GENERAL THEORY OF THE QUASI-CHEMICAL METHOD IN THE STATISTICAL THEORY OF SUPERLATTICES

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ABSTRACT

The generalization of the quasi-chemical method of Fowler and Guggenheim in the statistical theory of superlattices made by one of the authors is extended to a binary alloy of any composition. The formulae are very similar to those for the composition 1:1. The alloy $AuCu_3$ is treated in more detail.

1. INTRODUCTION.

In a recent paper one of the authors[1] has generalized the quasi-chemical method of Fowler and Guggenheim to any groups of sites in the case of a binary alloy with equal numbers of A and B atoms. It is the purpose of this paper to generalize this theory to any value of the concentration ratio of A and B atoms. For this purpose it is necessary to change the notation of the previous paper, and we shall adopt the notation proposed by Wang[2] in his generalization of Bethe's theory.

In the following treatment we shall confine ourselves to a binary alloy whose atoms are distributed in two classes of sites in the crystal, each site being surrounded by z neighbouring sites. Only interactions between neighbouring atoms will be taken into account, while those between more distant atoms will be neglected.

In Wang's notation the number of A atoms is denoted by $N\theta$, that of B atoms by $N(1-\theta)$, N being the total number of atoms. The number of α-sites is denoted by Nr, that of β-sites by $N(1-r)$. In a given distribution of atoms among the lattice sites the number of A atoms in α-sites is denoted by $Nr\theta_\alpha$, that in β-sites by $N(1-r)\theta_\beta$, so that

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[1] C. N. Yang, *J. Chem. Phys.* **13** (1945), 66; cited as I.

[2] J. S. Wang, *Phys. Rev.* **67** (1945), 98.

$$r\theta_\alpha+(1-r)\,\theta_\beta=\theta. \tag{1}$$

The numbers of B atoms in α- and β-sites are respectively $Nr(1-\theta_\alpha)$ and $N(1-r)\,(1-\theta_\beta)$. The (long-distance) orders, s, of the distribution is defined by

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

The purpose of the statistical theory of superlattices is to determine the equilibrium value of θ_α, or of s as a function of the temperature and the composition θ, and then deduce the energy of the alloy.

2. FUNDAMENTAL EQUATIONS OF THE QUASI-CHEMICAL METHOD.

In the quasi-chemical method we confine our attention to a group of sites chosen out of the whole crystal. The whole crystal is conceived as a superposition of such groups, all of identical form. Each group consists of a connected set of sites, but two different groups may have common sites.

Although the groups are all of identical form, they may differ in the nature of the sites they contain. For example, in the case of a group consisting of two nearest neighbouring sites in a face-centred cubic lattice, some of the groups will consist of α-β pairs and some β-β pairs, provided all the cube corners are α-sites and all the face centres are β-sites. The groups are therefore divided into a number of different types by the difference in the nature of the sites they contain.

In a given choice of the groups, let there be n-sites in each group with p pairs of nearest neighbouring sites, and let the total number of groups be M. Suppose that among the M groups there are l different types with Mc_λ groups of the type λ $(\lambda=1,2,\ldots.,l)$, such that $\sum c_\lambda=1$. Nevertheless, the sites of each group will be labelled by $1,2,\ldots.,n$ in one and the same way. It may happen that a site labelled with the number i is an α-site in one group and a β-site in another. Let q_i $(i=1,2,\ldots.,n)$ be a number specifying the state of occupation of the i-th site; $q_i=1$ if the i-th site is occupied by an A atom[3], $q_i=0$ if it is occupied by a B atom. In a given distribution of the atoms let $[q_1,q_2,\ldots.,q_n]_\lambda$ be the number of groups of the type λ having q_1 A atoms on the site 1, q_2 A atoms

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[3] It may be mentioned that the theory can be developed equally well by giving attention to the wrong atoms, as done in I, instead of to the A atoms.

on the site 2, etc, Since the total number of groups of the type λ is Mc_λ, we have

$$\sum_q [q_1\, q_2, \ldots, q_n]_\lambda = Mc_\lambda, \tag{3}$$

where the summation is taken over all possible values of the q's. Now since the fraction of α-sites occupied by A atoms is θ_α, and the fraction of β-sites occupied by A atoms is θ_β, it follows that the fraction of the groups of the type λ having the *i-th* site occupied by an A atom is θ_α or θ_β according as the *i-th* site in the type λ is an α-or a β-site. Hence

$$\sum_q q_i\, [q_1, q_2, \ldots, q_n]_\lambda = Mc_\lambda \theta_{\lambda i} \tag{4}$$

where $\theta_{\lambda i}$ is equal to θ_α if the *i-th* site in the type λ is an α-site and is equal to θ_β if it is a β-site.

The equations (3) and (4) suggest a chemical analogy. Imagine a gaseous assembly consisting of molecules with the chemical formulae

$$X^\lambda (Y_1{}^\lambda)_{q_1} (Y_2{}^\lambda)_{q_2} \ldots (Y_n{}^\lambda)_{q_n}.$$

If the number of such molecules be $[q_1, q_2, \ldots, q_n]_\lambda$, then the equations (3) and (4) can be interpreted as equations expressing that the variation in the numbers of the molecules are subject to the condition that the total numbers of the atoms X^λ, $Y_1^\lambda, \ldots, Y_n^\lambda$ shall remain fixed at the values Mc_λ, $Mc_\lambda \theta_{\lambda 1}, \ldots, Mc_\lambda \theta_{\lambda n}$, respectively. The basic assumption in the quasi-chemical method is that the equilibrium value of the number $[q_1, q_2, \ldots, q_n]_\lambda$ in the crystal is the same as the equilibrium value of the number of molecules in the corresponding chemical assembly with the chemical energy of combination equal to the configurational energy of our group in the distribution $(q_1, q_2, \ldots q_n)$. The configurational energy is a function of $q_1, \ldots q_n$ and is obviously the same for all types of groups. Let us denote this energy by χ. The equilibrium value of the number of molecules in a gaseous assembly is[4]

$$[q_1, q_2, \ldots, q_n]_\lambda = \xi_\lambda\, \mu_{\lambda 1}^{q_1}\, \mu_{\lambda 2}^{q_2} \ldots \mu_{\lambda n}^{q_n} e^{-\chi/kT} \tag{5}$$

where ξ_λ, $\mu_{\lambda 1}, \ldots, \mu_{\lambda n}$ are parameters to be determined by substituting (5) into (3) and (4), We shall assume (5) to be true for our groups in the alloy. It can be

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[4] See R. H. Fowler, *Statistical Mechanics*, 2nd ed., p. 163, eq. (478),

shown, as done in I, that the error of assuming (5) becomes negligibly small as the group of sites becomes very large.

Let us introduce the function φ_λ of $\mu_{\lambda i}$ defined by

$$\varphi_\lambda=\sum_q \mu_{\lambda 1}^{q_1}\cdots\mu_{\lambda r}^{q_n}\, e^{-\chi/kT}\,. \tag{6}$$

Then the substitution of (5) into (3) and (4) leads to

$$\xi_\lambda\varphi_\lambda=Mc_\lambda,\quad \xi_\lambda\mu_{\lambda i}\frac{\partial\varphi_\lambda}{\partial\mu_{\lambda i}}=Mc_\lambda\theta_{\lambda i}, \tag{7}$$

Eliminating ξ_λ, we obtain

$$\mu_{\lambda i}\frac{\partial}{\partial\mu_{\lambda i}}\ln\ \varphi_\lambda=\theta_{\lambda i}. \tag{8}$$

The parameters $\mu_{\lambda i}$ are *uniquely* determined by these equations, As $T\rightarrow\infty$ they approach the following limiting values

$$(\mu_{\lambda i})_{T=\infty}\ =\theta_{\lambda i}/(1-\theta_{\lambda i}). \tag{9}$$

The sum of the energies of all the M groups is

$$\sum_\lambda\sum_q\ [q_1,\ldots\ldots,q_n]_\lambda\chi=\sum_\lambda\ \xi_\lambda\, kT^2\frac{\partial\varphi_\lambda}{\partial T}$$

$$=MkT^2\sum_\lambda c_\lambda\ \frac{\partial}{\partial T}\ln\varphi_\lambda.$$

Now the sum of the pairs of nearest neighbours in the M groups is Mp, while that in the actual crystal is $\frac{1}{2}Nz$. Hence the average energy of the alloy will be $\frac{1}{2}Nz/Mp$ times the above expression, viz.,

$$E=\frac{Nz}{2p}kT^2\sum_\lambda c_\lambda\ \frac{\partial}{\partial T}\ln\varphi_\lambda. \tag{10}$$

3. THE FREE ENERGY AND THE EQUILIBRIUM DISTRIBUTION.

The average configurational energy can be expressed in terms of the configurational partition function $P(\theta_\alpha,\ \theta_\beta,\ T)$ by the well-known relation

$$E=kT^2\frac{\partial}{\partial T}P(\theta_\alpha,\ \theta_\beta,\ T).$$

Inversely the partition function can be obtained from the average energy by integration. We have

$$\ln P(\theta_\alpha, \theta_\beta, T) = \ln g(\theta_\alpha, \theta_\beta) + \int_\infty^T E \frac{dT}{kT^2}, \tag{11}$$

where

$$g(\theta_\alpha, \theta_\beta) = \frac{(Nr)!}{(Nr\theta_\alpha)!\,[Nr(1-\theta_\alpha)]!}\;\frac{[N(1-r)]!}{[N(1-r)\theta_\beta]!\,[N(1-r)(1-\theta_\beta)]!}$$

is the value of P in the limit of $T=\infty$.

The free energy F is related to the partition function by the simple relation

$$F = -kT \ln P(\theta_\alpha, \theta_\beta, T), \tag{12}$$

The integral in (11) can be evaluated with the help of a Legendre transformation in the same way as done in I. Let

$$\psi(\theta_\alpha, \theta_\beta, T) = \sum_\lambda c_\lambda \left(\ln \varphi_\lambda - \sum_i \theta_{\lambda i} \ln \mu_{\lambda i}\right). \tag{13}$$

It is easy to show that

$$\left(\frac{\partial \psi}{\partial T}\right)_{\theta_\alpha, \theta_\beta} = \sum_\lambda c_\lambda \left(\frac{\partial \ln \varphi_\lambda}{\partial T}\right)_{\mu_{\lambda i}},$$

and so

$$\int_\infty^T E \frac{dT}{kT^2} = \frac{Nz}{2p} \int_\infty^T \sum c_\lambda \frac{\partial}{\partial T} \ln \varphi_\lambda \, dT = \frac{Nz}{2p} \int_\infty^T \frac{\partial \psi}{\partial T} dT$$

$$= \frac{Nz}{2p}\{\psi(\theta_\alpha, \theta_\beta, T) - \psi(\theta_\alpha, \theta_\beta, \infty)\}.$$

The value of $\psi(\theta_\alpha, \theta_\beta, \infty)$ can be determined with the help of (9). When the result is substituted into (11) and (12), we obtain

$$F = -\frac{zNkT}{2p}\Big\{\sum_\lambda c_\lambda \left(\ln \varphi_\lambda - \sum_i \theta_{\lambda i} \ln \mu_{\lambda i}\right)$$

$$+ rD[\theta_\alpha \ln\theta_\alpha + (1-\theta_\alpha)\ln(1-\theta_\alpha)] + (1-r)D[\theta_\beta \ln\theta_\beta + (1-\theta_\beta)\ln(1-\theta_\beta)]\Big\}, \tag{14}$$

where $$D=n-\frac{2p}{z}.$$

In the derivation of (14) the following relation has been used:

$$\sum_{\lambda i} c_{\lambda} f(\theta_{\lambda i})=n[rf(\theta_{\alpha})+(1-r)\, f(\theta_{\beta})]. \tag{15}$$

This relation follows from the fact that among the total number of sites in the M groups, Mn in number. Mnr of which are α-sites and $Mn(1-r)$ are β-sites.

The equilibrium distribution is characterized by the value of the order s, which can be obtained by minimizing the free energy. If we regard F as a function of s, θ, T, we have

$$\left(\frac{\partial F}{\partial s}\right)_{\theta,T}=-\frac{2NkT}{2p}r(1-r)\{f_1(s,\theta)-f_2(s,\theta,T)\}. \tag{16}$$

with

$$f_1=D\ln\frac{\theta_{\alpha}(1-\theta_{\beta})}{\theta_{\beta}(1-\theta_{\alpha})}, \qquad f_2=\sum_{\lambda,i} c_{\lambda}\, \varrho_{\lambda i} \ln \mu_{\lambda i},$$

where $\varrho_{\lambda i}$ is $1/r$ or $-1/(1-r)$ according as $\theta_{\lambda i}$ is θ_{α} or θ_{β}. The equilibrium value of s is a solution of the equation

$$f_1(s,\theta)=f_2(s,\theta,T). \tag{17}$$

The solution will give a minimum of the free energy when

$$\frac{\partial f_1}{\partial s}<\frac{\partial f_2}{\partial s} \tag{18}$$

We shall now show that (17) is always satisfied by $s=0$. When $s=0$ we have $\theta_{\alpha}=\theta_{\beta}$ and $f_1=0$. Then $\theta_{\lambda i}=\theta$ and a solution of (8) is $\mu_{\lambda i}=\mu$, for all λ and i. Since the solution is unique, this is the only solution. Applying (15) to f_2 we obtain

$$f_2=\sum_{\lambda,i} c_{\lambda}\, \varrho_{\lambda i} \ln \mu=n \ln \mu\cdot\left(\frac{r}{r}-\frac{1-r}{1-r}\right)=0.$$

Hence (17) is satisfied by $s=0$.

When $T=\infty$ we have

$$f_2(s,\theta,\infty)=n\ \ln\frac{\theta_\alpha(1-\theta_\beta)}{\theta_\beta(1-\theta_\alpha)}=\frac{n}{D}f_1,$$

and the only solution is $s=0$.

When the temperature is below a certain critical temperature there will be at least one non-zero root s of (17). In the theory of Bragg and Williams[5] an equation of the form (17) is also obtained in which f_2 is a linear function of s. These authors have shown that in the case of $r=\frac{1}{2}$ the root $s>0$ gives a minimum of the free energy and the critical temperature is determined by the equation

$$\left(\frac{\partial f_1}{\partial s}\right)_{s=0}=\left(\frac{\partial f_2}{\partial s}\right)_{s=0}. \tag{19}$$

In the case of $r=\frac{1}{4}$, on the other hand, there are three roots of s ($s=0$ is one of them), of which the largest one, s^* say, gives an absolute minimum of the free energy when the temperature is below a certain critical temperature T_c determined by the condition that the free energy for the root $s=0$ is equal to that for the root s^*:

$$F(0,\theta,T_c)=F(s^*,\theta,T_c). \tag{20}$$

Since the difference between (19) and (20) is mainly due to the difference between the function f_1 in the two cases, we should expect the same equations (19) and (20) to apply to the present theory.

4. SOME GENERAL THEOREMS.

The energy χ depends on the interactions V_{AA}, V_{BB}, V_{AB} between pairs of atoms AA, BB, AB, respectively, in the form

$$\chi=p_{AA}\ V_{AA}+\ p_{BB}\ V_{BB}+\ p_{AB}\ V_{AB}, \tag{21}$$

where p_{AA}, p_{BB}, p_{AB} are respectively the number of nearest AA, BB, AB pairs in the group under consideration. The equilibrium property of the alloy depends, however, only on the combination

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[5] W. L. Bragg and E. J. Williams, *Proc. Roy. Soc.* **A 151** (1935), 540; E. J. Williams, *Proc. Roy. Soc.* **A 152** (1935), 231.

$$V=\tfrac{1}{2}(V_{AA}+V_{BB})-V_{AB} \tag{22}$$

of the interaction energies. We shall show that this is true in our theory. We proceed to prove the following theorem:

(*i*) *The free energy is changed by a constant when either* (*a*) *both* V_{AA} *and* V_{BB} *are replaced by* V *and* V_{AB} *by* 0, *or* (*b*) *both* V_{AB} *and* V_{BB} *are replaced by* 0 *and* V_{AA} *by* $2V$.

Suppose we have the replacement (a). Then χ is altered to

$$\chi'=(p_{AA}+p_{BB})V.$$

Now if z_i denotes the number of nearest neighbouring sites of the i-th site in the group under consideration. then we shall have

$$p_{AA}+p_{BB}+p_{AB}=p=\tfrac{1}{2}\sum_i z_i,$$

$$2p_{AA}+p_{AB}=\sum_i q_i z_i. \tag{23}$$

The difference between χ and χ' can be reduced to

$$\chi-\chi'=[V_{AB}-\tfrac{1}{2}(V_{AA}-V_{BB})]p+\tfrac{1}{2}(V_{AA}-V_{BB})\sum_q q_i z_i.$$

Let us denote by ξ_λ', $\mu'_{\lambda i}$ the parameters corresponding to the energy χ'. Then we have

$$[q_1,\dots,q_n]_\lambda=\xi_\lambda'(\mu'_{\lambda n})^{q_1}\dots(\mu'_{\lambda n})^{q_n}e^{-\chi'/kT}.$$

By comparing with (5) it is evident that the equilibrium property will be the same as in the case where χ is used if

$$\xi_\lambda'=\xi_\lambda\exp\{-[V_{AB}-\tfrac{1}{2}(V_{AA}-V_{BB})]p/kT\},$$

$$\mu_\lambda{}'_i=\mu_{\lambda i}\exp\{-\tfrac{1}{2}(V_{AA}-V_{BB})z_i/kT\}.$$

The relation between φ_λ and φ_λ' will be

$$\varphi_\lambda'=\varphi_\lambda\exp\{[V_{AB}-\tfrac{1}{2}(V_{AA}-V_{BB})]p/kT\}$$

and the difference between F and F' becomes

$$F-F'=-\frac{zNkT}{2p}\left[\sum_{\lambda} c_{\lambda}\left(\ln\frac{\varphi_{\lambda}}{\varphi_{\lambda}'}-\sum_{i}\theta_{\lambda i}\ln\frac{\mu_{\lambda i}}{\mu_{\lambda' i}}\right)\right]$$

$$=\frac{zN}{2p}\left\{\left[V_{AB}-\tfrac{1}{2}(V_{AA}-V_{BB})\right]p+\tfrac{1}{2}\sum_{\lambda, i}c_{\lambda}\,\theta_{\lambda i}z_i(V_{AA}-V_{BB})\right\}$$

$$=\tfrac{1}{2}zN\{V_{AB}+(\theta-\tfrac{1}{2})(V_{AA}-V_{BB})\},$$

which is a constant independent of the temperature. This proves the theorem for the replacement (a).

For the replacement (b) we have

$$\chi'=2p_{AA}V$$

and

$$\chi-\chi'=V_{BB}\,p+(V_{AB}-V_{BB})\sum q_i z_i.$$

The equilibrium property will be the same as in the case where χ is used if

$$\xi_{\lambda}'=\xi_{\lambda}\exp\{-V_{BB}\,p/kT\},$$

$$\mu_{\lambda i}'=\mu_{\lambda i}\exp\{-(V_{AB}-V_{BB})z_i/kT\}.$$

Then the same conclusion as in the case (a) follows.

We proceed to prove some further theorems.

(*ii*) *Two sites of the same nature* (namely, both are α-sites or both are β-sites) *situated symmetrically in the group have equal parameters* $\mu_{\lambda i}$.

It is easy to see that for two sites i and j which are situated symmetrically in the group the function φ_{λ} will be symmetrical in $\mu_{\lambda i}$ and $\mu_{\lambda j}$. Since by hypothesis $\theta_{\lambda i}=\theta_{\lambda j}$, eq. (8) will give equal values for $\mu_{\lambda i}$ and $\mu_{\lambda j}$.

(*iii*) ***If the parameters*** μ_i ***and*** μ'_i (we drop the subscript λ for simplicity) ***corresponding to the sets of values*** θ, s ***and*** θ', s' ***are connected by the relation*** $\mu_i\,\mu_i'=1$ (for all i), ***then***

$$\theta+\theta'=1, \qquad s=-s',$$

provided we use the replacement (a) in theorem (i).

When the replacement (a) has been made the energy will be symmetrical in A and B atoms, and the energy expression will be unaltered when $1-q_i$ is substituted for q_i. Thus we find (again drop the subscript λ)

$$\varphi(\mu_i)=\sum(\prod_i \mu_i{}^{q_i})e^{-\chi/kT}=\sum\Pi(\mu_i{}')^{-q_i}\,e^{-\chi/kT}$$

$$=\prod_i(\mu_i{}')^{-1}\sum\Pi(\mu'_i)^{1-q_i}\,e^{-\chi/kT}=\prod_i(\mu_i{}')^{-1}.\varphi(\mu_i{}'),$$

and consequently

$$\theta_i=\mu_i\frac{\partial\ln\varphi}{\partial\mu_i}=-\mu_i{}'\frac{\partial\ln\varphi}{\partial\mu_i{}'}=1-\theta_i{}'.$$

Since this is true for all i, we have $\theta=1-\theta'$ and $s=-s'$.

As corollaries of theorem (iii), we have

(*iv*) *If* $V_{AA}=V_{BB}=V$, $V_{AB}=0$, *then*

(*a*) $\ln\mu_i$ *is an odd function of* s *if* $\theta=\frac{1}{2}$, *and an odd function of* $\theta-\frac{1}{2}$ *when* $s=0$;

(*b*) *the derivatives* $\partial\ln\mu_i/\partial\theta$ *and* $\partial\ln\mu_i/\partial s$ *are unaltered when* θ *and* s *are simultaneously changed to* $1-\theta$ *and* $-s$;

(*c*) *when* $s=0$ *we have all* μ*'s equal, and* $\mu=0$ *when* $\theta=0$, $\mu=1$ *when* $\theta=\frac{1}{2}$, $\mu=\infty$ *when* $\theta=1$.

The last part (*c*) is not a direct consequence of (iii), but eq. (8) should also be used.

(*v*) *The critical temperature for an AB alloy* ($r=\frac{1}{2}$) *is symmetrical with respect to* $\theta=\frac{1}{2}$.

This is a consequence of (iv) (b). For the equation (19) for the determination of the critical temperature as a function of θ in the case of $r=\frac{1}{2}$, which reads

$$\frac{D}{\theta(1-\theta)}=\sum_{\lambda,i}c_\lambda\varrho_{\lambda i}\left(\frac{\partial}{\partial s}\ln\mu_{\lambda i}\right)_{s=0}, \tag{24}$$

is unaltered when θ is changed to $1-\theta$.

5. APPLICATION TO $AuCu_3$.

The face-centred cubic alloy $AuCu_3$ has been treated in I for the special case of $\theta=\frac{1}{4}$. We shall now remove this restriction, but shall still choose the tetrahedron as our group of sites. The tetrahedron consists of one α-site and three β-sites, and they are all of the same type. We have

$$r=\tfrac{1}{4},\quad z=12,\quad n=4,\quad p=6,\quad D=3.$$

Let us replace V_{AA} by $2V$ and V_{AB} and V_{BB} both by 0, and denote the parameter for the α-site by ν and that for the β-site by μ. using theorems (i) and (ii) in section 4. The function φ is

$$\varphi=(1+3\mu+3\eta\,\mu^2+\eta^3\,\mu^3)+\nu\,(1+3\eta\,\mu+3\eta^3\mu^2+\eta^6\mu^3), \tag{25}$$

where

$$\eta=e^{-2V/kT}.$$

Eq. (8) become

$$\nu\frac{\partial}{\partial\nu}\ln\varphi=\theta_\alpha,\qquad \mu\frac{\partial}{\partial\mu}\ln\varphi=3\theta_\beta, \tag{26}$$

where the factor 3 in the second equation is obtained by combining the three equations for the three β-sites.

The expression (14) for the free energy becomes

$$-F/NkT=\ln\varphi-\theta_\alpha\ln\nu-3\,\theta_\beta\ln\mu$$
$$+\tfrac{3}{4}[\theta_\alpha\ln\theta_\alpha+(1-\theta_\alpha)\ln(1-\theta_\alpha)]+\tfrac{9}{4}[\theta_\beta\ln\theta_\beta+(1-\theta_\beta)\ln(1-\theta_\beta)]. \tag{27}$$

The equation (17) for the determination of the equilibrium value of the degree of order becomes

$$3\ln\frac{\theta_\alpha(1-\theta_\beta)}{\theta_\beta(1-\theta_\alpha)}=4\ln\frac{\nu}{\mu} \tag{28}$$

In the case of $\theta=\frac{1}{4}$, the values of s and E as functions of the temperature are calculated and plotted in figs. 1 and 2. For other values of θ, the values of of s as a function of θ at $T=0$ and the values of the critical temperature as a function of θ are calculated and plotted in figs. 3 and 4. The method of calculation is:

For figs. 1 and 2, we first assume a value of η. We then assume a value of μ, and calculate the values of ν and s from (26), and substitute into (28), which is usually not satisfied. Next assume a different value of μ and repeat the calculation. The value of μ which satisfies (28) is finally obtained by interpolation, and the corresponding value of s deduced. The value of E is then determined by substituting the values of μ, ν, s into (10).

For the fig. 3 we assume a very small but non-zero value of η, and determine the values of μ and ν in orders of η. It is found that as θ varies from 0 to 1, the orders of μ and ν also vary from η^0 to η^{-3}. Giving a value of θ we assume a value of s and calculate μ and ν from (26), and substitute the results into (28). The value of s which renders (28) satisfied is then obtained by interpolation.

For the fig. 4 we first assume a value of η. Then assume a value of θ. The corresponding values of s and μ, ν which satisfy (26) and (28) are obtained by assuming successively different values of μ and determining the correct value of μ by interpolation. Determine also the value of μ corresponding to $s=0$. This value of μ is simply obtained from the special case of (26) in which $\theta_\alpha=\theta_\beta=\theta$ and $\mu=\nu$. Then calculate the values of $F/(NkT \ln 10)$ corresponding to both $s=0$ and the non-zero value of s and compare their values. Next assume a different value of θ and repeat the calculations. The value of θ which satisfies (20) is obtained by interpolation. To one value of T there are usually two values of θ satisfying (20).

From the figure 4 it is seen that the maximum critical temperature occurs at a composition $\theta=0.255$, which is slightly higher than the stoichiometric ratio $\frac{1}{4}$.

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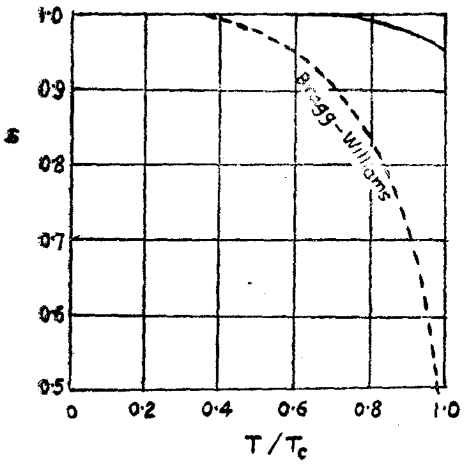

Fig. 1—The dependence of s on temperature for the AB_3 alloy in a face centred cubic alttice. $\theta=\frac{1}{4}$.

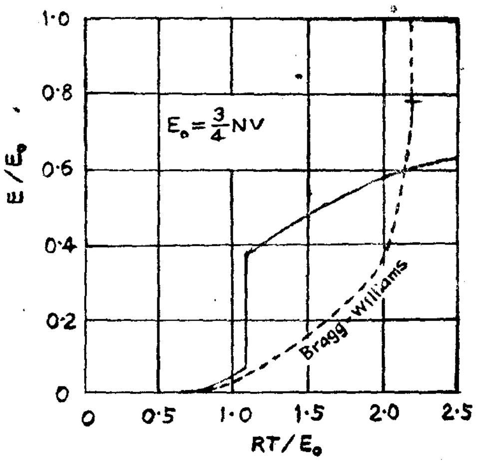

Fig. 2—The dependence of the configurational energy on temperature for the AB_3 alloy in a face-centred cubic lattice. $\theta=\frac{1}{4}$.

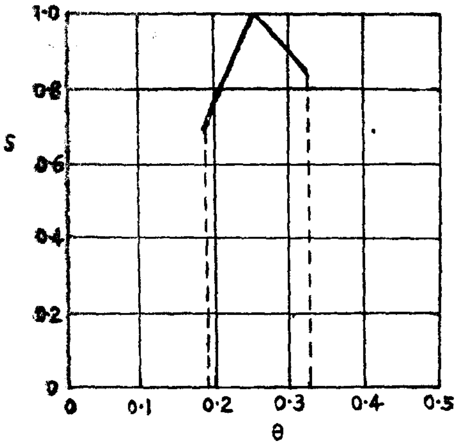

Fig. 3—Dependence of s on θ at $T=0$. for AB_3 alloy.

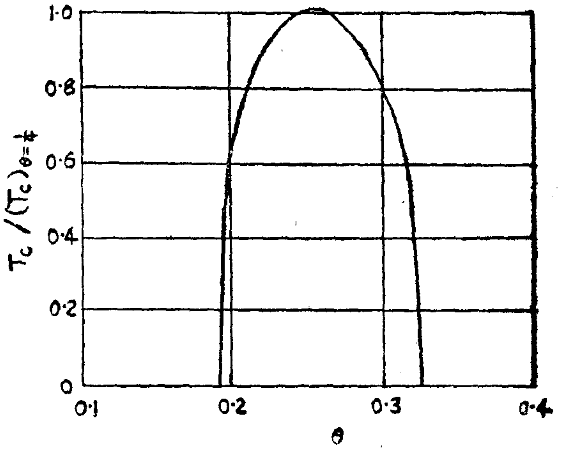

Fig. 4—Dependence of critical temperature on composition θ for AB_3 alloy.