

Comparing (9.7) and (5.10) we obtain the interesting result that

$$C(r_{-\infty} \cdots r_{-1} +_0 | r_{\infty}) = \frac{1}{2}(1+S). \quad (9.8)$$

The explanation of this identity would seem to be that the constraint of keeping an entire half-

line ordered provides sufficient knowledge to decide which sites in the lattice are α sites and which are β sites, in the sense of Section 5. The probability for finding a right atom would then be given in terms of the long range order by (9.8) or (5.6).

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Statistics of Two-Dimensional Lattices with Four Components†

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We have considered a two-dimensional square net consisting of four kinds of atoms supposing that only nearest neighbors interact and that there are only two distinct potential energies of interaction, one between like and one between unlike atoms. In extension of a method due to Onsager it is found that for the case where like atoms attract one another a simple "reciprocity" relation exists between the partition functions at pairs of temperatures "reciprocally" related to one another. As one temperature T tends to zero, the other T^* tends to infinity. If one further assumes that only one "Curie" transition point exists, the relation between T and T^* enables one to locate the Curie temperature. Predictions can be made concerning the nature of the transition point with results similar to those of Kramers and Wannier. The reciprocity relation for the case of attraction between like atoms is found to be not valid for the case where unlike atoms attract one another.

INTRODUCTION

IN a recent paper¹ on the statistics of two-dimensional ferromagnets, Kramers and Wannier have given a treatment of a model for cooperative phenomena. They discovered an important property of their system which expressed itself in the form of a simple symmetrical relation between the partition functions Z and Z^* at pairs of temperatures T and T^* , related in a certain symmetrical way. Any knowledge of the partition function Z at temperature T implies an equivalent amount of knowledge about Z^* at the related temperature T^* . The relation between T and T^* is a one to one relation; T decreases monotonically if T^* increases so that $T \rightarrow 0$ as $T^* \rightarrow \infty$. There is only one temperature at which $T = T^*$. Assuming

long range order at $T=0$ and absence of long range order at $T=\infty$, one will expect a Curie point. If the Curie point is the only temperature at which Z becomes singular, this temperature must be the one at which T and T^* become equal. Furthermore, one finds that the types of singularities which might occur at this transition are restricted by the relation between Z and Z^* . For example, if one assumes that there is no latent heat at the Curie point, the specific heat must be either continuous through the transition or infinite on both sides of the transition temperature.

Onsager² has been able to obtain the reciprocity relation discussed above from a more direct consideration of the form of the partition function. Moreover, his ingenious methods appear to lend themselves readily to generalization. Onsager proceeds by giving two formally different expressions for the partition function at a tempera-

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¹ H. A. Kramers and G. H. Wannier, *Phys. Rev.* **60**, 252 (1941).

² This method has not yet appeared in print. We are greatly indebted to Dr. Onsager for his permission to make use of it.

ture T and at a temperature T^* . He is then able to produce a transformation between T and T^* which brings the first form of $Z(T)$ into a simple relation with the second form of $Z(T^*)$.

In this paper, Onsager's methods have been extended to the study of two-dimensional square lattices containing four kinds of atoms in equal abundance. In addition to the assumption that only the interaction of nearest neighbors are important, the further assumption is made that there are only two distinct energies of interaction, one between like and the other between unlike atoms. It must not be supposed that this restriction reduces the problem to that of a crystal with only two kinds of atoms, for in the four-component lattice the *a priori* probability of finding a given kind of atom at a lattice point is $\frac{1}{4}$ and not $\frac{1}{2}$.

The detailed investigation will show that for the case where like atoms attract one another a simple symmetry or "reciprocity" relation, in the sense of Kramers and Wannier, exists. The relation does not exist, however, if like atoms repel each other. One can understand this result by using the following qualitative consideration. At low temperatures, for the case where like atoms attract one another, minimum energy is attained when the atoms separate into regions consisting exclusively of like atoms; at high temperatures the atoms should be randomly distributed on the lattice sites. One might, therefore, expect a transition point where the long range order disappears. The situation is different when unlike atoms attract one another. Using the letters A, B, C, D to denote the four kinds of atoms, if, as is assumed, the unlike pairs, $A-B, A-C, A-D$, etc., attract and have the same energy of interaction, there are many different states of minimum energy, and from the presence of an A atom on a given site, one can draw no conclusion about the occupant of a distant site. Therefore, there is no long range order at low temperatures and no reason to expect an order-disorder transition.

1. FIRST FORM OF THE PARTITION FUNCTION

Consider a two-dimensional square lattice consisting of four kinds of atoms A, B, C, D . Suppose that only nearest neighbors interact and that the energies of interaction between the various pairs of nearest neighbors are given by the following

scheme:

Pairs	$A-A$	$A-B$	$A-C$	$A-D$
	$B-B$			
	$C-C$	$C-D$	$B-D$	$B-C$
	$D-D$			
Energy	ϵ	ϵ'	ϵ''	ϵ'''

The reason for splitting the six pairs of unlike atoms into three groups of two equivalent pairs each will appear later. Eventually, $\epsilon', \epsilon'', \epsilon'''$ will be taken as equal.

The first form of the partition function is given in terms of four auxiliary functions of the temperatures u, x, y , and z defined by the relations

$$\begin{aligned} \exp(-\epsilon/kT) &= u+x+y+z, \\ \exp(-\epsilon'/kT) &= u-x+y-z, \\ \exp(-\epsilon''/kT) &= u-x-y+z, \\ \exp(-\epsilon'''/kT) &= u+x-y-z. \end{aligned} \quad (1)$$

By a "configuration", denoted by the general letter c , we shall mean any particular distribution of the A, B, C , and D atoms on the various available lattice sites. The partition function Z , by using the grand canonical ensemble, is defined by

$$Z = \sum_c \exp(-E_c/kT),$$

where E_c is the total energy associated with the configuration c , and the summation is taken over all possible configurations. Since E_c is a certain linear combination of $\epsilon, \epsilon', \epsilon'', \epsilon'''$, with integral coefficients, Z can also be written as

$$\begin{aligned} Z = \sum_c \left\{ \prod^c \exp\left(-\frac{\epsilon}{kT}\right) \prod^c \exp\left(-\frac{\epsilon'}{kT}\right) \right. \\ \left. \times \prod^c \exp\left(-\frac{\epsilon''}{kT}\right) \prod^c \exp\left(-\frac{\epsilon'''}{kT}\right) \right\}, \quad (2) \end{aligned}$$

where the numbers of factors in the various products depend, of course, on the configuration c . Since each pair of adjacent lattice sites contributes a factor to one of the four products in (2), we have, recalling the definitions of u, x, y , and z ,

$$Z = \sum_c \left\{ \prod_{\text{all pairs}}^c (u \pm x \pm y \pm z) \right\}, \quad (3)$$

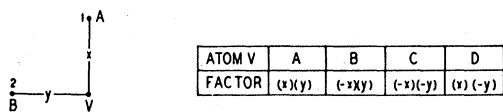


FIG. 1. An ineffective combination of lines.

where the product for each configuration is taken over all pairs of adjacent sites. This product can be evaluated by the following procedure: (i) for each pair of adjacent lattice sites, we choose a number which is either u , x , y , or z ; (ii) examining the pairs of atoms assigned by the configuration c to the pairs of adjacent sites we attach the proper $+$ or $-$ signs to the x , y , or z factors chosen in (i) and multiply together the u , $\pm x$, $\pm y$, $\pm z$ factors for this choice; (iii) we repeat the procedure of (ii) for all possible choices made in (i) and add the results together, the sum giving the required product in (3) for the given configuration c .

The choice indicated in (i) can be specified in a more geometrical way if we draw in the lattice connecting lines labeled with an x , y , or z between all pairs of adjacent lattice sites for which an x , y , or z is selected. No connecting line is drawn between a pair for which the letter u is chosen in (i). In this way the choice in (i) is equivalent to a "pattern" of x , y , and z lines running through the lattice. Any configuration c of atoms in the lattice may be adopted for any pattern of lines p . For a given pattern p , the choice of signs in (ii) is determined by the configuration c . Therefore, the partition function may be written in the form of a double sum, summations being carried out over all configurations c , and over all patterns p .

$$Z = \sum_c \sum_{\text{patterns}} \{ \prod^p u \prod^p \pm x \prod^p \pm y \prod^p \pm z \}. \quad (4)$$

The number of factors in each of the four products depends on the pattern p alone. The only effect of the configuration c is to influence the distribution of $+$ and $-$ signs.

There are many patterns, however, which do not effectively contribute to Z . In investigating the combinations of x , y , and z lines of a pattern which can intersect at a lattice point, we find that, under certain circumstances, there is a mutual cancellation of the four contributions to Z arising from a given pattern and four configurations which differ among themselves only in the identity of the atom at the lattice intersection

point in question. For example, suppose that at a point a single x line and a single y line terminate. For any configuration, the contribution to Z of a pattern containing this combination of x and y lines intersecting, will evidently have a factor $(\pm x)(\pm y)$ arising from these intersecting lines. Let us consider this factor for each of the four configurations obtained from some arbitrary initial one by successively changing the identity of the atom V at the point of intersection, keeping the identities of all other atoms fixed. Looking at the definition of u , x , y , z for the signs, we have (Fig. 1) an ineffective combination of lines. The sum of these contributions vanishes. The same result is found for other initial configurations which place other atoms at the points 1 and 2. We conclude, therefore, that any pattern which contains the combination $x y$ at a point, does not effectively contribute to Z .

A different result (Fig. 2) is obtained for the combination of intersecting lines $x y z$. All these factors are of the same sign; their total contribution does not vanish. The same conclusion is reached for other atoms at points 1, 2, and 3.

Examining in this manner all the various combinations of lines which can intersect at a point, we find that for those patterns which are effective for Z , "effective patterns" for short, the combinations of intersecting lines must be among the following types:

$$\begin{array}{cccc} x x & x y z & x x x x & x x y y \\ y y & & y y y y & x x z z \\ z z & & z z z z & y y z z. \end{array}$$

Figure 3 gives an example of a typical effective pattern.

The effective combinations listed above have the property that the signs of their contributions to Z remain unchanged however one changes the identity of the atom at the point of intersection. From this we can prove that the contributions to Z of a given effective pattern p , are positive for all configurations of atoms c , and therefore are all equal and independent of c . This is evident if we

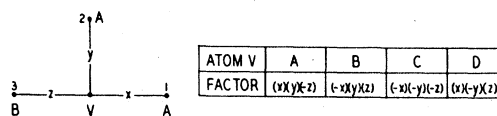


FIG. 2. An effective combination of lines.

consider that the contribution for a configuration of A atoms on all lattice points is surely positive, and that successive changes in the identities of the atoms at separate lattice points preserve the sign.

If N is the number of lattice sites, the total number of configurations is 4^N . Confining the summation to effective patterns and using the result of the previous paragraph, we can write as the final expression for the first form of the partition function

$$Z = 4^N \sum_{\text{eff. patt.}} u^{2N-(l+m+n)} x^l y^m z^n, \quad (5)$$

where l, m, n , are the total lengths (in units of the lattice distance) of the x, y, z lines, respectively, in one of the effective patterns contributing to the sum. Since there are $2N$ pairs of nearest neighbors when N is a large number and the factor u is chosen for all pairs of adjacent sites not included in the pattern, u appears to the power $2N - (l+m+n)$.

2. SECOND FORM OF THE PARTITION FUNCTION

The second form of the partition function is obtained by a geometrical procedure different from the one just used. For a given configuration, let us pick out all pairs of unlike nearest neighbors. Then, for each such pair, let us draw a separating line midway between the two atoms, this separating line being perpendicular to the line joining the pair and of length equal to the lattice distance. These separating lines will, from their definition, form the boundaries between regions in the lattice consisting of A atoms alone, B atoms alone, etc.

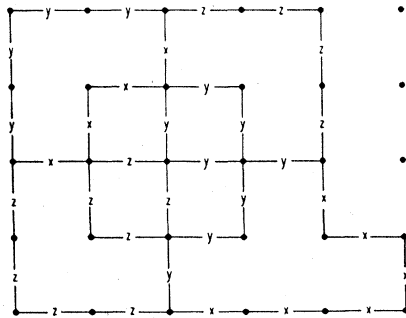


FIG. 3. A typical effective pattern.

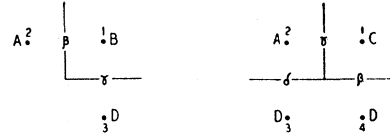


FIG. 4 (left). An impossible combination of lines.
FIG. 5 (right). A possible combination of lines.

Let us define four functions of the temperature $\alpha, \beta, \gamma, \delta$ by

$$\alpha = \exp\left(-\frac{\epsilon}{kT}\right), \quad \beta = \exp\left(-\frac{\epsilon'}{kT}\right),$$

$$\gamma = \exp\left(-\frac{\epsilon''}{kT}\right), \quad \delta = \exp\left(-\frac{\epsilon'''}{kT}\right) \quad (6)$$

and proceed to label the boundary lines according to the following scheme in accordance with the fact that the energy between an $A-B$ or $C-D$ pair is ϵ' and so on.

Pairs of	$A-B$	$A-C$	$A-D$
unlike atoms	$C-D$	$B-D$	$B-C$
Label of	β	γ	δ .
separating line			

In this way, each configuration has associated with it a pattern of β, γ, δ lines. These patterns are not entirely arbitrary, however. For example, we cannot have a single β line and a single γ line terminating at a point. In Fig. 4, a B atom was assumed at 1, and the atoms 2 and 3 written down in accordance with our labeling scheme. The result is a contradiction, since the atoms at 2 and 3 are not separated by any line and must therefore have the same identity.³ On the other hand, the combination $\beta \gamma \delta$ is possible, as Fig. 5 shows. If the identity of atom 1 is specified, the identities of atoms 2, 3, and 4 follow uniquely.

Examining all the cases, we find that the only possible combinations of β, γ, δ lines which can intersect at a point are among the following types:

$\beta\beta$	$\beta\gamma\delta$	$\beta\beta\beta\beta$	$\beta\beta\gamma\gamma$
$\gamma\gamma$		$\gamma\gamma\gamma\gamma$	$\beta\beta\delta\delta$
$\delta\delta$		$\delta\delta\delta\delta$	$\gamma\gamma\delta\delta$.

³ The argument holds only for the interior of the two-dimensional crystal. The resulting reciprocity relation is proved, therefore, only for the case where surface effects may be neglected.

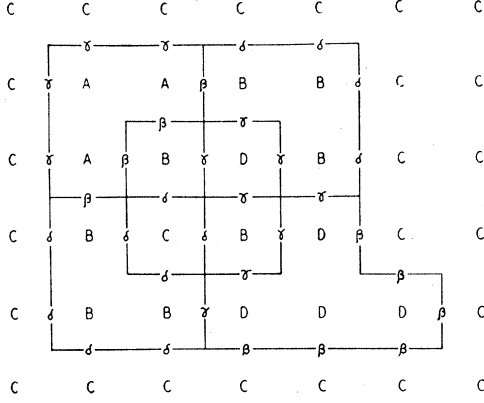


FIG. 6. β, γ, δ pattern identical with the x, y, z pattern of Fig. 3.

From this it can be concluded that, except for effects at the edges of the lattice which can be neglected when the lattice is very large, the patterns of β, γ, δ lines are geometrically identical with the effective patterns of x, y, z lines of the previous section. Figure 6 shows a pattern of β, γ, δ lines identical with the pattern of x, y, z lines of Fig. 3.

It is evident that each effective, or allowed, pattern of β, γ, δ lines is associated with exactly four distinct configurations. For if we give the identity of a particular atom in the lattice, the identities of all other atoms follow uniquely from the β, γ, δ pattern. The four configurations arise from the four possible identities of this particular atom. The energy of each of these configurations is

$$E_c = \{2N - (l + m + n)\}\epsilon + l\epsilon' + m\epsilon'' + n\epsilon''', \quad (7)$$

where l, m, n are the respective lengths (in units of the lattice distance) of the β, γ, δ lines of the associated pattern. Remembering the factor four and the definitions of $\alpha, \beta, \gamma, \delta$, we can write the partition function as a sum over patterns, instead of configurations, giving

$$Z = 4 \sum_{\text{eff. patt.}} \alpha^{2N - (l+m+n)} \beta^l \gamma^m \delta^n. \quad (8)$$

The next step is to compare the expressions (5) and (8).

3. THE RECIPROCITY RELATION

We now introduce the assumption that all pairs of unlike nearest neighbors interact with

the same energy; that is, we take $\epsilon' = \epsilon'' = \epsilon'''$. As a consequence $x = y = z$ and $\beta = \gamma = \delta$. For convenience we shall write the energies ϵ and ϵ' in the form

$$\begin{aligned} \epsilon &= -\omega + \phi \\ \epsilon' &= \omega + \phi \end{aligned} \quad (9)$$

and instead of the temperature, introduce as the new independent variable the quantity θ defined by

$$\theta = \exp(\omega/kT) = \alpha \exp(\phi/kT). \quad (10a)$$

We also define three new functions of the temperature U, X, η

$$\begin{aligned} U &= u \exp(\phi/kT), \\ X &= x \exp(\phi/kT), \\ \eta &= 1/\theta = \beta \exp(\phi/kT). \end{aligned} \quad (10b)$$

Then from (1), (9), (10) and the equality of x, y , and z , it follows that

$$\begin{aligned} \exp[(\omega - \phi)/kT] &= u + 3x \\ &= \exp(-\phi/kT)(U + 3X), \\ \exp[(-\omega - \phi)/kT] &= u - x \\ &= \exp(-\phi/kT)(U - X). \end{aligned} \quad (11)$$

The quantity ϕ can evidently be eliminated from these equations and one finds for U and X as functions of θ , the expressions

$$\begin{aligned} X &= \frac{1}{4}[\theta - (1/\theta)], \\ U &= \frac{1}{4}[\theta + (3/\theta)]. \end{aligned} \quad (12)$$

Let us now consider the partition function at two temperatures T and T^* which are, so far, unrelated to one another, writing $Z = Z(T)$ in the form (5) and $Z^* = Z(T^*)$ in the form (8). For $l + m + n$ we shall write t . Using (10) to express u, x, α, β in terms of U, X, θ, η we have

$$\begin{aligned} Z &= 4^N \sum_{\text{eff. patt.}} u^{2N-t} x^t \\ &= 4^N \exp(-2N\phi/kT) U^{2N} \sum_{\text{eff. patt.}} (X/U)^t, \end{aligned} \quad (13)$$

$$\begin{aligned} Z^* &= 4^N \sum_{\text{eff. patt.}} \alpha^{*2N-t} \beta^{*t} \\ &= 4 \exp(-2N\phi/kT^*) \theta^{*2N} \sum_{\text{eff. patt.}} (\eta^*/\theta^*)^t \\ &= 4 \exp(-2N\phi/kT^*) \theta^{*2N} \sum_{\text{eff. patt.}} (1/\theta^{*2})^t. \end{aligned} \quad (14)$$

By a "reciprocity" relation between Z and Z^* we understand the following. There shall exist a transformation $T^* = F(T)$ between the temperatures T and T^* having the two properties (i) if T is carried into T^* by the transformation, the transformation also carries T^* into T ; that is, if $T^* = F(T)$, then $T = F(T^*)$, (ii) for this transformation there shall exist a simple function $G(T)$ whose form is readily obtained without explicitly evaluating the partition function and which is such that

$$G(T)Z(T) = G(T^*)Z(T^*). \quad (15)$$

Moreover, with the possible exception of the points $T=0$ and $T=\infty$, $G(T)$ shall have no singularities for real temperatures. If these conditions are satisfied one can conclude that if $Z(T)$ has a singularity at T , $Z(T^*)$ will have a corresponding singularity at T^* .

A comparison between (13) and (14) suggests that the transformation between T and T^* is the one given implicitly in the condition

$$\theta^{*2} = U/X. \quad (16)$$

We shall verify that (16) leads to a reciprocity relation in the sense previously described.

Writing U and X in terms of θ we see that (16) is equivalent to

$$\theta^{*2} = (\theta^2 + 3)/(\theta^2 - 1). \quad (17)$$

Solving for θ^2 gives

$$\theta^2 = (\theta^{*2} + 3)/(\theta^{*2} - 1), \quad (18)$$

so that the transformation from T into T^* is of the required type.

Substituting (16) into (14) and comparing with the expression for Z in (13) we have

$$\begin{aligned} \frac{1}{4} \exp(2N\phi/kT^*)Z^* &= (U/X)^N \sum (X/U)^t \\ &= (4UX)^{-N} \exp(2N\phi/kT)Z. \end{aligned} \quad (19)$$

The relation to be derived is most simply expressed in terms of the N th root of Z , hereafter denoted by λ . This quantity may be regarded as the partition function per particle. In taking this N th root, however, we shall replace $4^{1/N}$ by unity. To this extent, and to the extent that effects due to the edge of the crystal are neglected, our method of deriving the reciprocity relation is

restricted to very large crystals. Writing $\lambda = Z^{1/N}$ and performing the N th root we have

$$\exp(2\phi/kT^*)\lambda^* = (4UX)^{-1} \exp(2\phi/kT)\lambda. \quad (20)$$

Using (12), (17), and (20) one may verify the expression

$$\exp(2\phi/kT)\lambda = (4U^*X^*)^{-1} \exp(2\phi/kT^*)\lambda^* \quad (21)$$

obtained in a formal way from (20) by interchanging starred and unstarred quantities. From (20) and (21) the symmetrical relation

$$\begin{aligned} (U^*X^*)^{-\frac{1}{2}} \exp(2\phi/kT^*)\lambda^* \\ = (UX)^{-\frac{1}{2}} \exp(2\phi/kT)\lambda \end{aligned} \quad (22)$$

readily follows. This has the form of a reciprocity relation.

If we define functions $f(\theta)$ and $\psi(\theta)$ by

$$\begin{aligned} f(\theta) &= 4\theta^{1+2\phi/\omega} / [(\theta^2 + 3)(\theta^2 - 1)]^{\frac{1}{2}}, \\ \psi(\theta) &= f(\theta)\lambda(\theta) \end{aligned} \quad (23)$$

the reciprocity is also expressed by

$$\psi(\theta^*) = \psi(\theta). \quad (24)$$

The $f(\theta)$ defined here plays the role of $G(T)$ of (15). Since its only singularities are at $\theta = \infty$ and $\theta = 1$ or $T = 0$ and $T = \infty$, this requirement on $G(T)$ is also satisfied.

In the formal procedure outlined so far it has not been specified whether like or unlike atoms attract one another. For the case where like atoms attract one another, we have ϵ' greater than ϵ and hence $\omega > 0$. The quantity θ is therefore greater than unity and from (17) θ^{*2} is positive and also greater than unity. Thus the transformation (17) is entirely consistent and the reciprocity relation (22) is valid.

However, for the case where like atoms repel one another, the energy ϵ' must be less than the energy ϵ , or ω must be negative. Consequently $\theta < 1$. From (17), θ^{*2} would then be negative and would not correspond to any real temperature T^* . The conclusion is, therefore, that for repulsion between like atoms no reciprocity relation, in the sense defined above, is found.

It has been pointed out in the introduction that long range order at low temperatures exists if like atoms attract but not when they repel each other. Therefore, in these two cases, an essentially

different behavior of the partition function at low temperatures is to be expected while no such difference at high temperatures is anticipated. Thus it is reasonable to find that a correlation between behaviors at high and low temperatures found for the one case does not hold for the other.

It must not be supposed that no relation of the form (15) can exist for the case of repulsion between like atoms. In fact an infinite number of such relations is possible. As an example, suppose T and T^* are related by $TT^* = T_0^2$. Let $G(T) = Z(T_0^2/T)$. Then we can evidently write

$$G(T)Z(T) = G(T^*)Z(T^*).$$

But now no conclusion about $Z(T)$ can be drawn since the form of $G(T)$ remains unknown as long as that of $Z(T)$ is not known.

Returning to the case of attraction between like atoms we see that from (17) T^* is a monotonically decreasing function of T . As T increases from 0 to ∞ , T^* decreases from ∞ to 0. There is only one temperature, which we shall denote by T_c , for which $T = T^*$. From (17) this occurs at

$$\theta_c = \exp(\omega/kT_c) = \sqrt{3}. \quad (25)$$

The interval from 0 to T_c is mapped by the transformation upon the interval from ∞ to T_c . Knowledge of λ on one of these intervals is equivalent, by (22), to knowledge of it on the other. If λ has any singularity at temperature T , it will have the same type of singularity at T^* . If it is assumed that only one singularity exists, it must then occur at temperature T_c , which we shall now call the critical temperature.

In Eq. (25) the quantity ω is half the difference between the energies of interaction between like and unlike atoms. The critical point for the two component system of Kramers and Wannier is

given by

$$\theta_c^2 = \exp(2\omega/kT_c) = 1 + \sqrt{2}, \quad (26)$$

where ω has the same significance as in our case. It will be noted that, for the same numerical value of ω , the transition occurs in our case at a temperature lower than the transition temperature of Kramers and Wannier by the ratio of $\ln(1 + \sqrt{2})$ to $\ln 3$ or by a factor of about 0.8. This may be due to the fact that in the four-component system the *a priori* probability favors disorder more than in the two-component system so that long range order breaks down at a lower temperature. This consideration gives support to the view that θ_c corresponds to the "Curie point."

The existence of the reciprocity relation (22) or (24) enables us to make certain limited statements concerning the nature of the hypothetical transition point. These conclusions are identical with those of Kramers and Wannier for lattices with two components. The energy E and specific heat C are given in terms of λ by

$$E = -Nd \log \lambda/d(1/kT) = -N\omega\theta d \log \lambda/d\theta,$$

$$C = dE/dT = (-\omega\theta/kT^2)(dE/d\theta).$$

From (17) and (24) we find for the possible discontinuities in E and C at the critical point

$$\Delta E = -2N\omega\theta_c(d \log \psi/d\theta)_{\theta_c+0}, \quad (27)$$

$$\Delta C = (\omega/kT_c^2)\Delta E.$$

Thus, if the energy is discontinuous, so is the specific heat. If $\Delta E = 0$ the specific heat is either continuous or becomes infinite at the transition temperature in such a way that the difference in its values at T and T^* tends to zero as T tends to T_c . This is about as far as one can go with the reciprocity relation alone.