Cooperative phenomena and influence of strain energy in alloys

P.L. CAVALLOTTI and R. BERGAMASCHI, Dipartimento di Chimica-Fisica Applicata, Politecnico di Milano, Milan, Italy
P.M. OSSI, Istituto di Ingegneria Nucleare, CESNEF, Politecnico di Milano, Milan, Italy

Abstract

Thermodynamic approximations for cooperative phenomena in solids are reviewed and a new approximation is proposed and developed. The method calculates the configurational free energy for Ising and Heisenberg model systems, from a series of quasi-chemical reactions, adopting a system renormalization solution strategy.
Magnetic and suitable order-disorder transformations are properly represented as higher order transitions. An elastic energy term is introduced to take into account the atomic size and shape change effects in metallic alloys. With this method we can distinguish when an ordering transition becomes first order. The method is also suitable for a theoretical calculation of the magnetic free energy contribution to ferromagnetic alloys.

Riassunto
Fenomeni cooperativi ed influenza dell'energia di deformazione nelle leghe
Vengono presentate le approssimazioni termodinamiche sui fenomeni cooperativi nei solidi ed è proposto e sviluppato un nuovo tipo di approssimazione. Con questo metodo si ottiene l'energia libera configurazionale per sistemi che seguono il modello di Ising o di Heisenberg, da una serie di reazioni quasichimiche, con una strategia di risoluzione in cui il sistema viene di volta in volta rinormalizzato. Le trasformazioni di fase magnetiche e quelle ordine-disordine, ad esse assimilabili, sono giustamente rappresentate come transizioni di ordine superiore. Per tenere conto degli effetti di dimensione degli atomi e di variazione di forma nelle leghe metalliche si introduce un contributo di energia elastica. In questo modo è possibile distinguere quando una transizione di ordinamento diventa del primo ordine. Con questo metodo è anche possibile valutare il contributo magnetico all'energia libera delle leghe ferromagnetiche.

Introduction

Cooperative phenomena play a fundamental role in crystals by determining many aspects of their phase transformations. They are particularly interesting for solutions with extended ranges of solubility, such as metallic solutions, and when phase changes with conservation of the lattice frame are considered, i.e. for coherent phase transformations.

During the last decade, many studies have been devoted to the thermodynamics of concentrated solid solutions (1) and some coherent phase diagrams have been calculated (1-5).

For concentrated solutions, the configurational part of the free energy is mainly an entropic term and methods have been proposed for calculating it. The main statistical models are, in order of complexity and approximation:

- the "mean field" or Bragg Williams (BW) model;
- the quasi-chemical (QC) approximation of Fowler and Guggenheim;
- the cluster variation (CV) method invented by Kikuchi (5).

The last method has recently been used to evaluate prototype coherent phase diagrams (4) from first principles. These diagrams were obtained with considerable computational efforts, but permit the evaluation of many interesting quantities, such as: long and short-range order parameters, critical fluctuation intensity, entropy changes. With these results, we can begin to understand the coherent transformations, which determine the early products in industrial phase transformations and the microstructure of the resulting alloy.

The statistical thermodynamic models so far proposed, although giving results and trends in general agreement with the experimental behaviour of alloys, fail to catch some special features of the phase transitions; for instance, critical transitions are interpreted as second order transformations at most, while they can be higher order transformations with specific heat increasing to an infinite value, at the critical temperature, T_C. The well known order-disorder transformation for β brass is interpreted only very approximately with these models.

The simplest physical model representing the ordering of an alloy is the same as adopted for a system of interacting anisotropic spins, in a vanishing magnetic field: the Ising model. Onsager (6) has shown that it is possible to obtain an exact solution of this problem for the two-dimensional square-lattice with the degree of occupation $\vartheta = \frac{1}{2}$. He has shown that the order-disorder transition of the Ising model is of the critical type, and that the failure in reproducing this important feature by the proposed approximations lies in the assumptions introduced to make the problem tractable.

Strategies have recently been proposed for solving this type of problem, based on the renormalization group (RG) method, which permit us to deal with problems involving many scales of length; that is, problems with fluctuations in physical quantities developing at all possible length scales (7-8). Critical phenomena are an example of this type of problem, where the whole spectrum of length scales must be taken into account.

Simple RG methods, such as the "spin decimation" transformation invented by Kadanoff (9-10) and the block-spin technique (11), have been used with great success to obtain data on 2D Ising models. In these methods some spins are held fixed while other spins are averaged, producing an effective interaction on the fixed spins. In the block-spin technique this involves three basic steps: division of the lattice into spin-blocks, averaging and replacement at the spins in the block with a single fixed spin having the average value, reduction of the dimensions of the system by giving to the fixed spins the original space. At every averaging step, fluctuations smaller than the block dimensions are eliminated.

These methods have a serious inherent limitation: severe truncations are needed in practical calculation to limit the number of parameters contained in interactions. Thus Monte Carlo RG has been developed and successfully applied to the 3D Ising model (12-13). An important consequence of the RG methods is that at T_C the thermodynamic potential of the system is independent of the system details at atomic level. Then, it seems possible to obtain a better approximation method starting from a good definition of the critical properties, instead of describing the atomic distribution starting from a very low (complete order) or very high (complete disorder) temperature. In a previous paper (14), it was shown that it is possible to improve the QC approximation value of the critical parameter $\frac{-\Delta\varepsilon}{2\,K_BT_C}$ were $\Delta\varepsilon$ is the interaction energy of a pair of atoms occupying two neighbouring positions and K_B the Bolzmann constant, by a simple modification of the partition function Q of the system. This modification can be interpreted, in the same frame of the QC reasoning, if we adopt a RG procedure (15). In this case, we must introduce, even at the critical temperature, two types of interaction, the direct interaction between atom pairs and the interactions between fixed atoms, when they represent the average value of the interacting atoms after the second step of the block-spins technique. This means that, even at T_C, we must consider two quasi-equilibrium reactions with different interaction energies. At T_C we can determine the characteristics of the blocks and of the averaging procedure. When T is less than or higher than T_C, to evaluate the thermodynamic potential of the system we must take into account the variation in the coupling strength, increasing at $T < T_C$ and decreasing at $T > T_C$ at each renormalization transformation, and the variation in the T of the system after each averaging, decreasing rapidly towards zero temperature at $T < T_C$ and increasing towards a state of maximum disorder at $T > T_C$.

In the following, we have tried to introduce these considerations into the evaluation of the free energy of systems following the Ising model.

Real systems do not closely follow the Ising model, except in the case of ferromagnetic salts with very low T_C. However, the Ising model is a good starting point for interpretation of the behaviour of alloys with respect to order-disorder transformations.

Kajitani and Cook (16) have shown that the free energy of these alloys can be considered as the sum of two components: one deriving from the Ising model and the other from the elasticity theory, as a result of two contributions: the size difference between atoms and the volume and shape change on ordering. With an improved approximation for the first chemical component, it is possible to obtain a better understanding of the ordering in real alloys.

Magnetic ordering has a strong effect on the shape of the miscibility gap in binary systems with a ferromagnetic and a magnetic component (17). The present empirical treatments will be reviewed and a suggestion for developments in this field advanced in the last paragraph.

Termodynamic quantities for Ising model systems

In the Ising model the species, such as atoms for alloys or spins for magnetic substances, occur at lattice sites and an interaction energy of the semi-classical type occurs between pairs of species. Spin interaction occurs only between the spin z components, whilst there is no interaction between the x and y components. This model corresponds to extreme magnetic anisotropy.

Other assumptions considered in the original model, and which could be removed in principle, regard the limitation of the spin value to the $s = \pm 1/2$ case and taking into account nearest neighbours' (nn) interactions only. Thus, only two spin orientations are possible, parallel or antiparallel; correspondingly there are only two occupation states for a site in a binary alloy AB: occupied by A or by B, and for a lattice gas: occupied or empty.

The QC approximation for a binary alloy assumes that, for a total of N_s sites, with N_A sites of type A and N_B sites of type B, the numbers of nn pairs N_{AA}, N_{BB} and N_{AB} (assumed equal to N_{BA}) are determined from the mass balance equations:

$$\frac{z\,N_A}{2} = N_{AA} + N_{AB}\,; \quad \frac{z\,N_B}{2} = N_{BB} + N_{AB} \qquad (1)$$

where z is the first shell coordination number and, from a quasi-equilibrium between the pair numbers, a consequence of a reaction between the pairs AA + BB = 2 AB, with the equilibrium constant:

$$K_{eq} = \frac{N^2_{AB}}{N_{AA} \cdot N_{BB}} = \exp \frac{\Delta\varepsilon}{K_BT} \qquad (2)$$

From Eqs. (1) and (2) we obtain:

$$N_{AB} = z\,N_s\,\vartheta\,(1-\vartheta)\,/\,(1+\beta) \qquad (3)$$

where $\vartheta = N_A/N_s$ and:

$$\beta = \{1-4\,\vartheta\,(1-\vartheta)\,[1-\exp(-\Delta\varepsilon/K_BT)]\}^{1/2} \qquad (4)$$

The free energy for the lattice configurations is obtained (14) from an entropic term taking into account the number of lattice configurations for the pairs:

$$\omega = (1/2\ z\ N_s)\ !\ /\ [N_{AA}\ !\ N_{BB}\ !\ (N_{AB}!)^2] \tag{5}$$

normalized to the right total number of configurations for the atoms, and an energy term taking into account the potentials for the single atoms and the potential of average force or nn interaction parameter:

$$-\ \Delta\varepsilon = \varepsilon_{AA} + \varepsilon_{BB} - 2\ \varepsilon_{AB} \tag{6}$$

The long range order parameter η is related to the occupation degree ϑ, through $\eta = 2\vartheta - 1$. The configurational free energy F_C as a function of η for the QC approximation (14), in the case $N_A = N_B = N_s/2$, is given by:

$$\frac{F_C - F_C\,(1)}{\tfrac{1}{2}\ N_s K_B T} =$$

$$= (1+\eta)\ln(1+\eta) + (1-\eta)\ln(1-\eta) - 2\ln 2 + \tag{7}$$

$$+ \frac{z}{2}\left[(1+\eta)\ln\frac{\beta+\eta}{1+\eta} + (1-\eta)\ \ln\frac{\beta-\eta}{1-\eta} - 2\ln\frac{\beta+1}{2}\right]$$

where $F_C\,(1)$ is the configurational free energy at $\eta = 1$. Eq. (7) represents an improvement with respect to the most simple BW approximation, because it takes into account the influence of the $\Delta\varepsilon$ parameter on the number of configurations, that is on the entropic term. Differentiating Eq. (7) twice with respect to η and equating it to zero, at T_C and $\vartheta = 1/2$, we obtain the critical parameter:

$\dfrac{-\ \Delta\varepsilon}{2K_BT_C}$ from the equation:

$$z/\beta_C + 2 - z = 0 \tag{8}$$

where $\beta_C = \exp\,(-\ \Delta\varepsilon/2K_BT)$. Eq. (8) gives:

$$\frac{-\ \Delta\varepsilon}{2K_BT_C} = \ln\frac{z}{z-2} \tag{9}$$

The numerical values of these parameters are a good measure of the accuracy of the free energy calculation near T_C. They are compared, for the various approximations, in Table 1.

The BW approximation gives $\dfrac{-\Delta\varepsilon}{2K_BT_C} = \dfrac{2}{z}$, that is a very rough approximation of the parameter.

Also the values obtained with Eq. (9) are far from the exact values for 2D Ising systems. The approximation is better for 3D systems, but even in this case BW approximation is out by about 25% and QC approximation by about 10%.

The CV method gives a better approximation of the configurational entropy S_C/K_B, summing over all possible distributions of the A and B atoms on the N_s sites the probability terms $x(J)\ln x(J)$, where $x(J)$ is the

TABLE 1 - Critical parameter $\dfrac{-\Delta\varepsilon}{2K_BT_C}$ for the Ising (s = 1/2) model

			APPROXIMATION						
	Lattice	z	BW (2/z)	QC $\left(\ln\dfrac{z}{z-2}\right)$	CV square or triangle	CV cube or tetrahedron	IQC z'/n	IQC $-\Delta\varepsilon/2K_BT_C$	Exact or best known[21]
1D		2	1	∞	∞		—	∞	∞
2D	Honeycomb	3	.66667	1.09861	—	—	3	1.33271	1.31696
	Square	4	.50000	.69315	.82554	—	2	.88137	.88137
	Triangular	6	.33333	.40547	.51083	—	3/2	.54130	.54931
	Kagomé	4	.50000	.69315	—	—	8/3	.92724	.93313[22]
	Diced	4	.50000	.69315	—	—	4/3	.82899	.8314 [22]
3D	Diamond	4	.50000	.69315	—	—	2/5	.73977	.73957
	Simple cubic	6	.33333	.40547	.43386	.43696	1/3	.44060	.44338
	BCC	8	.25000	.28768	.29572	.30815	1/3	.31756	.31481
	FCC	12	.16667	.18232	—	.19951	1/3	.20420	.20419

equilibrium probability that the system is in the configuration J. In the CV method the atomic distributions are described by introducing n-lattice points clusters (not only pairs) and their concentrations (or better expectation values) $x_n^{(s)}$ (J), where s is the cluster type among those containg n atoms.

We can write, in this case too, mass balance equations relating $x_n^{(s)}$ to $x_{n-1}^{(s)}$, and evaluate the number of configurations for the distribution of atoms, pairs or higher clusters in the lattice (1, 18). The entropy of the system is then approximated by a sum over small clusters (19).

$$S = K_B \, \Sigma_{n,s} \, \gamma_n^{(s)} \, \Sigma_J \, x_n^{(s)}(J) \ln x_n^{(s)}(J) \qquad (10)$$

where $\gamma_n^{(s)}$ are integers, determined by simple reported methods (20). The CV approximation is better than the QC approximation, because it takes into account closed configurations, ignored in the QC method.

The approximation results from the truncation of the cluster sizes to small ones, otherwise the number of independent variables (the correlation functions) becomes exceedingly large. The approximation of the critical parameters becomes about 7% for 2D systems and 2% for 3D systems, as reported in Table 1.

However , in critical conditions, fluctuations have an influence at every length scale, and the limitation of the considered cluster's size impedes the increase of the specific heat to the infinite value at T_C. On the other hand, at T_C the details of the system are not important if we adopt a renormalization group strategy solution; at every renormalization, the system does not change its behaviour. This means that for thermodynamic quantities it maintains its temperature. Then the QC approximation, if adequately corrected, can give better values of the critical parameter than the CV method.

What the QC approximation ignores is the interaction between the averaged spins, in the second step of the spin-block technique. We can take this into account in the same frame, introducing a second quasi-chemical equilibrium between pairs for the system after decimation; with varied interaction energy.

We have seen that it is possible to obtain very good values of the critical parameter, considering that the interaction energy after averaging is double; that is:

$$K^{I}_{eq} = \frac{{N^{I}_{AB}}^{2}}{N^{I}_{AA} \cdot N^{I}_{BB}} = \exp \frac{2\,\Delta\varepsilon}{K_B T} \qquad (11)$$

where N^{I}_{AB}, N^{I}_{AA} and N^{I}_{BB} are the number of pairs after averaging, subject to the mass balance constraints:

$$\begin{aligned} \frac{z'}{n}\,\frac{N_A}{2} &= N^{I}_{AA} + N^{I}_{AB} \\ \frac{z'}{n}\,\frac{N_B}{2} &= N^{I}_{BB} + N^{I}_{AB} \end{aligned} \qquad (12)$$

where z′ is the new nn coordination number for the fixed points, and n is the number of atoms which have been averaged. With this method we add a term to the free energy value in Eq. (7) of the type:

$$\frac{\Delta F_C}{\tfrac{1}{2}\, N_s K_B T} = \frac{z'}{2n}\left[(1+\eta)\ln\frac{\beta^{I}+\eta}{1+\eta} + (1-\eta)\ln\frac{\beta^{I}-\eta}{1-\eta} - 2\ln\frac{\beta^{I}+1}{2}\right] \qquad (13)$$

where

$\beta^{I} = \{1-(1-\eta^2)[1-\exp(-2\Delta\varepsilon/K_B T)]\}^{1/2}$ and

at T_C, $\beta^{I}_C = \exp(-\Delta\varepsilon/K_B T_C)$.

We must also take into account that we have increased the total number of configurations. Thus, we have introduced a parameter K_{ab}, function only of the temperature, which divides all the configuration terms of the free energy.

To obtain the critical parameter we differentiate twice the free energy with the new term, with respect to η, and equate it to zero at T_C and for $\eta = 0$, obtaining:

$$\frac{z}{\beta_C} + \frac{z'/n}{\beta_C^2} + 2 - z = 0 \qquad (14)$$

With the values of z′/n reported in Table 1 we obtain values of the critical parameter very near to the exact or best known ones; they differ by less than 1% for 3D Ising systems and less than 1.5% for 2D Ising systems. With this method it is also possible to distinguish between lattices with the same nn coordination number, but of different type, such as 2D square, Kagome or diced and 3D diamond. Examining the values of z′/n, it is possible to suggest a method for choosing the block. For 2D systems a good choice of z′ is that of the dual lattice, while n is the number of atoms averaged to obtain the dual lattice. For 3D systems the best choice for z′ is 2; that is, we must average the interactions of 5 or 6 atoms obtaining linear chains.

The free energy function near T_C is given by:

$$\begin{aligned} \frac{F_C}{N_s K_B T_C} = {} & \left(-z + \frac{2\tau}{\tau+1}\,\frac{z'}{n}\,\frac{z/4-1}{1+z'/2n} \right) \frac{-\Delta\varepsilon}{8 K_B T_C} + \\ & + \tau\,\frac{1-z/2}{2K_{ab}}\,[(1+\eta)\ln(1+\eta) + (1-\eta)\ln(1-\eta) - 2\ln 2] + \\ & + \frac{\tau}{4K_{ab}}\,\{z[(1+\eta)\ln(\beta+\eta) + (1-\eta)\ln(\beta-\eta) - 2\ln(\beta+1)] + \\ & + \frac{z'}{n}\,[(1+\eta)\ln(\beta^{I}+\eta) + (1-\eta)\ln(\beta^{I}-\eta) - 2\ln(\beta^{I}+1)]\} \end{aligned} \qquad (15)$$

In Eq. (15) a second energy term has been introduced to have a zero value for U_C at infinite T.

The best choice of the K_{ab} value at T_C

TABLE 2 - Critical values of thermodynamic quantities for 3D Ising (s = 1/2) models

Lattice	$-F_{cr}/N_sK_BT_C$				$-U_{cr}/N_sK_BT_C$			
	QC	CV[23]	IQC	Best App[21]	QC	CV[23]	IQC	Best App[21]
Diamond	.81095	—	.83405	.8335	.23105	—	.32332	.3232
Simple cubic	.75438	.8234	.77496	.77789	.12164	.2364	.21867	.21996
BCC	.73439	—	.75572	.75404	.082195	—	.17245	.17201
FCC	.71804	.7378	.74109	.74179	.049724	.1198	.15132	.15156

is $\left(1+\frac{3z'}{4n}\right)$; with this value it is possible to obtain a very good approximation for the F_C value at T_C, as shown in Table 2.

The U_C value at T_C depends on the behaviour of F_C as a function of T, because U_C is obtained from F_C through the relation:

$$-U_C=\tau^2\frac{\partial(F_C/\tau)}{\partial\tau}$$

where $\tau = T/T_C$ is the relative temperature of the system.

We have tried to see if it is possible to obtain a good approximation of the thermodynamic quantities with analytic expressions, even very near T_C, introducing τ functions in the exponential term of β and β^I, and in the series of terms deriving from the series of quasichemical reactions, consequence of the renormalization steps.

In fact, when the temperature T is greater or lower than T_C the system changes its actual T after each renormalization step, increasing T if $T > T_C$ or decreasing T if $T < T_C$ (7).

The two last right terms of eq. (15) become at $T < T_C$ or $T > T_C$ an infinite series of terms containing β_m and β^I_m, where:

$\beta_m = 1+(1-\eta^2)\,[1\text{-exp}(-f_1(\tau)\Delta\varepsilon/K_B\tau)]^{-\frac{1}{2}}$ and

$\beta^I_m = 1+(1-\eta^2)\,[1\text{-exp}(-2f_1(\tau)\Delta\varepsilon/K_B\tau)]^{-\frac{1}{2}}$ with

$f_1(\tau) = \tau^{2m-1}+\tau^{-2m}$ at $\tau<1$ and

$f_1\,(\tau)=2\tau^{-2m}-\tau^{1-2m+1}$

at $\tau>1$; and are multiplied by

$f_2\,(\tau)=(-a/(n^m\cdot(b-\tau-\tau^2-\tau^4))/K_a$ at $\tau<1$ and

$f_2(\tau) = (-a/(n^m\cdot(b\tau^2+b\tau^4-1))/K_a$ at $\tau>1$; with

$$K_a=1-\frac{a}{b-\tau-\tau^2-\tau^4}\sum_{m=1}^{\infty}\frac{\tau^m}{n^m}\quad\text{at } \tau<1 \text{ and}$$

$$K_a=1-\frac{a}{(b\tau^2+b\tau^4-1)\,(\tau^{1.5}+9\tau^{-1.5})}\sum_{m=1}^{\infty}\frac{1}{n^m}\text{ at } \tau>1.$$

Also K_{ab} value becomes a τ function; we have introduced the following expressions:

$$K_{ab}=\frac{z'}{n}\left(\frac{\alpha^2}{\beta-\tau^2}+\gamma\tau^2+\delta\tau^4+\varepsilon\tau^6\right)\text{ at } \tau<1\text{, and}$$

$$K_{ab}=1+\frac{z'}{2n}-\frac{z'}{n}\left(\frac{\alpha'^2}{\beta'\tau^{4.1\div4.7}-\tau^{-(5.9\div5.3)}}+\gamma'\tau^{-34}+\right.$$
$$\left.+\delta'\tau^{-2}+\varepsilon'\tau^{-4}\right)\text{ at } \tau>1$$

depending on the considered lattice and with the constraint $K_{ab}=1+\frac{3z'}{4n}$ at $\tau=1$.

The values of the internal energy at $\tau = 1$ are reported in Table 2, and the η and C_V/R values calculated for the diamond lattice in Figs. 1 and 2, together with the experimental data for the spontaneous magnetization and magnetic specific heat on the magnetic salt $DyP0_4$ (24), which closely follows the Ising model. The parameters introduced to obtain these data are:

- two parameters: a and b for the calculation of η as a function of τ at $\tau < 1$;
- one parameter: the value of $dK_{ab}/d\tau$ for obtaining the right value of $U_{crit}/N_sK_BT_C$;
- three parameters: γ, δ and ε for the calculation of C_V at $\tau < 1$ (α and β being fixed from the values of K_{ab} and $dK_{ab}/d\tau$ at $\tau = 1$);
- three parameters: γ', δ' and ε' for the calculation of C_V at $\tau > 1$ (α' and β' being fixed for the same preceding constraints).

These parameters and the temperature functions have been determined by a fitting procedure, and the results obtained show that it is indeed possible to obtain a very good approximation of the thermodynamic quantities for Ising model systems by analytic expressions with a

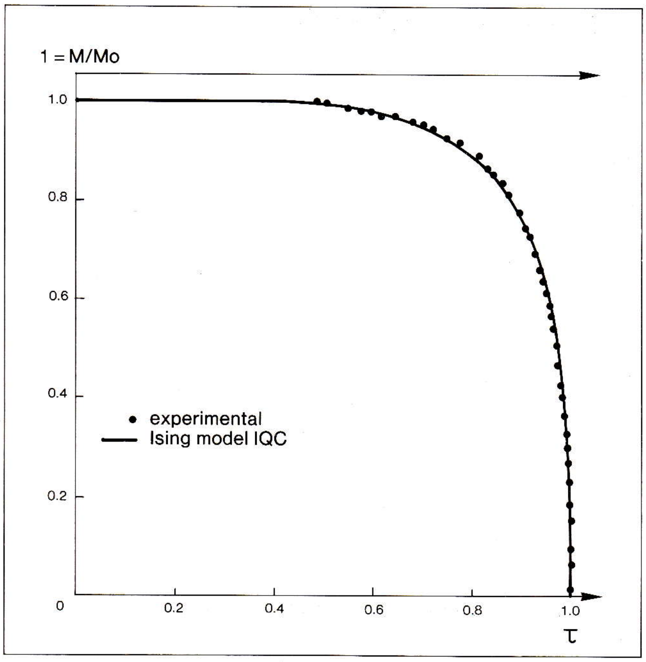
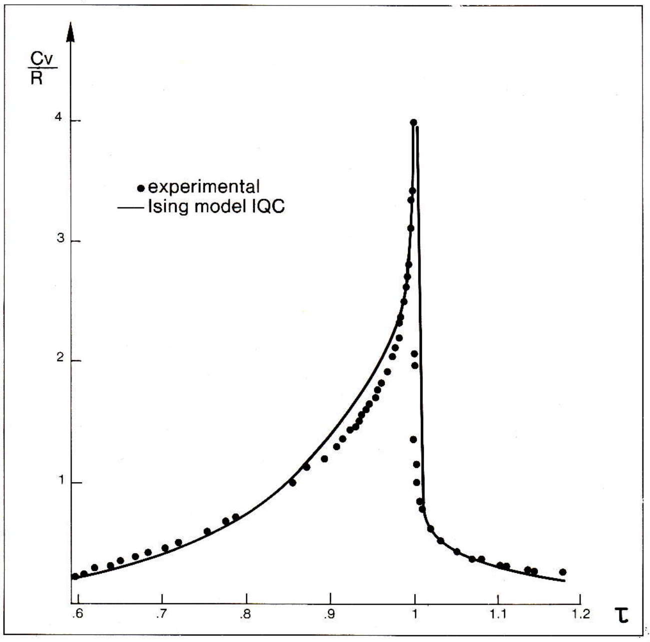


Fig. 1 - Temperature dependence of the order parameter for the diamond Ising lattice, calculated with the improved quasichemical (IQC) approximation. Comparison with the spontaneous magnetization of $DyPO_4$, derived from the magnetoelectric susceptibility (24).

Fig. 2 - Configurational specific heat calculated with the IQC approximation for the diamond Ising lattice. Comparison with the magnetic specific heat measured on $DyPO_4$ crystals (24).



limited number of parameters.

These calculations have been made so to be able to obtain values of the thermodynamic quantities from analytic expressions for application purposes. Thus, it is possible to compare experimental magnetic results with these values and to suggest how to change the analytic expression to follow the experimental results, if the system does not closely follow the Ising model. In the following we will show the application of these expressions in the study of order-disorder phenomena in typical alloys.

Order-disorder transformations in alloys

The Ising model is usually adopted to explain the ordering behaviour in binary alloys. However, this is not the only contribution to the configurational free energy of solid solutions; Cook and de Fontaine (25) have shown that an elastic free energy contribution must also be considered as a consequence of the different atomic sizes of A and B. Furthermore, Kajitani and Cook (16) have shown that the possibility of an overall change in crystal shape on ordering must be taken into account.

We have added this elastic energy contribution to the configurational free energy, calculated for the different lattices with the IQC approximation.

Ordering of β brass has been extensively studied, as a typical example of second-order ordering transition. Long range order dependence on the temperature has recently been measured by X-ray diffraction (26) and neutron diffraction (27), obtaining results in good agreement.

We calculated η from $\dfrac{\partial (F_C/R\,T_C)}{\partial \eta} = 0$, where F_C is the configurational free energy of the Ising lattice plus the elastic contribution suggested by Kajitani and Cook $\Delta F_{el}/RT_C = -c\,\eta^4$, with $c = .0299$.The results are presented in Fig. 3 and show the same type of approximation as obtained by Kajitani and Cook, from the Monte Carlo results of Flinn and McManus (28), for the same rigid Ising model, corrected, introducing the elastic energy term.

We have calculated the configuration specific heat for this ordering transition from the same configurational free energy. The results are presented in Fig. 4 and compared with measurements from thermal experiments. The results show a close agreement between the experimental values and the calculated ones for the disordered system. At $\tau < 1$ there is a marked discrepancy, which can be related to the difference shown in Fig. 3 for the long range order. It seems that the influence of the elastic energy term is not only an energetic influence, but there is an effect on the entropic term, which could be taken into account

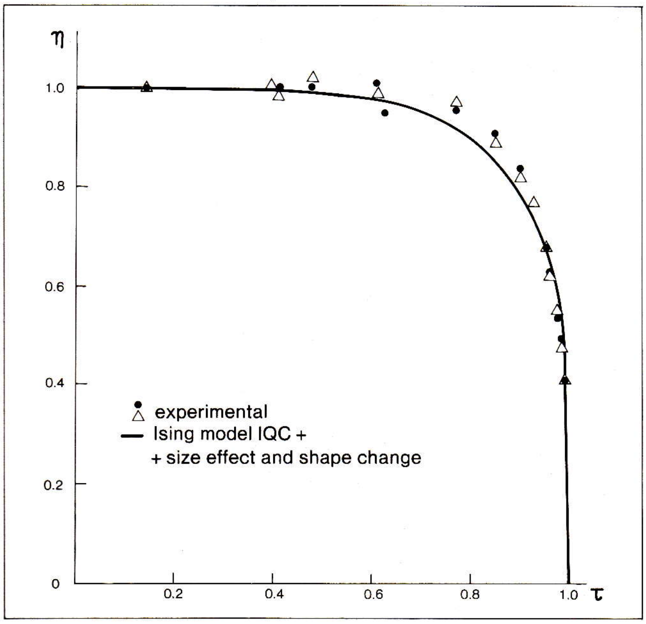


Fig. 3 - Order parameter η for β-brass, measured by neutron diffraction (27) and, calculated from the configurational free energy for the BCC Ising lattice plus an elastic term for size effect + shape change.

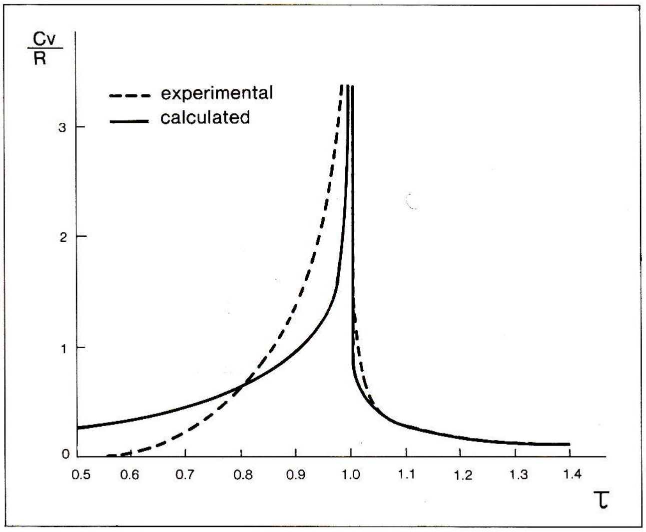


Fig. 4 - Configurational specific heat for the ordering reaction of β-brass, from thermal measurements (29) and calculated from the Ising model with IQC approximation with addition of an elastic energy (16).

varying the τ functions for the temperature change at each renormalization step.

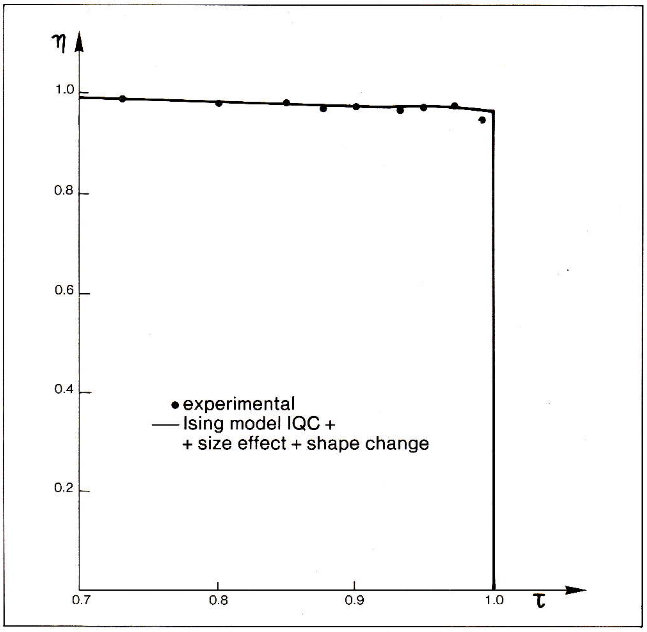


Fig. 5 - Order parameter η for Cu-Au alloy, measured by X-ray diffraction (31) and calculated from the configurational free energy for the FCC Ising lattice plus an elastic term for shape change (16).

We have also studied the ordering transformation in CuAu. This transition is first order with a finite latent heat at T_C. The addition of the elastic free energy term, with c = .251 according to Kajitani and Cook (16), makes the transition of the first order type, also in agreement with earlier results of Tachiki and Teramoto (30). The condition that the c value must satisfy, in order that the transition changes from higher order to first order, is obtained from the third derivate of the configurational free energy with respect to η, and is given by:

$$c > \frac{z}{16\beta_C} - \frac{z}{48\beta_C^3} + \frac{z'}{12n\beta_C^2} - \frac{z'}{24n\beta_C^4} - \frac{z-2}{24} \quad (16)$$

Calculation of η at T_C gives $\eta_C = 0.9665$ for CuAu, and this value is very close to the 0.97 value obtained by Roberts (31) by X-ray diffraction measurements. The dependence of η on τ is reported in Fig. 5 and it is much closer to the experimental values than that obtained by the CV method (32).

Magnetic ordering effect on phase stability of alloys

Magnetic ordering can influence alloys' phase stability, and as a consequence the phase equilibria in ferromagnetic alloys. This was shown a long time ago by Zener (33) for the Fe-Cr system; by Hillert, Wada and Wada (34) for Mn partition between austenite and ferrite or cementite; by Harvig, Kirchner and Hillert (35) for Cu solubility in ferrite; recently by Nishizawa, Hasebe and Ko (36) for Be, P, Zn solubility in ferrite and for Al, Ti, Zn solubility in Co; and by Nishizawa et al. (37) for the influence of magnetic ordering on the behaviour of miscibility gaps in ternary systems.

Sklarz and Wayman (37) have pointed out that the ferromagnetic transition also has an effect on the segregation of elements at the grain boundaries of iron alloys.
The magnetic free energy term is obtained empirically (17), integrating the magnetic specific heat, whose dependence on τ is given through a simple fitting expression.
Also, in this case an IQC approximation can be introduced. In fact, it is possible to describe the Heisenberg model, in which the spins interaction is isotropic, with reference, in this case, also to quasichemical equilibria.
Elliott (39) has shown that this is possible if we substitute in the expression of K_{eq} the relationship:

$$K_{eq} = \left(\exp \frac{\Delta\varepsilon}{K_B T} + 1\right)^2 \Big/ 4 \qquad (17)$$

However, in this case also, we ignore the interaction of the fixed point after each averaging, shown to be fundamental to a description of the system at T_C by the spins-block technique. If we introduce this second term, always doubling the interaction energy $\Delta\varepsilon$, we obtain an expression of the free energy which, differentiated twice with respect to η, gives at T_C and $\eta = 0$, the analogy of Eq. (14) for Heisenberg systems:

$$\frac{z}{2}\left(\frac{1}{\beta_C^2} + 1\right) + \frac{z'}{n} \cdot \frac{1}{\beta_C^4} + 2 - z = 0 \qquad (18)$$

The critical parameters obtained with Eq. (18) are reported in Table 3 for 3D Heisenberg models, together with the results of other methods (41) and of the best known values, obtained from high-temperature expansions (40). In this case, it is also possible to obtain very good values of the critical thermodynamic quantities $F_{cr}/N_s K_B T_C$ and $U_{cr}/N_s K_B T_C$, with an adequate choice of the parameters: $K_{ab} = 1$ and K_a at $\tau = 1$, as reported in Table 4.
In this way, it becomes possible to make a theoretical evaluation of the magnetic free energy contribution for ferromagnetic alloys.

TABLE 3 - Critical parameter $\frac{-\Delta\varepsilon}{2K_B T_C}$ for 3D Heisenberg (s = 1/2) models

		APPROXIMATION						
Lattice	z	mean field 2/z	Oguchi[41]	Constant coupling[41]	Bethe Peierls Weiss[41]	z′/n	IQC $-\Delta\varepsilon/2K_B T_C$	Exact or best known[40]
SC	6	.3333	.34965	.54915	.54025	1	.5974	.5952
BCC	8	.2500	.25707	.34674	.34483	1	.3998	.3968
FCC	12	.1667	—	.20276	—	1	.2508	.2488

TABLE 4 - Critical values of thermodynamic quantities for 3D Heisenberg (s = 1/2) models

Lattice	$-F_{cr}/N_s K_B T_C$		$-U_{cr}/N_s K_B T_C$	
	IQC (K_{ab} = 1)	Best Known[40]	IQC	Best Known[40]
SC	1.009	1.031	.590	.598
BCC	.926	.912	.465	.459
FCC	.895	.886	.433	.433

REFERENCES

(1) De Fontaine, D. Configurational thermodynamics of solid solutions. In H. Ehrenreich, F. Seitz and D. Turnbull (Eds). ***Solid state physics.*** *Academic, N. Y., 1979, Vol. 34, pp. 73-274.*

(2) De Fontaine, D. and R. Kikuchi. Fundamental calculations of coherent phase diagrams. In ***Applications of phase diagrams in metallurgy and ceramics,*** *NBS Publication SP-496, Gaithersburg Md., 1978, pp. 999-1026.*

(3) De Fontaine, D. Spinodal and equilibrium reactions. ***Physica*** *(Utrecht)* ***103*** *(1981), 57-66.*

(4) De Fontaine, D. Coherent phase diagrams in the cluster variation approximation. ***Mat. Res. Soc. Symp. Proc. 19*** *(1983), 149-162.*

(5) Kikuchi, R. A theory of cooperative phenomena. ***Phys. Rev. 81*** *(1951), 988-1003.*

(6) Onsager, L. Crystal Statistics. I A 2D model with an order-disorder transition. ***Phys. Rev. 65*** *(1944), 177-149.*

(7) Wilson, K. G. Problems in physics with many scales of length. ***Sci. Am. 241*** *(1979) (8), 158-179.*

(8) Wilson, K. G. Renormalization group and critical phenomena. ***Rev. Mod. Phys. 55*** *(1983), 583-598.*

(9) Wilson, K. G. Renormalization group: critical phenomena and the Kondo problem. ***Rev. Mod. Phys. 47*** *(1975), 773-840.*

(10) Kadanoff, L. P. and A. Houghton. Numerical evaluation of the critical properties of the 2D Ising model. ***Phys. Rev. B 11*** *(1975), 377-386.*

(11) Niemeijer, Th. and J.M.J. Van Leeuwen. Renormalization theory for Ising-like spin systems. In C. Domb and M.S. Green (Eds.), ***Phase transitions and critical phenomena.*** *Academic, London, 1976, Vol. 6, pp. 425-505.*

(12) Swendsen, R.H. Monte Carlo renormalization-group studies of critical phenomena. ***J. Appl. Phys. 53*** *(1982), 1920-4.*

(13) Swendsen, R.H. Monte Carlo renormalization-group studies of 2 D models. ***Surf. Sci. 125*** *(1983), 104-115.*

(14) Cavallotti, P.L. An improvement of the QC approximation for 2D lattice models. ***Surf. Sci. 83*** *(1979), 325-334.*

(15) Cavallotti, P.L. Thermodynamic models of interstitial iron-rich solid solutions. ***Gazz. Chim. It. 113*** *(1983), 145-251.*

(16) Kajitani, T. and H.E. Cook. On the influence of strain energy on order-disorder transformations. ***Acta Metall. 26*** *(1978), 1371-1378.*

(17) Inden, G. The role of magnetism in the calculation of phase diagrams. ***Physica*** *(Utrecht)* ***103 B*** *(1981), 82-100.*

(18) Burley, D.M. Closed form approximations for lattice systems. In C. Domb and M.S. Green (Eds.), ***Phase transition and critical phenomena.*** *Academic, London, 1972., Vol. 2, pp. 329-374.*

(19) Sanchez, J.M. and D. de Fontaine. Ordering in fcc lattices with first- and second-neighbor interactions. ***Phys. Rev. B 21*** *(1980), 216-228.*

(20) Gratias D., J.M. Sanchez and D. de Fontaine. Application of group theory to the calculation of the configurational entropy in the cluster variation method. ***Physica*** *(Utrecht)* ***113 A*** *(1982), 315-337.*

(21) Domb, C. Ising model. In C. Domb and M.S. Green (Eds.), ***Phase transitions and critical phenomena.*** *Academic, London, 1974, Vol. 3. pp. 357-484.*

(22) Syozi, I. Transformation of Ising models. In C. Domb and M.S. Green (Eds.), ***Phase transitions and critical phenomena.*** *Academic, London, 1972, Vol. 1, pp. 269-329.*

(23) Domb, C. On the theory of cooperative phenomena in crystal. ***Adv. Phys. 9*** *(1960), 149-244, 245-261.*

(24) De Jongh, L.J. and A.R. Miedema. Experiments on simple magnetic model systems. ***Adv. Phys. 23*** *(1974), 1-260.*

(25) Cook, H.E. and D. De Fontaine. On the elastic free energy of solid solutions. ***Acta Metall. 17*** *(1969), 915-924;* ***19*** *(1971), 607-616.*

(26) Chipman, B. and C.B. Walker. Long-range order in β-brass. ***Phys. Rev. Lett. 26*** *(1971), 233-6.*

(27) Rathmann, O. and J. Als-Nielsen. Long-range order in β-brass studied by neutron diffraction. ***Phys. Rev. B 9*** *(1974), 3921-6.*

(28) Flinn, P.A. and G.M. McManus. Monte Carlo Calculation of the order-disorder transformation in the body-centered cubic lattice. ***Phys. Rev. 124*** *(1961), 54-59.*

(29) Hultgren, R., P.D. Desai, D.T. Hawkins, M. Gleiser and K.K. Kelley. ***Selected values of the thermodynamic properties of binary alloys.*** *ASM, Metals Park OH, 1973, pp. 712-723.*

(30) Tachiki, M. and K. Teramoto. Long period superlattice in the Cu-Au alloy. ***J. Phys. Chem. Sol. 27*** *(1966), 335-348.*

(31) Roberts, B.W. X-ray measurements of order in Cu-Au. ***Acta Metall. 2*** *(1954), 597-603.*

(32) Kikuchi, R. and H. Sato. Caracteristics of superlattice formation in alloys of FCC structure. ***Acta Metall. 22*** *(1974), 1099-1112.*

(33) Zener, C. Impact of magnetism upon metallurgy. ***Trans. AIME 203*** *(1955), 619-630.*

(34) Hillert, M., T. Wada and H. Wada. The α-γ equilibrium in Fe-Mn, Fe-Mo, Fe-Ni, Fe-Sb, Fe-Sn and Fe-W systems. ***J. Iron Steel Inst. 205*** *(1967), 539-546.*

(35) Harvig, H., G. Kirchner and M. Hillert. On the ferrite-austenite equilibrium in the Fe-Cu system. ***Metall. Trans. 3*** *(1972), 329-332.*

(36) Nishizawa, T., M. Hasebe and M. Ko. Thermodynamic analysis of solubility and miscibility gap in ferromagnetic α-iron alloys. ***Acta Metall. 27*** *(1978), 817-828.*

(37) Nishizawa, T., S.M. Hao, M. Hasebe and K. Ishida. Thermodynamic analysis of miscibility gap due to ordering in ternary systems. ***Acta Metall. 31*** *(1938), 1403-1416.*

(38) Sklarz, K.E. and C. Wayman. The effect of ferromagnetism on intergranular segregation in iron. ***Acta Metall. 29*** *(1981), 341-9.*

(39) Elliott, R.J. Some properties of concentrated and diluted Heisenberg magnets with general spin. ***J. Phys. Chem. Sol. 16*** *(1960), 165-8.*

(40) Rushbrooke, G.S., G.A. Baker jr., and P.J. Wood. Heisenberg model. In C. Domb and M.S. Green (Eds.), ***Phase transition and critical phenomena.*** *Academic, London, 1974, Vol. 3, pp. 245-356.*

(41) Smart, J.S. ***Effective field theories of magnetism.*** *Saunders, Philadelphia, 1966.*