states at $T < T_c$. These were generally started either in perfectly ordered states or else cooled or heated from nearby equilibrium states. Starting from an ordered state was particularly important for obtaining stable values for the sublattice magnetization in a reasonable time and was crucial for $\alpha = 0$ when, because of the degeneracy of the ground state, our system of 2048 particles is not perfectly ordered on the four sublattices even at $T = 0$.

Plots of average energy, $E(T, \alpha)$ divided by $E(0, \alpha)$, versus $kT/E(0, \alpha)$, where $E(0, \alpha)/J = -2 - 3\alpha$ is the ground-state energy, are shown in Fig. 1. Plots of the average sublattice magnetization versus $T/T_c(\alpha)$ are shown in Fig. 2. $T_c(\alpha)$

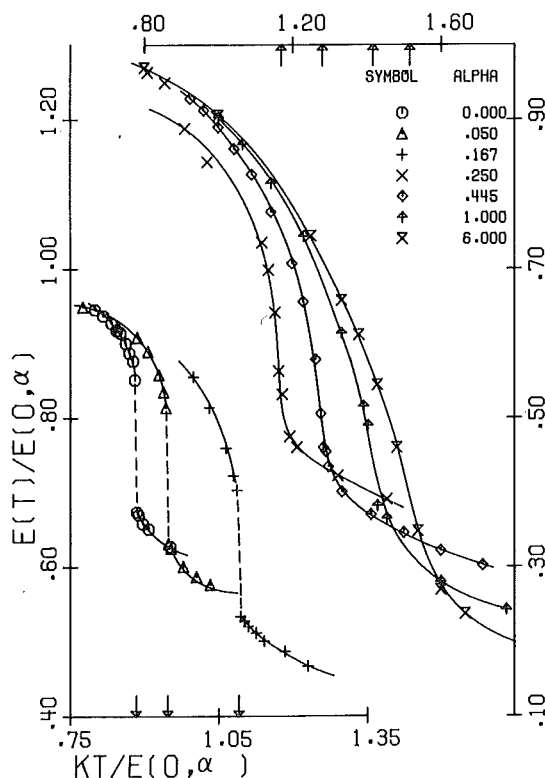


FIG. 1. $E(T, \alpha)/E(0, \alpha)$ vs $kT/E(0, \alpha)$ for values of α shown. The left and bottom scales are for the three smaller values of α where the discontinuities are indicated. The top and right scales are for $\alpha \geq 0.25$ where the transition is continuous. The transition points are indicated by arrows.

is here taken as the temperature where the energy graph has the steepest slope, without prejudice as to the order of the transition; see Table I. As seen from Fig. 2 the values of T_c obtained from the energy plots are consistent with those indicated by the magnetization.

In Fig. 3 we plot our values of $kT_c(\alpha)/E(0, \alpha)$ versus the variable x , the fraction of the ground-state energy due to the nnm interactions, $x = 3\alpha/(2 + 3\alpha)$ for $\alpha \geq 0$, to obtain a phase diagram of our system. For $x = 1$, the system splits into four independent simple-cubic lattices with nn ferromagnetic interactions. Extrapolation of our plots to $x = 1$ gives a value for the critical temperature within a few percent of that computed from extended series expansion.¹² It is generally accepted that the transition for this system, $x = 1$, is second order.

An inspection of Figs. 1 and 2 suggests that for small values of α there is an energy and sublattice magnetization discontinuity which is absent for large α . This gives strong evidence, but no proof, for a changeover from a first- to a second-order transition with the likelihood of a tricritical point around $\alpha \approx 0.25$, $x = 0.27$.

Critical exponents, metastable states.—Since phase transitions can be defined unambiguously only for infinite systems there is always a ques-

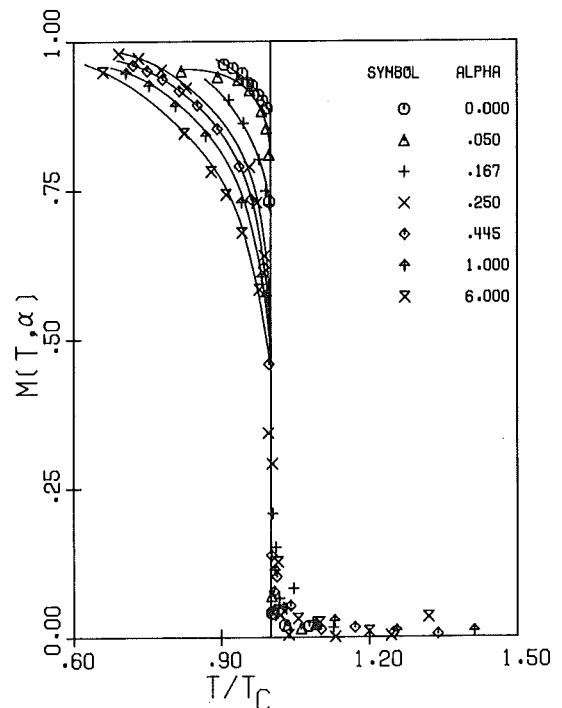


FIG. 2. Plots of the sublattice magnetization vs T/T_c for all α .

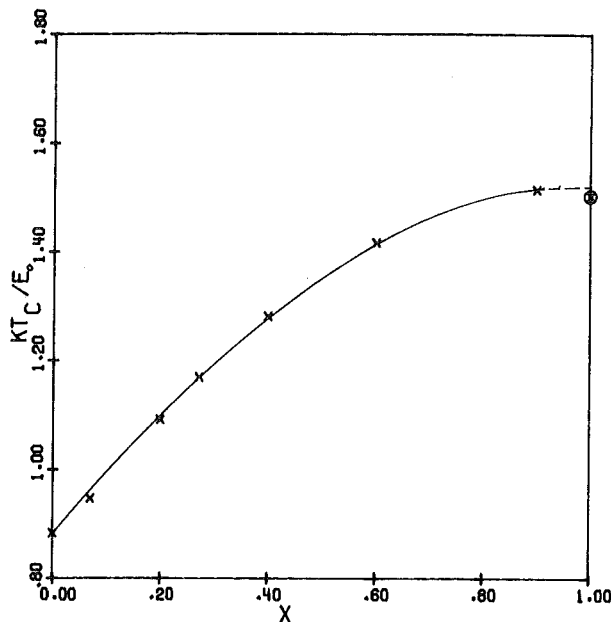


FIG. 3. Plot of $kT_c(\alpha)/E_0(\alpha)$ vs $x = 3\alpha/(2+3\alpha)$. The point at $x=1$ is the series-expansion value.

tion as to what can be deduced from computer simulations on small systems. This question has been discussed extensively^{13,14} for the case of a second-order transition, which corresponds here to large values of α . Strong arguments have been given for a scaling behavior of the observed critical temperature $T_c(N)$ with system size N . Carrying out simulations at $\alpha=6$ ($x=0.9$) for two additional values of N , $N=500$ and 4000 , and using the scaling relation¹³ $T_c(N) = T_c(\infty)[1 - a/N^{\lambda/3}]$, where $\lambda = 1/\nu$, $\nu = 0.64$, we estimate $kT_c(\infty)/4J \cong 7.8$ and the exponent β for the sublattice magnetization to be in the range $0.26-0.32$. The values of the specific heat for $T \leq T_c$ could be fitted reasonably well by the formula¹³

$$c/k = A[1 - T/T_c(\infty)]^{1/6} + b,$$

$$A \cong 1.4, \quad b = -2.0.$$

This is consistent with Ising-like behavior but is certainly no proof.⁹

At a first-order transition, the situation we have for small α , the probability distribution for the energy, $P(E, T)$, at a temperature T , will have two peaks, centered about the mean energy in each of the coexisting phases. In the limit of an infinite-size system one of the peaks dominates at any $T \neq \hat{T}_c$, the transition temperature in the infinite system. The ratio of the peak heights should behave asymptotically as $\exp[\varphi(T)N]$,

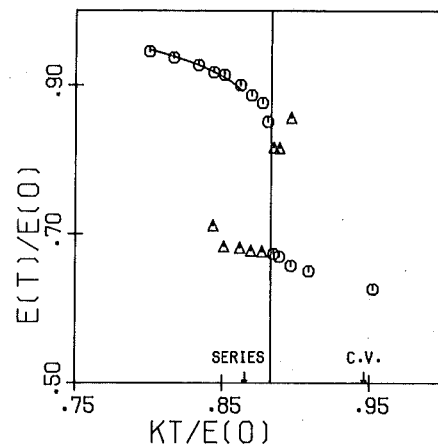


FIG. 4. The energy $E(T)/E(0)$ vs $kT/E(0)$ for $\alpha = 0$ is shown by circles. The triangles are the metastable points obtained by heating and cooling across T_c shown by the vertical line. The solid curve is given by the (2,2) Padé approximant (Ref. 6). The T_c given by both series and the cluster-variation method are shown.

where N is the size of the system and $\varphi(T) = 0$ for $T = \hat{T}_c$. For a finite system, $\langle(\Delta E)^2\rangle$ will have contributions both from the fluctuations inside each peak and from jumps between peaks. As may be expected, it is impossible to disentangle these different contributions unambiguously and no attempt was made to do so. The existence of the two peaks was manifest, however, in plots of energy versus time at $\alpha=0$ and 0.05 . Indeed, the secondary peak may, at any temperature, be related to a metastable state and these were observed at values of energy shown, for $\alpha=0$, in Fig. 4. While these values are not very precise, they support our belief that the transition for small α is first order.

Ground states, low-temperature phases, and series expansions.—The fcc system with an anti-ferromagnetic interaction $-J'$, $J' > 0$, between spins a distance L apart. This makes the degeneracy of the ground state equal to M , finite (but large), including always the maximally symmetric ground states discussed earlier. Slawny¹⁵ now shows that despite this M -fold degeneracy of the ground state the free energy is, at sufficiently low temperatures, given by the asymptotic series obtained from the expansion about the maximally symmetric ground states; i.e., no averaging over all ground states should be used. It seems very likely that this will also be the case for $J'=0$ or $L \rightarrow \infty$ —i.e., our system with $\alpha=0$ —when the degeneracy is infinite. This also suggests that the number of low-temperature phases

is only six, obtained from the maximally symmetric ground states.

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¹R. Kikuchi and H. Sato, *Acta Metall.* **22**, 1099 (1974).

²C. M. van Baal, *Physica (Utrecht)* **64**, 571 (1973).

³J. W. Cahn and S. Allen, *Acta Metall.* **20**, 423 (1972).

⁴A. Daniellian, *Physica (Utrecht)* **29**, 67 (1963).

⁵D. Betts and C. J. Elliot, *Phys. Lett.* **18**, 18 (1965).

⁶C. J. Elliot, Master's thesis, University of Alberta, 1965 (unpublished).

⁷I. M. Lifshitz, *Zh. Eksp. Teor. Fiz.* **11**, 255 (1941).

⁸I. M. Lifshitz, *Zh. Eksp. Teor. Fiz.* **14**, 353 (1944).

⁹D. Mukamel and S. Krinsky, *Phys. Rev. B* **13**, 5078 (1976).

¹⁰M. Hirabayashi, *J. Jpn. Inst. Met.* **15**, 565 (1951); R. L. Orr, J. Luciat-Labry, and R. Hultgren, *Acta Metall.* **8**, 431 (1960).

¹¹P. Bak, private communication.

¹²C. Domb, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1974), Vol. 3.

¹³M. E. Fisher, in *Critical Phenomena, Proceedings of the International School of Physics, "Enrico Fermi," Course LI*, edited by M. S. Green (Academic, New York, 1971).

¹⁴K. Binder, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1976), Vol. 5B, and references therein.

¹⁵J. Slawny, private communication.

TABLE I. The transition temperatures for different α 's.

α	$kT_c/4J$	$\Delta E/kT_c$
0.00	0.4415 ± 0.001	0.20
0.00 ^a	0.4733	0.25
0.05	0.5089 ± 0.0013	0.19
0.1667	0.6821 ± 0.0023	0.09
0.25	0.8036 ± 0.0032	
0.445	1.0672 ± 0.0029	
1.0	1.7699 ± 0.015	
6.0	7.5758 ± 0.142	

^aCluster variation (Ref. 1).