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29. ON THE THEORY OF PHASE TRANSITIONS

PART I

The question of continuous phase transitions (without latent heat) have been investigated from the general thermodynamical point of view. In doing this it becomes clear that such transitions can take place when the symmetry of the lattice changes. There are two possible types of transition, namely: (1) Curie points with a discontinuity in the specific heat, which lie on a curve in the  $p$ - $T$  diagram, (2) isolated points in the  $p$ - $T$  diagram which lie in a certain way on intersections of curves of normal phase transitions.

UP to the present time, among all phase transitions, Curie points, and so on, only the transition between a liquid and a gas has been fully investigated. It is known that the liquid-gas equilibrium curve in the  $p$ - $T$  diagram has an end point, and that a continuous transition between liquid and gas can be realised by going round it. As for transitions between a liquid and a crystal, or between different crystal modifications, the question about them has not been fully clarified. In a number of cases people talk about transitions connected with rotations of molecules; however it is not at all clear how rotations can lead to phase transitions, and in particular to discontinuities in the specific heat.

One even finds strange statements that there is no essential difference at all between liquids and crystals, and that continuous transitions between them are possible. However, liquids differ essentially from crystals in that they are isotropic in contrast to anisotropic crystals. Every transition from a crystal to a liquid or to a crystal of a different symmetry is associated with the disappearance or appearance of some elements of symmetry. But elements of symmetry are either present or absent; no intermediate case is possible. And so continuous transitions (in the sense that transitions between liquid and gas are continuous) connected with changes of the symmetry of the body are absolutely impossible.

Until recently the exact formulation of the very idea of the crystal lattice was lacking. Only quite recently Bethe and Peierls<sup>1</sup> have stressed the role of correlations at infinity in the crystal lattice.

Note that normal phase transitions between liquid and crystal or between different modifications where the state of the body, particularly the energy,

Л. Ландау, К теории фазовых переходов I, *Журнал Экспериментальной и Теоретической Физики*, 7, 19 (1937).

L. Landau, Zur Theorie der Phasenumwandlungen I, *Phys. Z. Sowjet.* 11, 26 (1937).

Л. Д. Ландау, К теории фазовых переходов II, *Журнал Экспериментальной и Теоретической Физики*, 7, 627 (1937).

L. Landau, Zur Theorie der Phasenumwandlungen II, *Phys. Z. Sowjet.* 11, 545 (1937).

changes discontinuously are not the main interest of the present investigation. Our main interest is in such transitions where the state of the body (particularly the energy) changes continuously even although the symmetry changes discontinuously. (See below for details.) We shall call these transitions the continuous ones. Let us emphasize once again that they are not continuous in the sense that transitions between liquid and gas are. At every moment we can tell that we have a body of this or that symmetry.

Usually the approach to this question is made difficult by the use of an idealized model of the lattice in which all atoms are placed in their positions and thermal motion is ignored.

These difficulties can be avoided if a distribution probability  $q(x, y, z)$  is used, where  $q(x, y, z) dx dy dz$  determines the probability for finding an atom in the given volume element of the body. If the body consists of different kinds of atoms then it would be possible to introduce several functions  $q_1, q_2, \dots$ , which would determine the probabilities for each kind of atom. Even in that case it would instead be possible to use only one distribution function. For instance we can determine that function as one which gives the mean

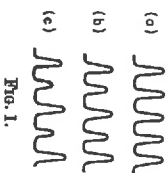


FIG. 1.

charge density at every point of the body (multiplied by  $dx dy dz$  it would give the charge in that volume). In the following, we shall talk simply about the "density"  $q(x, y, z)$ , meaning by that some function which determines the distribution of atoms in the body under consideration. Note that such a method based on the function  $q$  also has the advantage that it is possible in quantum mechanics as well.

The important feature of the function  $q$  is its symmetry, i.e. that group of co-ordinate transformations with respect to which  $q$  is invariant. The same group also determines the symmetry of the body. It is known that there are in all 230 possible different groups of transformations, i.e. types of symmetry. In isotropic bodies (liquids) obviously  $q = \text{const.}$

As already mentioned we shall consider here those transitions where, regardless of a discontinuity in the symmetry, the state of the body changes continuously. In other words the density  $q$  changes continuously. It is easy to see that such transitions are possible because even a very small change in the distribution of the atoms in the lattice is enough to change its symmetry. If for instance  $q$  is represented by the curve Fig. 1a (schematically drawn in one dimension) and some of the maxima decrease (Figs. 1b and 1c), then the symmetry changes as soon as the decreasing starts (the translational period of the lattice increases).

Let us consider a crystal with some density  $q_0$  which has a certain symmetry (we shall talk about the totality of symmetry transformations of  $q_0$  as the group  $g_0$ ). At the transition point the density starts to change and becomes  $q = q_0 + \delta q$ , where  $\delta q$  is small compared with  $q_0$ .  $\delta q$  also has some symmetry (group  $g$ ) which is lower than that of  $q_0$  (i.e. not all elements, that is symmetry transformations of  $q_0$ , are elements of symmetry of  $g$ ; the group  $g$  is a subgroup of the group  $g_0$ ). Then  $q = q_0 + \delta q$  has the same symmetry, because the sum of two functions has the same symmetry as the less symmetric term. We can therefore neglect the case where  $\delta q$  has a higher symmetry than  $q_0$ , since then  $q_0 + \delta q$  would have the same symmetry as  $q_0$ , so that no change in the symmetry of the body would take place.

Symmetry transformations from the group  $g_0$  which do not belong to the group  $g$  change  $\delta q$  into some other function. It is known from group theory that the function  $\delta q$  can be broken into a sum of functions the number of which is equal to the number of elements of the group  $g_0$ , in such a way that under every transformation of that group all these functions transform among themselves, i.e. become linear combinations of themselves.

Matrices of these linear transformations form the so-called "representation" of the group  $g_0$ . Further, all these functions into which  $\delta q$  is broken, can be separated into groups or "races", where all functions composing them again transformation among themselves. So we can write:

$$\delta q = \sum_{\alpha} \sum_{\beta} q_{\alpha\beta}^{(n)} \phi_{\beta}^{(n)}, \quad (1)$$

where  $n$  is the number of the race and  $\beta$  is the number of the function in the race.

Each of these races of functions can be used as a basis for the representation of the group. That representation is realised by the transformation matrices of the functions of that race. It is known that there exists an expansion of  $\delta q$ , into  $q^{(n)}$  where every race consists of the smallest possible number of functions (i.e. an irreducible partition, thus realising the "irreducible representation").

In (1) we shall suppose just such a partition. We could after all simply write it as  $\delta q = \sum_{\alpha} \sum_{\beta} q_{\alpha\beta}^{(n)}$ , because the functions  $q_{\alpha\beta}^{(n)}$  are not determined beforehand; in the future it will be convenient to consider the functions  $q_{\alpha\beta}^{(n)}$  somehow normalised.

Among all  $q_{\alpha\beta}^{(n)}$  there is always one function (which forms a "race" by itself) which is invariant with respect to all transformations of the group  $g_0$ . In the sum  $q_0 + \delta q$  we shall consider this function to belong to  $q_0$  so that  $\delta q$  has no such function.

The thermodynamic potential  $\Phi$ , of the body, is determined by the density  $q$ , i.e. depends on the form of the function  $q$ . In other words  $\Phi$  is a functional of  $q$ :  $\Phi = \Phi\{q\}$ ;  $\Phi$  depends also on the temperature  $T$  and the pressure  $p$  of the body as parameters. When  $p$  and  $T$  are given the form of the function  $q$  is determined from the condition that  $\Phi$  should have a minimum.

Let us expand the thermodynamic potential  $\Phi\{\epsilon_0 + \delta\epsilon\}$  in the state with density  $\epsilon = \epsilon_0 + \delta\epsilon$  in powers of  $\delta\epsilon$  (of course this expansion is not a normal power series; individual terms in the expansion are integral operators of  $\delta\epsilon$ ). Saying this in another way, we have an expansion in powers of  $\rho^{(n)}$  and  $\rho^{(p)}$ .

It can be seen that first order terms in the expansion are zero. The potential  $\Phi$  as the quantity which characterizes the physical properties of the body obviously should not change under any movements of the body, i.e. should be invariant under all possible co-ordinate transformations. If such a transformation changes  $\epsilon_0$  into  $\epsilon'_0$  and  $\delta\epsilon$  into  $\delta\epsilon'$ , then

$$\Phi\{\epsilon'_0 + \delta\epsilon'\} = \Phi\{\epsilon_0 + \delta\epsilon\}.$$

From this it can be seen that if  $\Phi$  is considered as a function only of  $\delta\epsilon$ , then  $\Phi$  is invariant only with respect to those transformations which do not change  $\epsilon_0$ , i.e. the transformation group  $\epsilon_0$ . Since the functions  $\rho^{(n)}$  under transformations of this group transform among themselves we can consider only the coefficients  $\rho^{(n)}$  to change under these transformations, because the expression for  $\Phi$  should be invariant with respect to transformations of these coefficients. In particular the coefficients of the powers of the  $\rho^{(n)}$  in the expression of  $\Phi$  will be invariants of the relevant degree. It is known that it is impossible to construct linear invariants from quantities transforming as an irreducible representation.

As to the terms of second order, they are known to separate into a sum of groups of terms consisting only of the quantities  $\rho^{(n)}$  (consequently of the functions  $\Phi^{(n)}$ ) belonging to one race.

The transition point is thus characterised by the fact that for a small change in  $T$  and  $p$ , an extra term  $\delta\epsilon$  appears in the density  $\epsilon_0$ . On one side of the transition point (which we shall call the "upper" side) terms of second order in the expansion are obviously essentially positive for all  $T$  and  $p$ . Thus the minimum is at  $\delta\epsilon = 0$  i.e. the state of the body corresponds to  $\epsilon = \epsilon_0$ ; that is, the body has a higher symmetry. On the other ("lower") side of the transition point terms of the second order are not essentially positive and thus to the minimum of  $\Phi$  corresponds some  $\delta\epsilon$  different from zero, which really determines the symmetry of the body. Consequently at the transition point itself the sum of all terms of the second order should be zero for any fixed  $\delta\epsilon$ .

For that it is obviously sufficient that any group of terms of second order belonging to one race becomes zero at the transition point. On the other hand the  $\delta\epsilon$  which make the sum zero are just those  $\delta\epsilon$  which can appear at the transition point.

After the functions  $\rho^{(n)}$  belonging to one of the races have been chosen such that the corresponding second order terms are equal to zero, then the rest of the  $\rho^{(n)}$  can be taken to be equal to zero. Then  $\delta\epsilon = \sum \rho^{(n)} \rho^{(n)}$  (summation only over functions of one race) is just that change of the density which makes the term of the second order vanish at the transition point, and is consequently physically realised. Therefore in future we shall only be concerned with that one race and shall drop the superscript  $(n)$ , specifying the race.

Because the functions  $\rho_i$  are determined by the condition that they should make the terms of the second order vanish at the transition point,  $\Phi$  can now be considered as a function only of the  $c_i$ , and the expansion in  $\delta\epsilon$  as an expansion in  $c_i$  where there are no terms of first order. As has been already said, the terms of the second order should form an invariant (with respect to all transitions of the group  $\epsilon_0$ ). In accordance with group theory such an invariant (in an irreducible representation) is a positive definite quadratic form, which, by suitable choice of the normalisation of the  $c_i$ , can always be written as the sum of squares. In this way terms of the second order (of the given race) have the form:

$$A \sum c_i^2. \quad (2)$$

At the transition point this expression need not be zero i.e. at that point  $A = 0$  ( $A$  is of course a function of  $p$  and  $T$ ).

In an analogous way terms of the third, fourth, ..., order are formed correspondingly from invariants of the third, fourth, ..., order. Terms of the third order can in some cases be absent. If, for instance, in a given race only one function  $\rho$  enters, then by acting with transformations of the group  $\epsilon_0$  the coefficient  $c$  can change sign. Therefore, in that case, all invariants and consequently all terms of odd orders are equal to zero.

If at a certain point (i.e. at specified  $p$  and  $T$ )  $A(p, T)$  should vanish, then, in order that this point really be a point of a continuous transition, it is necessary that the terms of third order are zero. Otherwise  $\Phi$  cannot have a minimum (as a function of  $c_i$ ) at that point, because that point would not correspond to a stable state of the body.

Two cases are possible:

1. Terms of the third order are identically zero (there are no invariants of third order). Transition points are determined from one condition:

$$A(p, T) = 0; \quad (3)$$

besides this terms of the fourth order should be positive definite. In that case transition points lie thus on a certain curve, which is determined by (3). This is the case of Curie points.

A physical state is realised and is determined by the coefficients  $c_i$  which correspond to the minimum of  $\Phi$  (at given  $p$  and  $T$ ). Define

$$\sum c_i^2 = \eta^2 \quad (4)$$

and

$$\frac{c_i}{\eta} = \gamma_i.$$

Then the expansion of  $\Phi$  is written in the form

$$\Phi = \Phi_0 + A\eta^2 + B(\gamma_i)\eta^4 + \dots,$$

where all coefficients are also functions of  $p$  and  $T$ .

Because the term of the second order does not depend on  $\gamma_i$  the values of  $\gamma_i$  can be obtained by finding the minimum of  $B(\gamma_i)$ . Having found these values

and substituting them into  $B(\gamma_i)$  we get

$$\Phi = \Phi_0 + A\eta^2 + B\eta^4 + \dots \quad (6)$$

where  $B = B(\varphi, T)$  is the minimum value of  $B(\gamma_i)$ . According to the above

$$B(\varphi, T) > 0. \quad (6)$$

Above the Curie point  $A > 0$ ; to the minimum of  $\Phi$  corresponds  $\eta = 0$ , i.e. the body has the symmetry  $\epsilon_0$ . At the Curie point  $A = 0$ , and below it  $A < 0$ . From the minimisation of  $\Phi$ , i.e. from  $\partial\Phi/\partial\eta = 0$ , we find

$$A + 2B\eta^2 = 0$$

or

$$\eta^2 = -\frac{A}{2B}. \quad (7)$$

Then

$$\Phi = \Phi_0 - \frac{A^2}{4B}.$$

The specific heat of the body is

$$C = -T \frac{\partial^2 \Phi}{\partial T^2} = C_0 + T \left( \frac{\partial A}{\partial T} \right)^2. \quad (8)$$

Terms which vanish at the Curie point are omitted.  $C_0$  is the specific heat of the body with the symmetry  $\epsilon_0$ , i.e. above the Curie point. Because of (8) we see that at the Curie point  $C > C_0$ . In this way at the Curie point the heat capacity has a discontinuity and it increases in going from a more to a less symmetric body (note, that one body is less symmetric than the other if its symmetry transformation group is a sub-group of the symmetry group of the other).

As was pointed out at the beginning of this case the coefficients  $\gamma_i$  are determined from  $B(\gamma_i)$ , i.e. they depend on the form of the terms of fourth order.

But all these terms depend also on  $p$  and  $T$ ; because of that the  $\gamma_i$  depend on  $p$  and  $T$  too. But the quantities  $\gamma_i$  determine the symmetry of  $\delta\epsilon_i$ , i.e. the symmetry of the crystal. Because of that it may happen that at different parts of the Curie point curve a transition takes place from a more symmetric crystal (where  $\delta\epsilon = 0$ ) to less symmetric crystals of different symmetries (i.e. where  $\delta\epsilon$  has a different symmetry).

In that case in the phase diagram there is a point of intersection of the Curie curve (curve I) with the phase transition curve (curve 2, Fig. 2); I is the most over into less symmetric phases II and III, where  $\delta\epsilon_{II} \neq 0$ ,  $\delta\epsilon_{III} \neq 0$ . Symmetry groups  $\delta\epsilon_{II}$  and  $\delta\epsilon_{III}$  are sub-groups of the symmetry group of the first phase. However they are not generally sub-groups of each other. Because of this the difference  $\delta\epsilon_{II} - \delta\epsilon_{III}$  cannot become zero; consequently between

phases II and III there should not be a Curie line, but a phase transition line. At the point  $B$  all three phases are identical; along the line  $AB$  the phases I and II are identical ( $\delta\epsilon_{II} = 0$ ); along  $BC$ :  $\delta\epsilon_{III} = 0$ .

It can further be shown, that the intersection of one Curie line with another can happen only at a point of the type shown in Fig. 3. If I is the most symmetric phase then the phases II and III have lower symmetries; their symmetry groups are sub-groups of the symmetry group of the phase I. Phase IV has even lower symmetry than II or III. Its symmetry group is simultaneously a subgroup of the symmetry groups of the phases II and III.

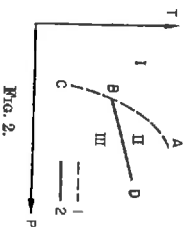


FIG. 2.

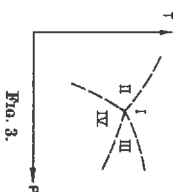


FIG. 3.

Finally, let us consider those cases where terms of fourth order in the expansion of  $\Phi$  also become zero at the transition point. For this it is necessary that the terms of the fourth order have only one coefficient which depends on  $p$  and  $T$ , together with which they would become zero. Otherwise the vanishing of fourth-order terms together with the condition  $A(p, T) = 0$  would give more than two equations with two unknowns ( $p$  and  $T$ ), which would generally have no solutions. For this it is required that only one invariant of the fourth order (formed from the  $c_i$ ) exists, i.e. the terms of the fourth order are identically equal to  $B(\varphi, T)\eta^4$  for arbitrary  $c_i$ .

If terms of the fourth order are equal to zero, then for the stability of the state (i.e. for  $\Phi$  to be a minimum) it is necessary for the term of the fifth order to be identically zero and the term of the sixth order to be positive. Two conditions,  $A = B = 0$  then determine an isolated point. That point is a  $\lambda$ -point whose properties have already been investigated by the author†. There it has been pointed out that  $\lambda$ -points are the points where the Curie curve goes over into the phase transition curve. Here I shall only consider an additional intersection of the Curie curve with the phase transition curve in bodies which are mixtures of two substances. In that case it appears that the specific heat does not become infinite but, as in pure substances, experiences only a finite jump.

The fact that the body is a mixture does not introduce anything essentially new into our considerations. The symmetry of the crystals, as before, determined by the density  $\rho$ , and the expansion of  $\Phi$  in the vicinity of a point of a continuous transition is

$$\Phi = \Phi_0 + A\eta^2 + B\eta^4 + \dots;$$

† In this earlier paper† the quantity  $\xi$  corresponds to  $\eta^2$ .

but now  $\Phi_0$ ,  $A$ ,  $B$  depend not only on  $p$  and  $T$  but on the concentration  $x$  of the mixture.

Let us prove that at the transition point of the Curie line into the phase transition line for mixtures (we shall in this case also call such a point a  $\lambda$ -point) the coefficient  $B$  in the expansion of  $\Phi$  should be zero. And indeed from this it will follow that the specific heat does not become infinite at that point (see equation (8)).

Let us investigate the neighbourhood of the  $\lambda$ -point. First we shall write conditions for the equilibrium of two phases on the transition curve (either a phase or a continuous transition). It is known that the thermodynamic potential  $\Phi$  is an additive quantity and because of that in mixtures it should be a homogeneous function of the first order of the number of particles of each kind. In particular for the mixture of two materials  $\Phi = N/(n/N)$ , where  $n$  and  $N$  are the numbers of both kinds of particles. The chemical potentials of each kind of particles are

$$\frac{\partial \Phi}{\partial N} = f - x \frac{\partial f}{\partial x}, \quad \frac{\partial \Phi}{\partial n} = \frac{\partial f}{\partial x}$$

(where  $x = n/N$ ). The equilibrium conditions are equality of the chemical potentials of both phases. In our case on one side of the transition point (where  $\eta = 0$ , i.e. in the more symmetric phase)  $\Phi = \Phi_0$ ; on the other side  $\Phi = \Phi_0 + A\eta^2 + B\eta^4$ . If  $x_0$  and  $x$  are the concentrations of both phases then the equilibrium conditions are

$$\frac{\partial \Phi_0}{\partial x_0} = \frac{\partial \Phi}{\partial x}$$

and

$$\Phi_0(x_0) - x_0 \frac{\partial \Phi_0}{\partial x_0} = \Phi - x \frac{\partial \Phi}{\partial x}.$$

Substituting  $\Phi = \Phi_0 + A\eta^2 + B\eta^4$ , we find from the first condition

$$\frac{\partial \Phi_0}{\partial x_0} = \frac{\partial \Phi_0}{\partial x} + \frac{\partial A}{\partial x} \eta^2$$

( $\partial A/\partial x$ , is not generally zero at the transition point and because of that it is possible to limit ourselves to the term in  $\eta^2$ ) or, expanding  $\partial \Phi_0/\partial x$  in a series:

$$\begin{aligned} \frac{\partial \Phi_0}{\partial x} &= \frac{\partial \Phi_0}{\partial x_0} + (x - x_0) \frac{\partial^2 \Phi_0}{\partial x_0^2} + \dots, \\ -\frac{\partial^2 \Phi_0}{\partial x_0^2} (x - x_0) &= \frac{\partial A}{\partial x} \eta^2. \end{aligned} \quad (9)$$

In the second condition to the same accuracy we put

$$\frac{\partial \Phi_0}{\partial x} \approx \frac{\partial \Phi_0}{\partial x_0}$$

and get

$$\Phi = \Phi_0(x_0) + \frac{\partial \Phi_0}{\partial x_0} (x - x_0).$$

Substituting here the expression for  $\Phi_0$  we find

$$A\eta^2 + B\eta^4 = \Phi_0(x_0) - \Phi_0(x) + (x - x_0) \frac{\partial \Phi_0}{\partial x_0}$$

and expanding  $\Phi_0(X_0) - \Phi_0(X)$  in a series:

$$A\eta^2 + B\eta^4 = -\frac{(x - x_0)^2}{2} \frac{\partial^2 \Phi_0}{\partial x_0^2}$$

Further substituting  $(x - x_0)$  from equation (9), then

$$A\eta^2 + B\eta^4 = \frac{(x - x_0)}{2} \frac{\partial A}{\partial x} \eta^2,$$

or

$$A + B\eta^2 = \frac{(x - x_0)}{2} \frac{\partial A}{\partial x}. \quad (10)$$

Also remember that one of the conditions for the stability of the state of the body, i.e. the condition that  $\Phi$  is a minimum, is  $\partial \Phi/\partial \eta = 0$  (in that phase where  $\eta \neq 0$ ). From this we get from (7):

$$\eta^2 = -\frac{A}{2B}.$$

Substituting this into (10), we find

$$A - (x - x_0) \frac{\partial A}{\partial x} = 0.$$

Substituting from here  $(x - x_0) = A/(\partial A/\partial x)$  and  $\eta^2 = -A/2B$  in equation (9), we find

$$\begin{aligned} \frac{\partial^2 \Phi_0}{\partial x_0^2} A &= \frac{\partial A}{\partial x} A \\ \frac{\partial A}{\partial x} &= \frac{\partial A}{\partial x} \frac{A}{2B} \end{aligned}$$

or

$$B = \frac{\left(\frac{\partial A}{\partial x}\right)^2}{2 \frac{\partial^2 \Phi_0}{\partial x_0^2}}. \quad (11)$$

From this it is obvious that at a  $\lambda$ -point  $B$  never becomes zero and that always  $B > 0$ . The last statement follows from (11) because  $\partial^2 \Phi_0/\partial x_0^2 > 0$  ORL 7a

according to the known thermodynamical inequalities for solutions. Furthermore the equation

$$A(x) + (x_0 - x) \frac{\partial A}{\partial x} = 0$$

can be written in the form  $A(x_0) = 0$  to the accepted approximation, i.e. the phase transition points for the more symmetric phase satisfy the same equation as the Curie curve.

In this way the neighbourhood of a  $\lambda$ -point has thus for mixtures the form shown in Fig. 4 (plotted along the co-ordinate axes are concentration and temperature). The dotted line is the continuous transition curve, i.e. the Curie curve. I is the more, and II the less symmetric phase. The line 10 goes continuously into the line 03; the line 02 branches away from it. The line 302 is the

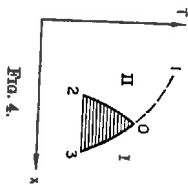


Fig. 4.

phase transition line; the shaded region 302 is the region of separation into two phases I and II, the concentrations of which are determined by the lines 03 and 02.

2. Let the term of third order in the expansion of  $\Phi$  now not be identically zero. The continuous transition in this case is only possible where terms of the second and third order are equal to zero. The first of these conditions gives again  $A(p, T) = 0$ . For the second condition to hold it is necessary for only one in variant of the third order to exist, i.e. the terms of third order should only possess one coefficient depending on  $p$  and  $T$ . Otherwise we would have too many equations which would not be possible to satisfy simultaneously. Let us again introduce the quantities  $\eta = c_1/\eta$ .

The term of third order should have the form

$$B(p, T) b(\eta) \eta^3$$

(it is assumed that there is only one invariant of the third order) and the expansion is

$$\Phi = \Phi_0 + A(p, T) \eta^2 + B(p, T) b(\eta) \eta^3 + C(p, T) \eta^4 + \dots \quad (12)$$

At a continuous transition point

$$A = B = 0.$$

Consequently the continuous transition points are in this case isolated, i.e. there is no Curie line. Therefore, such points should in some way lie on the

phase transition lines. Accordingly it is necessary to investigate the character of the phase transition line in the vicinity of such points.

In the neighbourhood of a continuous transition point of the type under consideration  $A$  and  $B$  are close to zero (but  $C > 0$ ). On the equilibrium curves of the more and less symmetric phase their thermodynamic potentials are equal, i.e.  $\Phi = \Phi_0$ , or

$$A\eta^2 + Bb\eta^3 + C\eta^4 = 0. \quad (13)$$

Besides that  $\partial\Phi/\partial\eta$  should be zero, as it should be for all possible equilibrium states, i.e.

$$\eta(2A + 3Bb\eta + 4C\eta^3) = 0. \quad (14)$$

These two equations should have a common solution different from zero (different from zero because the solution  $\eta = 0$  would mean that at the transition points  $\partial g = 0$ , i.e. a Curie line would exist and that as has already been mentioned is impossible).

It is easy to see that for this it is necessary that

$$B^2b^2 = 4AC \quad (15)$$

and

$$\eta = -\frac{Bb}{2C}. \quad (16)$$

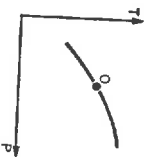


Fig. 5.

It could be thought that the continuous transition points considered simply lie on a phase transition curve like the point 0 in Fig. 5. However that is not so, but instead we shall now show that the point 0 should lie on the intersection of several phase transition curves.

Let us investigate points in the neighbourhood of 0 but not lying on phase transition curves. For them (as in every stable state)  $\partial\Phi/\partial\eta = 0$ . This equation has solutions  $\eta = 0$  and also solutions of the quadratic equation (14).

The solution  $\eta = 0$  corresponds to points which represent the state of the more symmetric phase ( $\partial g = 0$ ). In the second phase  $\eta$  is determined by equation (14). But quadratic equations have in general two solutions. At the point 0:  $A(p, T) = B(p, T) = 0$ ; in the neighbourhood of the point 0 the equation  $B(p, T) = 0$  determines a line. On that line (14) has two solutions with opposite signs

$$\eta = \pm \sqrt{-\frac{A}{2C}}. \quad (17)$$

That means that in the neighbourhood of the point 0 near to the line  $B = 0$  (14) has solutions with different signs, almost equal to each other in absolute value (because close to the line  $B = 0$ ,  $B$  is small). On one side of the line  $B = 0$ ,  $B$  is positive; there the negative solution of (14) corresponds to the stable state, otherwise by changing the sign of  $\eta$  it would be possible to decrease  $\Phi$ , i.e.  $\Phi$  would not have a minimum. By the same reason on the other side of the line  $B = 0$  (where  $B < 0$ ) the other solution of (14) becomes valid. Consequently the line  $B(\eta, T) = 0$  is also a phase transition line, where  $\eta$  changes sign discontinuously.

In this way the neighbourhood of the point 0 has the appearance shown in Fig. 6, i.e. at the point 0 the other phase transition line ends. The phase I is the more symmetric phase (in it  $\eta = 0$ ,  $A > 0$ ). On the phase transition line  $AB$ ,  $A = 0$ . The less symmetric phases II and III (where  $A < 0$ ) have the

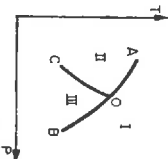


FIG. 6.

same symmetry (in them  $\eta$  differs only in sign, but this does not influence the symmetry of  $\Phi$ ). On the phase line  $CO$ ,  $B(\eta, T) = 0$ . At the point 0 all three phases become identical.

Let us determine the latent heat on the curves  $CO$  and  $AB$ . For the entropy we have

$$S = - \left( \frac{\partial \Phi}{\partial T} \right)_{\eta} = - \left( \frac{\partial \Phi}{\partial T} \right)_{\eta, \tau} - \left( \frac{\partial \Phi}{\partial \eta} \right)_{\eta, \tau} \frac{d\eta}{d\tau}.$$

But in all stable states  $\partial \Phi / \partial \eta = 0$ . Therefore

$$S = - \left( \frac{\partial \Phi}{\partial T} \right)_{\eta, \tau}.$$

Substituting (12), we find in the neighbourhood of the point 0 (i.e. for small  $\eta$ ):

$$S = S_0 - \frac{\partial A}{\partial T} \eta^2 \quad (18)$$

$S_0 = -\partial \Phi_0 / \partial T$  is the entropy of the phase I. Terms of higher orders can be neglected because unlike  $A$ ,  $\partial A / \partial T$  does not become zero.

Let us find the latent heat on the curve  $AB$ . On it  $\eta = -B\delta/2c$  (see equation (16)) and the latent heat of transition from the less symmetric to the more symmetric phase is

$$Q = T(S_0 - S) = \frac{\partial A}{\partial T} T \eta^2 = \frac{\partial A}{\partial T} \frac{T^2}{4C^2} B^2. \quad (19)$$

Near the point 0 the quantity  $B$  is a linear function of the distance along the curve from the point 0 (because at the point 0,  $B = 0$ ). In this way on the curve  $AB$ , near the point 0, the latent heat is proportional to the square of the distance from 0.

In order to find  $Q$  on the curve  $OC$  close to 0, write down the next term in the entropy  $S$ :

$$S = - \left( \frac{\partial \Phi}{\partial T} \right)_{\eta, \tau} = S_0 - \frac{\partial A}{\partial T} \eta^2 - \frac{\partial B}{\partial T} b \eta^3. \quad (20)$$

Since on the curve  $CO$  the quantity  $\eta$  is equal in absolute value in both phases, then the difference in entropy between phases II and III is  $2b \eta^3 \partial B / \partial T$ , where  $\eta$  is determined from (17). The latent heat is

$$Q = 2T \frac{\partial B}{\partial T} b \eta^3. \quad (21)$$

From (21) and (17) it can be seen that  $Q$  is proportional to  $(-A)^{3/2}$ , i.e. proportional to the distance from 0 to the power  $3/2$ .

Finally, it can be shown that when terms of fourth order have a complex structure new phase transition lines can appear. The neighbourhood of the point 0 then does not look as shown in Fig. 6, but as in Fig. 7.

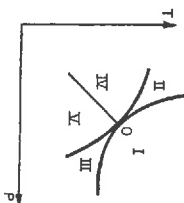


FIG. 7.

Phase I has the highest symmetry. Phases II and III have the same symmetry; the same applies to phases IV and V. At the point 0 all phases become identical, that is indeed the point of continuous transition. At the point 0 two of the phase transition curves have a common tangent and the third ends. Here we have assumed that two curves of phase transitions touch at the point 0. In the general case there may be several of them.

In part II of this paper it will be shown that in the case of transitions between liquids (i.e. isotropic bodies) and crystals terms of the third order are not identically zero. Therefore continuous transitions between liquids and crystals are only possible at isolated points of the type shown in Figs. 6 and 7. In particular Curie lines are impossible.

In the whole of the preceding part of the paper we have assumed that the symmetry properties of crystals are determined by the symmetry of the mean density function  $\rho$ . But the moving charges (electrons) in the body can create

in the crystal a mean current density  $f$  as well. Then the properties of the crystal will depend not only on the symmetry of the density  $\rho$  but also on the symmetry of  $f$ . Note that  $\int j dV$  over the whole volume of the crystal should be equal to zero. Otherwise that current would create a magnetic field and the crystal would possess some magnetic energy. That energy would very rapidly increase with an increase in the dimensions of the crystal and this would be energetically disadvantageous.

In the majority of bodies  $f = 0$ . In particular  $f \neq 0$  in ferromagnetic bodies. In the latter, in addition to this, the magnetic moment is not equal to zero in every part, i.e.  $\int [r \wedge j] dV \neq 0$  over an elementary cell. However not every body with  $f \neq 0$  is ferromagnetic, because although  $f \neq 0$ ,  $\int [r \wedge j] dV$  can be zero.

If  $f = 0$ , then the symmetry properties of the crystal are determined by the density  $\rho$ . It is known that there exists a limit to the number (230) of possible types of symmetry, i.e. space groups. If besides that  $f \neq 0$  then the classification of the types of symmetry follows from the properties of  $\rho$  and  $f$ ; then it is possible for there to be more than 230 space groups.

The presence of  $f \neq 0$  (crystals with  $f \neq 0$  we can call magnetic) does not introduce anything essentially new into the preceding discussion about transition points. At transition points the change in symmetry is then determined by  $\delta\rho$  and  $\delta j$ . As before only the transition points discussed above are possible.

Let us concentrate for a while on transitions connected with the appearance (or disappearance) of  $j$ , i.e. on transitions between magnetic and non-magnetic crystals. Since on one side of these points  $f = 0$ , then  $\delta j = j$ . As before we shall consider only the continuous transition points of this type, i.e. points where  $\delta j = j = 0$ , in the neighbourhood of which (on one side)  $j$  is small. Instead of expanding the thermodynamic potential  $\Phi$  in powers of  $\delta\rho$  we shall now have an analogous expansion in powers of  $j$ . In view of the symmetry of all the properties of the body in relation to the exchange of the future with the past the potential  $\Phi$ , in particular, cannot change when the sign of time is reversed. When such a change is made the density  $\rho$  does not change, but the current  $j$  has its sign reversed. From this it follows that in the expansion of  $\Phi$  in powers of  $j$  all terms with odd powers of  $j$  should be identically zero. It means that transitions connected with the appearance of  $j$  always belong to the case 1, i.e. Curie points are possible which form Curie lines, and under suitable conditions  $\lambda$ -points also. Such are the Curie points in ferromagnetic bodies. The discontinuities in the specific heats in chlorides of Fe, Cr, Ni at low temperatures are apparently of the same nature, there is also a  $\lambda$ -point in MnO. All these materials have  $f \neq 0$  below the transition point, and at the transition point  $f$  becomes zero (above that point  $f$  remains equal to zero). Until now we have been talking about transitions with a change in the symmetry of the crystal, but we have not discussed the physical nature of such changes which take place. Atoms in a crystal usually perform small oscillations about their equilibrium positions, i.e. the lattice points. In view of their smallness these oscillations cannot cause changes in the lattice symmetry.

This does not apply, of course, to the jump-like transitions when the atoms start oscillating around new equilibrium positions.

The continuous transitions with a change in the symmetry are always connected with a change in the ordering of the crystals, which follows when the number of places in the lattice where atoms of a given kind can reside is larger than the number of such atoms. There exists one particular distribution of the atoms in the lattice which is energetically most favourable. This is realised at sufficiently low temperatures. At higher temperatures the distribution of atoms deviates from this. As an example, let us consider a crystal formed from two kinds of atoms (binary mixture). The ideal configuration is that in which the atoms of different kinds are placed at lattice points in a definite order one relative to another (this is schematically shown in Fig. 8).



FIG. 8.

FIG. 9.

Such a crystal is said to be completely ordered. But every atom can in principle be found at any lattice point, i.e. there are more possible places for atoms of a given kind than there are atoms of that kind. Therefore, the crystal can also be incompletely ordered if some atoms are in "foreign" places, i.e. places at which, in the completely ordered crystal, should be atoms of the other kind. The probability, i.e. the density function  $\rho$  of finding atoms of one kind at lattice points in the completely ordered crystal can be represented schematically (in one dimension) by the curve in Fig. 9a, where the probability has a sharp maxima at every second lattice point. In the incompletely ordered crystal there appears some probability of finding atoms of a given kind at other (foreign) lattice points (Fig. 9b).

Finally the number of atoms of a given kind in the lattice residing at "own" places can be equal to the number of these atoms residing at their kind becomes equal at all lattice points (Fig. 9c). The crystal is then called disordered. It is easy to see that at the moment when this disorder appears the symmetry of the crystal changes (namely: the symmetry increases). That can be seen, for instance, in Fig. 9c; the curve c has, in comparison with curves a and b, an extra translational period equal to the distance between two neighbouring lattice points (the curves a and b have only a period equal to twice the distance between lattice points).

A second example is the crystal of  $\text{NH}_4\text{Cl}$ . This crystal has a lattice of the type NaCl, where at the lattice points are Cl and  $\text{NH}_4^+$ . The  $\text{NH}_4^+$  groups have the form of tetrahedra and in the  $\text{NH}_4\text{Cl}$  crystal they can be orientated in



two directions. If all  $NH_4$  groups are pointing in the same direction the crystal is completely ordered; if some of the groups  $NH_4$  are pointing in the opposite direction the crystal is incompletely ordered. Finally if the numbers of  $NH_4$  groups pointing in each direction are equal the crystal is disordered. Its symmetry has then changed, namely: the ordered crystal has the symmetry of a tetrahedron and the disordered the symmetry of a cube.

We can introduce the quantity "degree of order", which would characterize the deviation of the crystal from its ordered state; it is equal to 1 in the completely ordered crystal, decreases as a function of the deviation from the ordered state, and becomes zero in the disordered crystal. In our preceding discussions the transition from the function  $\varrho$  to  $\varrho + \delta\varrho$  corresponded to the continuous transition from the more to the less symmetric body, i.e. from the disordered crystal to the appearance of the beginning of orderliness. In this way  $\delta\varrho$

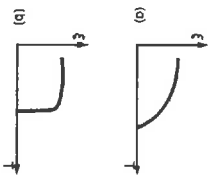


FIG. 10.

just determines how close the crystal is to complete disorder;  $\delta\varrho = 0$  in the disordered crystal. But we have seen that  $\delta\varrho$  is determined by the quantities  $\varrho_i$  which are moreover proportional to  $\eta$ . Obviously  $\eta$  can be chosen as the degree of order. In the above mentioned paper<sup>2</sup> we used as the degree of order always the positive quantity  $\xi = \eta^2$ .

At a continuous transition (for instance at a Curie point)  $\xi$  as a function of  $T$  has the form as shown in Fig. 10a. At the phase transition it becomes zero abruptly (Fig. 10b).

In the case of a binary mixture discussed above, the degree of order can be chosen in the following way. Let  $N_1$  be the number of atoms of a given kind residing at their places, and  $N_2$  at foreign places. In a disordered crystal  $N_1 = N_2$ . The probability of finding an atom in its place is proportional to  $N_1/(N_1 + N_2)$ , and in a foreign place  $N_2/(N_1 + N_2)$ . In a disordered crystal each of those fractions is equal to  $1/2$ . Therefore the deviations of the probabilities from their values in the disordered crystal are proportional to

$$\frac{N_1}{N_1 + N_2} - \frac{1}{2} = \frac{N_1 - N_2}{2(N_1 + N_2)}, \quad \frac{N_2}{N_1 + N_2} - \frac{1}{2} = \frac{N_2 - N_1}{2(N_1 + N_2)}$$

In this way  $\delta\varrho$  is proportional to the quotient  $(N_1 - N_2)/(N_1 + N_2)$ , which can indeed be chosen to be  $\eta$ .

In the case of transitions between magnetic and non-magnetic crystals atoms with differently orientated magnetic moments play the role of atoms of different

kinds. To a disordered crystal corresponds the case where the probabilities for an atom to have differently orientated moments are equal for every atom. In the case of the ferromagnetic state these probabilities cease to be equal, since the crystal as a whole has a magnetic moment. Finally in the case of magnetic, but not ferromagnetic, bodies the probabilities for different orientations of the moment for a single atom are also not equal, but in different atoms of the lattice the opposite orientation of the moments are more probable. In this way in this case the mean magnetic moments of different atoms have the opposite directions and the crystal as a whole does not have a magnetic moment.

#### CONCLUSIONS

1. The transitions between bodies of different symmetry (in particular between a liquid and a crystal) cannot happen continuously, in the same sense as the transition between a liquid and a gas above the critical point; at every moment the body has this or that symmetry.
2. Besides phase transitions the only other possible transitions are those continuous in the sense that at the transition point no abrupt change in the state of the body occurs (in particular there is no latent heat), but the symmetry changes suddenly. Such transitions are inevitably followed by a jump in the specific heat. These transitions are connected with a crystal becoming disordered.
3. The following types of continuous transitions with a change of symmetry are possible: (a) Curie points lying on a curve in the  $(p, T)$  diagram. These curves can intersect each other or the phase transition line in points of the kind shown in Figs. 2 and 3. The Curie line can go continuously into a the phase transition line. The point where this happens is a  $\lambda$ -point. At the  $\lambda$ -point of a pure substance the specific heat becomes infinite; if the body is a mixture the specific heat only experiences a finite jump. (b) Isolated continuous transition points. These points lie on the intersections of several phase transition lines (Figs. 6 and 7).
4. Continuous transitions are possible which are connected with the appearance or disappearance of the mean magnetic moments of every atom in the crystal (in particular such is the Curie point of ferromagnetic bodies). For such transitions case a) is appropriate.

#### PART II

The impossibility of the existence of crystals with a density function which depends only on one or two co-ordinates is proved. The question of transitions between a liquid and a crystal is discussed and it is shown that between them there cannot exist Curie points lying on a curve in the  $p$ - $T$  diagram. The question of the nature of liquid crystals is investigated.

In part II the question of transitions connected with a change in the symmetry of the body has been discussed from a general point of view. In this part we shall investigate the question of the relation between different states of matter from the same point of view.

<sup>†</sup> Referred to as I in the following.

1. THE IMPOSSIBILITY OF THE EXISTENCE OF CRYSTALS WITH DENSITY  $\rho$ , WHICH DEPENDS ON ONE OR TWO CO-ORDINATES

The density function  $\rho$  of a crystal (see I) is a function of all three co-ordinates  $x, y, z$ . The question arises, is the case possible where  $\rho$  is a function of only two, or even one, variable. A crystal with  $\rho = \rho(x)$  could be considered as consisting of atoms arranged in the form of parallel straight rows, where these rows are all equally orientated along the  $x$ -axis, but completely randomly placed with respect to each other. A crystal  $\rho = \rho(x, y)$  should have some how consist of parallel planes. In each of these planes atoms are distributed in a certain order; however the positions of these planes are undetermined.

Let us show that states of matter with density  $\rho$  depending only on one or two co-ordinates are impossible. We shall use a method applied by Peierls<sup>1</sup> to two-dimensional bodies. In particular let us determine the fluctuations in such a body.

Consider some deformation. Such a deformation is characterised by a displacement vector  $u(x, y, z)$  with the components  $u_i(x, y, z)$  at every point  $x, y, z$  of the body. The energy (more specifically the free energy) of the deformed body is determined, as it is known, by the deformation tensor  $u_{ik}$

$$u_{ik} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} \right).$$

The change  $\Delta F$  in the free energy per unit volume element of the body is known to be generally a quadratic function of all components of the tensor  $u_{ik}$ . The change in free energy of the whole body is  $V \Delta F$ , where  $V$  is the volume of the body.

The displacement vector  $u$  can be expanded in plane waves

$$u_i = \sum_f u_i^{(f)}, \quad u_i^{(f)} = a_i^{(f)} e^{i(f \cdot r)}, \quad (1)$$

obviously the fluctuation is

$$\overline{u_i^2} = \sum_f \overline{u_i^{(f)2}}. \quad (2)$$

The tensor  $u_{ik}$  which corresponds to a certain plane wave  $u_i^{(f)}$  is obviously proportional to the product of components  $u_i^{(f)}$  with components of the wave vector  $f$  [ $u_i^{(f)} = i(f_i u_k + u_k f_i)/2$ ]. The quadratic function  $\Delta F$  breaks into a sum of terms each of them depending only on  $u_i^{(f)}$  of one  $f$ .

Let us consider a body with density  $\rho = \rho(x)$ . Then it is easy to see that the free energy of the deformation in such a body does not depend on  $u_{xy}$  and  $u_{xz}$ . As a matter of fact these deformations exhibit themselves as nothing more than a displacement along the  $y$  and  $z$  directions. But in these directions

$\rho = \text{const}$ , and therefore such a displacement is not connected with a change in  $\rho$ , consequently neither with a change in  $F$ . Let us determine the mean value of  $u_{xx}^{(f)}$ . For this determine the part of the free energy which depends on  $u_{xx}^{(f)}$ . Since  $u_{xy}^{(f)}$  and  $u_{xz}^{(f)}$  do not enter  $\Delta F$  then the part of  $\Delta F$  we are looking for depends only on  $u_{xx}^{(f)}$ , i.e. on

$$u_{xx}^{(f)} = i f_x u_x^{(f)};$$

consequently  $\Delta F$  has the form

$$\Delta F = A u_{xx}^{(f)2} / f_x^2.$$

Since the probability of fluctuational to  $\exp(-\Delta F \cdot V/kT)$ , it is easy to see that

$$\overline{u_{xx}^{(f)2}} \sim \frac{kT}{AV f_x^2}. \quad (3)$$

In order to find the fluctuation of the displacement  $\overline{u_x^2}$  it is necessary to sum (3) over all characteristic frequencies. It is known that this summation can be replaced by an integration. For this (3) should be multiplied by the Debye distribution of characteristic oscillations, i.e. by  $V df_x df_y df_z$  and integrated over the range zero to the value of  $f$ , corresponding to the limiting Debye frequency. In this way

$$\overline{u_x^2} \sim \frac{kT}{A} \int \frac{df_x df_y df_z}{f_x^2}. \quad (4)$$

But this integral diverges like  $1/f_x$  when  $f_x = 0$ . So in this case the fluctuation is infinite.

But the infinite fluctuation results in the fact that the point to which a given value of the function  $\rho(x)$  corresponds can be placed within an arbitrary large distance; in other words the density  $\rho(x)$  "spreads" over the whole body. Saying this differently: no  $\rho(x)$  except  $\rho = \text{const}$  is possible.

If in a crystal  $\rho = \rho(x, y)$ , then in analogy to the above it can be shown that

$$\overline{u_x^2} \sim kT \int \frac{df_x df_y df_z}{\varphi_{II}(f_x, f_y, f_z)}, \quad (5)$$

where  $\varphi_{II}$  is a quadratic function of  $f_x$  and  $f_y$ , and similarly for  $\overline{u_y^2}$ .

This integral diverges logarithmically when  $f_x = 0, f_y = 0$ . So in this case also the fluctuation is infinite and therefore such crystals cannot exist.

In the case of  $\rho = \rho(x, y, z)$  it is easy to see that

$$\overline{u_x^2} \sim kT \int \frac{df_x df_y df_z}{\varphi_{III}(f_x, f_y, f_z)} \quad (6)$$

and similarly for  $\overline{u_y^2}$  and  $\overline{u_z^2}$ . This integral is obviously finite.

## 2. THE TRANSITION BETWEEN A LIQUID AND A CRYSTAL

Let us consider the possibility of transition from a liquid, i.e. an isotropic body, into a crystal, the continuous transition which was discussed in I (without latent heat).

Let  $\epsilon_0$  be the density function of the liquid. Since the liquid is isotropic  $\epsilon_0 = \text{const.}$  At the point of continuous transition  $\epsilon$  becomes  $\epsilon = \epsilon_0 + \delta\epsilon$ , where  $\delta\epsilon$  (and thus also  $\rho$ ) have the symmetry of the crystal. Expand  $\delta\epsilon$  in plane waves

$$\delta\epsilon = \sum_j q_j e^{i(r \cdot r_j)} \quad (7)$$

Here  $f$  are the reciprocal lattice vectors of the crystal. Since  $\rho$  is real we should have

$$q_j = a_j^* f_j \quad (8)$$

where the symbol \* signifies complex conjugate.

The thermodynamic potential  $\varphi$  of the crystal is a functional of  $\rho$  or, what is the same, a functional of  $\delta\epsilon$  (see I). If for  $\delta\epsilon$  we substitute expression (7), then  $\varphi$  will be a functional of the coefficients  $q_j$ . Near the transition point  $\varphi$  can be expanded in powers of  $q_j$ . Different terms of this expansion have the form

$$q_1, q_1, q_1, \dots$$

It is easy to see that in the expansion of  $\varphi$  the only terms which can exist are those for which  $f_1 + f_2 + \dots = 0$ . Actually  $\varphi$  should not change under a translation of the origin of co-ordinates, i.e. under the change of  $r$  into  $r + R$ , where  $R$  is an arbitrary constant vector. But under such an exchange  $q_j$  is multiplied by  $e^{i(r \cdot R)}$ , and the expression  $q_1, q_2, \dots$  by  $e^{i(f_1 + f_2 + \dots \cdot R)}$ . This factor is equal to 1 for all values of  $R$  only if  $f_1 + f_2 + \dots = 0$ .

From  $\sum f_j = 0$ , we have for terms of the first order  $f = 0$ , i.e. in the expansion of  $\varphi$  there are no terms of first order at all (see also I). Terms of second order should contain only products  $a_j, a_j$  or according to (8)  $|q_j|^2$ . The expansion of  $\varphi$  consequently has the form

$$\varphi = \varphi_0 + \sum_j A_j |q_j|^2$$

( $\varphi_0$  is the thermodynamic potential of the liquid, the  $A_j$  are constants which generally depend on pressure  $p$  and temperature  $T$  as well as  $f_j$ ). Because of the isotropy of the liquid we can conclude that the quantities  $A_j$  depend only on the magnitude, but not on the direction, of vector  $f$ .

Above the transition point  $\varphi$  has a minimum for all  $A_j$ , i.e. all  $A_j$  are positive. At a (continuous) transition point the second-order term should become zero for  $\delta\epsilon$  different from zero (see I). From this it follows that at the transition point one of the  $A_j$  should become zero, i.e. the curve  $A_j(f)$  touches the axis of the abscissae at the transition point (Fig. 11).

Touching at two points at the same time is highly improbable therefore at the transition point only one of the coefficients  $A_j$  becomes zero. From this it follows that, at the transition a point  $\delta\epsilon$  arises which corresponds to plane

waves with one definite wavelength, that wavelength which is determined by those values of  $f$  which correspond to the vanishing coefficient  $A_j$ . All  $q_j$  corresponding to other  $f$  are equal to zero. Designating that particular coefficient  $A_j$  simply by  $A$ , we have

$$\varphi = \varphi_0 + A \sum |q_j|^2 \quad (9)$$

where the summation is over  $f$  which differ only in their direction.

The terms of the third order have the form

$$\sum_{f_1, f_2, f_3} B_{f_1, f_2, f_3} q_{f_1} q_{f_2} q_{f_3}$$

where in every term  $f_1 + f_2 + f_3 = 0$ . But as has just been shown, at the transition point there arise periods which all have the same absolute magnitude. Therefore in the third-order terms also only those  $f_1, f_2, f_3$  which differ only in direction take part. The condition  $f_1 + f_2 + f_3 = 0$  means therefore that the vectors  $f_1, f_2, f_3$  should form an equilateral triangle. In all third-order terms these triangles have equal size (because the quantity  $f$  is determined by the second order term) and differ only in their orientation in space. Because of the isotropy of the liquid the coefficients  $B_{f_1, f_2, f_3}$  can depend only on the size, but not on the orientations, of these triangles. Therefore all  $B_{f_1, f_2, f_3}$  in the third-order terms are equal; their common value we shall denote by  $B$ . In this way the term of the third order has the form

$$B \sum q_{f_1} q_{f_2} q_{f_3}$$

where the summation is over  $f_1, f_2, f_3$  which form equal but differently oriented equilateral triangles. Adding this to (9) we have

$$\varphi = \varphi_0 + A(p, T) \sum |q_j|^2 + B(p, T) \sum q_{f_1} q_{f_2} q_{f_3} + \dots \quad (10)$$

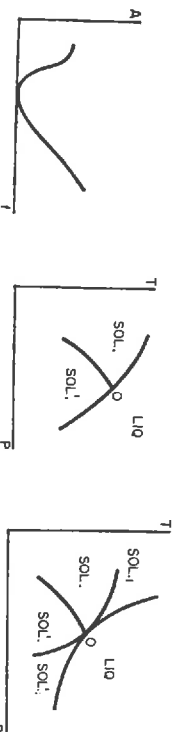


FIG. 11.

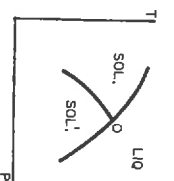


FIG. 12.

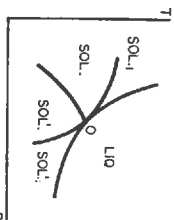


FIG. 13.

We see that the third-order term has only one coefficient  $B(p, T)$ . In other words we are dealing with the case analysed in I under case II. It means that between liquids and solid crystals there cannot be Curie points forming a line in the  $p$ - $T$  diagram, but continuous transitions are possible in isolated points which lie on intersections of ordinary phase transition lines, such as shown in Fig. 12 or in a more complicated case in Fig. 13. In those diagrams the point 0 is the point of continuous transition; Liq. indicates the liquid phase;

Sol., Sol', Sol'' are different solid phases. Sol, Sol' (in Fig. 12 the phases Sol., Sol', on the one hand and Sol'', Sol', on the other hand) have, in the vicinity of the point 0, equal symmetry and differ only in the sign of  $\delta\epsilon$ , i.e. they have  $\rho$  equal  $\rho = \epsilon_0 + \delta\epsilon$  (see I). In other words their lattices are such that in those places where in Sol. the probability of finding an atom has a maximum in the lattice Sol' it has a minimum, and vice versa. At the present time it is difficult to say to what extent such continuous transitions exist in nature.

### 3. LIQUID CRYSTALS

One often finds the opinion that liquid crystals represent bodies in which the molecules are arranged in "chains", oriented in one direction, i.e. bodies in which  $\rho$  is a function of one variable. However, it has been shown in section 1, that such bodies cannot exist.

Instead, we can imagine liquid crystals as bodies in which the molecules, or more precisely their centres of mass, are distributed completely randomly, as in ordinary liquids. Anisotropy of the liquid crystal is caused by the equal orientation of its molecules; for instance, if the molecules have an elongated shape, then all of them can be arranged with their axes in one direction. These ideas about the nature of liquid crystals can be formulated more precisely with the help of the density function.

If the body is isotropic, then  $\rho = \text{const}$ ; however, from  $\rho = \text{const}$  it does not follow that the body should necessarily be isotropic. If  $\rho = \text{const}$ , then this means that all positions of an atom, more precisely its centre of mass, in the body are equally probable. Nevertheless in this case different orientations in the body can be non-equivalent. Namely, when the position of any particular atom No. 1 is given, then the probability of different positions of a neighbouring atom No. 2 is a function of their relative positions (i.e. of the vector  $\mathbf{r}_{12}$  connecting atom No. 1 and 2). This probability  $\rho_{12}$  can depend on the direction of  $\mathbf{r}_{12}$ . Then the body will be anisotropic regardless of the fact that for every atom  $\rho = \text{const}$ . On the other hand, when this is so, the body will be a liquid since in it no displacement deformation is possible. If  $\rho = \text{const}$  then under any deformation, without a change of volume,  $\rho$  does not change, i.e. strictly speaking there is no deformation.

Such bodies ( $\rho = \text{const}$ ,  $\rho_{12}$  depends on the orientation) we can consider as liquid crystals. Thus we can talk about the symmetry of liquid crystals as the symmetry of the function  $\rho_{12}$ . But  $\rho_{12}$  is a function of the vector  $\mathbf{r}_{12}$ ; when the length of  $\mathbf{r}_{12}$  is changed without changing its direction, then  $\rho_{12}$  does not exhibit any periodicity (when  $\mathbf{r}_{12} \rightarrow \infty$ ,  $\rho_{12}$  obviously tends to  $\rho^2$ ). In other words  $\rho_{12}$  has no translational symmetry. Therefore the possible symmetry groups of  $\rho_{12}$ , i.e. of liquid crystals, are not the 230 space groups, but point groups. Of course the number of these groups is not limited to 32 as in solid crystals; the symmetry of liquid crystals should be classified in the same way as the symmetry of molecules. In particular, symmetry axes of any (and not only of the second, third, fourth and sixth) order are possible. In particular, liquid crystals are possible with total axial symmetry. It is experimentally

known that certain liquid crystals are uniaxial. It would be very interesting to establish whether they possess total axial symmetry or simply have axes of higher than second order.

In principle, liquid crystals with cubic symmetry are possible. Such crystals are impossible to distinguish from ordinary crystals in their optical properties. It is possible that liquid He II is such a crystal. (He II does not exhibit double refraction).<sup>3</sup>

If all particles considered are the same then  $\rho_{12}$  obviously has a centre of symmetry. Actually, if on the left of atom No. 1 we have atom No. 2, then standing at the position of atom No. 2 we will have atom No. 1 on the right; in view of the equality of these atoms we conclude that the values of  $\rho_{12}$  should be equal for two anti-parallel but equal  $\mathbf{r}_{12}$ . If the crystal consists of different atoms then it is possible that  $\rho_{12}$  does not have a centre of symmetry.

Let us consider the possibility of continuous transitions between liquid crystals and liquids (continuous in the sense that there is no discontinuity in the state).

In the case of a continuous transition  $\rho_{12}^{(0)}$  becomes  $\rho_{12}^{(0)} + \delta\rho_{12}$  in a similar way to that in which  $\rho_0$  became  $\rho_0 + \delta\rho$  before.  $\rho_{12}^{(0)}$  relates to the liquid and is therefore isotropic;  $\delta\rho_{12}$  has the symmetry of the liquid crystal.

It is shown in I at a continuous transition point there appear functions  $\delta\rho$ , in the present case  $\delta\rho_{12}$ , having certain symmetry properties which characterized irreducible representations of the symmetry group  $\rho_{12}^{(0)}$ , i.e. in the present case symmetry groups of rotations about the origin of co-ordinates. It is known that functions which characterize irreducible representations of the rotation group either change their sign under inversion (reflection in the origin of co-ordinates) or do not. In the second case the crystal which is being formed has a centre of symmetry. In the first case it has not. The thermodynamic potential  $\Phi$  of the body should be invariant with respect to every possible transformation, in particular with respect to inversions. Therefore if the crystal, i.e.  $\delta\rho$ , has no centre of symmetry then all terms of odd powers in the expansion of  $\Phi$  in powers of  $\delta\rho_{12}$  in particular the terms of third order, are identically equal to zero. In other words we have the case analysed as the case I, namely; continuous transitions are possible as Curie points lying on a curve in the diagram.

If  $\delta\rho_{12}$  has a centre of symmetry then terms of the third order are not generally speaking identically equal to zero. In this case we have the case II of part I, i.e. only isolated points of continuous transition are possible, similar to continuous transitions between a liquid and a solid crystal (section 2).

It is experimentally known that He II becomes an ordinary liquid not at Curie points, i.e. we have the case I. This means, according to what has been said above, that if He II is a liquid crystal it need not have a centre of symmetry. Since, on the other hand, He II consists of identical atoms it should be assumed that the absence of a centre of inversion is caused by the fact that the atoms of He II themselves have asymmetric electron shells. In view of a certain strangeness of such an assumption, the assumption itself about He II being a liquid crystal becomes somehow doubtful.

## 4. SURFACE PHASES

The surface of separation of two isotropic, i.e. liquid, phases can generally speaking be anisotropic. Apparently in some cases this has been observed. But as it has been shown in section 1, that crystals in which  $\rho$  is a function of only two coordinates are impossible. In particular the existence of two dimensional "solid" crystals, i.e. crystals with anisotropic  $\rho$ , are impossible. Therefore anisotropic surface should be two dimensional "liquid" crystals, i.e. in them the molecules, more precisely their centres of mass, are randomly distributed, but not all of them are equally orientated ( $\rho = \text{const}$ ,  $\epsilon_{11}$  is anisotropic).

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## 30. ON THE THEORY OF SUPERCONDUCTIVITY

In this paper it is shown that at average values of the magnetic field different from zero a superconductor must break up not into two regions, viz. a superconducting and a non-superconducting one, but into a large number of alternating superconducting and non-superconducting layers. This circumstance provides an explanation for the existence of Peierls' intermediate state.

## 1. THE INTERMEDIATE STATE

Rutgers and Gorter<sup>1</sup> have shown that a number of the properties of superconductors may be explained by supposing that the superconducting and non-superconducting states are two phases, the superconducting phase being characterised by the fact that a magnetic field does not penetrate it, i.e. its magnetic permeability  $\mu = 0$ . If a superconductor is placed in a magnetic

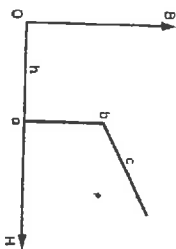


Fig. 1.

field, then on increasing this field the relation between the induction  $B$  and the magnetic field  $H$  is illustrated by the curve in Fig. 1. While the metal is superconducting  $B = 0$ ; when the magnetic field reaches a critical value, which we shall denote by  $h$ , the body goes over to the non-superconducting phase.  $B$  then increases with  $H$  according to the formula  $B = H$  ( $\mu$  is practically equal to 1). Experiment shows that the section  $ab$  of the curve shown also corresponds to a certain actually realisable state of the body. Thus, a superconducting sphere placed in a magnetic field does not divide into two parts—a superconducting and a non-superconducting one—but a uniform magnetic field, which is not, however, equal to the external field, appears within it. With increase in the latter the field within the sphere also increases, approaching the external one. The state corresponding to the indicated section of the  $B-H$  curve was analysed by Peierls<sup>2</sup> and called "intermediate" by him.

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