

... VARIATION OF INTERACTION ENERGY WITH CHANGE OF LATTICE CONSTANTS AND CHANGE OF DEGREE OF ORDER*

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ABSTRACT

The change of lattice constants due to order-disordering process in a superlattice is investigated by using the condition of minimum free energy in Bethe's theory. It is found that the interaction energy depends on the degree of order when the external pressure is kept constant. The specific heat at constant pressure given by the theory is compared with experiment. Another source of the variation of interaction energy is the change of atomic arrangements. This is also investigated from the viewpoint of Wang's formulation of the free energy in Bethe's approximation.

1. INTRODUCTION

The binary alloy CuAu is face-centred cubic when disordered and tetragonal when ordered. This change of lattice form has been studied by Wilson¹ on the basis of Bethe's theory of superlattices, and his result agrees well with Gorsky's measurements². He employed the condition of minimum energy at constant entropy for obtaining the equilibrium lattice constant under a given external pressure. But instead of using the correct entropy expression in Bethe's theory

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1 A. H. Wilson, *Proc. Camb. Phil. Soc.* 34, 81 (1938).

2 Gorsky, *Zeit. f. Phys.*, 50, 64 (1928).

(which was unknown at that time), he replaced the condition of constant entropy by that of constant long-distance order, which amounts to using Bragg-Williams' entropy as an approximation. It will be shown in the present paper that Bethe's theory can be consistently applied throughout the calculation if the condition of minimum free energy at constant temperature is used. The explicit expression of the free energy is, however, not required in the actual calculation.

The change of lattice constants evidently affects the interaction energy between the atoms, and must consequently produce a change in the configurational energy and the specific heat of the crystal. We shall see that this effect is in the right direction to bring the theory into closer agreement with experiment, because it tends to make the energy increase more rapidly near the critical temperature. An actual calculation of the specific heat at variable lattice constant but constant external pressure is made in §3.

Now the interaction energy is also influenced by change in the atomic arrangement. Mott³ has shown from an investigation of the electronic distribution in superlattices that the interaction energy decreases as the degree of order decreases. The actual relation between the two is, however, very complicated. A linear dependence of the average interaction energy upon the degree of order has been assumed by Lin⁴ in attempting to explain the occurrence of the maximum critical temperature of a face-centred alloy at the atomic ratio 1:3. This assumption will now be examined in the light of the free energy in Bethe's approximation⁵. In this way it is found that the interaction energy as a function of the degree of order must satisfy certain equations obtained from a set of conditions of consistency. This same set of conditions of consistency makes also

³ N. F. Mott, *Proc. Phys. Soc.* **49**, 258 (1937).

⁴ U. C. Lin, *Chinese J. Phys.* **3**, 182 (1939).

⁵ Wang, "Free Energy in the Statistical Theory of Order-Disorder Transformations", *Science Report of National Tsing Hua University*, series A, 30-th Anniversary Memorial Number (1941) printed but failed to appear.

possible the calculation of the energy of the crystal without appealing to Bragg-Williams' theory as Lin did.

2. THE VARIATION OF LATTICE CONSTANTS

We shall form the partition function at constant lattice constants l_1 and l_2 and then obtain their equilibrium values from the equations determining the generalized reactions. Let $\frac{1}{2}zNm$ be the number of A-B neighbours in the crystal. If $g(m)$ is the number of arrangements of the atoms for given value of m , and $W(l_1, l_2, m)$ the configurational energy of the crystal, the configurational partition function is

$$f(m, T, l_1, l_2) = g(m) e^{-W/kT}.$$

The equilibrium value \bar{m} of m is determined from the condition of maximum f :

$$\frac{\partial}{\partial m} \log f(\bar{m}, T, l_1, l_2) = 0.$$

The generalized reactions are given by

$$\begin{aligned} L_1 &= kT \frac{d}{dl_1} \log f(\bar{m}, T, l_1, l_2) = kT \frac{d\bar{m}}{dl_1} \frac{\partial}{\partial \bar{m}} \log f + kT \frac{\partial}{\partial l_1} \log f \\ &= kT \frac{\partial}{\partial l_1} \log f = - \frac{\partial}{\partial l_1} W(l_1, l_2, \bar{m}). \end{aligned} \quad (1)$$

To study the change of lattice form in CuAu we divide the face-centred lattice into four simple cubic sublattices 1, 2, 3, 4. Let the shortest distance between the sites of 1 and 2, or 3 and 4 be l_1 , that between the sites of 1 and 3, 1 and 4, 2 and 3 or 2 and 4 be l_2 , so that the former is the distance between neighbouring Au-Au or Cu-Cu atoms and the latter that between neighbouring Au-Cu atoms when the crystal is perfectly ordered. The interaction energies V_{AA}, V_{AB} and V_{BB} are function of l_1, l_2 . If the number of sites of each sublattice

is $\frac{1}{2}N$, the number of pairs of sites between sublattices 1 and 2 must be $4(\frac{1}{2})N = 2N$. I denote by m_{12} the fraction of A-B pairs among these. Then the number of

$$\text{A-A pairs is } \frac{1}{2} \left[4 \left(\frac{N}{2} \theta_1 + \frac{N}{2} \theta_2 \right) - 2Nm_{12} \right] = N[\theta_1 + \theta_2 - m_{12}],$$

$$\begin{aligned} \text{B-B pairs is } \frac{1}{2} \left[4 \left(\frac{N}{2} \{1 - \theta_1\} + \frac{N}{2} \{1 - \theta_2\} \right) - 2Nm_{12} \right] \\ = N[2 - \theta_1 - \theta_2 - m_{12}], \end{aligned}$$

where θ_i is the fraction of sites of sublattice i occupied by A atoms. Thus the interaction energy between the atoms on sublattices 1 and 2 is

$$N[(\theta_1 + \theta_2 - m_{12})V_{AA}(l_1) + 2m_{12}V_{AB}(l_1) + (2 - \theta_1 - \theta_2 - m_{12})V_{BB}(l_1)].$$

Writing $c = \frac{1}{4}(\theta_1 + \theta_2 + \theta_3 + \theta_4)$ and $V = \frac{1}{2}(V_{AA} + V_{BB}) - V_{AB}$

we get the energy of the whole crystal

$$\begin{aligned} W = N[4cV_{AA}(l_1) + 4(1-c)V_{BB}(l_1) - 2(m_{12} + m_{14})V(l_1)] \\ + N[8cV_{AA}(l_2) + 8(1-c)V_{BB}(l_2) \\ - 2(m_{13} + m_{24} + m_{14} + m_{23})V(l_2)]. \quad (2) \end{aligned}$$

With this value for W , (1) becomes

$$\begin{aligned} L_1 = -N[4cV'_{AA}(l_1) + 4(1-c)V'_{BB}(l_1) \\ - 2(\bar{m}_{12} + \bar{m}_{14})V'(l_1)], \quad (3) \end{aligned}$$

and

$$\begin{aligned} L_2 = -N[8cV'_{AA}(l_2) + 8(1-c)V'_{BB}(l_2) \\ - 2(\bar{m}_{13} + \bar{m}_{14} + \bar{m}_{23} + \bar{m}_{24})V'(l_2)]. \quad (4) \end{aligned}$$

To solve for l_1 and l_2 as functions of T we must first know the \bar{m} 's, which are usually very complicated. Wilson¹ discussed the values of l_1 and l_2 only in the cases when the alloy is disordered and when the order is nearly perfect. We shall also confine our attention to these cases.

(i) *Disordered*. In this case there is no difference between the four sublattices so that all the \overline{m}_{ij} 's are equal to \overline{m} . (3) and (4) reduce to

$$\begin{aligned} L_1 &= -N[4cV_{AA}'(l_1) + 4(1-c)V_{BB}'(l_1) - 4\overline{m}V'(l_1)], \\ L_2 &= -N[8cV_{AA}'(l_2) + 8(1-c)V_{BB}'(l_2) - 8\overline{m}V'(l_2)]. \end{aligned} \quad (5)$$

If $L_1 = L_2 = 0$ this shows that $l_1 = l_2$, so that the crystal is cubic.

(ii) *Order nearly perfect*. When $c = \frac{1}{2}$, and the order is nearly perfect,

$$\theta_1 = \theta_2 \approx 1, \quad \theta_3 = \theta_4 \approx 0, \quad \theta_1 + \theta_3 = 1, \quad \theta_1 - \theta_3 = s.$$

There are only a few B atoms on sublattices 1 and 2. Hence approximately

$$\overline{m}_{12} = (1 - \theta_1) + (1 - \theta_2) \approx 2\theta_3 = 1 - s.$$

By the same reason we can obtain the number of A-A pairs of neighbours between the sublattices 1 and 3:

$$N(\theta_1 + \theta_3 - \overline{m}_{13}) = 4(\frac{1}{2}N\theta_3).$$

Thus

$$\overline{m}_{13} = \theta_1 - \theta_3 = s.$$

We can now write down all the \overline{m} 's:

$$\overline{m}_{12} = \overline{m}_{34} = 1 - s, \quad \overline{m}_{13} = \overline{m}_{14} = \overline{m}_{23} = \overline{m}_{24} = s.$$

The equations are correct to the first order of $(1-s)$. Substituting them into (3) and (4) we obtain

$$L_1 = -2N[V_{AA}'(l_1) + V_{BB}'(l_1) - 2(1-s)V'(l_1)],$$

and
$$L_2 = -4N[V_{AA}'(l_2) + V_{BB}'(l_2) - 2sV'(l_2)].$$

These are exactly equations (27) in Wilson's paper, from which an expression of the degree of tetragonality in agreement with Gorsky's measurements² can be obtained.

3. THE EFFECT OF THE CHANGE OF LATTICE CONSTANTS ON THE INTERACTION ENERGY

In the alloy CuAu the gold atoms and the copper atoms are in contact when the order is perfect. Since the copper atom is somewhat smaller than the gold atom, the size of the crystal must increase when gold atoms exchange their positions with copper atoms. Thus with increasing disorder the distance between the atoms increases and hence the interaction energies diminish. The disordering process is therefore effected with more ease near the critical temperature than it is at lower temperatures; and we expect the specific heat at constant pressure to possess a steeper and higher maximum at the critical temperature than the specific heat at constant volume.

Now we shall calculate in length the specific heat at constant pressure of the alloy β -brass, which forms the simplest type of superlattice that can be studied statistically. Bethe's method will be used.

The configurational energy of the crystal is, in Easthope's⁶ notations:

$$W = -N_{AB} V + \frac{1}{2} N z \{ c(V_{AA} - V_{BB}) + V_{BB} \}. \quad (6)$$

Substitution of this expression into (1) gives

$$0 = -\bar{m}V'(l) + c[V_{AA}'(l) - V_{BB}'(l)] + V_{BB}'(l),$$

when the pressure is put equal to zero. Now the variation of V is not very large, so that to a sufficient approximation we may assume the linear relations

$$(V_{AA}'(l) - V_{BB}'(l))/V'(l) = -K_0 + K_1 V \quad (7)$$

$$\text{and} \quad V_{BB}'(l)/V'(l) = -J_0 + J_1 V. \quad (8)$$

These three last equations give, after eliminating $V_{AA}'(l)$ and $V_{BB}'(l)$:

6. Easthope, *Proc. Camb. Phil. Soc.* 33, 502 (1937); 34, 68 (1938).

$$V = \frac{\bar{m} + (cK_0 + J_0)}{cK_1 + J_1} \quad (9)$$

We have already seen that V increases as \bar{m} increases, hence $cK_1 + J_1$ must be positive. The other constant $cK_0 + J_0$ must also be positive in order that V may be positive with only a relatively small variation.

We can now start from (9) and the equations given by Easthope⁶ for the determination of \bar{m} as a function of the temperature and V to obtain the specific heat at constant pressure:

$$C_p = \frac{dW}{dT} = \left(\frac{\partial W}{\partial \bar{m}} \right)_l \frac{d\bar{m}}{dx} \frac{dx}{dT} + \left(\frac{\partial W}{\partial l} \right)_{\bar{m}} \frac{dl}{dT} = \left(\frac{\partial W}{\partial \bar{m}} \right)_l \frac{d\bar{m}}{dx} \frac{dx}{dT} \quad (10)$$

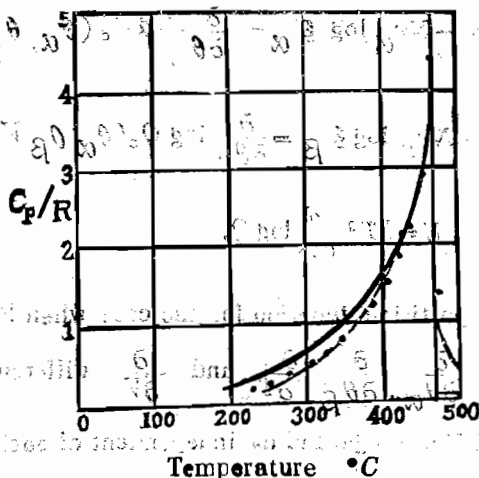
$$\text{But} \quad \frac{dx}{dT} = (xV/kT^2) / (1 + \frac{x}{kT} \frac{dV}{d\bar{m}} \frac{d\bar{m}}{dx}) \quad (11)$$

Hence by (6)

$$C_p = \frac{\frac{1}{2} N_2 k x (\log x)^2 \left(- \frac{d\bar{m}}{dx} \right)}{1 + \frac{x \log x}{\bar{m} + (cK_0 + J_0)} \left(- \frac{d\bar{m}}{dx} \right)} \quad (12)$$

The value of this expression is calculated for the case $c = \frac{1}{2}$, the constant $cK_0 + J_0$ being assumed to be 1.79 to make $(C_p)_{T_c} = 5.1R$. The result is plotted in the accompanying figure together with Moser's and Sykes and Wilkinson's experimental data.⁷

7. H. Moser, *Phys. Zett.* 37, 737 (1936); C. Sykes and H. Wilkinson, *J. Inst. Metals* 61, 223 (1937).



: Moser's experiment
 — Sykes and Wilkinson's experiment

Fig. Configurational specific heat of β -brass.

4. THE EFFECT OF THE ATOMIC DISTRIBUTION ON

THE INTERACTION ENERGY

As has already been mentioned, the interaction energy depends in some very complicated manner upon the degree of order on account of the change of atomic distribution. To study the effect of such a dependence Lin⁴ has assumed a linear relationship

$$V = V_0(1 - \alpha c + \beta m_{AA}) \quad (13)$$

between the interaction energy: V and the fraction of A-A pairs of neighbours: m_{AA} . In this section we shall study the general nature of the variation of V in the light of the theory of the free energy in Bethe's approximation given by Wang⁵.

The fundamental equations in Wang's paper are (45), (46) and (39) with ξ_α and ξ_β given by (47), (48), (49) and (50). These equations are still assumed to be valid now V becomes a function of θ_α , θ_β and T . They may be put into the form:

$$\frac{d}{d\theta_\alpha} \log Q = -Nr_\alpha \log \xi_\alpha = \frac{\partial}{\partial \theta_\alpha} \log Q_0(\theta_\alpha, \theta_\beta, V/T), \quad (14)$$

$$\frac{d}{d\theta_\beta} \log Q = -Nr_\beta \log \xi_\beta = \frac{\partial}{\partial \theta_\beta} \log Q_0(\theta_\alpha, \theta_\beta, V/T), \quad (15)$$

$$E = kT^2 \frac{d}{dT} \log Q, \quad (16)$$

where Q_0 is the partition function for the case when V is a constant, if we denote by $\frac{\partial}{\partial \theta_\alpha}$, $\frac{\partial}{\partial \theta_\beta}$, $\frac{\partial}{\partial T}$ and $\frac{\partial}{\partial V}$ differentiations when

θ_β , θ_α , T and V are regarded as independent of each other, and by

$\frac{d}{d\theta_\alpha}$ the operator $\frac{\partial}{\partial \theta_\alpha} + \frac{dV}{d\theta_\alpha} \frac{\partial}{\partial V}$, (14) and (15) mean that we

have assumed with Lin that the equilibrium values of θ_α and θ_β are given by the same equation as in Bethe's approximation. (16) gives the energy of the crystal.

Consistency of (14) and (15) requires

$$\frac{d}{d\theta_\alpha} \left(\frac{\partial}{\partial \theta_\beta} \log Q_0 \right) = \frac{d}{d\theta_\beta} \left(\frac{\partial}{\partial \theta_\alpha} \log Q_0 \right),$$

$$\text{i. e.} \quad \frac{dV}{d\theta_\alpha} \frac{\partial^2}{\partial V \partial \theta_\beta} \log Q_0 = \frac{dV}{d\theta_\beta} \frac{\partial^2}{\partial V \partial \theta_\alpha} \log Q_0. \quad (17)$$

Upon the hypothesis of nearest neighbour interaction the energy in Wang's paper becomes

$$(E_0) = kT^2 \frac{\partial}{\partial T} \log Q_0 = zNVm_{AA}. \quad (18)$$

But Q_0 depends on T and V through V/T , so that

$$\frac{\partial^2}{\partial V \partial \theta_\alpha} \log Q_0 = -\frac{T}{V} \frac{\partial^2}{\partial T \partial \theta_\alpha} \log Q_0 = -\frac{\partial E_0}{\partial \theta_\alpha} / kTV.$$

Substituting this equation and a similar one into (17) we obtain

$$\frac{\partial E_0}{\partial \theta_\beta} \frac{dV}{d\theta_\alpha} = \frac{\partial E_0}{\partial \theta_\alpha} \frac{dV}{d\theta_\beta}, \quad (18)$$

which become, if $\frac{\partial E_0}{\partial V} \frac{dV}{d\theta_\alpha} \frac{dV}{d\theta_\alpha}$ is added to both sides,

$$\frac{dE_0}{d\theta_\beta} \frac{dV}{d\theta_\alpha} = \frac{dE_0}{d\theta_\alpha} \frac{dV}{d\theta_\beta}.$$

This shows that V and E_0 are connected by a relation independent of θ_α and θ_β , i. e.

$$V = V(E_0, T). \quad (19)$$

A consequence of this result is that the coefficient α in Lin's relation (13) must be zero. This makes, however, the maximum critical temperature for the AB type of superlattices to shift to a value of the concentration different from $\frac{1}{2}$, which contradicts experimental results. One way out of the difficulty is to make some other assumption regarding the dependence of V on the degree of order, such as a quadratic dependence

$$V = V_0 \left[1 + \beta m_{AA}^2 - \frac{\beta(z-1)}{2c(cz-1)} m_{AA}^4 \right]. \quad (20)$$

Let us now try to find E in the general case. From (14) and (16) we get

$$\begin{aligned} \frac{dE}{d\theta_\alpha} &= kT^2 \frac{d}{dT} \left(\frac{\partial}{\partial \theta_\alpha} \log Q_0 \right) = kT^2 \frac{d(V/T)}{dT} \frac{\partial}{\partial \theta_\alpha} \frac{\partial}{\partial (V/T)} \log Q_0 \\ &= -\frac{T^2}{V} \frac{d(V/T)}{dT} \frac{\partial E_0}{\partial \theta_\alpha}. \end{aligned} \quad (21)$$

Similarly $\frac{dE}{d\theta_\beta} = -\frac{T}{V} \frac{d(\frac{V}{T})}{dT} \frac{\partial E_0}{\partial \theta_\beta}$.

Hence $\frac{dE}{d\theta_\alpha} \frac{\partial E_0}{\partial \theta_\beta} = \frac{dE}{d\theta_\beta} \frac{\partial E_0}{\partial \theta_\alpha}$.

Just as (18) leads to (19), this last equation leads to

$$E = E(E_0, T).$$

Substituting this into (21) we obtain

$$\frac{\partial E}{\partial E_0} \left(\frac{\partial E_0}{\partial \theta_\alpha} + \frac{\partial E_0}{\partial V} \frac{dV}{d\theta_\alpha} \right) = \frac{\partial E_0}{\partial \theta_\alpha} \left(1 - \frac{T}{V} \frac{dV}{dT} \right).$$

But (19) gives

$$\frac{dV}{d\theta_\alpha} = \frac{\frac{\partial E}{\partial \theta_\alpha} \frac{\partial V}{\partial E_0}}{1 - \frac{\partial V}{\partial E_0} \frac{\partial E_0}{\partial V}} \quad \text{and} \quad \frac{dV}{dT} = \frac{\frac{\partial V}{\partial T} + \frac{\partial V}{\partial E_0} \frac{\partial E_0}{\partial T}}{1 - \frac{\partial V}{\partial E_0} \frac{\partial E_0}{\partial V}}.$$

Hence
$$\begin{aligned} \frac{\partial E}{\partial E_0} &= \left(1 - \frac{\partial V}{\partial E_0} \frac{\partial E_0}{\partial V} \right) \left(1 - \frac{T}{V} \frac{\partial V}{\partial T} \right) \\ &= 1 - \frac{\partial V}{\partial E_0} \frac{\partial E_0}{\partial V} - \frac{T}{V} \frac{\partial V}{\partial T} + \frac{T}{V} \frac{\partial V}{\partial E_0} \frac{\partial E_0}{\partial T}. \end{aligned}$$

Now E_0/V is a function of $\theta_\alpha, \theta_\beta$ and V/T , so that

$$\frac{\partial E_0}{\partial V} = -\frac{T}{V} \frac{\partial E_0}{\partial T} + \frac{E_0}{V}.$$

Hence
$$\frac{\partial E}{\partial E_0} = 1 - \frac{E_0}{V} \frac{\partial V}{\partial E_0} - \frac{T}{V} \frac{\partial V}{\partial T} \quad (22)$$

If V depends on m_{14} only, and not on T , we have

$$\frac{\partial E}{\partial E_0} = 1 - \frac{E_0}{V} \frac{\partial V}{\partial E_0} = V \frac{d(E_0/V)}{dE_0}.$$

The boundary condition is given by the case when there are no A atoms, i. e. when $\theta_\alpha + \theta_\beta = 0$. In this case $m_{AA} = 0$, $E_0 = E = 0$.

Hence

$$E = \int_0^{E_0} \left(V \frac{d(E_0/V)}{dE_0} \right) dE_0 = zN \int_0^{m_{AA}} V dm_{AA}. \quad (23)$$

If the assumption (20) is made, the energy of the crystal is

$$E = zNV \left[m_{AA} + \frac{\beta}{2} m_{AA}^2 - \frac{\beta(z-1)}{6c(cz-1)} m_{AA}^3 \right].$$

When β is not large, this differs very little from Bethe's original expression in numerical value. The specific heat is

$$C_V = zNV \frac{dm_{AA}}{dT} = zNV \frac{dm_{AA}}{dx} \frac{1}{1 + \frac{x}{kT} \frac{dV}{dx}} = zNkx(\log x) \frac{dm_{AA}}{dx} \frac{1}{1 + \frac{x}{kT} \frac{dV}{dx}} \frac{dm_{AA}}{dx}.$$

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