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# Critical Behavior of Solid Solutions in the Order-Disorder Transformation

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A discussion of critical phenomena in the order-disorder transformation from the standpoint of the theories of Bethe and Kirkwood is presented. A comparison of the two theories is undertaken, and the best values of the transition temperatures and heat capacity anomalies,  $\Delta C_v$ , for the simple cubic and body-centered cubic lattices are tabulated. The influence of anomalies in the coefficients of expansion and compressibility on the anomaly in the heat capacity  $C_p$  is investigated.

THE theory of order and disorder in solid solutions originally formulated by Bragg and Williams<sup>1</sup> has been elaborated on the basis of a more detailed crystalline model by Bethe<sup>2</sup> and by Kirkwood.<sup>3</sup> It is the purpose of the present article to compare the methods of Bethe and Kirkwood particularly in the results they give at the order-disorder transition temperature. For this purpose, a new formulation of the Bethe method is employed, which has the advantage of yielding closed expressions for the thermodynamic functions of the crystal. The new formulation will be described in detail in a later article. The results of the two methods were previously believed to differ significantly only in the magnitude of the heat capacity anomaly at the critical temperature.<sup>4</sup> We shall show that this discrepancy is removed by a more precise use of the method of moments at the critical temperature. The anomaly in  $C_v$  for a body-centered cubic crystal remains about one-fourth the observed anomaly in  $C_p$  for  $\beta$ -brass as measured by Sykes and Moser. Eisenschitz<sup>5</sup> has suggested that this difference is due to a real anomaly in  $C_p - C_v$  associated with anomalies in the coefficients of expansion and compressibility of the crystal. We shall discuss the possibilities of this view.

We take as our model a binary solid solution consisting of  $N_0$  atoms of type 1 and  $N_0$  atoms of type 2, the crystal being built up of two interpenetrating simple lattices  $A$  and  $B$  of  $N_0$  sites each, occupied by a total number of atoms

$N$ , equal to  $2N_0$ . We denote by  $N_1^A$  and  $N_1^B$  the numbers of atoms of type 1 on the respective lattices and by  $x_1^A$  and  $x_1^B$  the atom fractions of component 1 on the two lattices. The long range order of the crystal is defined in the usual manner.

$$s = x_1^A - x_1^B. \quad (1)$$

A configuration of the crystal may be uniquely specified by a set of numbers  $\xi_1, \dots, \xi_{N_0}, \eta_1, \dots, \eta_{N_0}$  where  $\xi_a$  states the number of atoms of type 1 in site  $a$  of lattice  $A$  and  $\eta_b$  the number of atoms of type 1 in site  $b$  of lattice  $B$ . Each variable  $\xi_a$  and  $\eta_b$  has a domain of two values, zero and unity. The configurational partition function of the crystal for a fixed degree of long range order may be written as follows,

$$f = \sum_{\substack{\xi_1, \dots, \xi_{N_0}=0 \\ \sum \xi_a = N_1^A}}^1 \sum_{\substack{\eta_1, \dots, \eta_{N_0}=0 \\ \sum \eta_b = N_1^B}}^1 \exp(-2\alpha \sum_{a,b=1}^{N_0} \lambda_{ab} \xi_a \eta_b), \quad (2)$$

$$N_1^A = (N/4)(1+s), \quad N_1^B = (N/4)(1-s),$$

$$\alpha = V/kT, \quad V = (V_{11} + V_{22})/2 - V_{12},$$

where  $V_{11}$ ,  $V_{22}$ , and  $V_{12}$  are the mutual potential energies of the indicated types of nearest neighbor pair and the zero of energy is that of the completely ordered crystal at absolute zero. The neighbor matrix  $\lambda_{ab}$  is characterized by the fact that  $\lambda_{ab}$  is unity if sites  $a$  and  $b$  are nearest neighbors and zero otherwise. Evidently we may write

$$\sum_{a=1}^{N_0} \lambda_{ab} = \sum_{b=1}^{N_0} \lambda_{ab} = z, \quad (3)$$

where  $z$  is the number of nearest neighbors of any site. If it is desired to take account of interactions of higher order than those of nearest

<sup>1</sup> Bragg and Williams, Proc. Roy. Soc. London **A145**, 699 (1934); **151**, 540 (1935); **152**, 231 (1935).

<sup>2</sup> Bethe, Proc. Roy. Soc. London **A150**, 552 (1935).

<sup>3</sup> Kirkwood, J. Chem. Phys. **6**, 70 (1938).

<sup>4</sup> See Nix and Shockley, Rev. Mod. Phys. **10**, 1 (1938).

<sup>5</sup> Eisenschitz, Proc. Roy. Soc. London **168A**, 546 (1938).

neighbors, the generalization of the neighbor matrix is obvious. For simplicity we shall assume only nearest neighbor interaction here. Since the partition function  $f$  reduces to the total number of configurations consistent with the specified degree of long range order, for vanishing  $\alpha$ , we may define a function  $G(\alpha, s^2)$ , vanishing for  $\alpha$  equal to zero, by the relation

$$f = \left(\frac{1+s}{2}\right)^{-N(1+s)/2} \left(\frac{1-s}{2}\right)^{-N(1-s)/2} e^{NzG(\alpha, s^2)}, \quad (4)$$

where the first factor is equal to the total number of configurations for fixed  $s$ . From the form of the partition function (2), it is obvious that  $G$  is an even function of  $s$  and therefore a single valued function of  $s^2$ . The configurational free energy, equal to  $-kT \log f$  may be expressed as follows,

$$-F/NkT = -\left(\frac{1+s}{2}\right) \log \left(\frac{1+s}{2}\right) - \left(\frac{1-s}{2}\right) \log \left(\frac{1-s}{2}\right) + zG(\alpha, s^2). \quad (5)$$

Determination of the equilibrium degree of long range order by minimization of the free energy at constant  $\alpha$  leads to the condition

$$\log \frac{1+s}{1-s} = 4zs \frac{\partial G}{\partial (s^2)}. \quad (6)$$

Assuming  $G(\alpha, s^2)$  to be an analytic function of  $s^2$ , we may write

$$G(\alpha, s^2) = G_0(\alpha) + s^2 G_1(\alpha) + s^4 G_2(\alpha) + \dots \quad (7)$$

For a phase change of the second kind, Eq. (6) has no real solutions other than  $s=0$  for values of  $\alpha$  less than a critical value satisfying the equation,

$$2zG_1(\alpha_c) = 1 \quad (8)$$

with a critical temperature  $T_c$  equal to  $V/k\alpha_c$ . For values of  $\alpha$  greater than  $\alpha_c$ , there exist two nonvanishing real solutions,  $\pm s$ , of minimum free energy, yielding a unique equilibrium value of  $s^2$ . The approximate forms of  $G(\alpha, s^2)$  which we shall discuss satisfy these conditions, although it has not been rigorously proved that the exact form does.

The heat capacities  $C_v^+$  and  $C_v^-$  just above and just below the critical temperature have the form

$$\frac{C_v^- - C_v^+}{Nk} = \frac{6[z\alpha_c dG_1/d\alpha]^2}{1 - 12zG_2(\alpha_c)}, \quad (9)$$

$$C_v^+/Nk = z\alpha_c^2 d^2 G_0/d\alpha^2.$$

For the calculation of the discontinuity in the heat capacity at the critical temperature a knowledge of  $G_1(\alpha)$  and  $G_2(\alpha)$  is sufficient.<sup>5</sup> However, since  $\Delta C_v$  is extremely sensitive to the value of  $G_2(\alpha_c)$ , the latter must be known with accuracy.

We may now discuss the forms of  $G(\alpha, s^2)$  provided by the several theories of order and disorder. In a later paper, we shall find for the Bethe theory

$$G(\alpha, s^2) = -\left(\frac{1+s}{4}\right) \log \left[\frac{2(y+s)}{(y+1)(1+s)}\right] - \left(\frac{1-s}{4}\right) \log \left[\frac{2(y-s)}{(y+1)(1-s)}\right], \quad (10)$$

$$y = [s^2 + (1-s^2)e^{2\alpha}]^{\frac{1}{2}}.$$

Expansion in powers of  $s^2$  yields

$$G_0(\alpha) = \left(\frac{1}{2}\right) \log \left(\frac{1+e^{-\alpha}}{2}\right); \quad G_1(\alpha) = \frac{1-e^{-\alpha}}{4} \quad (11)$$

$$G_2(\alpha) = \frac{1}{24} \left[1 - \frac{3}{2}e^{-\alpha} + \frac{1}{2}e^{-3\alpha}\right].$$

From Eqs. (8) and (11), one obtains for the critical value of  $\alpha$

$$\alpha_c = \log [z/(z-2)]. \quad (12)$$

The discontinuity of the heat capacity at the critical temperature follows from Eqs. (9), (11), and (12).

$$\frac{\Delta C_v}{Nk} = \frac{3z^2}{8} \frac{z-1}{z-2} \left[ \log \left( \frac{z}{z-2} \right) \right]^2. \quad (13)$$

For a simple cubic lattice,  $z=6$ ,  $\Delta C_v/Nk$  has the value 1.78 and for a body-centered lattice,  $z=8$ , the value 1.70. The Bragg and Williams value is 1.50.

<sup>5</sup> See Borelius, Ann. d. Physik 20, 57 (1934).

TABLE I.

APPROXIMATION	$z=6, \zeta=3$		$z=8, \zeta=11$	
	$kT_c/V$ *	$\Delta C_v/Nk$	$kT_c/V$	$\Delta C_v/Nk$
0	3.00	1.50	4.00	1.50
1	2.57	1.75	3.55	1.69
2	2.49	1.78	3.49	1.70
3	2.44	1.86	3.41	1.81
$B_1$	2.47	1.78	3.48	1.70
$B_2$	2.37	1.94		

In the Kirkwood theory,\* the exact configurational partition function is expanded in powers of  $\alpha$ , leading to the following expression for  $G(\alpha, s^2)$

$$G(\alpha, s^2) = \sum_{n=1}^{\infty} (-1)^n \alpha^n \lambda_n / (Nz)(n!), \quad (14)$$

where the Thiele semi-invariants  $\lambda_n$  are related to the moments  $M_n$  of the sum

$$2 \sum_{a, b=1}^{N_0} \lambda_{ab} \eta_b \xi_a$$

in the following manner

$$\sum_{m=1}^n \binom{n-1}{m-1} \lambda_m M_{n-m} = M_n; \quad n=1, 2, \dots \quad (15)$$

The moment  $M_n$  is an *a priori* average of the sum,

$$\left( 2 \sum_{a, b} \lambda_{ab} \xi_a \eta_b \right)^n$$

over all crystalline configurations of fixed  $s$ . The method of calculation has been described by Kirkwood.<sup>3</sup> The first four moments have been calculated and are presented below

$$\begin{aligned} \lambda_1/Nz &= (1-s^2)/4, \\ \lambda_2/Nz &= (1-s^2)^2/8, \\ \lambda_3/Nz &= -s^2(1-s^2)^2/4, \\ \lambda_4/Nz &= (1-s^2)^2[2(1-3s^2)^2 + 3\zeta(1-s^2)^2]/16, \end{aligned} \quad (16)$$

$$\zeta = (1/z) \left[ \sum_{a'=1 \neq a}^{N_0} z_{aa'}^2 - z^2 \right],$$

where  $z_{a'a}$  is the number of common neighbors

\* For convenience, certain changes in notation from reference 3 have been made in the present article. The present  $\alpha$  differs from the  $\alpha$  of reference 3 by a factor  $2/Z$ .

on lattice  $B$  of the pair of sites  $a'$  and  $a$  on lattice  $A$ . For a simple cubic lattice  $\zeta$  is equal to 3 and for a body-centered lattice 11. We remark that characteristics of the crystal structure other than the coordination number  $z$  begin to appear at the fourth moment. Expansion of the right-hand side of Eq. (10) in powers of  $\alpha$  shows that the  $G(\alpha, s^2)$  of the Bethe theory is accurate to the third moment but is incorrect in the fourth moment.

For the calculation of the discontinuity of the heat capacity at the critical temperature, we expand the  $G(\alpha, s^2)$  of Eqs. (14) and (16) in powers of  $s^2$  with the result,

$$G_0(\alpha) = -\alpha/4 + \alpha^2/16 + (2+3\zeta)\alpha^4/384 + \dots$$

$$G_1(\alpha) = \alpha/4 - \alpha^2/8 + \alpha^3/24 - (4+3\zeta)\alpha^4/96 + \dots \quad (17)$$

$$G_2(\alpha) = \alpha^2/16 - \alpha^3/12 + (22+9\zeta)\alpha^4/192 + \dots$$

With the aid of Eq. (8) and the expansion (17) for  $G_1(\alpha)$ , the critical value of  $\alpha$  may be expanded in powers of  $1/z$ .

$$\alpha_c = (2/z)[1 + 1/z + 4/3z^2 + (3+\zeta)/z^3 + \dots]. \quad (18)$$

Use of the series (17) and (18) in Eq. (9) and expansion in powers of  $1/z$  yields for the heat capacity discontinuity

$$\Delta C_v/Nk = (3/2)[1 + 1/z + 2/3z^2 + 3(1+\zeta)/z^3 + \dots]. \quad (19)$$

To obtain terms of order  $z^{-4}$  in the expansions (18) and (19), the fifth moment is required. The critical temperatures and the heat capacity anomalies computed by Eqs. (18) and (19) and by Bethe's first ( $B_1$ ) and second ( $B_2$ ) approximations are presented in Table I, for the simple cubic and the body-centered cubic lattices. The Bethe first approximation, valid to the third moment in the energy, does not differ significantly from the Kirkwood second approximation in which terms including the third moment are retained. The Bethe second approximation deviates somewhat from the Kirkwood third approximation in which the fourth moment is retained. It has not been verified whether the Bethe second approximation, which is extremely tedious to analyze, is valid to the fourth moment or not. The values of  $kT_c/V$  and  $\Delta C_v/Nk$ , presented in

Table II, appear to represent the best approximations obtainable from the assembled calculations. In Kirkwood's original first approximation, based on the second moment of energy, the values 2.37 and 4.1 were obtained for  $kT_c/V$  and  $\Delta C_v/Nk$ . These values are obtained if the linear and quadratic terms of the expansions (17) are substituted into Eqs. (8) and (9) without the subsequent expansion in powers of  $1/z$ . Due to the extreme sensitivity of the right-hand side of Eq. (9) to the value of  $G_2(\alpha_c)$ , this procedure leads to the abnormally high value 4.1 for the heat capacity anomaly. The expansion in powers of  $1/z$  employed here avoids this difficulty. Exact values of the coefficients in the series (18) and (19) to terms of degree one less than the order of the last moment retained are provided by the method.

Eisenschitz<sup>5</sup> has raised the question of the reality of the heat capacity anomaly at the transition temperature. It is of course true that for a finite lattice, the partition function is an analytic function of the reciprocal temperature and that on the basis of statistical mechanics the mean energy and heat capacity are, strictly speaking, continuous functions of the temperature. However, as Eisenschitz has shown, the derivative  $-dC_v/dT$  is of the order  $N^{1/2}$  at the critical temperature, where  $N$  is the total number of atoms. In any macro-crystal  $N$  is so large that a physical discontinuity would be observed, since the mathematical continuity would be obscured not only by the practical limit of precision of measurement but also by the theoretical limit of precision imposed by the fluctuation theory of statistical mechanics on the measurement of any thermodynamic function. However, Eisenschitz goes a step further, maintaining that the effective thermodynamic unit of a crystal is a molecular domain composed of approximately  $10^4$  atoms, small enough to reveal the mathematical continuity of  $C_v$ . His argument for such an assumption does not seem adequate to us, nor does the experimental evidence for a

finite slope in the heat capacity curve of  $\beta$ -brass at the transition point seem conclusive enough to give empirical justification for the assumption. Eisenschitz points out that exactly at the critical temperature, it is no longer correct to approximate the complete partition function

$$\sum_{s=-1}^{+1} f(s)$$

by its maximum term, as we have done. On the basis of the Bragg and Williams approximation (our zero approximation) he computes a value 0.6 for  $C_v/R$ . Because of an error in his transformation of the sum over  $s$  to an integral, this value should properly be 0.8. For an infinite lattice, this value has no significance since  $C_v$  is not a single valued function of the temperature at  $T_c$ . We also believe that it has no physical significance for a finite lattice of macroscopic dimensions, since it can easily be shown that at a temperature satisfying the relation  $|T - T_c|/T_c \geq N^{-1/2}$  the error in approximating the partition function,

$$\sum_{s=-1}^{+1} f(s),$$

by its maximum term is of the order  $N^{-1/2}$ . Unless the Eisenschitz domains are admitted, these points become trivial. It is of course true that domains of the type encountered in ferromagnetism enter into the formation of superlattices, but they are of essentially macroscopic dimensions and contain a sufficient number of atoms to give the observed physical discontinuities. Were the independent domains as small as Eisenschitz maintains, sharp superlattice lines in the x-ray reflections from an ordered crystal would not be observed.

There is a large discrepancy between the observed anomaly in  $C_p$  as given by the data of Sykes and Moser for  $\beta$ -brass and the calculated anomaly in  $C_v$  for a body-centered cubic lattice. The discrepancy is doubtless due in part to deficiencies in the theory, such as the neglect of the coupling between lattice vibrations and configuration and the simplifying assumptions concerning the atomic interactions, but seems far too large to account for on this basis alone. From thermodynamics we know that

TABLE II.

LATTICE	$kT_c/V$	$\Delta C_v/Nk$
Simple Cubic	2.4	1.9
Body-Centered Cubic	3.4	1.8

$$C_p - C_v = \beta^2 v T / \kappa \quad (20)$$

$$\beta = \frac{1}{v} \left( \frac{dv}{dT} \right)_p; \quad \kappa = -\frac{1}{v} \left( \frac{dv}{dp} \right)_T,$$

where  $\beta$  and  $\kappa$  are the coefficients of expansion and compressibility. Eisenschitz has made the important suggestion that there is a large anomaly in  $C_p - C_v$  at the critical temperature due to the dependence of the interaction energy of neighbors,  $V$ , on the expansion of the lattice. He has undertaken the calculation of  $C_p$  in zero approximation without explicit use of Eq. (20), using the partition function at constant pressure. Reasonable assumptions concerning the dependence of  $V$  on the volume of the crystal lead to an anomaly in  $C_p$  for  $\beta$ -brass of the experimental magnitude. Eisenschitz's essential results can perhaps be obtained in a more simple fashion by the use of thermodynamics and our partition function (4). From Eq. (5), we easily obtain the following equation of state,

$$p = p' + \gamma \bar{E} / v \quad (21)$$

$$\gamma = -(v/V)(dV/dv)$$

where  $\bar{E}$  is the mean configurational energy,  $v$  is the volume and  $p'$  is the pressure due to non-configurational contributions to the free energy, and  $p$  is the total pressure. We remark that  $p$ ,  $\bar{E}$ , and  $p'$  as well as the derivatives of  $p'$  must be continuous functions of the temperature. Moreover  $\bar{E}$  depends explicitly only on  $\alpha$  and  $s^2$  and the equilibrium value of  $s^2$  is a function of  $\alpha$  alone. Therefore  $\bar{E}$  depends implicitly on the volume only through the variable  $\alpha$ . Using these facts, we may compute the anomalies in the coefficients of expansion and compressibility from the equation of state,

$$\Delta\beta = (\gamma_0 \kappa_+ \Delta C_v / v) \frac{1 + \gamma_0 \beta_+ T_c}{1 - \gamma_0^2 \kappa_+ T_c \Delta C_v / v}, \quad (22)$$

$$\Delta\kappa = \frac{\gamma_0^2 \kappa_+^2 T_c \Delta C_v / v}{1 - \gamma_0^2 \kappa_+ T_c \Delta C_v / v},$$

where  $\beta_+$  and  $\kappa_+$  are the coefficients of expansion and compressibility just above the critical temperature and  $\gamma_0$  is the value of  $\gamma$  at the critical temperature. In a similar manner, the anomaly  $\Delta C_p$  may be calculated from Eqs. (20) and (21)

$$\Delta C_p = \frac{(1 + \gamma_0 \beta_+ T_c)^2}{1 - \gamma_0^2 \kappa_+ T_c \Delta C_v / v} \Delta C_v. \quad (23)$$

It is interesting to apply Eq. (23) to the case of  $\beta$ -brass. The critical temperature is 740°K and  $\Delta C_p / R$  is approximately 8 according to the measurements of Sykes and Moser. Approximating  $\beta_+$  and  $\kappa_+$  by the mean coefficients of copper and zinc and using the theoretical value 1.8 for  $\Delta C_v / R$ , we find that the experimental value of  $\Delta C_p$  corresponds to a value of  $\gamma_0$  of about 2.3. While no objection can be made to the magnitude of this value, it is difficult to obtain a good theoretical check on  $\gamma$ . Eisenschitz represents  $\gamma$  as a function of the volume by a two-constant equation, which we shall not discuss here.

While Eisenschitz's proposal doubtless disposes of an important part of the discrepancy between theory and experiment, the necessity of introducing empirical constants in comparison of theory and experiment may well obscure real discrepancies of smaller magnitude. Since  $\Delta C_v / R$  is the only quantity predicted by the theory involving no parameters to be determined from experiment, it would be extremely desirable to have experimental values of this quantity itself. Measurements of the anomalies of the coefficients of expansion and compressibility as well as of  $C_p$  would provide the necessary information for an adequate test of the theory. Data<sup>6</sup> at present available are inadequate for a quantitative test.

<sup>6</sup> Grube, Schönmann, Vaupel and Weber, *Zeit. f. Anorg. u. Allgem. Chemie* **201**, 41 (1931).  
Matsuda, *Sci. Rep. Tohoku Imp. Univ.* **11**, 223 (1922).