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Order-disorder transformations in ferromagnetic binary alloys

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Order-disorder transformations in binary body-centered-cubic alloys with two ferromagnetic components are studied within the mean-field approximation. Only pairwise interactions between nearest neighbors are included. Special attention is given to the temperature dependence of the specific heat in several kind of alloys and discontinuities of the specific heat at the critical temperatures are calculated. Three different situations are analyzed; i.e., (i) Θ_0 (spatial order-disorder critical temperature) $<\Theta_M$ (Curie temperature), (ii) $\Theta_M<\Theta_0$, and (iii) $J_{AB}<<J_{AA}, J_{BB}$ where J_{IJ} are the Ising exchange integrals for the alloy A_xB_{1-x} with spins S_A and S_B. The Fe-Co system is studied within this model, and the results are compared with experimental data.

I. INTRODUCTION

Order-disorder phonomena in alloys have been investigated for many years and copious data for the bulk are available. But, although these phenomena are well understood in paramagnetic alloys, studies in magnetic systems are still lacking. Experimentally it is well established that there is an interdependence between magnetism and spatial long-range order.[1] However, theoretical analyses for the spatial order-disorder transformations in magnetic systems, as in FeCo, are usually carried out ignoring the magnetic properties.[2] Recently it has been shown that in alloys with two magnetic species the interplay of the two phenomena may lead to results completely different from those predicted by theories that take into account only one of the effects.[3-6] In a mean-field theory, Tahir-Kheli and Kawasaki[3] studied the temperature dependence of the order parameters and Morán-López and Falicov[4,5] analyzed in detail the phase diagrams (temperature concentration) for different kinds of alloys. In particular it was shown that the asymmetry of the ordering curve of Fe_xCo_{1-x} is obtained if magnetism is included.[5] Studies of the temperature dependence of the order parameters in the Bethe approximation have been published also.[6]

In this paper we study further the interplay of atomic and magnetic ordering within the model used by Morán-López and Falicov.[5] It is a mean-field theory where the interatomic forces and the magnetic interactions are assumed to be pairwise between nearest neighbors only. Here, we examine in detail the temperature dependence of the specific heat in alloys with several bulk behaviors and we calculate the discontinuities in the specific heat at the critical temperatures by means of a formalism outlined recently.[7]

Our concern in this paper is to explore the changes in the specific heat produced by the interdependence of the two phenomena. Then we study the problem within the simple mean-field theory. An obvious restriction of this model is that short-range-order correlations cannot be taken into account. These effects would modify our mean-field results mainly near the transition temperatures.

II. THEORY AND CALCULATION

We consider a body-centered-cubic binary alloy A_xB_y $(y=1-x)$ with two ferromagnetic components with spins S_A and S_B.

In order to describe the spatial long-range order, the bcc lattice is subdivided into two equivalent sublattices α and β. All α sites have β sites as nearest neighbors and vice versa. In the perfectly ordered case of the $A_{0.5}B_{0.5}$ alloy, all α sites are occupied by A atoms and all β sites by B atoms.

In the disordered case the probabilities of finding an A atom in the α and β sublattices are the same.

The magnetic properties of the system are described by means of the probabilities $p_\nu(I,m)$, of finding an atom I ($I=A,B$) with spin $S_z=m$ ($-S_I \le m \le S_I$) in the sublattice ν ($\nu=\alpha,\beta$). The total number of probabilities is then $2(2S_A+1)+2(2S_B+1)$ and they are normalized by

$$\sum_{I,m} p_\nu(I,m)=1, \quad \nu=\alpha,\beta \; . \tag{2.1}$$

The average concentration x of species A is given in terms of the probabilities by

$$\tfrac{1}{2}\sum_{\nu,m} p_\nu(A,m)=x \; . \tag{2.2}$$

At zero temperature we have for the $A_{0.5}B_{0.5}$ alloy that

$$p_\alpha(A,S_A)=p_\beta(B,S_B)=1,$$

and the rest of the p's are equal to zero. Above the Curie temperature we have

$$p_\nu(A,S_A)=p_\nu(A,S_A-1)\cdots=p_\nu(A,-S_A) \; , \tag{2.3}$$

$$p_\nu(B,S_B)=p_\nu(B,S_B-1)\cdots=p_\nu(B,-S_B) \; , \tag{2.4}$$

$$\nu=\alpha,\beta \; .$$

At finite temperature, the equilibrium values for the probabilities are found by minimizing the free energy $F=U-TS$, by means of the natural iteration method,[8] and subject to the three constraints (2.1) and (2.2).

The contributions to the internal energy U are the chemical nearest-neighbor interactions U_{AA}, U_{BB}, and U_{AB} and the Ising exchange integrals J_{AA}, J_{BB}, and J_{AB} (defined positive for ferromagnetic coupling). For the case $S_A=S_B=\frac{1}{2}$, the internal nal energy can be written as

$$U=U_C+U_M \; , \tag{2.5}$$

where

$$U_C(\eta)=U_C(0)-\tfrac{1}{8}NZW_C\eta^2 \tag{2.6}$$

and

$$U_M(\xi_I)=-\tfrac{1}{8}NZ\sum_{I,I'}\xi_\alpha(I)\xi_\beta(I')J_{II'} \; . \tag{2.7}$$

Here, N is the total number of atoms, Z is the coordination number and the spatial long-range order parameter η, and the four magnetic long-range order parameters $\xi_\nu(I)$ are defined by

$$\eta\equiv[p_\alpha(A)-p_\beta(A)] \tag{2.8}$$

and

$$\xi_\nu(I)\equiv p_\nu(I\uparrow)-p_\nu(I\downarrow) \; , \tag{2.9}$$

respectively.

In Eq. (2.6) W_C is the chemical contribution to the effective heat of mixing[9] and is defined by

$$W_C\equiv U_{AA}+U_{BB}-2U_{AB} \; . \tag{2.10}$$

The entropy is given by the expression

$$S=-\tfrac{1}{2}kN\sum_{I\nu m}[p_\nu(I,m)\ln p_\nu(I,m)] \; . \tag{2.11}$$

We now define two basic parameters: an unperturbed Curie temperature Θ_M

$$8k\Theta_M\equiv Z(xJ_{AA}+yJ_{BB})+Z[(xJ_{AA}-yJ_{BB})^2+4xyJ_{AB}^2]^{1/2} \; , \tag{2.12}$$

which is the Curie temperature[10] for $U_C=0$, and an unperturbed ordering temperature Θ_0

$$k\Theta_0=ZxyW_C \; , \tag{2.13}$$

which is the ordering temperature in nonmagnetic systems. Thus, three situations are possible, i.e., (i) $\Theta_0<\Theta_M$, (ii) $\Theta_M<\Theta_0$, and (iii) $\Theta_0<\Theta_M$, $J_{AB}<<J_{AA}$, J_{BB}, depending on the values of the parameters $J_{II'}$, W_C, and x. The temperature dependence of the order parameters as well as the phase diagrams in all those cases were studied in detail in Ref. 5. Here we study the temperature dependence of the specific heat

$$C=T\frac{\partial S}{\partial T} \tag{2.14}$$

and its discontinuity at the critical temperatures.

In the cases (i) and (ii) mentioned above, there are two critical temperatures T_1 and T_2 ($T_1<T_2$). At the lower critical temperature where a second-order phase transition takes place one of the order phenomena disappears. A more complicated situation occurs in case (iii).

Recently it has been shown that in systems with coupled order parameters, there are extra contributions to ΔC at $T=T_1$, not present in systems with only one kind of order.[7] It was shown that if the two phases are characterized by the order parameters ξ_i ($i=1,2,\ldots,N_1$) and ζ_i ($i=1,2,\ldots,N_2$) such that $\xi_i=0$ for $T\ge T_1$ and $\zeta_i=0$ for $T\ge T_2$, the specific heat at $T_1^{\pm}$ is given by

$$C(T_1^-)=-(\xi_1^0)^2\frac{\partial S}{\partial \xi_1^2}\bigg|_{T_1}+T_1\left[\left(\frac{\partial S}{\partial \tilde{\xi}_i}\tilde{\xi}_i'\right)_{T_1}+\frac{\partial S}{\partial \zeta_i}\bigg|_{T_1}\zeta_i'(T_1^-)\right], \tag{2.15}$$

and

$$C(T_1^+)=T_1\frac{\partial S}{\partial \zeta_i}\bigg|_{T_1}\zeta_i'(T_1^+) . \tag{2.16}$$

Here,

$$\tilde{\xi}_i\equiv\frac{\xi_i}{\xi_1}\quad (i\neq 1),$$

$$\tilde{\xi}_i'=\frac{\partial\tilde{\xi}_i}{\partial T}\bigg|_{T=T_1}, \tag{2.17}$$

and

$$\zeta_i'(T_1^{\pm})=\frac{\partial\zeta_i}{\partial T}\bigg|_{T=T_1^{\pm}} .$$

At the higher temperature T_2 only one kind of order is present and ΔC is calculated by means of the regular Landau theory for phase transitions.[11]

We now apply the above formalism to the three following situations.

A. $\Theta_0<\Theta_M$

In this case the order-disorder critical temperature is no longer given by Eq. (2.13) but by a completely different equation.[5] We denote this temperature by T_0. The parameters that vanish at $T=T_0$ are

$$\xi_1=\eta\ ,\quad \xi_2=\xi_\alpha(A)-\xi_\beta(A)\ ,\quad \xi_3=\xi_\alpha(B)-\xi_\beta(B)\ ,\quad N_1=3\ , \tag{2.18}$$

and the parameters that remain finite at $T=T_0$ are

$$\zeta_1=\xi_\alpha(A)+\xi_\beta(A)\qquad \zeta_2=\xi_\alpha(B)+\xi_\beta(B)\ ,\quad N_2=2\ . \tag{2.19}$$

The specific heat at $T_0^{\mp}$ is then given by

$$C(T_0^-)=\frac{1}{8}(\xi_1^0)^2\left[\frac{(1+\tilde{\xi}_2)^2}{2x+\zeta_1}+\frac{(1-\tilde{\xi}_2)^2}{2x-\zeta_1}+\frac{(1+\tilde{\xi}_3)^2}{2y-\zeta_2}+\frac{(1-\tilde{\xi}_3)^2}{2y+\zeta_2}\right]-\frac{kT_0}{4ZW_C}\left[\zeta_1'(T_0^-)\ln\left[\frac{2x+\zeta_1}{2x-\zeta_1}\right]+\zeta_2'(T_0^-)\ln\left[\frac{2y+\zeta_2}{2y-\zeta_2}\right]\right], \tag{2.20}$$

and

$$C(T_0^+)=-\frac{kT_0}{4ZW_C}\left[\zeta_1'(T_0^+)\ln\frac{2x+\zeta_1}{2x-\zeta_1}+\zeta_2'(T_0^+)\ln\frac{2y+\zeta_2}{2y-\zeta_2}\right] . \tag{2.21}$$

Equations (2.20) and (2.21) are evaluated by solving ten and four coupled equations, respectively.

At temperatures higher than T_0, the spatial order is lost and the system remains ferromagnetic up to the temperature Θ_M. This phase is characterized by only two order parameters, ζ_1 and ζ_2. Near Θ_M, it can be shown that

$$\zeta_2=-\frac{J_{AB}}{\left[J_{BB}-\frac{4kT}{Zy}\right]}\zeta_1 . \tag{2.22}$$

Thus, the specific heat at Θ_M^-, is calculated by the Landau theory[11] for systems with only one type of order, and it is given by

$$C(\Theta_M^-)=\frac{\zeta_0^2}{8x^2yJ_{AB}}\left[xyJ_{AB}^2+\left[\frac{4k\Theta_M}{Z}-xJ_{AA}\right]^2\right] . \tag{2.23}$$

Here,

$$\zeta_0^2=\frac{3}{xy}[(xJ_{AA}-yJ_{BB})^2+4xyJ_{AB}]^{1/2}\left[J_{AB}\left[\frac{4k\Theta_M}{ZxyJ_{AB}}-\frac{J_{AA}}{yJ_{AB}}\right]^3-\frac{1}{x^3}\left[J_{BB}-\frac{4k\Theta_M}{Zy}\right]\right]^{-1}, \tag{2.24}$$

and Θ_M is given by Eq. (2.12).

B. $\Theta_M < \Theta_0$

In this case, at $T=\Theta_0$ there is a second-order transition between an ordered paramagnet ($T<\Theta_0$) and a disordered one ($T>\Theta_0$). There is also, in general, a lower temperature T_M at which a second-order transition between an ordered ferromagnet ($T<T_M$) and an ordered paramagnet ($T_M<T<\Theta_0$) occurs. In this situation we have

$$\begin{aligned}&\xi_1 \equiv \xi_\alpha(A)\ ,\\ &\tilde{\xi}_2 \equiv \xi_\beta(A)/\xi_\alpha(A)\ ,\\ &\tilde{\xi}_3 \equiv \xi_\alpha(B)/\xi_\alpha(A)\ ,\\ &\tilde{\xi}_4 \equiv \xi_\beta(B)/\xi_\alpha(A)\ ,\quad N_1=4\ ,\end{aligned} \tag{2.25}$$

and

$$\zeta_1 \equiv \eta\ ,\quad N_2=1\ . \tag{2.26}$$

Applying the mentioned general theory[7] we find that the specific heat at $T_M^{\mp}$ is given by

$$C(T_M^-) = -\tfrac{1}{4}\eta'(T_M^-) + \tfrac{1}{4}(\xi_1^0)^2 \left[\frac{1}{x+\frac{1}{2}\eta} + \frac{\tilde{\xi}_2^2}{x-\frac{1}{2}\eta} + \frac{\tilde{\xi}_3^2}{y+\frac{1}{2}\eta} + \frac{\tilde{\xi}_4^2}{y-\frac{1}{2}\eta} \right], \tag{2.27}$$

and

$$C(T_M^+) = -\tfrac{1}{4}\eta'(T_M^+)\eta\ . \tag{2.28}$$

At $T>T_M$ the system becomes paramagnetic and the problem reduces to calculating the specific heat of a normal order-disorder transition. The specific heat $C(\Theta_0^-)$ is given by

$$C(\Theta_0^-) = \frac{3}{2}\frac{xy}{x^3+y^3}\ . \tag{2.29}$$

C. $\Theta_0 < \Theta_M$, $J_{AB} << J_{AA}$, J_{BB}

In this situation the low-temperature behavior is different from that discussed in Sec. II A. Because of weak magnetic exchange between dissimilar atoms the system becomes paramagnetic, in the $A_{0.5}B_{0.5}$ alloy, at the temperature T_M' where the chemical order is strong and becomes ferromagnetic again at a higher temperature T_0 where the system is disordered enough to take advantage of the strong exchange interactions J_{AA} and J_{BB}.

The calculation of C at T_M' corresponds to the case discussed in Sec. II B where $\Theta_M<\Theta_0$, and the the calculation of C at Θ_M corresponds to disordered ferromagnetic systems [Eq. (2.34)]. At $T=T_M'$, the situation is much more complicated and only numerical results for C are presented.

III. RESULTS AND DISCUSSION

The Fe_xCo_x system is a metallic ordering alloy with bcc crystal structure and with Curie temperatures higher than the spatial order-disorder transition temperatures.[12] Then it belongs to the alloys described in Sec. II A. This system, as all the magnetic transition metals, presents localized and itinerant properties.[13] Therefore, it is evident that a description of this alloy by a spin-$\frac{1}{2}$ Ising model is not fully adequate It is, however, interesting to consider our model is a simple interpolation scheme for this system. The phase diagram was studied within this model and it was shown that its main features can be obtained.[5] The four parameters J_{FeFe}, J_{FeCo}, J_{CoCo}, and W_C were obtained from the three experimental values of Θ_M at $x=0.4$, 0.5, and 0.6 and from T_0 at $x=0.5$. It is worth noticing that the Curie temperature at those concentrations coincides with a change of crystal structure from bcc to fcc. However, it is not clear from the experiment if this last change of phase drives the system to the paramagnetic state. Based on a mean-field theory one would expect the opposite, since the Curie temperature is proportional to the coordination number, but a more careful study would be necessary. Here we are mainly interested in the change of the specific heat at the order-disorder temperature.

We applied the theory described in Sec. II A to this system. Our results are presented in Figs. 1 and 2. The temperature dependence of the specific heat is shown in Fig. 1. We see that $C(T_0^-)$ is much larger (5.408) than the one we would obtain in an ordering paramagnetic alloy (1.5). This enhancement shows clearly the interplay between magnetism and spatial order. We show also in this figure the experimental results.[14] Here, we subtracted the lattice and electronic contribution to C.

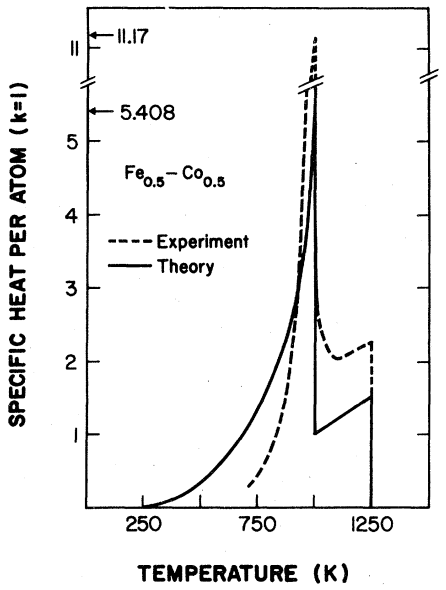

FIG. 1. Temperature dependence of the specific heat C for a $Fe_{0.5}Co_{0.5}$ alloy. The arrows mark the peak values of C at the order-disorder transition temperature.

Our results are in a good qualitative agreement to the experiment, but $C(T_0^{\mp})$ and $C(\Theta_M^{-})$ are smaller than those experimentally observed. However, it is expected that the quantitative difference would be smaller if we would formulate the theory in the Bethe approximation, taking into account short-range spin correlations.

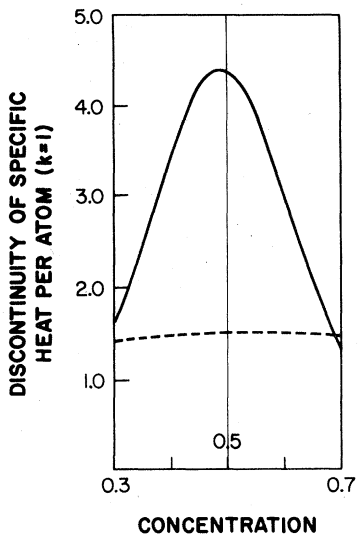

FIG. 2. Discontinuity in the specific heat of the Fe-Co system as function of the iron concentration x at the order-disorder transition temperature (full line) and at the Curie temperature (dashed line).

In Fig. 2 we show the results for ΔC at $T=T_0$ (full line) and at $T=\Theta_M$ (dashed line) as a function of the alloy concentration. We see that $\Delta C(T_0)$ is asymmetric with respect to $x=0.5$, a feature not possible to obtain in our simple model if magnetism is not included.

The results for an alloy of the type discussed in Sec. II B are shown in Figs. 3 and 4. The parameters used in Fig. 3 are $J_{AA}=1.0$, $J_{AB}=0.5$, $J_{BB}=2.0$, $W_C=1.2$, and $x=0.5$. Here, we show the temperature dependence of the order parameters η and $\bar{\xi}=\frac{1}{2}\sum_{I,\nu}\xi_\nu(I)$ [Fig. 3(a)] and the temperature dependence of the specific heat (solid line) and of the entropy [dashed line Fig. 3(b)]. In Fig. 4 we show the concentration dependence of ΔC at T_M for the range $x_1 \le x \le x_2$, where $\Theta_M \le \Theta_0$. We

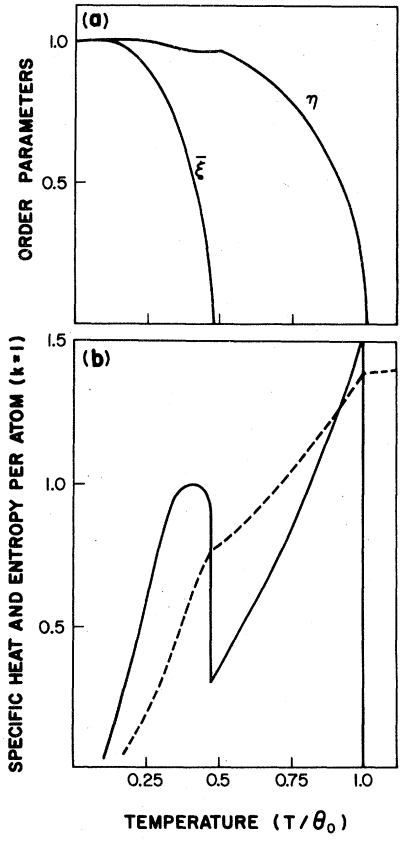

FIG. 3. (a) Temperature dependence of the spatial long-range order parameter η and average magnetization $\bar{\xi}$ for the case $\Theta_M<\Theta_0$ and the set of parameters $J_{AA}=1.0$, $J_{AB}=0.5$, $J_{BB}=2.0$, $W_C=1.2$, and $x=0.5$. (b) Specific heat (full line) and entropy (dashed line) for the same alloy, showing that the phase transitions at T_0 and T_M are of the second kind.

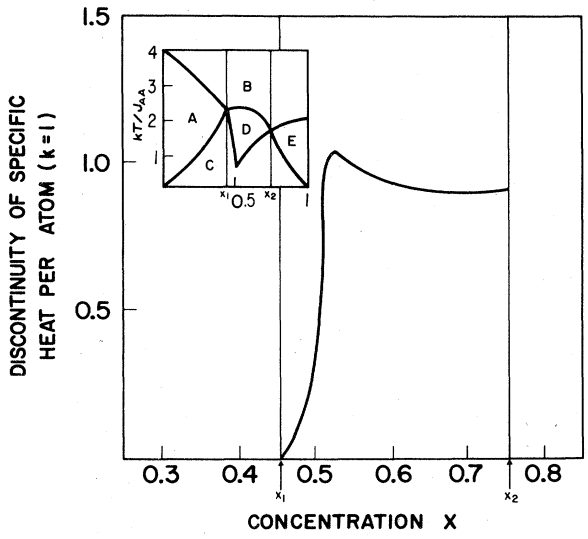

FIG. 4. Discontinuity of specific heat at T_M as a function of the concentration of A atoms in an alloy with the same parameters as those in Fig. 3. The inset figure shows the range $x_1 \leq x \leq x_2$ on the phase diagram where $\Theta_M \leq \Theta_0$. The different phases are A and E disordered ferromagnets, B disordered paramagnets, C ordered ferromagnets, and D ordered paramagnets.

show in the inset figure the phase diagram for this alloy. The different phases are A and E disordered ferromagnets, B disordered paramagnets, C ordered ferromagnets, and D ordered paramagnets.

Figures 5–7 contain results for the third kind of alloy discussed in Sec. II, i.e., $\Theta_0 < \Theta_M$ and $J_{AB} << J_{AA}, J_{BB}$. The parameters used are $J_{AA} = 1.0$, $J_{AB} = 0.25$, $J_{BB} = 2.0$, $W_C = 1.0$. In Fig. 5 we show the temperature dependence of η, ξ, C, and S for an alloy with $x = 0.5$. In this case, we have three critical temperatures: T'_M at which the system becomes paramagnetic at low temperatures, T_0 at which the system becomes ferromagnetic and spatially disordered, and Θ_M the Curie temperature at high temperatures. At each of these temperatures there is a discontinuity in the specific heat. This is shown in Fig. 5(c). We show here also the temperature dependence of the entropy. In Fig. 6 we display the results for an alloy with $x = 0.45$ and the same parameters as in Fig. 5. In this case there are only two transition temperatures T_0 and Θ_M. The paramagnetic gap present for $x = 0.5$ vanishes, but there is a discontinuity in $\bar{\xi}$ at $T = T_0$. We see that there are two main differences in C as compared with the results for $x = 0.5$: (i) the discontinuity at $T = T'_M$ becomes a shoulder

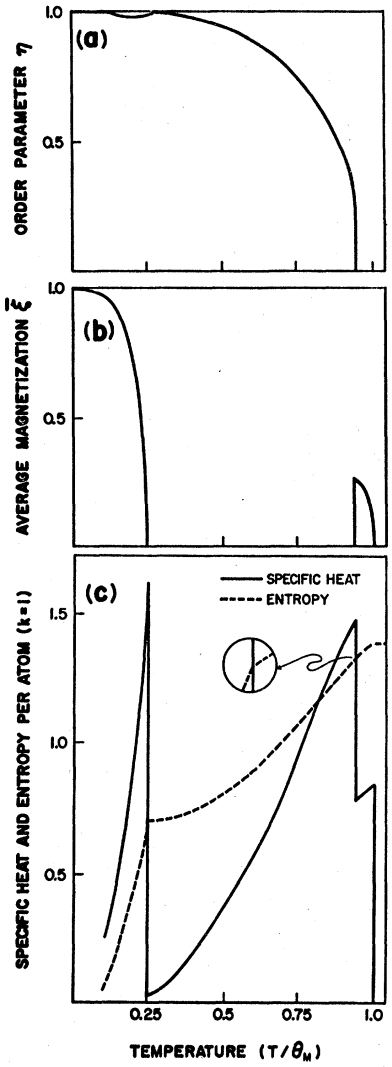

FIG. 5. Temperature dependence of (a) η, (b) $\bar{\xi}$, and (c) C (full line) and S (dashed line) for an alloy with $J_{AA} = 1.0$, $J_{AB} = 0.25$, $J_{BB} = 2.0$, $W_C = 1.0$, and $x = 0.5$.

and (ii) the finite C at $T = T_0$ becomes infinite.

The results for ΔC at T'_M for concentrations $x_1 \leq x \leq x_2$ as well as the phase diagram are presented in Fig. 7. The phases A, B, C, D, and E are the same as those of Fig. 4. The results of ΔC are similar to those displayed in Fig. 4, except the sharp increase of the region near x_1, where the systems pass through four phases as one increases the temperature.

All our results stress the strong interdependence of magnetism and spatial long-range order. Experiments on this kind of systems would be desirable to check the validity of our theory.

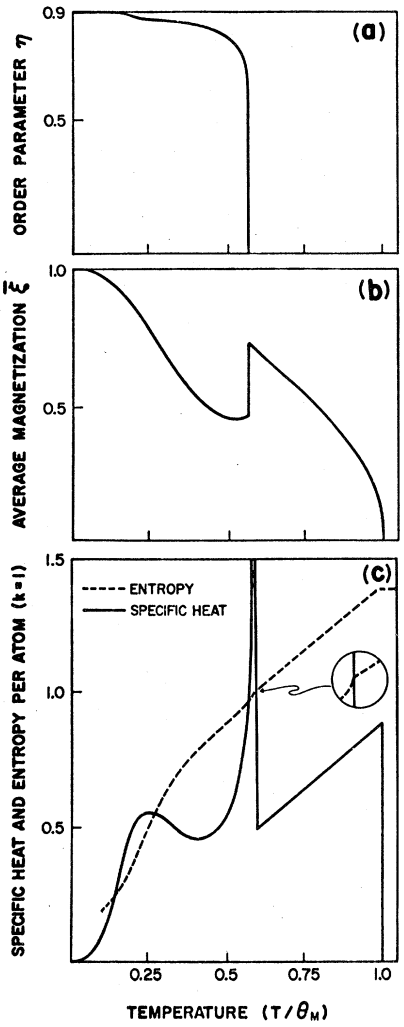

FIG. 6. Same as Fig. 5 with $x=0.45$. Note that, as compared with Fig. 5, the discontinuity at $T=T_M'$ becomes a shoulder and C becomes infinite at $T=T_0$.

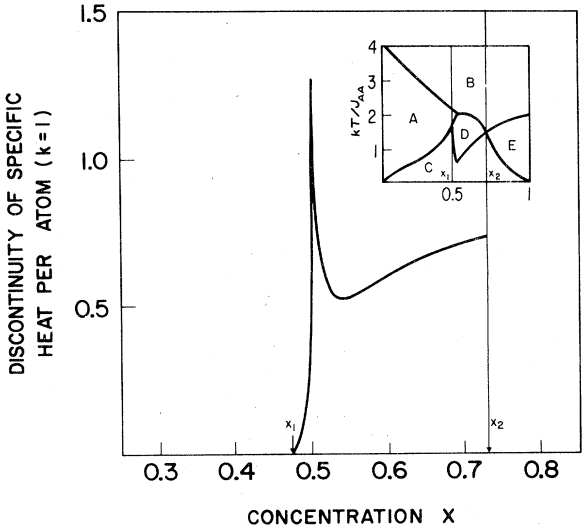

FIG. 7. Discontinuity of the specific heat at T_M as a function of the concentration of A atoms in an alloy with same parameters as those in Fig. 5. The inset figure shows the range $x_1 \leq x \leq x_2$ on the phase diagram where $\Theta_M < \Theta_0$. The phases marked A, B, C, D, and E are the same as those in Fig. 4.

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