

90 YEARS



## ON THE THEORY OF PHASE TRANSITIONS

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The question about continuous phase transitions (without latent heat) is 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 realized by going around 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 related to rotations of molecules; however, it is not at all clear how rotation can lead to phase transition and, in particular, to a jump of the specific heat.

One even finds the strange statement 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. Therefore, continuous transitions (in the same sense that transitions between liquid and gas are continuous) connected with change of the symmetry of the body are absolutely impossible.

Until recently, the exact formulation for the notion of crystal lattice was lacking. Only quite recently, Bethe and Peierls 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, is changed discontinuously, are not the main interest of the present investigation. Our main interest is in such transitions where the state of the body (specifically 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 same sense as 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  $\rho(x, y, z)$  is used, so that  $\rho(x, y, z)dxdydz$  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  $\rho_1, \rho_2, \dots$ , which would determine the probabilities for each kind of atoms. 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 charge density at every point of the body. In the following, we shall talk simply about the "density"  $\rho(x, y, z)$  as some function which is chosen in a certain way and determines the distribution of atoms in the body under consideration. Note that such a method based on the function  $\rho$ , has also the advantage that it is possible in quantum mechanics as well.

The important property of the function  $\rho$  is its symmetry, i.e. that group of coordinate transformations, with respect to which  $\rho$  is invariant. The same group determines the symmetry of the body. As is known, there are altogether 230 possible different groups of

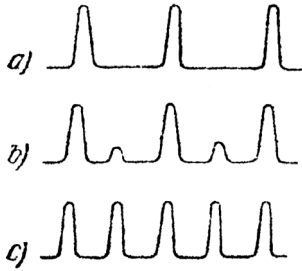


Fig. 1

transformations, i.e. types of symmetry. In isotropic bodies (liquids), obviously,  $\rho = \text{const}$ .

As already mentioned, we consider here those transitions where, in spite of a discontinuity in the symmetry, the state of the body changes continuously. In other words, the density  $\rho$  changes continuously. It is easy to see that such transitions are possible because even a very small change in the distribution of atoms in the lattice is enough to change its symmetry. If, for instance,  $\rho$  is represented by the curve like that in Fig. 1, *a* (schematically drawn in one dimension) and some of the maxima decrease (Figs. 1, *b* and 1, *c*), 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  $\rho_0$  which has a certain symmetry (we shall talk about the totality of symmetry transformations  $\rho_0$  as about the group  $\rho_0$ ). At the transition point, the density starts to change and becomes  $\rho = \rho_0 + \delta\rho$ , where  $\delta\rho$  is small compared with  $\rho_0$ . The quantity  $\delta\rho$  has also some symmetry (group  $\delta\rho$ ) which is lower than that of  $\rho_0$  (i.e. not all elements of the symmetry transformations  $\delta\rho$  are elements of the symmetry  $\rho_0$ ; the group  $\delta\rho$  is a subgroup of the group  $\rho_0$ ). Then  $\rho = \rho_0 + \delta\rho$  has the same symmetry, because the sum of two functions has the same symmetry as the less symmetric term. Therefore, if  $\delta\rho$  would have a higher symmetry than  $\rho_0$ , then  $\rho_0 + \delta\rho$  would have the same symmetry as  $\rho_0$ , so that no change in the symmetry of the body would take place.

Symmetry transformations from the group  $\rho_0$  which do not belong to the group  $\delta\rho$  change  $\delta\rho$  into some other function. It is known from group theory that the function  $\delta\rho$  can be split into a sum of functions, the number of which is equal to the number of elements of the group  $\rho_0$ , 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  $\rho_0$ . Further, all these functions, into which  $\delta\rho$  is split, can be separated into

groups or “races”, where all functions composing them again are transformed among themselves. So we can write

$$\delta\rho = \sum_n \sum_i c_i^{(n)} \varphi_i^{(n)}, \quad (1)$$

where  $n$  is the number of a race, and  $i$  is the number of a 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 realized by the transformation matrices of the functions of that race. It is known that there exists an expansion of  $\delta\rho$  into  $\varphi_i^{(n)}$ , where every race consists of the smallest possible number of functions (thus realizing the “irreducible representation”).

In (1), we suppose just such a partition. We could after all simply write it as  $\delta\rho = \sum_n \sum_i \varphi_i^{(n)}$ , because the functions  $\varphi_i^{(n)}$  are not determined beforehand, but it will be convenient in the future to consider these functions somehow normalized.

Among all  $\varphi_i^{(n)}$ , there is always one function (which forms a “race” by itself) which is invariant with respect to all transformations of the group  $\rho_0$ . In the sum  $\rho_0 + \delta\rho$ , we consider this function to belong to  $\rho_0$  so that  $\delta\rho$  has no such function.

The thermodynamic potential  $\Phi$  of the body is determined by the density  $\rho$ , i.e. depends on the form of the function  $\rho$ . In other words,  $\Phi$  is a functional of  $\rho$ :

$$\Phi = \Phi\{\rho_0 + \delta\rho\}.$$

In addition,  $\Phi$  depends also on the temperature  $T$  and the pressure  $p$  of the body as on the parameters. When  $T$  and  $p$  are given, the form of the function  $\rho$  is determined from the condition that  $\Phi$  should have a minimum.

Let us expand the thermodynamic potential  $\Phi\{\rho_0 + \delta\rho\}$  in the state with density  $\rho_0 + \delta\rho$  in powers of  $\delta\rho$  (of course, this expansion is not an ordinary power series; individual terms in the expansion are integral operators of  $\delta\rho$ ). In other words, we have an expansion in powers of  $\varphi_i^{(n)}$  and  $c_i^{(n)}$ .

It can be seen that the first-order terms in this expansion are zero. It is obvious that the potential  $\Phi$  as the quantity characterizing the physical properties of the body should not be changed under any movements of the body, i.e. it should be invariant under all possible coordinate transformations. If some transformation changes  $\rho_0$  into  $\rho'_0$  and  $\delta\rho$  into  $\delta\rho'$ , then

$$\Phi\{\rho_0 + \delta\rho\} = \Phi\{\rho'_0 + \delta\rho'\}.$$

From this, it can be seen that if  $\Phi$  is considered as a functional only of  $\delta\rho$ , then  $\Phi$  is invariant only with respect to those transformations which do not change  $\rho_0$ , i.e. the transformations of the group  $\rho_0$ . Since the functions  $\varphi_i^{(n)}$  transform among themselves under transformations of this group, we can consider that only the coefficients  $c_i^{(n)}$  are changed under these transformations, so that the expression for  $\Phi$  should be invariant with respect to transformations of these coefficients. In particular, the coefficients in the expansion of  $\Phi$  with respect to the powers of  $c_i^{(n)}$  are the invariants of the corresponding degree.

It is known that it is impossible to construct linear invariants from quantities transforming as an irreducible representation. Therefore, the expansion starts from terms of the second order. The single invariant of the second order which can be composed from the above-mentioned quantities is a positive definite quadratic form. It always can be reduced to the sum of squares by a suitable choice of the normalization.

Thus, the beginning of the expansion of  $\Phi$  can be written in the following way:

$$\Phi\{\rho_0 + \delta\rho\} = \Phi\{\rho_0\} + \sum_n A^{(n)} \sum_i c_i^{(n)2}, \quad (2)$$

where the coefficients  $A^{(n)}$  depend on the functions  $\varphi_i^{(n)}$  and also on the parameters  $T$  and  $p$ .

Let us study the behavior of this expression in the  $p, T$ -plane near the transition point. This point is characterized in the following way. On one side of the transition point (which we call the "upper" side), the body is described by the density  $\rho_0$ , i.e.  $\delta\rho = 0$  corresponds to the stable equilibrium state. On the other ("lower") side of the transition point, a little addition  $\delta\rho$  arises. This situation can be obviously described in such a way: above the transition point, all the quantities  $A^{(n)}$  in (2) have only positive values and, consequently, the minimum of the second term in (2) is realized for all  $c_i^{(n)} = 0$ , i.e. at  $\delta\rho = 0$ . The minimum at  $\delta\rho$  different from zero arises if at least one term from  $A^{(n)}$  becomes negative. Both regions are separated by the points, at which the given  $A^{(n)}$  is positive for all  $\varphi$  and equals to zero only for one definite kind of the function  $\varphi$ . Then just that addition to  $\rho_0$ ,

$$\delta\rho = \sum_i c_i^{(n)} \varphi_i^{(n)},$$

physically occurs, which makes vanish  $A^{(n)}$  and which is transformed, in particular, according to the representation of a given number  $n$ . Hereinafter, we consider just this  $\delta\rho$  with definite functions  $\varphi_i^{(n)}$ . In

(2), all terms of the sum, apart from the  $n$ -th term, are identically equal to zero, and we write down the following relation, by dropping the superscript  $n$ :

$$\Phi = \Phi_0 + A \sum c_i^2 + \dots$$

A necessary condition for the existence of the point of a continuous transition has the form

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

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

Two cases are possible.

I. Terms of the third order are identically zero (there are no invariants of the third order). Then, for the existence of a transition point, it is necessary and sufficient that condition (3) be fulfilled, and terms of the fourth order should be positive. Thus, in this case, transition points lie on a certain curve in the  $p, T$ -plane which is determined by Eq. (3). This is the case of Curie points.

It can be seen that such a case can be realized, i.e. invariants of the third order can be absent. This is clear from the following example. If the race under investigation has only one function, then the coefficient  $c$  at definite transformations can change the sign. In that case, all invariants of odd orders are obviously equal to zero.

Define

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

and

$$c_i/\eta = \gamma_i.$$

Then the expansion of  $\Phi$  takes 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

$$\Phi = \Phi_0 + A\eta^2 + B\eta^4, \quad (5)$$

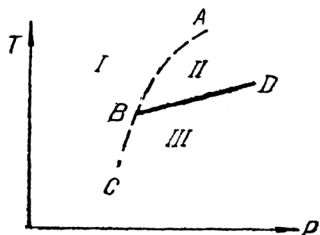


Fig. 2

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

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

Above the Curie point,  $A > 0$ ;  $\eta = 0$  corresponds to the minimum of  $\Phi$ , i.e. the body has the symmetry  $\rho_0$ . At the Curie point,  $A = 0$ , and  $A < 0$  below it. From the minimization of  $\Phi$ , i.e. from  $\partial\Phi/\partial\eta = 0$ , we obtain

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

or

$$\eta^2 = -A/(2B). \quad (7)$$

Then

$$\Phi = \Phi_0 - A^2/(4B).$$

The specific heat of the body is

$$c = -T \frac{\partial^2 \Phi}{\partial T^2} = c_0 + \frac{T}{2B} \left( \frac{\partial A}{\partial T} \right)^2. \quad (8)$$

Terms which vanish at the Curie point are omitted. The quantity  $c_0$  is the specific heat of the body with the symmetry  $\rho_0$ , i.e. above the Curie point. By virtue of (8), we see that  $c > c_0$  at the Curie point. Thus, at the Curie point, the heat capacity has a jump, and it increases in going from a more to a less symmetric body (we recall that one body is less symmetric than the other body if its symmetry transformation group is a subgroup of the symmetry group of the other one).

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

But all these terms depend also on  $p$  and  $T$ ; because of that, the  $\gamma_i$  depend on  $p$  and  $T$  as well. But the quantities  $\gamma_i$  determine the symmetry of  $\delta\rho$ , i.e. the symmetry of the crystal. Therefore, it may happen that, on different parts of the curve of Curie points, the

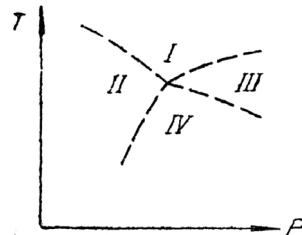


Fig. 3

transition takes place from a more symmetric crystal (where  $\delta\rho = 0$ ) to less symmetric crystals of different symmetries (i.e. where  $\delta\rho$  has a different symmetry).

In that case in the phase diagram, there is a point of intersection of curve  $AC$  of Curie points with phase transition curve  $BD$  (in Fig. 2); I is the most symmetric phase ( $\delta\rho = 0$ ); along curves  $AB$  and  $BC$  at Curie points, it goes over into less symmetric phases II and III, where  $\delta\rho_{II} \neq 0$  and  $\delta\rho_{III} \neq 0$ , respectively.

The symmetry groups  $\delta\rho_{II}$  and  $\delta\rho_{III}$  are subgroups of the symmetry group of first phase I. However, they are not, generally speaking, subgroups of each other. Because of this, the difference  $\delta\rho_{II} - \delta\rho_{III}$  cannot become zero. Hence, between phases II and III, there should not be a Curie line, but a phase transition line. At point  $B$ , all three phases are identical; along line  $AB$ , phases I and II are identical ( $\delta\rho_{II} = 0$ ); and  $\delta\rho_{III} = 0$  along  $BC$ .

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

Finally, let us consider those cases where terms of the 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 the 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  $c_i$ ) exist, i.e. the terms of the fourth order should be identically equal to  $B(p, T)\eta^4$  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 that the term of the fifth order be identically zero, and the term of the sixth order 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 [1]. There, it was pointed out that the  $\lambda$ -point ( $B = 0$ ) is a point where the Curie curve ( $B > 0$ ) goes over into the phase transition curve ( $B < 0$ ).

Here, we additionally consider only the intersection of the curve of Curie points with the phase transition curve in bodies which are mixtures of two substances. In that case, it turns out that the specific heat does not become infinite, as that in pure substances, but exhibits 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 crystal is, as before, determined by the density  $\rho$ , and the expansion of  $\Phi$  in the vicinity of the point of a continuous transition is

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

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

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

Let us investigate the vicinity of the  $\lambda$ -point. First, we write conditions for the equilibrium of two phases on the transition curve (it makes no difference, phase transitions or continuous ones). It is known that the thermodynamic potential  $\Phi$  is an additive quantity, and, therefore, it should be a homogeneous function of the first order of the number of particles of each kind in mixtures. In particular, for a mixture of two materials,  $\Phi = Nf(n/N)$ , 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 the equality of the chemical potentials of both phases. In our case,  $\Phi = \Phi_0$  on one side of the transition point (where  $\eta = 0$ , i.e. in the more symmetric phase); 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  $\Phi = \Phi_0 + A\eta^2 + B\eta^4$ , the first condition yields

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

( $\partial A/\partial x$  is, generally speaking, not equal to zero at the transition point, and, therefore, it is possible to limit ourselves to the term with  $\eta^2$ ) or

$$-\frac{\partial^2 \Phi_0}{\partial x_0^2} (x - x_0) = \frac{\partial A}{\partial x} \eta^2, \quad (9)$$

by expanding  $\partial \Phi_0/\partial x$  in a series:

$$\frac{\partial \Phi_0}{\partial x} = \frac{\partial \Phi_0}{\partial x_0} + (x - x_0) \frac{\partial^2 \Phi_0}{\partial x_0^2} + \dots$$

In the second condition, we put

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

with the same accuracy and get

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

Substituting the expression for  $\Phi$ , we find

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

Expanding  $\Phi_0(x_0) - \Phi_0(x)$  in series, we have

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

Further, substituting  $(x - x_0)$  from Eq. (9), we obtain

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

or

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

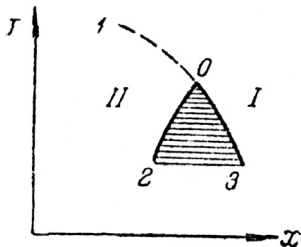


Fig. 4

Taking value of  $\eta^2$  from (7), we find

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

Substituting  $(x - x_0) = A/(\partial A/\partial x)$  and  $\eta^2 = -A/(2B)$  from the above equation into (9), we get

$$\frac{\partial^2 \Phi_0}{\partial x_0^2} \bigg/ \frac{\partial A}{\partial x} = \frac{\partial A}{\partial x} \frac{1}{2B}$$

or

$$B = \frac{1}{2} \left( \frac{\partial A}{\partial x} \right)^2 \bigg/ \frac{\partial^2 \Phi_0}{\partial x_0^2}. \quad (11)$$

One can see from this that, at the  $\lambda$ -point,  $B$  never becomes zero, and always  $B > 0$ . The last statement follows from Eq. (11), because  $\partial^2 \Phi_0/\partial x_0^2 > 0$  according to the well-known thermodynamical inequalities for solutions. Further, in the accepted approximation, the equation

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

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

Thus, the neighborhood of the  $\lambda$ -point for solutions has the form shown in Fig. 4 (plotted along the coordinate axes being concentration and temperature). The dotted line is the continuous transition curve, i.e. the Curie curve. Regions I and II are, respectively, the more and less symmetric phases. Line 10 goes continuously into line 03; line 02 branches away from it. Line 302 is the phase transition line; shaded region 302 is the region of separation into two phases I and II, the concentrations of which are determined by lines 03 and 02.

II. Let now the third-order term in the expansion of  $\Phi$  do not equal zero identically. In this case, the continuous transition is possible only if terms

of the second and third orders are equal to zero. The first of these conditions gives again  $A(p, T) = 0$ . For the second condition to hold, it is necessary that only one invariant of the third order exist, i.e. the third-order terms should only possess one coefficient depending on  $p$  and  $T$ . Otherwise, one would have too many equations, which cannot be satisfied simultaneously.

Let us introduce the quantities  $\gamma_i = c_i/\eta$  again. Then, the third-order term should have the form

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

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

$$\begin{aligned} \Phi = \Phi_0 + A(p, T)\eta^2 + B(p, T)b(\gamma_i)\eta^3 + \\ + C(p, T, \gamma_i)\eta^4 + \dots \end{aligned} \quad (12)$$

At the continuous transition point,

$$A = B = 0.$$

Consequently, the continuous transition points are isolated in this case, i.e. there is no Curie line. Therefore, such points should lie in some way on the phase transition lines. Accordingly, it is necessary to investigate the character of these lines in the vicinity of such points.

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

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

In addition, as for all possible states, the relation  $\partial\Phi/\partial\eta = 0$ , should be true, i.e.

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

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,  $\delta\rho = 0$ , i.e. a Curie line would exist, which is impossible, as has already been mentioned). It is easy to see that this requires that the relations

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

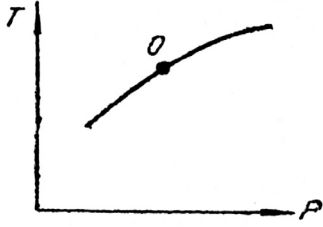


Fig. 5

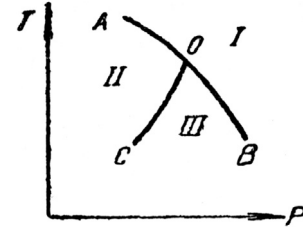


Fig. 6

and

$$\eta = -Bb/(2C) \quad (16)$$

be fulfilled.

It could be thought that the continuous transition points under study simply lie on a phase transition curve like the point  $O$  in Fig. 5. However, that is not so. We now show that point  $O$  should lie on an intersection of several phase transition curves.

Let us investigate points which are located in the neighborhood of  $O$ , but do not lie on phase transition curves. For them (as in every stable state),  $\partial\Phi/\partial\eta = 0$ . This equation has the solution  $\eta = 0$  and also solutions of the quadratic equation (14).

The solution  $\eta = 0$  corresponds to points which represent the state of the more symmetric phase ( $\delta\rho = 0$ ). In another phase,  $\eta$  is determined from the quadratic equation (14). But quadratic equations have generally two solutions. At point  $O$ ,  $A(p, T) = B(p, T) = 0$ . In a neighborhood of point  $O$ , the equation  $B(p, T) = 0$  determines a line. On that line, Eq. (14) has two solutions with opposite signs:

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

This means that, in the neighborhood of point  $O$  near to the line  $B = 0$ , Eq. (14) has solutions with different signs, almost equal to each other in absolute value (because  $B$  is small near the line  $B = 0$ ). But, on one side of the line  $B = 0$ ,  $B$  is positive. There, the negative solution of Eq. (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 Eq. (14) is realized. Hence, the line  $B(p, T) = 0$  is also a phase transition line, where  $\eta$  changes the sign.

In this way, the neighborhood of point  $O$  has the form shown in Fig. 6, i.e. the other phase transition line ends at point  $O$ . Phase I is the more symmetric phase (in it,  $\eta = 0, A > 0$ ). On phase transition line  $AB$ ,  $A = 0$ .

Less symmetric phases II and III (where  $A < 0$ ) have the same symmetry (in them,  $\eta$  differs only by sign, but this does not influence the symmetry of  $\rho$ ). On phase line  $CO$ ,  $B(p, T) = 0$ . At point  $O$ , all three phases become identical.

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

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

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

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

Substituting (12), we find, in the neighborhood of point  $O$ , (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 phase I. Terms of higher orders can be neglected because  $\partial A/\partial T$ , unlike  $A$ , does not become zero.

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

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

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

In order to find  $Q$  on curve  $OC$  close to  $O$ , we take also the next term in the entropy  $S$  into account:

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

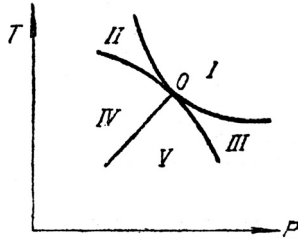


Fig. 7

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

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

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

Finally, it can be shown that, when the fourth-order terms have complex structure, new phase transition curves can appear. Then neighborhood of point  $O$  does not look as that shown in Fig. 6, but as in 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 point  $O$ , all the phases become identical. It is, indeed, the point of a continuous transition. At point  $O$ , two of the phase transition curves have a common tangent, and the third curve ends. Here, we have assumed that only two phase transition curves touch at point  $O$ . In the general case, there may be several of them.

It will be shown in the sequel of this paper that terms of the third order are not identically zero in the case of transitions between liquids (i.e. isotropic bodies) and crystals. At isolated points of the type shown in Figs. 6 and 7. In particular, Curie lines are impossible.

In the preceding part of this paper, we assumed that the symmetry properties of crystals are determined by the symmetry of the mean density function  $\rho$ . But the moving charges (electrons) can create a mean current density  $\mathbf{j}$  in the crystal 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  $\mathbf{j}$ . Note that  $\int \mathbf{j} dV$  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 the dimensions of the crystal, and this would be energetically disadvantageous.

In the majority of bodies,  $\mathbf{j} = 0$ . In particular,  $\mathbf{j} \neq 0$  in ferromagnetic bodies, where the magnetic moment is not equal to zero in every part, i.e. the integral  $\int [\mathbf{r} \times \mathbf{j}] dV$  over an elementary cell is not zero. However, not every body with  $\mathbf{j} \neq 0$  is ferromagnetic, because, although  $\mathbf{j} \neq 0$ ,  $\int [\mathbf{r} \times \mathbf{j}] dV$  can be equal to zero.

If  $\mathbf{j} = 0$ , then the symmetry properties of the crystal are determined by the density  $\rho$ . It is known that there exists a limited number (230) of possible types of symmetry, i.e. space groups. If, in addition,  $\mathbf{j} \neq 0$ , then the classification of the types of symmetry follows from the properties of  $\rho$  and  $\mathbf{j}$ . In this case, more than 230 space groups are admissible.

The presence of  $\mathbf{j} \neq 0$  (such crystals can be called magnetic) does not introduce anything essentially new into the preceding discussion about transition points. At transition points, a change in the symmetry is then determined by  $\delta\rho$  and  $\delta\mathbf{j}$ . As before, only the transition points discussed above are possible.

Let us concentrate for a while on the transitions related to the appearance (or disappearance) of  $\mathbf{j}$ , i.e. on the transitions between magnetic and non-magnetic crystals. Since, on one side of these points,  $\mathbf{j} = 0$ , we have  $\delta\mathbf{j} = \mathbf{j}$ . As before, we consider only the continuous transition points of this type, i.e. points, where  $\delta\mathbf{j} = \mathbf{j} = 0$  and  $\mathbf{j}$  is small in their neighborhood (on one of the sides). Instead of expanding the thermodynamic potential  $\Phi$  in powers of  $\delta\rho$ , we now have an analogous expansion in powers of  $\mathbf{j}$ . In view of the symmetry of all the properties of the body with respect to the exchange of the future with the past, the potential  $\Phi$ , in particular, cannot vary when the sign of time is reversed. The density  $\rho$  does not vary under such a transformation, but the current  $\mathbf{j}$  reverses its sign. It follows from this that, in the expansion of  $\Phi$  in powers of  $\mathbf{j}$ , all terms with odd powers of  $\mathbf{j}$  should be identically zero. This means that the transitions related to the appearance of  $\mathbf{j}$  always belong to case I, i.e. Curie points which form Curie lines are possible. Moreover, under suitable conditions, the  $\lambda$ -points are also possible. Such are the Curie points in ferromagnetic bodies. The jumps in the specific heats in chlorides of Fe, Cr, and Ni at low temperatures are apparently of the same nature, as well as the  $\lambda$ -point in MnO. All these materials have  $\mathbf{j} \neq 0$  below the transition point, and, at the transition point,  $\mathbf{j}$  becomes zero (above that point,  $\mathbf{j}$  remains equal to zero).

Until now, we have been talking about the transitions with a change in the symmetry of the crystal, but we have not discussed the physical nature of changes which take place. Atoms in a crystal usually perform small



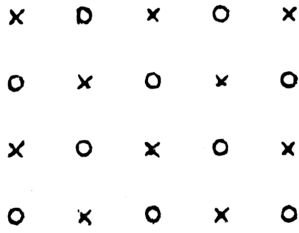


Fig. 8

oscillations about their equilibrium positions, i.e. about the lattice points. In view of their smallness, these oscillations cannot cause changes in the lattice symmetry. This is not applied, of course, to the jump-like transitions, when the atoms start to oscillate around new equilibrium positions.

The continuous transitions with a change in the symmetry are always related to a change in the order of the crystals, which may occur 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 arrangement of the atoms in the lattice which is energetically most favorable. This is realized at sufficiently low temperatures. At higher temperatures the arrangement of atoms deviates from this particular arrangement.

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).

Such a crystal is said to be completely ordered. But every atom can in principle be situated 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 “wrong” places, i.e. places, at which should be atoms of the other kind in the completely ordered crystal. The probability, i.e. the density function  $\rho$ , to find atoms of one kind at lattice points in the completely ordered crystal can be represented schematically (in one dimension) by the curve in Fig. 9,*a*, where the probability has a sharp maximum at every second lattice point. In the incompletely ordered crystal, there appears some probability to find atoms of a given kind at other (“wrong”) lattice points (Fig. 9,*b*).

Finally, the number of atoms of a given kind in the lattice residing at “wrong” points can be equal to the number of these atoms residing at their “own” places. This means that the probability to find atoms of a given

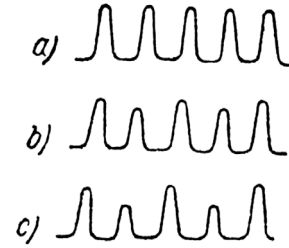


Fig. 9

kind becomes the same at all lattice points (Fig. 9,*c*). The crystal is then called disordered. It is easy to see that, at the time moment when this disorder appears, the symmetry of the crystal changes (namely, the symmetry increases). That can be seen, for instance, in Fig. 9,*c*; the curve *c* has, in comparison with curves *a* and *b*, an extra translational period equal to the distance between two neighboring lattice points (the curves *a* and *b* have only a period which is equal to the double distance between lattice points).

A second example is the crystal of  $\text{NH}_4\text{Cl}$ . This crystal has a lattice of the  $\text{NaCl}$  type, where at the lattice points are  $\text{Cl}$  and  $\text{NH}_4$ .  $\text{NH}_4$  groups have the form of a tetrahedron and can be oriented in the crystal of  $\text{NH}_4\text{Cl}$  in two directions. If all  $\text{NH}_4$  groups are pointing in the same direction, the crystal is completely ordered; if some of  $\text{NH}_4$  groups are pointing in the opposite direction, the crystal is incompletely ordered. Finally, if the numbers of  $\text{NH}_4$  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 one has the symmetry of a cube.

We can introduce the quantity “degree of order” which would characterize the deviation of a crystal state from the ordered one; 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  $\rho$  to  $\rho + \delta\rho$  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,  $\delta\rho$  just determines how close the crystal is to the complete disorder;  $\delta\rho = 0$  in the disordered crystal. But we have seen that  $\delta\rho$  is determined by the quantities  $c_i$  which are, in turn, proportional to  $\eta$ . Obviously,  $\eta$  can be chosen as the degree of order. In the above-mentioned paper [2], we used the always positive quantity  $\xi = \eta^2$  as the degree of order.

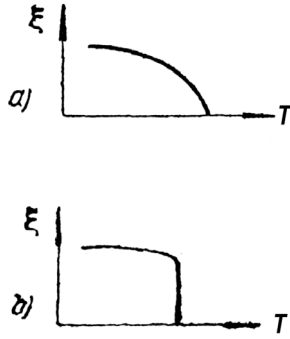


Fig. 10

At a continuous transition,  $\xi$  as a function of  $T$  has the form shown in Fig. 10, *a*. At the phase transition, it becomes zero stepwise (Fig. 10, *b*).

In the case of the 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 “wrong” places. In a disordered crystal,  $N_1 = N_2$ . The probabilities to find an atom in its and wrong places are proportional to  $N_1/(N_1 + N_2)$  and  $N_2/(N_1 + N_2)$ , respectively. 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

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

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

In this way,  $\delta\rho$  is proportional to the ratio

$$(N_1 - N_2)/(N_1 + N_2)$$

which can indeed be chosen to be  $\eta$ .

In the case of transitions between magnetic and non-magnetic crystals, atoms with differently oriented magnetic moments play the role of atoms of different kinds. The case where the probabilities for an atom to have differently oriented moments are equal for every atom corresponds to a disordered crystal. In the case of the ferromagnetic state, these probabilities cease to be equal, and there appears a magnetic moment inherent in the crystal as a whole. Finally, in the case of magnetic, but not ferromagnetic, bodies, the probabilities for different orientations of the moment for a single atom are not equal either, but, in different atoms of the lattice, the opposite orientation of the moments

is more probable. Thus, 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 symmetries (in particular, between a liquid and a crystal) cannot happen continuously, contrary to 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 jump 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 related to transition of a crystal to the disordered state.

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 the phase transition line or each other at points of the kind shown in Figs. 2 and 3. The Curie line can go continuously into 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 which are related to the appearance or disappearance of the mean magnetic moment of every atom in the crystal (in particular, such is the Curie point of ferromagnetic bodies) are possible. For such transitions, case (a) holds.

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Lev Davidovich Landau was the outstanding physicist-theorist of the XX century, Full Member of the Academy of Sciences of the USSR, the Nobel Prize winner in physics (1962) “For pioneer investigations in the theory of condensed matter and especially of liquid helium”.

During 1932–1937, he was Head of the Department of Theoretical Physics at the Ukrainian Physical-Technical Institute in Kharkov (now NSC “Kharkov Institute of Physics and

Technology” of NAS of Ukraine), L.D. Landau headed a chair at Kharkov State University also. Since 1937, he was Head of the Theoretical Department of the Institute for Physical Problems of the Academy of Sciences of the USSR in Moscow. He is a founder of the Kharkov’s scientific school of theoretical physics.

L.D. Landau’s investigations cover practically all branches of theoretical physics, ranging from fluid mechanics to quantum field theory [1]. L.D. Landau predicted the existence of neutron stars (W. Baade, F. Zwicky, L.D. Landau), he constructed a general theory of phase transitions of the second order (1936–1937). The Ginzburg-Landau equation is of great importance in the theory of superconductivity. The Landau levels, Landau diamagnetism, and Landau–Lifshits equation are well known in physics. L.D. Landau constructed the theory of superfluid liquid helium-II [2] and the theory of the Fermi liquid [3–5]. L.D. Landau’s investigations in plasma physics and in the theory of magnetism are of great importance. L.D. Landau formulated the theory of a two-component neutrino (independently of A. Salam, T. Lee, and C. Yang, 1957) and proposed the principle of conservation of the combined parity in the weak interactions of elementary particles [6].

A significant part in the L.D. Landau’s heritage belongs to the world-famous “Course of Theoretical Physics” written jointly with E.M. Lifshits in many volumes.

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