STATISTICAL THEORY OF SUPERLATTICES OF THE TYPE AB IN A QUADRATIC AND A SIMPLE CUBIC LATTICE*

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(Received September 22, 1948)

ABSTRACT

Wang's generalization of Bethe's theory of superlattices is applied to the cases of quadratic and simple cubic lattice. Only neighbour interaction is taken into consideration. All the calculations are carried out to the second approximation.

The variation of the critical temperature with composition is calculated. The degree of order, the energy and the specific heat are calculated for the special case of equal numbers of A and B atoms at various temperatures. It is found that the results differ very little from those obtained by Bethe in the second approximation. In the case of the simple cubic lattice the discontinuity of the specific heat is found to be only slightly larger than that obtained by Bethe.

1. INTRODUCTION

The problem of superlattices in alloys was first studied by Bragg and Williams. They attempted to connect the physical properties of the alloy at a given temperature with the degree of order in the distribution of atoms in the alloy as a whole by assuming that there is an average energy in maintaining the order. Later Bethe gave an improved theory in which the order of the alloy is regarded as set up by the interaction between neighbouring atoms. In Bethe's method the equilibrium properties of the alloy are determined by an indirect method without evaluating the partition function. Thus this method in its original form is not applicable to problems in which a knowledge of the partition function is required.

To mend this defect Professor J. S. Wang[1] has given a method of obtaining an approximate expression for the partition function in Bethe's theory. In this method the partition function is obtained by integrating the configurational energy of the alloy obtained from a generalization of

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* Based on an M. Sc. dissertation, National Tsing Hua University, 1948.

[1] J. S. Wang, *Phys. Rev.* **67** (1945), 98-106.

Bethe's theory. The equilibrium values are determined by means of the usual formulae in statistical mechanics in terms of the partition function.

In the present paper the author applies Wang's general theory to the special cases of quadratic and simple cubic lattices, working to the second approximation. For simplicity only interactions between nearest neighbours are taken into account. Special emphasis is laid on the case of alloy with equal numbers of A and B atoms so that a direct comparison with Bethe's original results can be made.

2. GENERAL FORMULAE

In the present problem of superlattices in a binary alloy consisting of two kinds of atoms A and B in a quadratic and simple cubic lattice the lattice points are divided equally into two classes α and β, each class having $\frac{1}{2}N$ sites, where N is the total number of sites. Let θ_α and θ_β be the fractions of α and β sites occupied by A atoms. Then if $N\theta$ is the total number of A atoms, we have

$$\theta_\alpha + \theta_\beta = 2\,\theta. \tag{1}$$

The degree of order, s, is defined by

$$s = \theta_\alpha - \theta_\beta. \tag{2}$$

Our problem is to determine the equilibrium values of s and of the energy by the method of statistical mechanics. The usual procedure in statistical mechanics is to construct the partition function and derive all equilibrium properties from it. Unfortunately this procedure does not work when the atoms have strong interactions with one another, and approximate methods have to be used.

In Wang's generalization of Bethe's theory an approximate expression for the energy is obtained from a local grand partition function, which is constructed for a group of a few sites around a given central site. The partition function is then obtained by integrating the energy expression thus obtained and the equilibrium value of s is derived from the partition function by the usual formula. Two ways of obtaining the energy expression have been given, of which one is particularly convenient in the case of interaction only between nearest neighbours and will be chosen in the present paper. The group of sites for the construction of the local grand partition function to the second approximation consists of the central site, the first shell sites which are nearest neighbours to the central site, and the second shell sites which are nearest neighbours to the first shell sites. The second shell sites are divided into two subgroups, the medium sites and the corner sites, the former being nearer to the central site than the latter. (See fig. 1 for the positions of these sites in a quadratic lattice.) Accordingly, there are altogether four kinds of sites in the case of the second approximation. An A atom on each kind of sites is provided with a parameter, which is determined by the condition that the fraction of A atoms on these sites determined by the local grand partition function is equal to θ_α or θ_β according as the sites are α or β sites.

In the special cases of a quadratic and a simple cubic lattice with neighbour interaction the general formulae in Wang's paper can be greatly simplified. For a central α-site, all the first shell sites are β sites, and all the second shell sites are α sites. Hence we have only four parameters, λ_α for the central site, $\varepsilon_{1\beta}$ for each first shell site, $\varepsilon_{2\alpha}$ for each medium site, and $\varepsilon_{3\alpha}$ for each corner site. We shall write these simply as λ_α, ε_1, ε_2, ε_3. Similarly for a central β-site we have the parameters λ_β, $\zeta_{1\alpha}$, $\zeta_{2\beta}$, $\zeta_{3\beta}$, which will be written simply as λ_β, ζ_1, ζ_2, ζ_3. Again we shall simplify the notation $z_{1\alpha\beta} = z_{1\beta\alpha}$, $z_{2\alpha\alpha} = z_{2\beta\beta}$, $z_{3\alpha\alpha} = z_{3\beta\beta}$ to z, z_2, z_3. Then the equations for the determination of the parameters are[1]

$$\theta_\alpha = \lambda_\alpha \frac{\partial}{\partial \lambda_\alpha} \log K_\alpha, \tag{3}$$

$$z\,\theta_\beta = \varepsilon_1 \frac{\partial}{\partial \varepsilon_1} \log K_\alpha, \quad z_2\,\theta_\alpha = \varepsilon_2 \frac{\partial}{\partial \varepsilon_2} \log K_\alpha, \quad z_3\,\theta_\alpha = \varepsilon_3 \frac{\partial}{\partial \varepsilon_3} \log K_\alpha, \tag{4}$$

where K_α is the local grand partition function for a central α-site, and is given by

$$K_\alpha = F + \lambda_\alpha F_\eta,$$

where
$$F = F(\varepsilon_1, \varepsilon_2, \varepsilon_3) = \Sigma\,\gamma\,\varepsilon_1^{n_1}\,\varepsilon_2^{n_2}\,\varepsilon_3^{n_3}\,\eta^{m_1} \tag{5}$$

$$F_\eta = F(\eta\, \varepsilon_1, \varepsilon_2, \varepsilon_3),$$

$$\eta = e^{-V/kT}, \qquad V = V^{AA} + V^{BB} - 2V^{AB}.$$

In the expression for F, n_1 runs from 0 to z, n_2 from 0 to z_2, n_3 from 0 to z_3, m_1 is the number of AA pairs among the $n_1 + n_2 + n_3$ A atoms, γ is the number of arrangements for a given set of values of n_1, n_2, n_3, m_1, and the summation is taken over all values of n_1, n_2, n_3, m_1. The parameters λ_β, ζ_1, ζ_2, ζ_3 satisfy a set of similar equations with an interchange of the roles played by θ_α and θ_β.

Equation (3) can be written in the form

$$\frac{\theta_\alpha}{1 - \theta_\alpha} = \frac{\lambda_\alpha F_\eta}{F}. \tag{6}$$

Eliminating λ_α in (4) by (6), we obtain

$$\begin{aligned} z\, \theta_\beta &= (1 - \theta_\alpha)\, \varphi_1 + \theta_\alpha\, \varphi_{1\eta}, \\ z_2\, \theta_\alpha &= (1 - \theta_\alpha)\, \varphi_2 + \theta_\alpha\, \varphi_{2\eta}, \\ z_3\, \theta_\alpha &= (1 - \theta_\alpha)\, \varphi_3 + \theta_\alpha\, \varphi_{3\eta}, \end{aligned} \tag{7}$$

where

$$\varphi_\nu = \varphi_\nu(\varepsilon_1, \varepsilon_2, \varepsilon_3) = \varepsilon_\nu \frac{\partial}{\partial \varepsilon_\nu} \log F,$$

and

$$\varphi_{\nu\eta} = \varphi_\nu(\eta\, \varepsilon_1, \varepsilon_2, \varepsilon_3).$$

Here for the sake of simplicity the notation for φ_1 is chosen differently from Wang's original notation (which is ψ_1).

Similarly for a central β-site we have

$$\theta_\beta = \lambda_\beta \frac{\partial}{\partial \lambda_\beta} \log K_\beta, \qquad \text{or} \qquad \frac{\theta_\beta}{1 - \theta_\beta} = \frac{\lambda_\beta G_\eta}{G}, \tag{8}$$

$$\begin{aligned} z\, \theta_\alpha &= (1 - \theta_\beta)\, \chi_1 + \theta_\beta\, \chi_{1\eta}, \\ z_2\, \theta_\beta &= (1 - \theta_\beta)\, \chi_2 + \theta_\beta\, \chi_{2\eta}, \\ z_3\, \theta_\beta &= (1 - \theta_\beta)\, \chi_3 + \theta_\beta\, \chi_{3\eta}, \end{aligned} \tag{9}$$

where

$$K_\beta = G + \lambda_\beta G_\eta,$$

$$G = G(\zeta_1, \zeta_2, \zeta_3) \equiv F(\zeta_1, \zeta_2, \zeta_3),$$

$$G_\eta = G(\eta \zeta_1, \zeta_2, \zeta_3),$$

$$\chi_\nu = \zeta_\nu \frac{\partial}{\partial \zeta_\nu} \log G. \tag{10}$$

Here again the notation χ_ι is different from Wang's original notation (which is ω_ι).

Equations (35) and (36) in Wang's paper[1] for the energy E_1 and the partition function Q reduce in the present case to

$$E_1 = \frac{Nz}{4\mu} k T^2 \frac{\partial}{\partial T} (\log K_\alpha + \log K_\beta), \tag{11}$$

and

$$\begin{aligned}\log Q = \frac{N}{2} \left[\frac{z}{2\mu} (1 + z + z_2 + z_3) - 1 \right] [\theta_\alpha \log \theta_\alpha + (1 - \theta_\alpha) \log (1 - \theta_\alpha) \\ + \theta_\beta \log \theta_\beta + (1 - \theta_\beta) \log (1 - \theta_\beta)] \\ + \frac{Nz}{4\mu} [\log K_\alpha - \theta_\alpha \log \lambda_\alpha - z\, \theta_\beta \log \varepsilon_1 - z_2\, \theta_\alpha \log \varepsilon_2 - z_3\, \theta_\alpha \log \varepsilon_3] \\ + \frac{Nz}{4\mu} [\log K_\beta - \theta_\beta \log \lambda_\beta - z\, \theta_\alpha \log \zeta_1 - z_2\, \theta_\beta \log \zeta_2 - z_3\, \theta_\beta \log \zeta_3],\end{aligned} \tag{12}$$

where μ is the number of pairs of nearest neighbouring sites in the group of the sites under consideration, which includes the central site, the first shell sites and the second shell sites. The equilibrium value of s is determined by the equation

$$2 \frac{\partial}{\partial s} \log Q = \frac{\partial}{\partial \theta_\alpha} \log Q - \frac{\partial}{\partial \theta_\beta} \log Q = 0. \tag{13}$$

in which the differentiation is taken with η kept constant. Substituting the expression (12) for Q in (13) and using (3) and (4), we obtain

$$-\frac{8\mu}{Nz}\frac{\partial}{\partial s}\log Q =$$

$$-D\log\frac{\theta_\alpha(1-\theta_\beta)}{\theta_\beta(1-\theta_\alpha)}+\log\frac{\lambda_\alpha}{\lambda_\beta}-z\log\frac{\varepsilon_1}{\zeta_1}+z_2\log\frac{\varepsilon_2}{\zeta_2}+z_3\log\frac{\varepsilon_3}{\zeta_3}=0. \qquad (14)$$

where

$$D = 1 + z + z_2 + z_3 - \frac{2\mu}{z}.$$

When the value of s determined by this equation is substituted into (11) we obtain the equilibrium value of the energy.

It is seen that $s = 0$ is always a solution of (14). For when $s = 0$ we have, by (2), $\theta_\alpha = \theta_\beta$, and the two classes of sites α and β become equivalent, so that $\lambda_\alpha = \lambda_\beta$, $\varepsilon_1 = \zeta_1$, $\varepsilon_2 = \zeta_2$, $\varepsilon_3 = \zeta_3$. In this case, therefore, every term in (14) is zero.

In general the equation (14) has three real roots, one of which is $s = 0$ and the two other roots are equal in numerical value but are opposite in sign, one being obtained from the other by interchanging the quantities for a central α site with those for a central β site. The non-zero root exists when the temperature is below a certain critical temperature, at which the three roots all become zero. The critical temperature is therefore determined by the condition that the equation (14) has a multiple root:

$$\left(\frac{\partial^2}{\partial s^2}\log Q\right)_{s=0} = 0, \qquad (15)$$

which reduces, by (14), to

$$\frac{D}{\theta(1-\theta)}-\left\{\frac{1}{\lambda_\alpha}\left(\frac{\partial\lambda_\alpha}{\partial\theta_\alpha}-\frac{\partial\lambda_\alpha}{\partial\theta_\beta}\right)+\frac{z}{\varepsilon_1}\left(\frac{\partial\varepsilon_1}{\partial\theta_\alpha}-\frac{\partial\varepsilon_1}{\partial\theta_\beta}\right)-\frac{z_2}{\varepsilon_2}\left(\frac{\partial\varepsilon_2}{\partial\theta_\alpha}-\frac{\partial\varepsilon_2}{\partial\theta_\beta}\right)\right.$$

$$\left.-\frac{z_3}{\varepsilon_3}\left(\frac{\partial\varepsilon_3}{\partial\theta_\alpha}-\frac{\partial\varepsilon_3}{\partial\theta_\beta}\right)\right\}_{s=0}=0, \qquad (16)$$

in which use has been made of the relations

$$\left(\frac{\partial \varepsilon_\nu}{\partial \theta_\alpha}\right)_{s=0} = \left(\frac{\partial \zeta_\nu}{\partial \theta_\beta}\right)_{s=0}, \qquad \left(\frac{\partial \varepsilon_\nu}{\partial \theta_\beta}\right)_{s=0} = \left(\frac{\partial \zeta_\nu}{\partial \theta_\alpha}\right)_{s=0}.$$

In the special case of equal numbers of A and B atoms, ($\theta = \frac{1}{2}$), the parameters for central β site bear simple relations with those for central α site. From the expression of F given in (5) with the consideration that γ is unaltered when n_1, n_2, n_3 are changed respectively to $z - n_1$, $z_2 - n_2$, $z_3 - n_3$ while m_1 changes to $m_1 + (z-1)\left(\frac{z}{2} - n_1\right) + 2\left(\frac{1}{2} z_2 - n_2\right) + \frac{1}{2} z_3 - n_3$ we can easily obtain the relation[2]

$$F(\varepsilon_1, \varepsilon_2, \varepsilon_3) = \eta^{z(z-1)} \varepsilon_1^{z} \varepsilon_2^{z_2} \varepsilon_3^{z_3} F(\varepsilon_1^{-1} \eta^{-z+1}, \varepsilon_2^{-1} \eta^{-2}, \varepsilon_3^{-1} \eta^{-1}). \tag{17}$$

Differentiating with respect to the parameters, we obtain for φ_ν the relation

$$\varphi_\nu(\varepsilon_1, \varepsilon_2, \varepsilon_3) = z_\nu - \varphi_\nu(\varepsilon_1^{-1} \eta^{-z+1}, \varepsilon_2^{-1} \eta^{-2}, \varepsilon_3^{-1} \eta^{-1}). \tag{18}$$

Similarly we have

$$\chi_\nu(\zeta_1, \zeta_2, \zeta_3) = z_\nu - \chi_\nu(\zeta_1^{-1} \eta^{-z+1}, \zeta_2^{-1} \eta^{-2}, \zeta_3^{-1} \eta^{-1}). \tag{19}$$

Using (7), (9), (18) and (19), the transformation

$$\varepsilon_1 \longrightarrow \zeta_1^{-1} \eta^{-z}, \qquad \varepsilon_2 \longrightarrow \zeta_2^{-1} \eta^{-2}, \qquad \varepsilon_3 \longrightarrow \zeta_3^{-1} \eta^{-1}$$

changes θ_α to $1 - \theta_\beta$ and θ_β to $1 - \theta_\alpha$. Therefore at $\theta = \frac{1}{2}$ a possible solution is

$$\varepsilon_1 = \zeta_1^{-1} \eta^{-z}, \qquad \varepsilon_2 = \zeta_2^{-1} \eta^{-2}, \qquad \varepsilon_3 = \zeta_3^{-1} \eta^{-1}.$$

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[2] Let X^{AA}, X^{BB}, X^{AB} denote respectively the numbers of pairs AA, BB, AB. we have

$$2 X^{AA} + X^{AB} = (z-1) n_1 + 2 n_2 + n_3,$$

$$2 X^{BB} + X^{AB} = (z-1)(z - n_1) + 2(z_2 - n_2) + (z_3 - n_3).$$

Thus

$$X^{BB} - X^{AA} = \frac{1}{2} z(z-1) + z_2 + \frac{1}{2} z_3 - (z-1) n_1 - 2 n_2 - n_3.$$

Since (see equation (23) of § 3) $z_2 = \frac{1}{2} z(z-2)$, $z_3 = z$ we have

$$X^{BB} - X^{AA} = z(z-1) - (z-1) n_1 - 2 n_2 - n_3.$$

These relations make the above consideration obvious. A more direct method is to use equation (22).

From general considerations in statistical mechanics we conclude that this is the only solution.

Thus for $\theta = \frac{1}{2}$ we have, from (17),

$$F(\varepsilon_1, \varepsilon_2, \varepsilon_3) = \eta^{z(z-1)} \varepsilon_1^{z} \varepsilon_2^{z_2} \varepsilon_3^{z_3} F(\eta \zeta_1, \zeta_2, \zeta_3)$$

$$= \eta^{z(z-1)} \varepsilon_1^{z} \varepsilon_2^{z_2} \varepsilon_3^{z_3} G(\eta \zeta_1, \zeta_2, \zeta_3)$$

$$F(\eta \varepsilon_1, \varepsilon_2, \varepsilon_3) = \eta^{z^2} \varepsilon_1^{z} \varepsilon_2^{z_2} \varepsilon_3^{z_3} G(\zeta_1, \zeta_2, \zeta_3).$$

From (6) and (8) we obtain immediately

$$\lambda_\alpha = \lambda_\beta^{-1} \eta^{-z}.$$

Using these relations, (14) finally assumes the form

$$-D \log \frac{\theta_\alpha}{1-\theta_\alpha} + \log \lambda_\alpha - z \log \varepsilon_1 + z_2 \log \varepsilon_2 + z_3 \log \varepsilon_3 = 0. \qquad (20)$$

This is the equation used in the following two sections.

3. THE QUADRATIC LATTICE

In this section we shall consider the special case of the quadratic lattice in detail. The group of sites under consideration is shown in the figure.

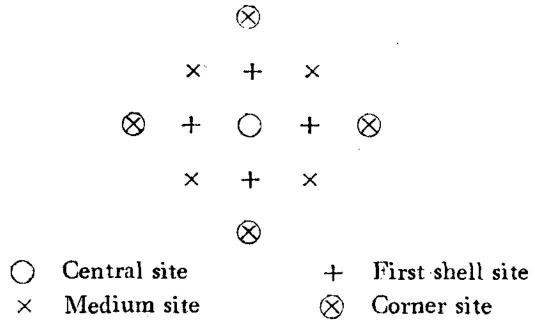

Fig. 1.

The expression of F as given by (5) can be simplified by the following method. Let us introduce the new notations

$$n_1 = n, \qquad n_2 = n_{20} + n_{21} + n_{22}, \qquad n_3 = n_{30} + n_{31}.$$

The second subscripts 0,1,2, mean that the A atom under consideration has 0,1, or 2 A atoms as nearest neighbours (the central site being excluded). We have

$$m_1 = n_{21} + 2\,n_{22} + n_{31}$$

and

$$F = \Sigma\,\chi\,\varepsilon_1{}^n\,\varepsilon_2{}^{n_{20} + n_{21} + n_{22}}\,\varepsilon_3{}^{n_{30} + n_{31}}\,\eta^{n_{21} + 2\,n_{22} + n_{31}}.$$

Denote by m_{AA}, $m_{AB} = 2m$, m_{BB} the numbers of adjacent AA, AB, and BB atoms in the first shell. In the quadratic and simple cubic lattice each site in the first shell has $z - 2$ adjacent sites. Hence we have

$$(z-2)\,n = m_{AB} + 2\,m_{AA} = 2\,m + 2\,m_{AA},$$

$$(z-2)\,(z-n) = m_{AB} + 2\,m_{BB} = 2\,m + 2\,m_{BB}.$$

But m_{AA}, m_{AB}, m_{BB} just give the maximum possible values of n_{22}, n_{21}, n_{20} for given values of n and m. Hence we have

$$max.\ n_{20} = \left(\frac{1}{2}z - 1\right)(z-n) - m, \quad max.\ n_{21} = 2\,m,$$

$$max.\ n_{22} = \left(\frac{1}{2}z - 1\right)n - m, \quad max.\ n_{30} = z - n, \quad max.\ n_{31} = n.$$

In the expression for F let us first make a partial sum over the possible configurations arising from a given set of values of n and m. We can write F in the form

$$F = \Sigma\,g_{nm}\,\varepsilon_1{}^n\,Q_{nm}, \tag{21}$$

where g_{nm} is the number of arrangements for a given set of values of n and m. For a quadratic lattice they are given in the following table.

Table of g_{nm} for a quadratic lattice

n	0	1	2	2	3	4
$2m$	0	2	2	4	2	0
g_{nm}	1	4	4	2	4	1

The function Q_{nm} is evidently given by

$$Q_{nm} = \Sigma \binom{max.\ n_{20}}{n_{20}} \binom{max.\ n_{21}}{n_{21}} \binom{max.\ n_{22}}{n_{22}} \binom{max.\ n_{30}}{n_{30}} \binom{max.\ n_{31}}{n_{31}} \times$$
$$\varepsilon_2{}^{n_{20}+n_{21}+n_{22}}\, \varepsilon_3{}^{n_{30}+n_{31}}\, \eta^{n_{21}+2n_{22}+n_{31}},$$

the summation being taken over all possible values of n_{20}, etc., for given n and m. Substituting into it the maximum values obtained above, we have immediately

$$Q_{nm} = (1+\varepsilon_2)^{(\frac{1}{2}z-1)z}(1+\varepsilon_3)^z \left(\frac{1+\varepsilon_2\eta^2}{1+\varepsilon_2}\right)^{n(\frac{1}{2}z-1)} \left(\frac{1+\varepsilon_3\eta}{1+\varepsilon_3}\right)^n \times$$
$$\left[\frac{(1+\varepsilon_2\eta)^2}{(1+\varepsilon_2)(1+\varepsilon_2\eta^2)}\right]^m. \qquad (22)$$

Since z_2 and z_3 are, by definition, respectively the maximum values of n_2 and n_3, therefore

$$z_2 = max.\, n_{20} + max.\, n_{21} + max.\, n_{22} = \frac{1}{2}z(z-2),$$
$$z_3 = max.\, n_{30} + max.\, n_{31} = z. \qquad (23)$$

Further, we have, by definition,[2]

$$\mu - z = X^{AA} + X^{BB} + X^{AB}.$$

Making use of (23) and the equations in footnote 2, we have

$$\mu = z^2.$$

Thus

$$D = 1 + z + z_2 + z_3 - \frac{2\mu}{z} = z_2 + 1.$$

For the quadratic lattice we have

$$z = z_2 = z_3 = 4, \qquad \mu = 16, \qquad D = 5.$$

Introducing the symbols

$$
\begin{aligned}
u &= \varepsilon_1 \left(\frac{1 + \varepsilon_2 \eta^2}{1 + \varepsilon_2} \right)^{(\frac{1}{2}z - 1)} \left(\frac{1 + \varepsilon_3 \eta}{1 + \varepsilon_3} \right), \\
v &= \frac{(1 + \varepsilon_2 \eta)^2}{(1 + \varepsilon_2)(1 + \varepsilon_2 \eta^2)},
\end{aligned}
\tag{24}
$$

we can put (21) into the more serviceable form

$$
F = (1 + \varepsilon_2)^{(\frac{1}{2}z - 1)z} (1 + \varepsilon_3)^z \Sigma g_{nm} u^n v^m. \tag{25}
$$

To make further formulation simpler we introduce the functions A, B, C defined by

$$
A = \Sigma g_{nm} u^n v^m, \qquad B = \frac{u}{z} \frac{\partial}{\partial u} \log A, \qquad C = \frac{v}{z_2} \frac{\partial}{\partial v} \log A. \tag{26}
$$

Similar to F_η we understand by A_η, B_η, C_η those functions obtained from A, B, C by replacing the argument u by $u\eta$ (or ε_1 by $\varepsilon_1 \eta$).

Substituting (25) and (26) into (6) and (7) we obtain the following four equations determining λ_α, ε_1, ε_2, ε_3 as functions of θ_α, θ_β, and η :

$$
\lambda_\alpha = \frac{\theta_\alpha}{1 - \theta_\alpha} \frac{A}{A_\eta}, \tag{27}
$$

$$
\theta_\beta = (1 - \theta_\alpha) B + \theta_\alpha B_\eta, \tag{28}
$$

$$
\begin{aligned}
\theta_\alpha = {} & \frac{\varepsilon_2}{1 + \varepsilon_2} + \theta_\beta \left(\frac{1}{1 + \varepsilon_2} - \frac{1}{1 + \varepsilon_2 \eta^2} \right) \\
& - \left(\frac{1}{1 + \varepsilon_2} + \frac{1}{1 + \varepsilon_2 \eta^2} - \frac{2}{1 + \varepsilon_2 \eta} \right) [(1 - \theta_\alpha) C + \theta_\alpha C_\eta],
\end{aligned}
\tag{29}
$$

$$
\theta_\alpha = (1 - \theta_\beta) \frac{\varepsilon_3}{1 + \varepsilon_3} + \theta_\beta \frac{\eta \varepsilon_3}{1 + \eta \varepsilon_3}. \tag{30}
$$

We now apply these equations to the study of the variation of the critical temperature with composition. Since it is immaterial whether the alloy contains a fraction θ of A atoms or a fraction θ of B atoms, the curve of critical temperature against composition must be symmetrical with respect to $\theta = \frac{1}{2}$. From (16) we see that we need also the derivatives of the parameters, which can be obtained from equations (27) to (30) by differentiation[3].

In making numerical calculations we choose a definite kT/V (corresponding to a definite temperature). Assume a value for ε_3 and determine ε_1, ε_2 by solving (28) and (29) by the method of successive approximations. With ε_1, ε_2 determined the value of λ_α is obtained from (27). We then calculate the derivatives of λ_α, ε_1, ε_2, ε_3 with respect to θ_α and θ_β by solving a set of simultaneous linear equations derived from (27) to (30). All the values obtained are substituted into (16) to see if it is satisfied. If not, we start this process with a new value for ε_3. Repeat this method a number of times until (16) is satisfied. In this way we obtain a value for θ which gives the composition of the alloy with the preassigned value of kT/V as its critical value for kT/V. In this way we obtain the curve as shown in fig. 2. In the case of the first approximation a closed expression has been obtained by Easthope[4]. This is also plotted in fig. 2. for comparison. It is seen that for a definite composition the critical value of kT/V is lower in the case of the second approximation.

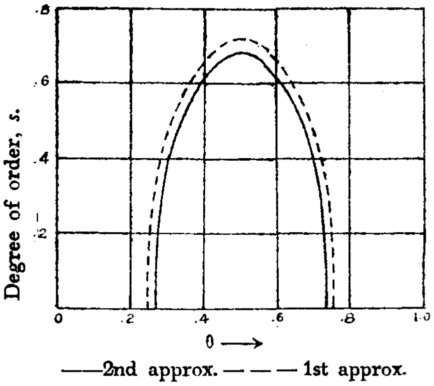

Fig. 2. Quadratic lattice

Let us now study exclusively the case of equal numbers of A and B atoms ($\theta = \frac{1}{2}$). First of all we wish to calculate the degree of order corresponding to various values of kT/V. We now require besides equations (28) to (30) also equation (20) with $\theta_\alpha = 1 - \theta_\beta$. Corresponding to a definite kT/V, we start with a value assumed for ε_3 and determine θ_α, ε_2, ε_1, as before. The values thus obtained are substituted into (20) to see if they are the equilibrium values corresponding to the given value of kT/V. This method is repeated a number of times until (20) is satisfied. The values of s thus obtained are plotted against kT/V in fig. 3.

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[3] For the formulae see Appendix I.

[4] C.E. Easthope, *Proc. Camb. Phil. Soc.* **33** 1937 , 502.

We are now in a position to calculate the equilibrium values of E_1 corresponding to various kT/V. We shall use equation (11) in the following explicit form

$$E_1 = \frac{NV}{2}\left\{\theta_\beta\left[\frac{(z-2)\eta^2\varepsilon_2}{1+\varepsilon_2\eta^2} + \frac{\varepsilon_3\eta}{1+\varepsilon_3\eta}\right] + \theta_\alpha B_\eta \right.$$
$$\left. + (z-2)\left(\frac{1}{1+\varepsilon_2\eta^2} - \frac{1}{1+\varepsilon_2\eta}\right)\left[(1-\theta_\alpha)C + \theta_\alpha C_\eta\right]\right\}. \quad (31)$$

The equilibrium values of E_1, as obtained from (31) by substituting into it the equilibrium values of the parameters, are plotted against kT/V in fig. 4.

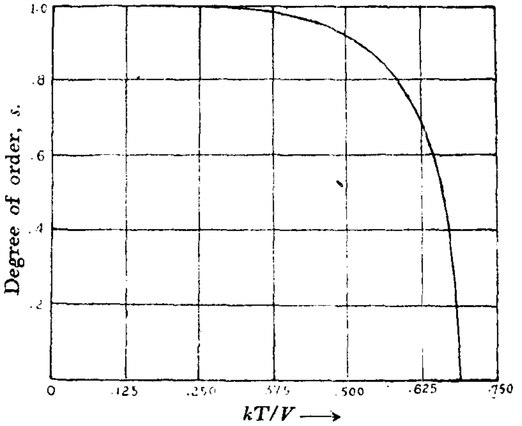

Fig. 3. Quadratic lattice $\theta = \frac{1}{2}$

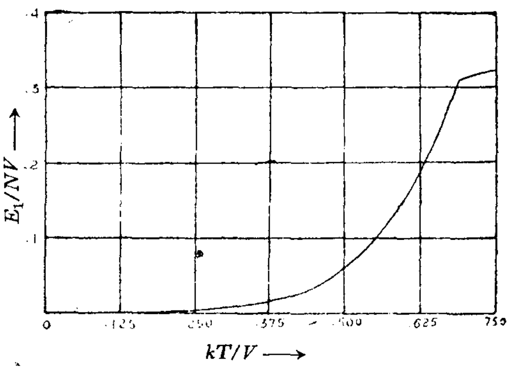

Fig. 4. Quadratic lattice $\theta = \frac{1}{2}$

Although the specific heats can be obtained by differentiating (31) with respect to temperature, the formula thus obtained is very complicated and the calculation is too laborious. Therefore we have adopted the method of numerical differentiation with finite differences applied to the calculated values of the energy. At the critical temperature the method of differences is not advisable. However, an exact formula for the specific heat at the critical temperature can be obtained by means of an expansion[5] similar in nature to that used by Bethe in his determination

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[5] For an explanation of the method see Appendix II.

of the critical temperature. In this way we obtain the following results. For the sake of comparison they are tabulated side by side with the results obtained by Bethe[6] in the case of the first approximation.

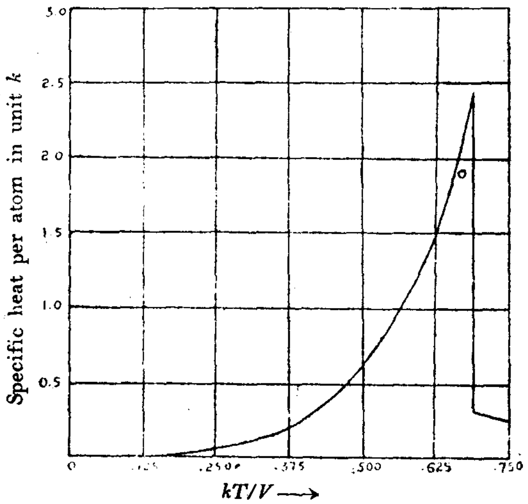

Fig. 5. Quadratic lattice $\theta = \frac{1}{4}$

	Present method	Bethe's 1st approx.
Specific heat per atom	$2.442\ k(T = T_c - 0)$	$2.14\ k(T = T_c - 0)$
	$0.3164\,k(T = T_c + 0)$	$0.214\,k(T = T_c + 0)$
Variation of s near T_c	$s = 1.731\sqrt{\frac{T_c - T}{T_c}}$	$s = 1.553\sqrt{\frac{T_c - T}{T_c}}$

4. THE SIMPLE CUBIC LATTICE

The calculations in the present section are similar to those in the preceding section. The only difference is that the z's differ from those for the quadratic lattice. According to Bethe's original formulation of the second approximation, the first shell sites are at a distance a from the central site, while the medium and corner sites are respectively at distances $\sqrt{2}\,a$ and $2\,a$ from the central site. As there are sites at a distance $\sqrt{3}\,a$ from the central site, it seems that one should include them

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[6] Bethe, *Proc. Roy. Soc.* **150** (1935), 552.

in the group of sites under consideration. It may be noted, however, that the introduction of the second shell is considered to have effect only on the first shell sites when we are dealing with the case of neighbour interaction. Therefore in the second approximation we need not consider those sites at distance $\sqrt{3}\,a$ from the central site, because they are neither nearest neighbours of the central site nor nearest neighbours of the first shell sites. Thus in the present case we may imagine the group of sites to be situated in three mutually perpendicular planes, each plane containing the sites arranged in the form shown in fig. 1.

The constants z, z_2, z_3, μ and D now assume the values

$$z = 6, \qquad z_2 = 12, \qquad z_3 = 6, \qquad \mu = 36, \qquad D = 13.$$

Since in deriving equations (21) to (30) the arguments used are not restricted to the case of quadratic lattice, and these equations hold also for the case of simple cubic lattice with the z's replaced by the present values. The values of g_{nm}, however, are different from those for the quadratic lattice. They are tabulated in the following table

Table of g_{nm} for a simple cubic lattice

n	0	1	2	2	3	3	4	4	5	6
$2m$	0	4	6	8	8	6	8	6	4	0
g_{nm}	1	6	12	3	12	8	3	12	6	1

The explicit forms of A, B, C in (25) are therefore quite different for the two types of lattice.

For the simple cubic lattice the variation of the critical temperature with composition is studied as before. We again make use of equations (27) to (30) and (16) with the present z's and g's. The results obtained are plotted in fig. 6.

For the case of $\theta = \frac{1}{2}$, equations (27) to (31) and (20) are again used to obtain curves of order against kT/V, E_1 against kT/V, and specific heat against kT/V. They are shown in figs. 7, 8, 9. In these figures Bethe's original results[6] for the second approximation are also plotted in dotted lines.

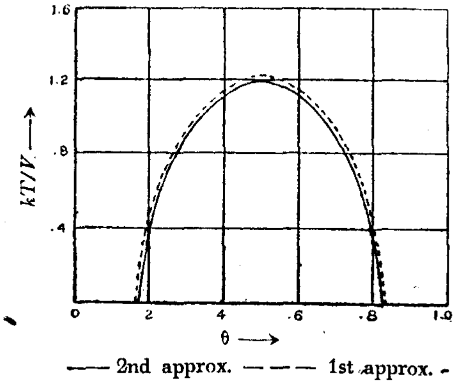

Fig. 6. Simple cubic lattice

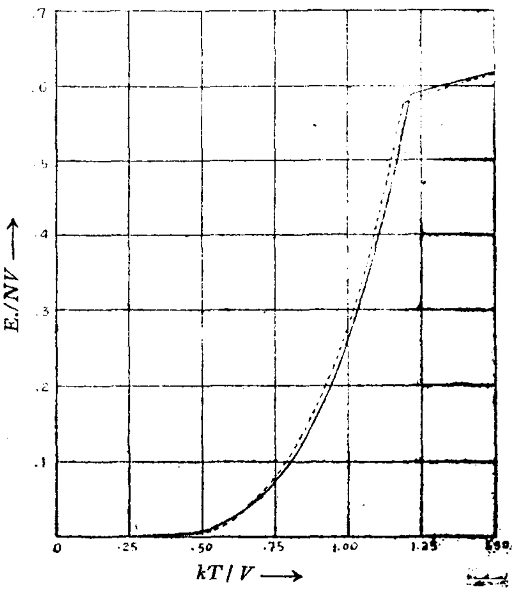

Fig. 8. Simple cubic lattice $\theta = \frac{1}{2}$

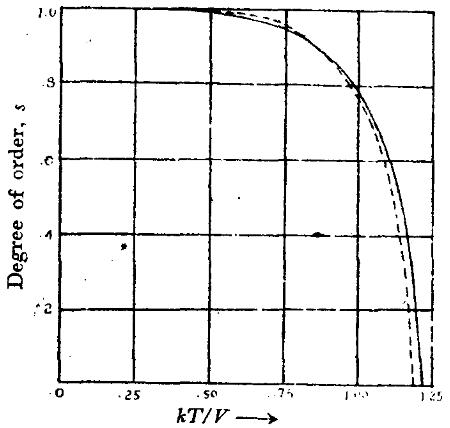

Fig. 7. Simple cubic lattice $\theta = \frac{1}{2}$

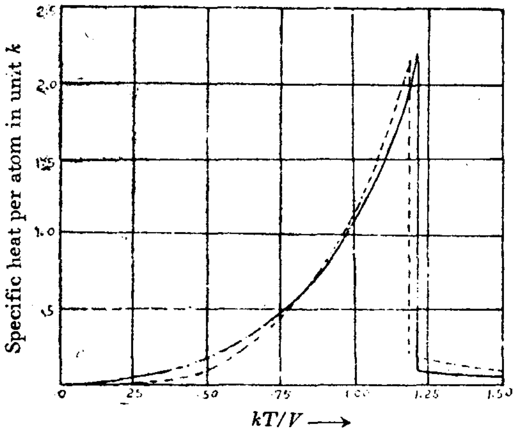

Fig. 9. Simple cubic lattice $\theta = \frac{1}{2}$

At the critical temperature an expansion is made. This enables us to calculate the specific heat at the critical temperature and the behaviour of s near it. They are all given in the following table.

	Present method	Bethe's 2nd Approx.
Critical value of η_c	0.4396	0.4303
Specific heat per atom	$2.17\ k(T = T_c - 0)$	$2.14\ k(T = T_c - 0)$
	$0.104\,k(T = T_c + 0)$	$0.203\,k(T = T_c + 0)$
Variation of s near T_c	$s = 2.62\sqrt{\frac{T_c - T}{T_c}}$	$s = 2.32\sqrt{\frac{T_c - T}{T_c}}$

It is seen that although the discontinuity of the specific heat is now a little more marked, the results obtained by the two methods are essentially the same when we are face to face with the large discrepancies between experimental results and theoretical predictions.

Finally I wish to thank Professor J. S. Wang for suggesting this problem and for his constant advice during the course of investigation.

APPENDIX I

The equation determining the critical temperature is, according to (16),

$$\frac{D}{\theta(1-\theta)} + \left\{ \frac{z}{\varepsilon_1}\left(\frac{\partial \varepsilon_1}{\partial \theta_\alpha} - \frac{\partial \varepsilon_1}{\partial \theta_\beta}\right) - \frac{z_2}{\varepsilon_2}\left(\frac{\partial \varepsilon_2}{\partial \theta_\alpha} - \frac{\partial \varepsilon_2}{\partial \theta_\beta}\right) - \frac{z_3}{\varepsilon_3}\left(\frac{\partial \varepsilon_3}{\partial \theta_\alpha} - \frac{\partial \varepsilon_3}{\partial \theta_\beta}\right) \right.$$
$$\left. - \frac{1}{\lambda_\alpha}\left(\frac{\partial \lambda_\alpha}{\partial \theta_\alpha} - \frac{\partial \lambda_\beta}{\partial \theta_\beta}\right) \right\}_{s=0} = 0. \qquad \text{(I—1)}$$

By making use of equation (27) and the equation obtained by partially differentiating it with respect to s we succeed in eliminating λ_α and its derivatives in (I – 1). The equation now becomes

$$\frac{1}{\theta(1-\theta)} + \frac{1}{\varepsilon_1}\left(\frac{\partial \varepsilon_1}{\partial \theta_\alpha} - \frac{\partial \varepsilon_1}{\partial \theta_\beta}\right)_{s=0}(1 - B + B_\eta)$$
$$- \frac{1}{\varepsilon_2}\left(\frac{\partial \varepsilon_2}{\partial \theta_\alpha} - \frac{\partial \varepsilon_2}{\partial \theta_\beta}\right)_{s=0}\left(\frac{1}{2}z - 1\right)\left[\left(\frac{1}{1+\varepsilon_2} - \frac{1}{1+\varepsilon_2\eta^2}\right)(B - B_\eta)\right.$$
$$\left. + \left(\frac{1}{1+\varepsilon_2} + \frac{1}{1+\varepsilon_2\eta^2} - \frac{2}{1+\varepsilon_2\eta}\right)(C - C_\eta) + 1\right]$$

$$-\frac{1}{\varepsilon_3}\left(\frac{\partial\varepsilon_3}{\partial\theta_\alpha}-\frac{\partial\varepsilon_3}{\partial\theta_\beta}\right)_{s=0}\left[\left(\frac{1}{1+\varepsilon_3}-\frac{1}{1+\varepsilon_3\eta}\right)(B-B_\eta)+1\right]=0. \tag{1—2}$$

Besides equations (28), (29), (30) we require also equations determining the derivatives of the parameters. They are obtained by differentiating (28), (29), (30) and are found to be

$$B-B_\eta-1=\sum_\nu\frac{1}{\varepsilon_\nu}\left(\frac{\partial\varepsilon_\nu}{\partial\theta_\alpha}-\frac{\partial\varepsilon_\nu}{\partial\theta_\beta}\right)_{s=0}\left[(1-\theta)\,\varepsilon_\nu\frac{\partial}{\partial\varepsilon_\nu}B+\theta\,\varepsilon_\nu\frac{\partial}{\partial\varepsilon_\nu}B_\eta\right], \tag{I—3}$$

$$1+(C-C_\eta)\left(\frac{1}{1+\varepsilon_2}+\frac{1}{1+\varepsilon_2\eta^2}-\frac{2}{1+\varepsilon_2\eta}\right)+\frac{1}{1+\varepsilon_2}-\frac{1}{1+\varepsilon_2\eta^2}$$

$$=\left(\frac{1}{1+\varepsilon_2}+\frac{1}{1+\varepsilon_2\eta^2}-\frac{2}{1+\varepsilon_2\eta}\right)\sum_\nu\frac{1}{\varepsilon_\nu}\left(\frac{\partial\varepsilon_\nu}{\partial\theta_\alpha}-\frac{\partial\varepsilon_\nu}{\partial\theta_\beta}\right)_{s=0}\times$$

$$\left[(1-\theta)\,\varepsilon_\nu\frac{\partial}{\partial\varepsilon_\nu}C+\theta\,\varepsilon_\nu\frac{\partial}{\partial\varepsilon_\nu}C_\eta\right]$$

$$+\frac{1}{\varepsilon_2}\left(\frac{\partial\varepsilon_2}{\partial\theta_\alpha}-\frac{\partial\varepsilon_2}{\partial\theta_\beta}\right)_{s=0}\left[\frac{\varepsilon_2}{(1+\varepsilon_2)^2}+\theta\left\{\frac{\eta^2}{(1+\varepsilon_2\eta^2)^2}-\frac{1}{(1+\varepsilon_2)^2}\right\}\right.$$

$$\left.+\left\{\frac{2\eta}{(1+\varepsilon_2\eta)^2}-\frac{1}{(1+\varepsilon_2)^3}-\frac{\eta^2}{(1+\varepsilon_2\eta^2)^2}\right\}\{(1-\theta)\,C+\theta\,C_\eta\}\right], \tag{I—4}$$

$$\frac{1}{1+\varepsilon_3}+\frac{\varepsilon_3\eta}{1+\varepsilon_3\eta}=\frac{1}{\varepsilon_3}\left(\frac{\partial\varepsilon_3}{\partial\theta_\alpha}-\frac{\partial\varepsilon_3}{\partial\theta_\beta}\right)_{s=0}\left\{(1-\theta)\,\frac{\varepsilon_3}{(1+\varepsilon_3)^2}+\theta\,\frac{\varepsilon_3\eta}{1+\varepsilon_3\eta}\right\}, \tag{I—5}$$

In making numerical calculations we calculate $\frac{1}{\varepsilon_r}\left(\frac{\partial\varepsilon_r}{\partial\theta_\alpha}-\frac{\partial\varepsilon_\nu}{\delta\theta_\beta}\right)$ from (I — 3), (I — 4), (I — 5) with the values of ε_r calculated from (28), (29), (30). All these values are then substituted into (I — 2) to see if they are the equilibrium values.

APPENDIX II

To investigate the behaviour of the alloy near the critical temperature we make the following expansion. The method is the same for both types of lattice; only the numerical constants involved are different for the two cases. For simplicity here we give an account for the case of the quadratic lattice.

To carry out the expansion it is found convenient to eliminate θ_α, θ_β, ε_1 from all equations. In particular equation (20) becomes

$$5 \log \eta + \log \varepsilon_3 + 9 \log \frac{1 + \varepsilon_3}{1 + \varepsilon_3 \eta} + 4 \log u + 4 \log \frac{1 + \varepsilon_2}{\varepsilon_2 (1 + \varepsilon_2 \eta^2)} - \log \lambda_\alpha = 0. \tag{II—1}$$

Since at $s = 0$

$$\varepsilon_2 = \eta^{-1}, \qquad \varepsilon_2 = \eta^{-\frac{1}{2}}, \qquad \varepsilon_1 = \eta^{-2}, \qquad \lambda_\alpha = \eta^{-2}, \qquad u = \eta^{-\frac{1}{2}},$$

for $s \doteq 0$ we can write $\varepsilon_2 = \eta^{-1}(1 + \delta)$,

and let

$$\varepsilon_3 = \eta^{-\frac{1}{2}}(1 + \varepsilon_{31}\,\delta + \varepsilon_{32}\,\delta^2 + \varepsilon_{33}\,\delta^3 + \cdots),$$

$$\lambda_\alpha = \eta^{-2}(1 + \lambda_1\,\delta + \lambda_2\,\delta^2 + \lambda_3\,\delta^3 + \cdots),$$

$$u = \eta^{-\frac{1}{2}}(1 + u_1\,\delta + u_2\,\delta^2 + u_3\,\delta^3 + \cdots).$$

For v we have

$$v = \frac{4\eta}{(1+\eta)^2}\left[1 + \frac{(1-\eta)^2}{4(1+\eta)^2}\,\delta^2 + \cdots\right] = v_0\left[1 + \frac{(1-\eta)^2}{4(1+\eta)^2}\,\delta^2 + \cdots\right],$$

with $$v_0 = \frac{4\eta}{(1+\eta)^2}.$$

Equations (28), (29), (30), and (II − 1) become

$$\Sigma (4 - n)\, g_{nm}\, \eta^{-\frac{n}{2}}\, v_0^m \left[\left\{(n-2)\,u_1 - \frac{\lambda_1}{2}\right\}\right.$$
$$\left. + \left\{(n-2)\left(u_2 - \frac{u_1^2}{2}\right) - \frac{1}{2}\left(\lambda_2 - \frac{\lambda_1^2}{2}\right)\right\}\delta\right.$$

$$+ \Bigl\{ (n-2)\Bigl(u_3 - u_1 u_2 + \frac{u_1^3}{3}\Bigr) - \frac{1}{2}\Bigl(\lambda_3 - \lambda_1 \lambda_2 + \frac{\lambda_1^3}{3}\Bigr) + \frac{1}{3!}\Bigl((n-2)u_1 - \frac{\lambda_1}{2}\Bigr)^3$$

$$+ \Bigl((n-2)u_1 - \frac{\lambda_1}{2}\Bigr) \frac{m(1-\eta)^2}{4(1+\eta)^2} \Bigr\} \delta^2 \Bigr] = 0. \qquad \text{(II—2)}$$

$$\frac{(1-\eta)^2}{4\eta(1+\eta)} \Sigma m\, g_{nm}\, \eta^{-\frac{n}{2}} v_0^m \Bigl[1 - \frac{1}{2}\delta + \Bigl\{ \frac{1}{2}\Bigl((n-2)u_1 - \frac{\lambda_1}{2}\Bigr)^2 + \frac{(1-\eta)^2}{4(1+\eta)^2}$$

$$+ \frac{m(1-\eta)^2}{4(1+\eta)^2} \Bigr\} \delta^2 \Bigr] + \Sigma g_{nm}\, \eta^{-\frac{n}{2}} v_0^m \Bigl[\Bigl\{ 2(n-2)u_1 - \lambda_1 + \frac{2}{1+\eta} \Bigr\}$$

$$+ \Bigl\{ 2(n-2)\Bigl(u_2 - \frac{u_1^2}{2}\Bigr) - \Bigl(\lambda_2 - \frac{\lambda_1^2}{2}\Bigr) - \frac{1}{1+\eta} \Bigr\} \delta$$

$$+ \Bigl\{ 2(n-2)\Bigl(u_3 - u_1 u_2 + \frac{u_1^3}{3}\Bigr) - \Bigl(\lambda_3 - \lambda_1 \lambda_2 + \frac{\lambda_1^3}{3}\Bigr) + \frac{1}{3}\Bigl((n-2)u_1 - \frac{\lambda_1}{2}\Bigr)^3$$

$$+ \frac{1}{1+\eta}\Bigl((n-2)u_1 - \frac{\lambda_1}{2}\Bigr)^2 + \frac{1-\eta}{(1+\eta)^2}\Bigl((n-2)u_1 - \frac{\lambda_1}{2}\Bigr) + \frac{1+\eta^2}{(1+\eta)^3}$$

$$+ \frac{m(1-\eta)^2}{4(1+\eta)^2}\Bigl(2(n-2)u_1 - \lambda_1 + \frac{2}{1+\eta}\Bigr) \Bigr\} \delta^2 \Bigr] = 0, \qquad \text{(II—3)}$$

$$\Sigma \dot{g}_{nm}\, \eta^{-\frac{n}{2}} v_0^m \Bigl[\Bigl\{ \frac{2}{1+\eta^{\frac{1}{2}}}\varepsilon_{31} + 2(n-2)u_1 - \lambda_1 \Bigr\} + \Bigl\{ \frac{2}{1+\eta^{\frac{1}{2}}}\Bigl(\varepsilon_{32} - \frac{1}{2}\varepsilon_{31}^2\Bigr)$$

$$+ 2(n-2)\Bigl(u_2 - \frac{u_1^2}{2}\Bigr) - \Bigl(\lambda_2 - \frac{\lambda_1^2}{2}\Bigr) \Bigr\} \delta$$

$$+ \Bigl\{ \frac{2}{1+\eta^{\frac{1}{2}}}\Bigl(\varepsilon_{33} + \frac{2 + 3\eta^{\frac{1}{2}} + 3\eta}{6(1+\eta^{\frac{1}{2}})^2}\varepsilon_{31}^3 - \varepsilon_{31}\varepsilon_{32}\Bigr) + 2(n-2)\Bigl(u_3 - u_1 u_2 + \frac{u_1^3}{3}\Bigr)$$

$$- \Bigl(\lambda_3 - \lambda_1 \lambda_2 + \frac{\lambda_1^3}{3}\Bigr) + \frac{1}{4!}\Bigl(\frac{2}{1+\eta^{\frac{1}{2}}}\varepsilon_{31} + 2(n-2)u_1 - \lambda_1\Bigr)^3$$

$$+ \frac{m(1-\eta)^2}{4(1+\eta)^2}\Bigl(\frac{2}{1+\eta^{\frac{1}{2}}}\varepsilon_{31} + 2(n-2)u_1 - \lambda_1\Bigr) \Bigr\} \delta^2 \Bigr] = 0, \qquad \text{(II—4)}$$

$$\Bigl\{ \frac{10 - 8\eta^{\frac{1}{2}}}{1+\eta^{\frac{1}{2}}}\varepsilon_{31} - \frac{8\eta}{1+\eta} + 4u_1 - \lambda_1 \Bigr\} + \Bigl\{ \frac{10 - 8\eta^{\frac{1}{2}}}{1+\eta^{\frac{1}{2}}}\Bigl(\varepsilon_{32} - \frac{1}{2}\varepsilon_{31}^2\Bigr)$$

$$+\frac{4\,\eta}{1+\eta}-\left(\lambda_2-\frac{\lambda_1^2}{2}\right)+4\left(u_2-\frac{u_1^2}{2}\right)\Bigg\}\,\delta$$

$$+\left\{\frac{10-8\eta^{\frac{1}{2}}}{1+\eta^{\frac{1}{2}}}\left(\varepsilon_{33}+\frac{2+3\eta^{\frac{1}{2}}+3\eta}{6\,(1+\eta^{\frac{1}{2}})^2}\,\varepsilon_{31}^3-\varepsilon_{31}\,\varepsilon_{32}\right)+4\left(u_3-u_1\,u_2+\frac{u_1^3}{3}\right)\right.$$

$$-\left(\lambda_3-\lambda_1\,\lambda_2+\frac{\lambda_1^3}{3}\right)-\frac{2\eta^{\frac{1}{2}}\,(1-\eta)}{3\,(1+\eta^{\frac{1}{2}})^3}\,\varepsilon_{31}^3-\frac{4\,\eta\,(3+3\,\eta+2\,\eta^2)}{3\,(1+\eta)^3}$$

$$\left.+\frac{1}{4!}\left(\frac{10-8\eta^{\frac{1}{2}}}{1+\eta^{\frac{1}{2}}}\,\varepsilon_{31}-\frac{8\,\eta}{1+\eta}+4\,u_1-\lambda_1\right)^3\right\}\,\delta^2=0\,. \qquad \text{(II—5)}$$

In these equations a common factor δ has been cancelled out.

Let us introduce the following notations

$$A_\theta=\Sigma\,g_{nm}\,\eta^{-\frac{n}{2}}\,v_0^m,\qquad A_0\,\langle n\rangle=\Sigma\,n\,g_{nm}\,\eta^{-\frac{n}{2}}\,v_0^m,\qquad A_0\,\langle m\rangle=\Sigma\,m\,g_{nm}\,\eta^{-\frac{n}{2}}\,v_0^m,$$

$$A_0\,\langle n^2\rangle=\Sigma\,n^2\,g_{nm}\,\eta^{-\frac{n}{2}}\,v_0^m.$$

It is found that if we multiply (II — 2), (II — 3), (II — 4) respectively by

$$a=\frac{2\,[4\,A_0-A_0\,\langle n\rangle\,]}{A_0\,A_0\,\langle n^2\rangle-A_0^2\,\langle n\rangle},$$

$$b=-\,\frac{1}{A_0}\left[4\,\eta^{\frac{1}{2}}-4+\frac{\{4\,A_0-A_0\,\langle n\rangle\}^2}{A_0\,A_0\,\langle n^2\rangle-A_0^2\,\langle n\rangle}\right],$$

$$c=-\,\frac{5-4\eta^{\frac{1}{2}}}{A_0}\,,$$

and add them to (II — 5), we obtain an expression of the form

$$P+R\,\delta+W\,\delta^2=0.$$

In this expression P and R are functions of η only, whereas W involves u_1, λ_1, ε_{31} as well. Putting $\delta=0$ we obtain the condition for critical temperature. This condition can be explicitly written down :

$$\left[\frac{2}{1+\eta}+\frac{(1-\eta)^2}{4\,\eta\,(1+\eta)}\,\frac{A_0\,\langle m\rangle}{A_0}\right]\left[4-4\,\eta^{\frac{1}{2}}+\frac{\{4\,A_0-A_0\,\langle n\rangle\}^2}{A_0\,A_0\,\langle n^2\rangle-A_0^2\,\langle n\rangle}\right]=\frac{8\,\eta}{1+\eta}.$$

This is actually equivalent to using equation (16), the only difference being that at present all the equations are differentiated with respect to ε_2 rather than s.

With the critical value η_c determined we can expand η about η_c or T about T_c. We expand P and R in this way, and it is found that they all begin with the term $(T_c - T)/T_c = \xi$. Write

$$P = P'\xi + \cdots, \quad R = R'\xi + \cdots.$$

In W we replace all variables by their critical values. At the critical temperature the values of u_1, λ_1, ε_{31} can be obtained by setting in (II − 2), (II − 3), (II − 4) and solving the simultaneous linear equations thus obtained. In this way we obtain an equation of the form

$$P'\xi + R'\xi\delta + W_c\delta^2 + \text{terms of higher order} = 0,$$

where W_c stands for the value of W at the critical temperature. In order that this expression vanishes identically we must have

$$P'\xi + W_c\delta^2 = 0, \quad \text{etc.}$$

Thus

$$\delta = \sqrt{\frac{P'}{W_c}\xi} = 2.835\sqrt{\frac{T_c - T}{T_c}}.$$

The order s, on making an expansion in δ, assumes the form

$$s = \frac{\lambda_1 A_0 - 2u_1\{A_0\langle n\rangle - 2A_0\}}{2A_0}\delta + \cdots$$

Hence to the first order

$$s \propto \sqrt{\frac{T_c - T}{T_c}}.$$

Substituting critical values into the above expression for s we obtain

$$s = 1.731\sqrt{\frac{T_c - T}{T_c}}.$$

The energy E_1 is expanded along similar lines. A rather complicated calculation gives finally

$$E_1 = \frac{NV}{16}\left[4.877 - 3.486\,\frac{T_c - T}{T_c} - 2.913\,\delta^2\right].$$

The part involving δ^2 is the cause for the discontinuity of the specific heat at the critical temperature, because above the critical temperature all parameters are simple powers of η as mentioned above.

中 文 提 要

平面方格及立方格中 A B 型超格之理論

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本文應用王氏之理論於平面方格及立方格中 AB 型超格。所有計算皆作到第二次近似值，惟僅考慮到鄰近原子間之相互作用。所計算者有臨界溫度與合金成分之關係，秩序之程度，內能，及比熱。凡 Bethe 氏曾經計算過者與本文計算結果相較，均相差無幾。