PHASE TRANSFORMATIONS IN CRYSTALLINE BODIES (CURRENT STATE OF THE PROBLEM)

I. I. Novikov

UDC 536.7

Reciprocal transformations of phases of materials (according to the current concept, we have to distinguish between four phases of a material — crystalline, liquid, gaseous, and plasma) constitute one of the most interesting physical phenomena. A large number of works, including those of a fundamental character, are devoted to the study of phase transformations. This interest, which is not weakening with time, is caused not only by the great importance of phase transformations for practical use, since some of the phases possess unique properties (e.g., superconductivity, ferromagnetism, etc.), but also by the purely cognitive value, since during phase transformations there appear the most essential main features of the makeup of the material. The current physical theory is still far from the complete understanding of the mechanism of phase transformations, although a lot has been done in this direction. The state of the problem is well characterized by the following saying of Uhlenbeck [1]: "Up to now we have not any clear idea about the process of melting; in this case the situation is completely unclear. There are merely certain vague views." Although in a number of different phase transformations melting is not regarded as the most complex one, there nevertheless is no sufficient clarity in relation to it; even to a greater degree this applies to other transformations. "Although here also a lot has been done, this problem in many aspects remains open," states Uhlengeck. However, so definite is the statement of Ginzburg [2]: noting that up to now there is not any satisfactory theory of phase transitions, in particular, of the second kind, since even in the best of them "the Landau theory in the general case has no explanation of the anomalous temperature variation of heat capacity and other quantities," he considers that "creation of a sequential theory of phase transitions..., and generalization of all results... remains one of the central problems of physics of solids,"

In the following we consider only those phase transformations which take place between crystalline phases. Reciprocal transformations of crystalline phases received the name polymorphism. It is appropriate here to avoid the confusion sometimes encountered about what is included under the term polymorphism. According to [3], "polymorphism is the property of a material to exist in several crystalline or liquid crystalline phases — polymorphic modifications which differ in the structure and in physical properties... . Special polymorphic forms are encountered during phase transitions of the second kind in seignette-electrics, ferromagnetics..., superconductivity, and others." From this we see that under polymorphism we understand in fact all forms of transformations in crystalline phases, i.e., transitions both of the first and second kinds.

The concept of phase transitions of different kinds arises, as we know, from thermodynamics, which allows the conditions of equilibrium of phases to be formulated in the most general form. These conditions consist of equality of temperatures T of the phases coexisting in equilibrium, equality of their pressures p (only providing that on the boundary of separation of the phases there act no other forces in comparison with the pressure), and equality of the chemical potential φ of both phases. It should be emphasized that thermodynamics does not explain the very fact of existence of different phases; it merely determines the conditions of equilibrium, if it is known that the material exists both in the form of phase I and in the form of phase II. The third condition of equilibrium is most meaningful in the physical sense; it establishes the character of variation of the thermal parameters on the curve of phase equilibrium, in particular, the dependence of p on T in the case of known $\varphi(p, T)$, and, furthermore, contains foundations for a classification of phase transformations, proceeding from the singularities of the functions $\varphi(p, T)$. If the chemical potential during transition from one phase into another is characterized by

---

A. A. Baibakov Institute of Metallurgy, Academy of Sciences of the USSR, Moscow.
Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 39, No. 6, pp. 1118-1132, December, 1980. Original article submitted July 4, 1979.

0022-0841/80/3906-1391$07.50

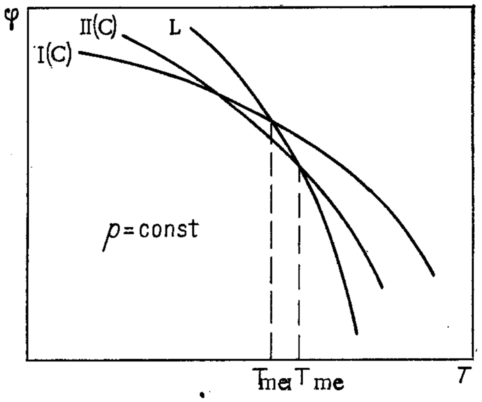

Fig. 1. Phase diagram φ, T [I(C), II(C), crystalline phases; L, liquid phase].

different values of the first partial derivatives (we recall that $\left(\frac{\partial\varphi}{\partial p}\right)_T=v, \left(\frac{\partial\varphi}{\partial T}\right)_p=-s$), then such a transition is called a transition of the first kind; if, however, the values of the first derivatives of the chemical potential of both phases are the same and difference exists only in the second and subsequent partial derivatives, then the phase transition is a transition of the second kind. In the case of phase transitions of the second kind, in contrast to phase transitions of the first kind, there is no heat being produced or absorbed, nor is there jump variation in the volume; to make up for it, there appear jumps in the heat capacity, compressibility, and other thermodynamic quantities.

Thermodynamics, in addition to the formulation of the condition of equilibrium of phases, allows us to draw certain additional conclusions of general nature, in particular, about the preferential direction in which phase transitions take place under some external action or another. In order to make the subsequent exposition understandable, we recall that a crystalline body constitutes an ordered state of a system consisting of a huge number of structural particles — atoms (more precisely, their ion frameworks). Such ordered states are characterized by a certain macroscopic quantity, called the order parameter. A nonzero value of the order parameter signifies a lower degree of symmetry in comparison with an isotropic condition which possesses greater symmetry and, respectively, the zero value of order parameter; the larger the numerical value of the order parameter, the lower the degree of symmetry. The magnitude of the order parameter is connected with the deviation of the density of ion frameworks forming the crystal lattice, from a homogeneous distribution; because of completely determined positions of nodes in space, characteristic to a crystal, the translational and rotational symmetry is not realized to the full extent, a consequence of this being a nonzero value of the order parameter. Side by side with a spatial symmetry, we have to distinguish a symmetry connected with ferromagnetic, seignette-electric, and superconductive states of crystalline bodies. In the first two cases the role of the order parameter is played by the summary magnetic or electric moment, while in the third case the order parameter is connected with Cooper pairs of free valency electrons of a metal crystal. External actions influence the degree of orderedness of the original state and lead to a variation of the magnitude of the order parameter, either directly or by means of variation of other parameters of the system, as a result of which in the final analysis the order parameter undergoes a variation. Examples of such actions are in the first case the action of a strong external magnetic field on the superconductor; in the second case it is the action of temperature, leading at sufficiently high values of T to a variation, as a result of thermal fluctuations, of the order parameter and to establishment of a new degree of symmetry.

Temperature effects are of particularly great interest; therefore, it is appropriate to confine ourselves in the following to the consideration of only those phase transformations in crystalline solids which are attained by temperature variation (e.g., by heating of the body as a result of supplying heat from outside, or by cooling when removing heat), while maintaining the pressure on the body unaltered; phase transitions taking place when the pressure is increased will not be considered here.

A stable state of the body corresponds, as we know, to the minimum of the Gibbs energy: $\Phi = I(T, p) - TS(T, p)$. Therefore, it is clear that in the case of high temperatures, independently of the magnitude and functional dependence of enthalpy I, increase in the entropy S is favorable, since it leads to a decrease in Φ. Physically, this signifies

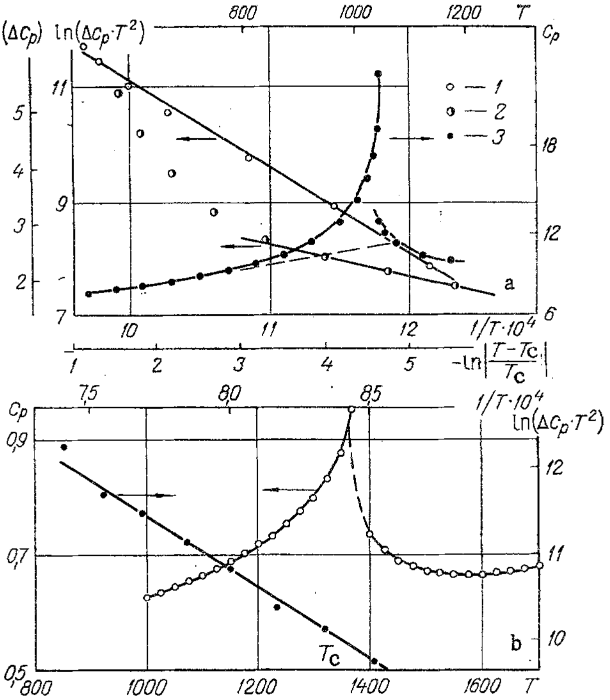

Fig. 2. Heat capacity: a) iron (1 — exponential relation, 2 — power relation) and b) cobalt in the region of the Curie point. T, °K; c_p, J/kg·T·10³; 1/T·10⁴, °K⁻¹.

disordering of the original state and raising of the degree of symmetry. It follows from what has just been said, e.g., that in the case of a phase transition of the first kind taking place with a rise in the temperature, the entropy of the crystalline phase being formed is greater than the initial value, i.e., during transition heat will be absorbed (in other words, the latent heat of transition will be positive). The last conclusion could be drawn also on the basis of the Le Chatelier principle: since a stable system always counteracts an external action, heating of the original crystalline phase must initiate in the system processes leading to absorption of heat during a phase transition.

From this principle there follows yet another important result, according to which the heat capacity in the region of a phase transition must undergo a growth, i.e., will always be greater than before or after the phase transition; the largest value of heat capacity will be attained at the point of transition. This anomaly has the most general validity, i.e., applies to all phase transitions and constitutes an expression of the fact that during approach to the point of transformation in the body there are stimulated processes tending to slow down the transition to the new phase. An increase in the heat capacity is precisely a process of this kind: since a phase transition is characterized by an intersection or merger of the isobars of the chemical potentials φ_I and φ_{II} of the two phases (I(C) and II(C) in Fig. 1), an increase in the heat capacity of the original phase signifies an increase in the angle coefficient of the curve φ_I and its rotation toward the curve φ_{II}; this tendency of the curve φ_I to become parallel to φ_{II} and not to intersect with it, manifests itself in the tendency to hinder the phase transition. If positiviness of the latent heat during a phase transition takes place with an increase in the temperature, and an anomalous increase in the heat capacity in the region of the phase transition are unconditional thermodynamic rules, then for the order parameter there is no such rigid rule, and the latter does not always change in the same direction (i.e., decrease) as the temperature increases. Nevertheless, phase transitions taking place with an increase in the temperature, in an overwhelming majority of cases, lead to lowering of the degree of orderedness and to a decrease in the order parameter. In connection with this, in the well-known course of theoretical physics by Landau and Lifshits [4] there is stated that in a huge majority of all known cases the more symmetric phase corresponds to the higher temperatures, while the less symmetric phase corresponds to the lower temperatures. However, this tendency manifests

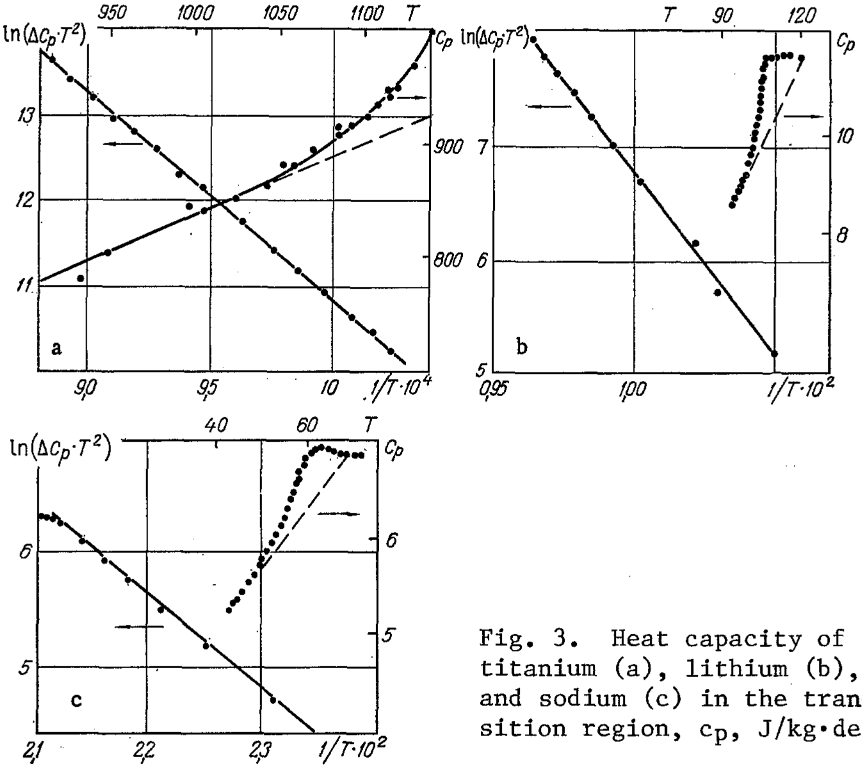

Fig. 3. Heat capacity of titanium (a), lithium (b), and sodium (c) in the transition region, c_p, J/kg•deg.

itself only as a whole, i.e., for the entire set of the phase transitions possible in the given material; at intermediate stages deviations are possible. A good example is iron, which up to the temperature 1182°K has a bcc lattice, then goes into a fcc lattice and at 1661°K again assumes a bcc lattice. The fcc lattice, being more densely packed, has a somewhat lower degree of symmetry in comparison with the bcc lattice. The violation of the order of change of symmetry during the first phase transition, when a less symmetric phase is formed in spite of an increase in the temperature, is caused apparently by electronic effects, but as yet there is no complete explanation [5]. In the region of high temperatures, iron, just as the overwhelming majority of other elements, has a bcc lattice.

The possibility of predicting, while proceeding from the thermodynamic considerations, the direction in which the physical properties change during a phase transition is very interesting and can be illustrated, side by side with the latent heat of transition, by a number of examples. For example, it can be expected that a phase transition attained when the temperature is changed under the conditions $p = \text{const}$, must be characterized in the region of transition by a decrease of the elastic moduli of the crystal, its electrical conductivity and thermal conductivity, and by an increase of the absolute value of the coefficient of linear expansion. It should, however, be noted that forecasts of this kind, which most often rest on the principle of Le Chatelier, are not always convincing and in a number of cases have a preliminary character; therefore, the final answer remains after the experiment.

It is also of interest to determine the energy characteristics of the sequence of crystalline phases. We take tentatively as such a characteristic the melting temperature, actual or virtual, of each phase. The virtual temperature is introduced because if the first crystalline phase is transformed into the second, then under the given pressure the first phase is not observed in the state of melting and, consequently, we can talk about its melting temperature merely tentatively, in the sense that if the transition into the second phase was not occurring, then the first phase would melt when heated up to temperature T_{meI}. From the general form of the isobars of the chemical potential of crystalline and liquid phases in the case of a phase transition of the first kind (Fig. 1) we see that as a consequence of the condition $\left(\frac{\partial\varphi}{\partial T}\right)_p = -s < 0$, the temperature T_{meI} will always be less than T_{me} and, consequently, the sequence of phase transitions in crystalline bodies is such that the virtual temperature of melting of each of the phases is higher than that of the preceding phase. It can also be said that any phase transformation in a crystalline

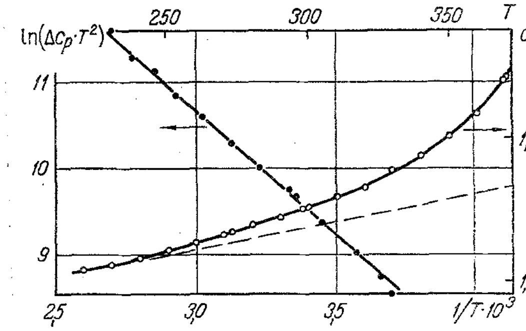

Fig. 4. Heat capacity of sodium near melting point.

body translates it into a state with a larger energy of bond, which precisely for this reason is capable of existing at higher temperatures in comparison with the initial phase.

From what has been said above, it follows that thermodynamics appears effective not only in the case of a precise formulation of the conditions of equilibrium of phases, but also when we determine the character of variation at least of some of the thermodynamic quantities dependent on the external conditions under which the phase transition takes place; in particular, thermodynamics allows us to forecast the probable sequence of phases being formed.

The possibilities of thermodynamics are by no means exhausted by this. Although thermodynamics is not in a position to indicate the mechanism by means of which phase transitions are effected, we nevertheless are able to analyze, on its basis, the phase transformation mechanisms which are considered as probable, and to establish the most appropriate of them, i.e., the most "suitable" one from the energy viewpoint, which in fact turns out to be the preferred mechanism. Such an approach becomes completely clear if we bear in mind that in the final analysis a phase transition constitutes an energy transformation. In the case of transitions of the first kind, both the internal energy and the enthalpy change; during phase transitions of the second kind their derivatives change and, in addition, constituents of free energy assume other values (e.g., at the Curie point the surface energy connected with the domain wall becomes zero). Consequently, phase transitions in all cases are accompanied by excitations of the energy structure of the material, with each such excitation being characterized by a definite energy spectrum. As was shown for the first time by Landau, the state and properties of any condensed system can be described by means of the concept of quasiparticles which are nothing else than elementary excitations. With reference to polymorphous transitions, this means that during the approach to the point of transition in the original phase there arise conditions which are favorable to formation of a sufficiently large number of quasiparticles; a result of this in the final analysis is the phase transition itself. After the occurrence of the phase transition the number of these quasiparticles sharply falls because of the increase of energy of their formation [6].

The concept of quasiparticles constitutes an extremely convenient means of describing complex interactions in condensed systems consisting of many particles, since it becomes possible to obtain in a comparatively simple way perfectly satisfactory estimates. With reference to phase transformations in crystalline bodies, this method is also interesting in view of the circumstance that we in fact know beforehand the most important thermodynamic feature of the quasiparticles responsible for the phase transition, and their chemical potential being zero [7, 8]. In a contrary case quasiparticles could not be freely forming and disappearing.

As is known from the theory of nonideal diluted solutions, the chemical potential of the dissolved material, the concentration of which is c, equals per single particle [9]

$$\varphi' = \varphi'_0 + kT \ln c, \tag{1}$$

where φ'_0 differs, because of the interaction between the particles of the dissolved material and the solvent, from the chemical potential of the particle of the dissolved material in a free state. Quasiparticles can be regarded as a certain substance dissolved in a solid body, and the body itself as a solvent. The difference $\varphi' - \varphi'_0$ equals $i' - i'_0 - T(s' - s'_0)$, with, according to what has been said above, $\varphi' = 0$, $i'_0 - i'$ being the energy of formation of a quasiparticle E, while $s'_0 - s' = \Delta s'$ is the increment of the entropy of the crystal as a result of appearance in it of a single quasiparticle, connected with a variation of the spectrum of oscillations of the lattice, after subtraction of the quantity of entropy of displacement. Consequently,

$$c = \exp\left\{\frac{\Delta s'}{k}\right\} \exp\left\{-\frac{E}{kT}\right\}. \tag{2}$$

The first term on the right-hand side represents the so-called entropy multiplier. Its role is important when we compute the concentration of quasiparticles, but it does not influence determination of the energy of formation of quasiparticles E from experimental data, proceeding from relation (2). Therefore, in a number of cases we put the entropy multiplier equal to a constant or even take [6]

$$c = \exp\left\{-\frac{E}{kT}\right\}. \tag{2a}$$

Expressions (2) and (2a) have a thermodynamic origin and are used for the subsequent analysis.* By means of (2) we can easily determine the variation of the heat capacity in the region of phase transition. Since with an increase of the temperature by dT, the concentration of quasiparticles varies by dc, while for the formation of a single quasiparticle energy E is expended, the amount of heat required amounts to $E(\partial c/\partial T)dT$. Consequently, the contribution of quasiparticles toward the heat capacity will be

$$\Delta c_p = \frac{E^2 N}{kT^2} \exp\left\{\frac{\Delta s'}{k}\right\} \exp\left\{-\frac{E}{kT}\right\}. \tag{3}$$

The quantity Δc_p characterizes the increase (growth) of heat capacity in the region of phase transition, i.e., the "peak" of heat capacity. From Eq. (3) we see that

$$\ln(\Delta c_p T^2) = \ln \frac{E^2 N}{kT^2} \exp\left\{\frac{\Delta s'}{k}\right\} - \frac{E}{kT},$$

i.e., in semilogarithmic coordinates $\ln(\Delta c_p T^2)$, $1/T$ the increase of heat capacity in the region of phase transition is described by a straight line relation; the tangent of the angle of inclination of the experimental straight line, taken with the minus sign, is numerically equal to the energy of formation of quasiparticles E.

The increase in heat capacity itself in the region of phase transition is determined from the experimental values of heat capacity as follows. It is assumed that beyond the limits of the region of phase transition the contribution of quasiparticles toward heat capacity is negligibly small and the latter varies with temperature according to a linear law, since the anharmonic and electronic constituents of heat capacity are proportional to T. Therefore, we can assume approximately that in the absence of quasiparticles heat capacity would vary in the region of phase transition along the tangent to the experimental curve $c_p(T)$, drawn to a certain initial point corresponding to the boundary of the region of phase transition (this point corresponds to a negligibly small contribution toward c_p of quasiparticles, and is therefore to a certain degree conditional). Since the temperature effect of the transition region is much less than the absolute magnitude of the temperature of phase transition, a linear approximation seems to be justified. Nevertheless, there remains a certain indeterminacy in the drawing of the tangent, a circumstance which might affect the computations, from experimental data for c_p, of the amount of energy of formation of quasiparticles; to reduce the indeterminacy we have to carry out measurements with a small step in the temperature. In the case of phase transitions of the second kind, we also have to take into account the contribution toward heat capacity from spin interaction, which at the Curie point amounts to $3R/2$.

Experimental data referring to heat capacity and also, as will be seen in the following, to certain other properties, well confirm the assumption that phase transitions in crystalline bodies are effected by quasiparticles; in any case, in semilogarithmic coordinates the growth in heat capacity observed in experiment in the region of phase transition is described by a straight line relation in complete agreement with expression (3).

---

*Expression (2a) coincides with the well-known expression for concentration of vacancies obtained from statistical considerations.

Next we have to determine the nature, i.e., the type of quasiparticles responsible for the transition. The method of their identification is obvious. Having determined from results of measurement of heat capacity or some other property the energy of formation of quasiparticles responsible for the phase transformation, and having compared it with the values of the energy of formation of known quasiparticles, we can determine what these quasiparticles are.

In Figs. 2 and 3a we have presented the data of heat capacity measurements of iron, cobalt, and titanium [10-12] in the region of phase transitions. Experimental points in semilogarithmic coordinates lie perfectly on a straight line, thus confirming the correctness of the viewpoint developed above, concerning the mechanism of phase transformations. The values of the energy of quasiparticle formation found from these measurements amounted, respectively, to 1.2, 1.8, 2 ± 0.2 eV. In the literature there are presented values of the energy of vacancy formation in Fe from 0.8 to 1.4 eV. As is seen, the energy of formation of quasiparticles, found from the measurement of heat capacity of iron, in the region of phase transition practically coincides with the energy of vacancy formation. Therefore, we can conclude that in crystalline bodies most probably vacancies are responsible for phase transitions. In connection with this, the data on titanium is most significant, on the example of which the expediency of using semilogarithmic coordinates, for representing the temperature dependence of heat capacity in the region of phase transitions, was demonstrated for the first time. In the case of a phase transition of the first kind, before there appears a new crystalline structure, the bcc in the given case $\alpha\text{-}T_i$, the part of nodes of the crystal lattice (hcp in the given case) occupied by atoms must first be freed by formation of vacancies, for the rearrangement of the structure to be possible at all. During phase transformations of the second kind, e.g., at the Curie point, formation of vacancies apparently ensures the emergence or vanishing of the Bloch wall separating domains from one another.

In Fig. 3b and c we have presented the data on the heat capacity of Li and Na [13-15] in the region of phase transitions (transition from hcp to bcc lattice). In these cases also the growth of heat capacity varies, when approaching the point of transformation, along a straight line in semilogarithmic coordinates. The same course of the temperature dependence is observed for steels and rare-earth elements. All this allows us to draw a conclusion about the general, i.e., universal character of the relation (3) thus established, concerning the variation of heat capacity in the region of phase transitions.*

The conclusion about the decisive role of vacancies in processes of transformation of crystalline phases does not appear unexpected, if we recall that already Frenkel and Ubellode [17, 18] pointed to the inevitability of vacancy formation, and furthermore in a rapidly growing amount when the melting point is approached, a circumstance fully confirmed by experiment. On this basis, the process of melting is often interpreted as a vacancy effect. This viewpoint has in our opinion the most general importance, i.e., can be extended to all phase transformations in crystalline bodies (and not only to melting), since the crystal cannot "sense" beforehand into which new form — type of order or disorder — it will have to go, and therefore it behaves in all cases, more or less, identically. The role of vacancies in the case of phase transitions of the first kind is regarded, as was already mentioned earlier, fairly obvious. Phase transitions of the second kind, in the case of a comparatively small variation of external parameters, as we know, are easily transformed into transitions of the first kind. Already from this we can conclude that phase transformations both for the first and second kinds must be realized in the same way, most probably, via formation of vacancies. In the case of phase transitions of the first kind, these apparently are vacancies of the Schottky type (since the characteristic relaxation times here are fairly long). As for phase transitions of the second kind, for which the new phase arises at once within the entire volume (in contrast to phase transitions of the first kind, when the new phase appears first in the form of small embryos which grow with time), a more detailed investigation is necessary, since at the first glance formation of Frenkel pairs is not excluded. About formation of a considerable number of vacancies in the pretransitional state of the crystal, i.e., when the transition point is being approached, there

---

*In Fig. 2a we have represented also the analysis of the experimental data of c_p of iron in a power relation arising from the theory of scale representations. As is seen, this relation is suitable only for a narrow temperature interval; conversely, the exponential relation is fulfilled within a broad region of temperature.

speak plain experimental facts. In particular, during observation of mutual diffusion of molybdenum and titanium, we discover that at temperatures sufficiently close to the temperature of phase transformation in titanium (e.g., by 5-10 less than it), there occurs considerable and at the same time practically one-sided diffusion of molybdenum into titanium, as was to be expected, if a large number of vacancies are formed in titanium.

It should be noted that the idea of special quasiparticles, by means of which phase transitions are effected, is not at all new and has been discussed in the literature. Thus, e.g., in [19] it is mentioned that as such quasiparticles (called phasons) there may serve bonded electron states in fluctuations of the original phase, in which the rearrangement of the configuration of atoms or spins responsible for the new phase has taken place.

Information about the mechanism of phase transformations can be obtained from observation of the anomaly of the velocity of sound, which consists of reduction in the velocity as the point of phase transition is approached; after passing the point of transition, the velocity of sound increases. The reduction in the velocity of sound is caused by the decrease of elastic moduli of the crystal mentioned earlier; the magnitude of this reduction can be easily established, if we assume that vacancies are responsible for the phase transition. Indeed, the increase of the number of vacancies as the point of phase transition is approached, signifies decrease of the number of ion frames at the nodes of the crystal lattice, a circumstance leading to reduction of the bond forces acting in the crystal, a characteristic of which is provided by the elastic moduli. The number of ion frames per unit volume decreases as a result of formation of vacancies from n to n $-$ γnc (where γ is a certain coefficient), so that μ is a function of the form $\mu = f[n(1 - \gamma c)]$. The concentration of vacancies c at the point of transition is less than 1%; therefore, this function can be expanded by powers of c and terms of the second and higher orders can be neglected. Then

$$\mu = \mu_0 - \gamma c,$$

where the index 0 refers to a region far away from the transition point. Having substituted here the value of c from (2) and taking into account the fact that the velocity of sound is proportional to $\sqrt{\mu}$, we have

$$a_0^2 - a^2 \sim \exp\left\{-\frac{E}{kT}\right\}. \tag{4}$$

From this it follows that in semilogarithmic coordinates $\ln(a_0^2 - a^2)$, 1/T the temperature dependence of the variation of the square of the velocity of sound must be represented by a straight line (the angle of inclination of which to the 1/T axis will give the energy E). An analysis of experimental data shows that this dependence well agrees with experimental [16]. This is yet another, independent of the data on heat capacity, confirmation that phase transformations are effected via formation of vacancies. We note that the anomaly of the velocity of sound and heat capacity well correlate with one another, leading to the same values of energy of vacancy formation. We note that such a definite dependence must reveal in the region of phase transition also those other properties which, similar to the sound velocity, are proportional to a power of the elastic modulus μ, in particular, sound absorption.

It is of interest to consider, further, the temperature behavior of the coefficient of linear expansion in the region of phase transition. If we proceed from formation of vacancies during the phase transition, then, bearing in mind that the volume of all vacancies being formed amounts by order to the quantity b^3cN, where b is a lattice parameter, it is easy to see that the variation of the linear dimension l of a body with temperature will be proportional to $\sqrt[3]{c}$. According to this, the increment of the coefficient of linear expansion $\alpha = \sigma(l/l_0)/\sigma T$ in the region of phase transition is

$$\Delta\alpha = \frac{E}{3kT^2}\exp\left\{-\frac{E}{3kT}\right\}. \tag{5}$$

This relation* was experimentally confirmed in tests of steels [16]. It should, however, be noted that expression (5) refers to the case where the vacant contribution toward α is substantially greater than all others, a circumstance which does not always occur. We know,

---

*It is interesting to note that the indices of the degree of exponents in the expressions for $\Delta\alpha$ and Δc_p are different, as a consequence of which the ratio in the region of phase transitions, apparently, turns out to be variable, i.e., deviation from the law of Grüneisen takes place.

e.g., in certain crystals we observe a decrease, and not an increase of α in the region of phase transition.

An analysis of a large number of direct experimental results thus leads to the conclusion that the anomalies of physical properties of crystals in the region of polymorphic transformations are caused by formation of quasiparticles of the vacancy type in the pretransition states. In connection with this, it is appropriate to focus attention on the following two instances of no little importance. First, from the fact that the concentration of quasiparticles at the point of polymorphic transition is less than 1%,* we see that the bond forces in the crystal are extremely sensitive toward the concentration of quasiparticles. Already from tests concerned with the measurement of the concentration of vacancies close to the melting point, it was known that the concentration of vacancies in a crystal cannot exceed a certain value (of order 1%) without the crystal being destroyed. In other words, it is sufficient to have altogether about 1% vacancies, for the original crystal to lose its stability. Something analogous takes place also in the case of polymorphic transitions: during approach to the point of transition, the concentration of quasiparticles (according to what has been said above, apparently, of vacancies) comparatively rapidly increases to a certain limit value (less than 1%) at which the original structure of the crystal no longer can exist, and goes into a new crystalline structure which is stronger at the given temperature. The phase being formed will be distinguished by a larger value of the energy of quasiparticle formation. As a consequence of the increase of the energy of quasiparticle formation, the number of quasiparticles beyond the point of transition sharply falls, a circumstance which causes the characteristic form of anomaly of physical properties in the region of phase transition.

The energy of formation of quasiparticles in the new phase E_2 can be approximately determined from the comparison of the experimental values of heat capacity at the point of transition and on the right of it by means of the expression (3).† From the fact that the energy of quasiparticle formation (under which in the following we often understand vacancies) in the given case is greater than in the preceding case, it follows that the hierarchy of crystalline phases in the final analysis is determined by the bond energy or, which generally is equivalent, by the energy of vacancy formation. The circumstance that the stability of a crystal and, consequently, the magnitude of bond is extremely sensitive to vacancy concentration, gives rise to a fairly strong anomaly of various properties in the region of phase transitions, particularly notable in the case of heat capacity, which sometimes varies by factor of two.

Determination of energy of vacancy formation from the anomaly of the temperature dependence of physical properties in the region of phase transitions of crystalline phases is a new method which has a number of advantages in comparison with the known methods, in particular, in relation to accuracy. This is completely clear from the comparison of Figs. 3b and 4: the temperature interval when determining the energy of vacancy formation from the growth of the heat capacity, while approaching the melting point, is much greater than in the region of polymorphic phase transition, and, respectively, the accuracy is less. In addition, as a consequence of the lower temperature, it is simpler to carry out measurements in the region of transitions of crystalline phases, than close to the melting temperature. At the same time, it becomes possible to determine the energy of vacancy formation at temperatures which are intermediate in relation to the melting point. It is expedient to consider the problem of dependence of E on T. In [8] a theoretical expression for E at the melting temperature was substantiated. It was also shown there that E equals the difference

---

*The concentration c can be computed from experimental data, e.g., for c_p by means of expression (3), taking into account the fact that the coefficient in front of the exponent, including in the general case the entropy multiplier, is determined in semilogarithmic coordinates from the point of intersection of the line $\ln(\Delta c_p T^2)$ with the ordinate axis.

†On the right of the transition point, close to it, the variation of the enthalpy Δi of all quasiparticles amounts to $\Delta(cE) = c_1(E_2 - E_1) - E_1(c_1 - c_2)$. Since $E_2 - E_1 \ll E_1$, while $\varphi = 0$, the second term is much larger than the first and, respectively $\Delta i = -E_1 c_1 \exp\{(E_2 - E_1)kT\}$, while c_p is proportional to $(E_1 E_2 - E_1)/kT^2)\exp\{(E_2 - E_1)/kT)/kT\}$, a fact which is well confirmed by experiments with nickel. It should be noted, by the way, that for Ni the computation of E_1 from the data on heat capacity is made difficult in view of the comparative closeness of the temperatures of Debye and Curie, as a consequence of which the value of the spin constituent of heat capacity differs from 3/2·R.

of the chemical potentials φ_α of an atom at the node of the crystal lattice at T = 0 and an atom located at the given temperature T outside the crystal, i.e., emerging from it. The chemical potential of a free atom is easily determined by means of transition along the elasticity curve of saturated vapor from the melting temperature to the given temperature T, and it is $\varphi_\alpha(T_{me}) - \psi(T)$, where $\psi(T) = \int_T^{T_{me}} \left(v_a \frac{dp}{dT} - s_a \right) dT$; respectively, $E(T) = E(T_{me}) + \psi(T)$.

Experimental data on heat capacity (see Fig. 2b and 3a, c) reveal a one-sided slight deviation of the experimental points from a straight line in the immediate vicinity of the phase transition temperature (for titanium, e.g., a few degrees from the transition point). This is connected with fluctuations developing in the immediate vicinity of the transition point. In the case of phase transitions of the second kind the order parameter, as we know, fluctuates especially strongly. These fluctuations, taking into account the fact that both phases do not differ very much, promote translation of one phase into the other (e.g., the ordered one into the disordered one); in the case of phase transitions of the first kind, such fluctuations lead to repeated occurrence of a phase transformation in different parts of the body.

The concept of quasiparticles by means of which a phase transition is effected allows us further to forecast the behavior of the transfer properties of the crystal in the region of phase transformation. Since electrical conductivity and thermal conductivity of metal crystals is connected basically with the electronic subsystem (the electronic constituent is substantially greater than the lattice system), while quasiparticles will, as follows from their very nature, scatter free valency electrons, we have to expect a decrease in the electrical conductivity and thermal conductivity in the region of phase transition. Some of the experimental data found in the literature confirms these conclusions. However, as yet there is no completely reliable data, as a consequence of complexity of the measurements. It can also be expected that the diffusion coefficient at the point of phase transition undergoes an anomalous change because of the jumplike growth of the energy of vacancy formation, but reliable data here also in lacking.

As was more than once mentioned, the quasiparticles responsible for phase transformations in crystals are, apparently, vacancies. Weighty arguments, in part discussed above, speak in favor of this, but as yet the problem cannot be considered as finally solved. Accordingly, relations (3)-(5) presented above determine the vacancy contribution (and in a more general level — the contribution of quasiparticles responsible for the phase transition) to some physical property of the crystal or another in the region of phase transition.

If we proceed from the vacancy mechanism of phase transitions in crystals, then it becomes fairly clear how we displace the point of phase transition into a region of higher or, conversely, into a region of lower temperatures; the possibility of such a displacement has a great practical importance. It is obvious that for the phase transition to take place at a higher temperature, in comparison with that observed usually, we have to make formation of vacancies more difficult in the pretransition state of the crystal. This can be achieved, e.g., by preliminary cooling of the crystal to a temperature less than the usual transition temperature, and then by nonequilibrium (rapid) heating to a temperature close to the transition point. As a result of this, the crystal will be starved of vacancies and the phase transition takes place at a temperature which is higher than the usual one, when the vacancy concentration is at equilibrium. The vacancy starvation of a crystal can apparently be achieved also by certain other external actions, but the crystal will be in a nonequilibrium state and, if the external actions are not repeated, the transition temperature rapidly decreases to the usual one. An exception is all-sided compression of the crystal, leading to the equilibrium concentration of vacancies being reduced $\exp\{\sigma \cdot v_\alpha / dT\}$ times. However, as a consequence of the dependence of the energy of vacancy formation on the degree of compression, the transition temperature will pass through a minimum in the case of certain materials, i.e., at the beginning with an increase in σ it will decrease, but subsequently, when a certain value of σ is reached, it will increase. Taking into account the fact that the concentration of vacancies in thin testpieces (the dimension of which is less than the length of a free passage of vacancies) is less than the equilibrium concentration, we can, proceeding from the reasoning developed above, expect that in sufficiently thin films and especially in individual crystals the temperature of phase transitions will be higher than that usually observed in comparatively thick testpieces. The value of the transition temperature can be influenced by flows of vacancies, being formed, e.g., during deformation, and also by the number of sources of them, etc. A more radical change of the temperature of phase transition can be attained by alloying the crystal with other elements. At the same time, in order to raise the temperature of phase transition, we have to introduce alloying elements which give rise to the energy of vacancy formation in comparison with the original crystal. Particularly effective will be those alloying elements which lead to anomalously large change in the energy of vacancy formation. Regrettably, all these conclusions, although they seem very likely, cannot be illustrated by concrete examples, first and foremost because of insufficient knowledge about the energy of vacancy formation at various temperatures. We note in passing that the majority of these conclusions remain valid also in the case where the quasiparticles responsible for phase transitions are different from vacancies.

Thus, analysis of experimental data and theoretical reasoning show that anomalies of physical properties of crystals in the region of phase transitions of the first and second kinds to a considerable extent are determined by formation of quasiparticles in the crystal during the pretransition period, to which schematically reduces in fact the mechanism of phase transitions; these quasiparticles apparently are vacancies. Account of the contribution of quasiparticles responsible for transformation of crystalline phases allows us to formulate the laws of variation (anomalies) of properties in the region of phase transitions, these laws having a universal character. The contribution of quasiparticles towards physical properties in the region of phase transition of crystals is expressed by a universal relation, and namely the variation of a given property in the region of phase transition, i.e., its anomaly, is equated to the product of integer degrees of the energy of quasiparticle formation E and temperature of the form $E^{\alpha}/k^{\gamma}T^{\beta}$ by an exponential whose index represents the ratio of the energy E, or a fraction of it, to the quantity kT. In semilogarithmic coordinates, this relation is depicted by a straight line. This relation, established for the first time, is valid for both types of phase transitions (of the first and second kinds) and well agrees with experiment. For certain properties the contribution of quasiparticles responsible for the phase transition can be predominant; for other properties this contribution might be comparable with the contribution caused by the thermal and calorific equations of state of the crystal.

NOTATION

T, absolute temperature; p, pressure; φ, chemical potential; S, s, entropy; v, specific volume; v_a, activation volume; Φ, energy of Gibbs; I, i, enthalpy; k, Boltzmann constant; R, gas constant; σ, stress; c, equilibrium concentration of quasiparticles; E, energy of quasiparticle formation; c_p, heat capacity in the case $p = \text{const}$; N, Avogadro's number; n, number of ion frames per unit volume; μ, modulus of elasticity; a, velocity of sound; T_C, temperature of the Curie point; α, coefficient of linear expansion; b, parameter of crystal lattice.

LITERATURE CITED

1. G. Uhlenbeck, "Fundamental problems of statistical mechanics," Usp. Fiz. Nauk, 103, No. 2, 275-318 (1971).
2. V. L. Ginzburg, "Which problems of physics and astrophysics are now considered to be particularly important and interesting?" Usp. Fiz. Nauk, 103, No. 1, 87-120 (1971).
3. Physics Encyclopedic Dictionary [in Russian], Vol. 4, Sovet-skaya Éntsiklopediya, Moscow (1965).
4. L. D. Landau and E. M. Lifshits, Statistical Physics [in Russian], GITTL, Moscow (1951), pp. 428-451.
5. U. Yum-Rozeri, "On the structure of iron alloys," Usp. Fiz. Nauk, 88, No. 1, 125-148 (1966).
6. I. I. Novikov, Topical Problems of Modern Thermodynamics. Review on Thermophysical Properties [in Russian], IVT AN SSSR, No. 3, Moscow (1977), pp. 3-42.
7. Yu. B. Rumer and M. Sh. Ryvkin, Thermodynamics, Statistical Physics and Kinetics [in Russian], Chap. 3, Nauka, Moscow (1972), pp. 161-167.
8. I. I. Novikov, "On energy characteristics of the vacancy in metals," Izv. Akad. Nauk SSSR, Met., No. 6, 172-174 (1976).
9. D. Ter-Haar and G. Bergeland, Elementary Thermodynamics [Russian translation], Chap. 6, Mir, Moscow (1968), pp. 135-137.

10. D. C. Wallace, P. H. Sidles and G. C. Danielson, "Specific heat of high purity iron by a pulse heating method," J. Appl. Phys., 31, No. 1, 168-176 (1960).
11. M. Braun and R. Kohlhaas, "Die spezifische Wärme des Kobalt zwischen 50 und 1400°C," Z. Naturforsch., No. 19a, 663-670 (1964).
12. S. V. Boyarskii and I. I. Novikov, "The character of temperature dependence of heat capacity of Ti close to a polymorphic transformation," Teplofiz. Vys. Temp., 16, No. 3, 534-536 (1978).
13. D. L. Martin, "The specific heat of sodium from 300 to 475°K," Phys. Rev., 154, No. 3, 571-575 (1967).
14. D. L. Martin, "The specific heat of sodium from 20 to 300°K: the martensite transformation," Proc. R. Soc., A254, No. 1279, 433-443 (1960).
15. D. L. Martin, "The specific heat of lithium from 20 to 300°K: the martensite transformation," Proc. R. Soc., A254, No. 1279, 444-454 (1960).
16. I. I. Novikov, V. G. Goncharov, K. I. Obydalo, V. V. Roshchupkin, R. I. Raskina, and N. A. Semashko, "The density and coefficient of linear expansion of tool steels of heightened heat resistance," Izv. Akad. Nauk SSSR, Met., No. 5, 73-75 (1978).
17. A. Ubellode, Melting and Crystal Structure [Russian translation], Chap. 2, Mir, Moscow (1969), pp. 123-130.
18. Ya. I. Frenkel, An Introduction to the Theory of Metals [in Russian], Chap. 3, Nauka, Moscow (1972), pp. 218-222.
19. M. A. Krivoglaz, "Fluctuation states of electrons," Usp. Fiz. Nauk, 111, No. 4, 617-654 (1973).