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Comparison of approximate methods for the study of antiferromagnetism in the fcc lattice

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The study of antiferromagnetism in the fcc lattice by means of different approximate methods has resulted in varied and not always consistent results. An improved approximation of the cluster-variation method is used here to calculate the phase diagram of a model fcc system with nearest-neighbor antiferromagnetic interactions. Comparison with recent Monte Carlo simulations indicates that, despite some discrepancies near the triple-point region, the cluster-variation method provides a convenient technique for the study of phase equilibria in three-dimensional systems.

The Ising model in the fcc lattice with antiferromagnetic interactions has been investigated by a number of different statistical-mechanics approximations: molecular field or Bragg-Williams,[1] quasichemical,[2] cluster-variation method (CVM),[3–8] real-space renormalization group,[9] and, more recently, Monte Carlo (MC) simulations.[10–13]

The Bragg-Williams and quasichemical approximations are clearly inadequate for the treatment of antiferromagnetism in the fcc lattice with nearest-neighbor interactions, while the only renormalization-group calculation which the authors are aware of has fared very poorly in this case.[9] On the other hand, the MC simulations and the CVM calculations seem to capture most of the essential features of the phase diagram, although discrepancies between both methods are still apparent. In this Brief Report we compare available results from both techniques and report on a phase diagram calculation in the tetrahedron-octahedron approximation of the CVM.

Thus far, two different approximations of the CVM have been used to study fcc lattices with antiferromagnetic interactions, namely, the tetrahedron[3–6] and the tetrahedron-octahedron approximations.[7,8] The antiferromagnetic or ordering alloy models which have been investigated include systems with (i) first-neighbor pair interactions,[3,4] (ii) first- and second-neighbor pair interactions,[7,8] and (iii) first-neighbor pairs and many-body interactions.[3,5,6]

The calculations with many-body interactions were carried out in the lowest meaningful level of approximation of the CVM with the intent of describing phase equilibria in the binary CuAu[5] and the ternary CuAgAu systems.[6] Very satisfactory agreement with the real phase diagrams was obtained. Despite the obvious interest on simple models which are able to describe real systems, the above calculations cannot, of course, settle the question of reliability of a given CVM approximation for antiferromagnetic interactions.

The effect of second-neighbor pair interactions on ordering in fcc lattices has been studied in the tetrahedron-octahedron approximation.[7,8] The calculations were carried out for values of the ratio ϵ of second- to first-neighbor interactions between 0 and 0.5. The predicted phase diagrams displayed a rather complex topology, the correctness of which could not be ascertained at the time the calculations were performed. Recent MC simulations for $\epsilon = 0.25$ have made possible, however, a detailed evaluation of the CVM results. The transition temperature obtained by Phani, Lebowitz, and Kalos[10] at a point of concentration $c = 0.5$ for $\epsilon = 0.25$ differs by less than 3% from that calculated by the CVM. A complete MC phase diagram calculation, again for $\epsilon = 0.25$, has been undertaken very recently by Bond and Ross.[11] The MC and the CVM results agree remarkably well near first-order transitions with the major discrepancies occurring near second-order transitions. The overall agreement is nevertheless quite close.

The binary fcc Ising model with nearest-neighbor antiferromagnetic pair interactions ($\epsilon = 0$) has been investigated in the Bragg-Williams,[1] quasichemical,[2] and CVM (tetrahedron) approximations.[3,4] A comparison of the predictions of the mean-field approximations used so far have been given by de Fontaine and Kikuchi.[5]

Recent MC simulations by Binder[12] for the case $\epsilon = 0$ have, in addition to confirming the reliability of the CVM near stoichiometry, clearly indicated appreciable discrepancies near the triple point where the disordered (fcc) and the two ordered phases present in the phase diagram—$L1_0(AB)$ and $L1_2(A_3B)$—coexist. Whereas the tetrahedron approximation of

the CVM predicts a triple point occurring at relatively high temperature ($T_t \simeq 0.8\ T_0$ with T_0 the $L1_0$ transition temperature at stoichiometry), the MC simulations seem to indicate that the triple point occurs at $T=0$. In view of such discrepancies, Binder concluded that CVM was affected by serious deficiencies for the description of ordering in fcc lattices. It was speculated that the deficiencies originated from the inability of the CVM to describe the " frustrated" fcc lattice with first-neighbor antiferromagnetic interactions which, as it is well known, has highly degenerate ground states. It should be pointed out, however, that the MC results were compared with the lowest meaningful approximation of the CVM. Thus it seems natural to inquire whether higher approximations will bring the CVM into closer agreement with the MC simulations or if, as it has been suggested,[12] there are serious deficiencies in the CVM for the description of ordering in fcc lattices.

In order to clarify the question of reliability of the CVM, we report here the results of a phase diagram calculation in the tetrahedron-octahedron approximation for the fcc lattice with first-neighbor antiferromagnetic pair interactions only. For $\epsilon=0$, there are only two ordered ground states present in the phase diagram, namely, the $L1_0$ structure occurring at stoichiometry AB and the $L1_2$ structure at stoichiometry A_3B. Thus the phase diagram calculation by the CVM entails the characterization and minimization of the free-energy functional for three phases: disordered, $L1_0$, and $L1_2$. For the derivation of the CVM free-energy functional in the tetrahedron-octahedron approximation, the reader is referred to Refs. 7 and 14. The approximation in question was used for binary Ising models with ferromagnetic nearest-neighbor pair interactions[14] and for antiferromagnets with ϵ in the range 0 to 0.5.[7,8] For the values of ϵ investigated (0.25, 0.35, and 0.45), the ordered ground states are somewhat more complex than the $L1_0$ and $L1_2$ structures occurring for $\epsilon \leq 0$.[7,8]

In the disordered state, there are 10 variational parameters corresponding to the 10 correlation functions associated with the octahedron, the tetrahedron, and with their respective subclusters.[7,14] Due to the loss of symmetry on ordering, the 10 multisite correlation functions split into 27 and 22 correlation functions for the $L1_0$, and $L1_2$ structures, respectively. Thus the number of nonlinear algebraic equations arising from the minimization conditions (10, 27, and 22 for the disordered, $L1_0$ and $L1_2$ phases, respectively) is such that they can be solved very efficiently by the Newton-Raphson method.

The temperature-external field (chemical potential or magnetic field) and temperature-composition phase diagrams predicted by the tetrahedron-octahedron approximation are shown in Figs. 1 and 2, respectively. At stoichiometry, the transitions occur

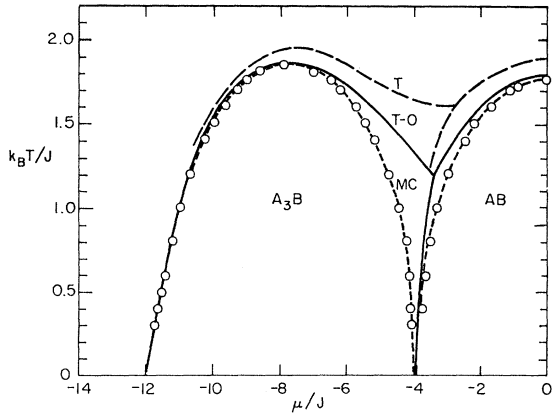

FIG. 1. Temperature-chemical potential phase diagram, both coordinates being normalized by the first-neighbor pair interaction energy J, calculated for an fcc lattice by various methods: Monte Carlo simulation (Ref. 14) (MC, short dashes); CVM tetrahedron approximation (Refs. 3 and 4) (T, long dashes); and present tetrahedron-octahedron approximation (T-O, full curve).

at $k_BT/J=1.87$ for A_3B and $k_BT/J=1.79$ for AB, where J is the nearest-neighbor exchange interaction. The transition temperatures at stoichiometry agree remarkably well with the values of 1.86 and 1.76 predicted by the MC simulations for the A_3B and the AB ordering reactions, respectively.[12]

The same figures show for comparison the phase diagrams calculated in the tetrahedron approximation

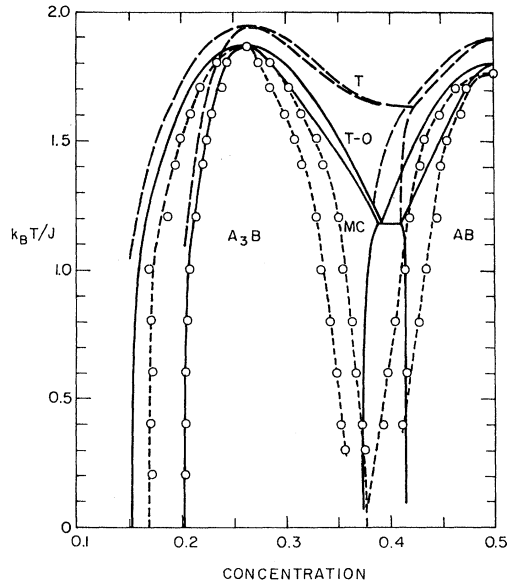

FIG. 2. Temperature-composition phase diagram corresponding to Fig. 1, with curves labeled similarly.

of the CVM and via the MC simulations. As seen in Fig. 1, the discrepancies with the MC calculations near the triple point persist although there is marked improvement with respect to the tetrahedron approximation. The agreement is particularly good, in fact, within the uncertainties of the MC calculations, for large values of the external field (i.e., away from stoichiometry). Thus the observation that the CVM fails away from stoichiometry[12] does not seem to be completely valid in general.

Further predictions of the CVM are provided by the CVM-calculated curves given in Figs. 3 and 4, which show, respectively, the long-range order parameter versus temperature for the $L1_0$ and $L1_2$ structures, and the Warren-Cowley short-range order parameter α_1 versus concentration for different temperatures. Note that at temperatures $k_BT/J=1.6$ both ordered- and disordered-phase regions are traversed. For $k_BT/J=2$, the plot of Fig. 4 is in apparent qualitative discrepancy with the MC results of Binder, which show a sharp decrease in $-\alpha_1$ near the triple point concentration.[12] The strong decrease in $-\alpha_1$ is, however, absent in more recent MC simulations,[13] in close agreement with the present CVM results.

As shown here, the overall degree of accuracy obtained with relatively low levels of approximation of the CVM, such as the tetrahedron and the tetrahedron-octahedron approximations, is, in the author's opinion, quite remarkable. The agreement between CVM and MC calculations is perhaps more impressive for the more complex $\epsilon=0.25$ phase diagram, as shown by Bond and Ross.[11] The most serious discrepancy observed in fcc lattices with first-neighbor antiferromagnetic pair interactions concerns the location of the triple point. However, one can obtain marked improvement by choosing larger clusters in the free-energy expansion, as indicated by the comparison of the tetrahedron and tetrahedron-octahedron approximations. An important consideration for the evaluation of the phase diagram of Figs. 1 and 2 is the simplicity of the model together with the ease of computation. In particular, since in the CVM one calculates grand potentials (or free energies) directly, the construction of the phase diagram does not require the detailed data analysis of the MC method.

A final and very important consideration concerns the application of the CVM to real alloy systems which, of course, cannot be expected to behave as the simple Ising model investigated here. In real alloy systems, one expects a longer range of temperature and concentration-dependent pair interactions, elastic interactions, and, possibly, many-body interactions. The characterization of such interactions are beyond the capabilities of existing theories and therefore one must introduce a number of phenomenological parameters into the statistical model. Therefore it is of the utmost importance to have a sufficiently reliable thermodynamic model that would allow repeated calculations for different values of the energy parameters without excessive use of computer time and data interpretation. The CVM appears to fulfill such requirements. Thus it seems reasonable to expect that the systematic use of the CVM in the future will contribute significantly to the understanding of ordering in real alloy systems.

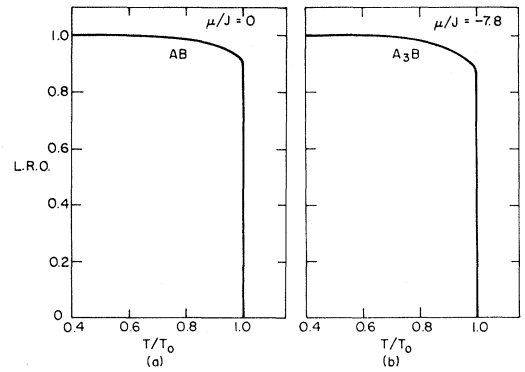

FIG. 3. Long-range order parameter vs reduced temperature (T_0 is transition temperature) calculated according to the CVM T-O approximation (a) at the stoichiometric composition of the AB ordered phase ($\mu=0$), and (b) close to the stoichiometry of the A_3B phase ($\mu/J=-7.8$).

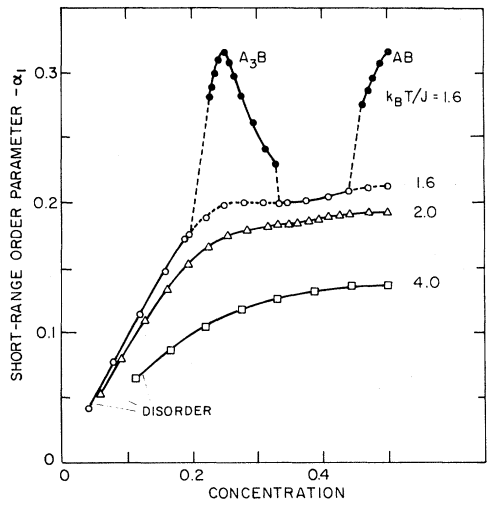

FIG. 4. Short-range order parameter α_1 vs concentration according to the CVM T-O approximation for various values of the normalized temperature k_BT/J. Note that for the value 1.6 of this parameter, both ordered- and disordered-phase regions are traversed, full symbols being used for the ordered phases, and open symbols for the disordered phase (stable or metastable).

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