

Scientific Session of the Division of General Physics and Astronomy and the Division of Nuclear Physics of the Academy of Sciences of the USSR (27–28 November 1985)

Usp. Fiz. Nauk **149**, 325–342 (June 1986)

A Joint Scientific Session of the Division of General Physics and Astronomy and the Division of Nuclear Physics of the Academy of Sciences of the USSR was held on November 27 and 28, 1985, at the S. I. Vavilov Institute of Physics Problems of the Academy of Sciences of the USSR. The following reports were presented at the session.

November 27

1. *A. A. Sobyenin*. General properties of systems with a “double” critical point.
2. *I. L. Fabelinskiĭ, S. V. Krivokhizha, and L. L. Chaĭkov*. Experimental studies of solutions with a “double” critical point.
3. *A. A. Volkov, G. V. Kozlov, E. G. Kryukova, and A. A.*

Sobyenin. New results on the dynamics of Rochelle salt crystals (a system with a “double” critical point).

November 28

4. *B. A. Volkov and O. A. Pankratov*. Electronic structure of quasicubic crystals: energy bands, dielectric properties, and defects in narrow-gap semiconductors.
 5. *L. A. Fal’kovskiiĭ*. The origin of electron spectra of group V semimetals.
 6. *B. A. Volkov and O. A. Pankratov*. Inverted contact in semiconductors—a new inhomogeneous structure with a two-dimensional gas of zero-mass electrons.
- Summaries of the reports are given below.

A. A. Sobyenin. *General properties of systems with a “double” critical point.* During the last several years the attention of physicists studying phase transitions (PT) became attracted by a class of systems in which the ordered state exists in a limited temperature interval between the upper (T_{c1}) and lower (T_{c2}) critical points (second-order PT points); these two critical points (CP) approach each other and merge into one (“double”) critical points (Fig. 1) at a certain x_0 when the pressure, material composition or any other parameter x characterizing the state of the system is changing. The phase diagrams of the type shown in Fig. 1 are observed in crystals from the Rochelle salt group (see, e.g., Ref. 1 and, further in this set of summaries the report of A. A. Volkov *et al.*), in liquid binary mixtures with the upper and lower mixture CPs (see below the report of I. L. Fabelinskiĭ *et al.*), in liquid crystal systems undergoing second-order PT from a nematic into a smectic A-phase,²⁻⁴ and in some other materials.

An increased interest in systems with “double” CPs can be explained by a number of reasons. First of all, the fact itself that with a temperature decrease such systems can make transitions from the ordered into a disordered state is unusual and requires a microscopic explanation. Secondly, the behavior of such systems near the “double” CPs differs significantly from their behavior near the regular points along the lines of second-order PTs (which are characterized by relatively small changes in values of the derivatives dT_c/dx and d^2T_c/dx^2). In particular, the temperature dependences of many physical quantities show here much larger anomalies than those for the case of regular PTs of second

type, when at the same time for some quantities (for example, the heat capacity) the corresponding anomalies disappear. Thirdly, because of the special features of systems with “double” critical points mentioned above (a special shape of the phase diagram and a sharp temperature dependence of some physical quantities), it is possible to carry out for them much more complete and rigorous experimental verification of theoretical predictions (either for Landau’s theory or the fluctuation theory of PT) than can be done for regular cases.

The major characteristic properties of materials with a “double” CP can be seen already in Landau’s theory of PTs, in which the density of nonequilibrium thermodynamic potential of a system is expanded in a power series of the order parameter η and its spatial derivatives:

$$\Phi(\eta; T, x) = \Phi_0(T, x) + \frac{A(x, T)}{2} \eta^2 + \frac{B(x, T)}{4} \eta^4 + \dots + \frac{D(x, T)}{2} (\nabla\eta)^2; \quad (1)$$

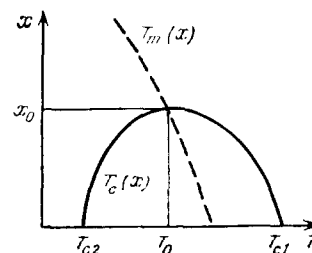


FIG. 1.

here the coefficients B and D should be assumed to be positive for the case of second-order PTs to guarantee the stability of the system; the coefficient A changes sign on the lines of phase transitions $T_c(x)$, with $A > 0$ for a disordered phase and $A < 0$ for an ordered phase.

The main distinguishing characteristic feature of systems with "double" CPs is the property that the usual assumption about linearity of the temperature dependence of the coefficient $A(x, T)$ in the phase transition area is not applicable to these systems. In fact, it is easy to see that due to a nonmonotonic behavior of the curve $T_c(x)$ the temperature dependence of the coefficient A in systems with a "double" CP is also nonmonotonic⁶ (Fig. 2), in particular, in the area $x < x_0$, where there are two PTs, the minimum of the curves describing temperature dependence of the coefficient A is located below the abscissa axis, it touches the temperature axis at the point T_0 for $x = x_0$, and in the region $x > x_0$ the minimum of the $A(T)$ curves moves above the abscissa axis in accordance with the fact that phase transitions in the system do not occur when $x > x_0$.

The existence of minima on the $A(T)$ curves makes it convenient to expand the function $A(x, T)$ in a power series in terms of the deviation of the temperature T from the minimum temperature $T_m(x)$ (and not from the critical temperature $T_c(x)$), as is done in the usual case):

$$A(x, T) = A_0(x) + A_2(x)t^2 + A_3(x)t^3 + \dots, \quad (2)$$

$$t \equiv [T - T_m(x)] T_0^{-1}.$$

This approach allows a significant reduction in the number of unknown phenomenological coefficients used in the theory (in comparison with the usually used expansion of the function $A(x, T)$ in a power series in terms of $\varepsilon = [T - T_c(x)]/T_c(x)$ independently near the upper and lower CPs) and a description of both the shape of the PT line [it can be found from the condition $A(x, T) = 0$] and the behavior of physical quantities in the entire area near the "double" CP, including the region $x > x_0$, where PTs are absent. However, the temperature dependences of a number of physical quantities—the susceptibility $\chi = 1/A$, the correlation radius of the order parameter $r_k = (D/A)^{1/2}$, the characteristic frequency of the "soft" mode $\omega_0 \sim A^{1/2}$, the relaxation time of the order parameter $\tau \sim \chi \sim 1/A$, etc., have the sharply expressed anomalies caused by an anomalous temperature dependence of the coefficient A .

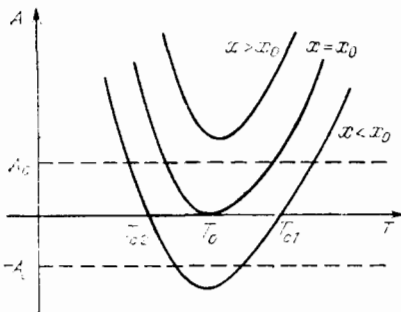


FIG. 2.

We note that the same nonmonotonic dependence of the coefficient A will be observed also near any other point on the $T_c(x)$ curve if one approaches it along directions parallel to the tangent to the PT curve at a given point. In this sense all points on the PT curve are equivalent.^{10,11} However, usually the curvature of PT lines is small, and it is possible to approach them along the tangent directions only for systems with double CPs.

Besides, for some physical quantities (such as, e.g., heat capacity) it is exactly the double CP that is the singled-out point.

It can be seen from Eq. (2) that as the double CP is approached at which $A_0(x_0) = 0$, the anomalies of physical quantities that contain the coefficient A increase. Thus, susceptibility and the relaxation time of the order parameter increase according to $\chi \sim \tau \sim t^{-2}$, which differs sharply from the usual Curie law ($\chi \sim \tau \sim |t|^{-1}$), the correlation radius increases as $r_k \sim |t|^{-1}$ (instead of $r_k \sim |t|^{-1/2}$), and the characteristic frequency of the "soft" mode decreases proportionally to $|t|$ (instead of $\omega_0 \sim |t|^{1/2}$, for the usual case). At the same time the anomalies of quantities containing the derivatives of the coefficient A with respect to the temperature decrease significantly near the "double" point. For example, the "discontinuities" of the heat capacity $\Delta C = -T\partial^2(A^2/4B)/\partial T^2$ at the points T_{c1} and T_{c2} decrease proportionally to the square of the relative distance between these points ($\Delta C \sim [(T_{c1} - T_{c2})/2T_0]^2$). A large (by several orders of magnitude) decrease of the anomaly in the heat capacity was found in all systems with a double CP in which this anomaly has been studied.

It is well known^{7a} that in a number of systems (the only exception among the materials that are of interest to us are Rochelle salt crystals^{7b}) the approximation of the Landau theory breaks down in a certain temperature interval near the CP line that is determined from the condition

$$|A| \leq \left(\frac{3k_B T B}{8\pi D^{3/2}} \right)^2 \equiv A_c. \quad (3)$$

Inside the corresponding interval of the A values (indicated in Fig. 2 by the dashed lines) the expression (1) for the density of thermodynamic potential of the system changes in the following way^{8,9}:

$$\Phi = \Phi_0 + \frac{A_0 A_2}{4B_0} \left| \frac{A}{A_c} \right|^{3\nu} + \frac{A}{2} \left| \frac{A}{A_c} \right|^{2\nu - \sigma - 1} \eta^2 + \frac{B_0}{4} \left| \frac{A}{A_c} \right|^{\nu - 2\sigma} \eta^4 + \frac{D_0}{2} \left| \frac{A}{A_c} \right|^{-\sigma} (\nabla \eta)^2; \quad (4)$$

here the function $A(x, T)$ is determined, as before, by the expression (2); $\nu \sim 2/3$ —is the so-called "critical exponent" of the correlation radius ($r_k \sim |A/A_c|^{-\nu}$); $\sigma \sim 10^{-2}$ is a small "critical exponent" characterizing the behavior of the correlation function $\langle \eta(r)\eta(0) \rangle \sim r^{-[1 + (\sigma/\nu)]}$ for $A = 0$. The values of the coefficients B_0 and D_0 can be assumed to be equal, within the order of magnitude, to their values in the Landau theory of PTs.

From (4) and (2) it follows (see also Refs. 10 and 11) that in "double" CPs the effective values of susceptibility exponents ($\chi \sim |t|^{-\nu_{\text{eff}}}$), the correlation radius ($r_k \sim |t|^{-\nu_{\text{eff}}}$) and the quantities related to them are dou-

bled, in exactly the same way as in the region of applicability of the Landau theory for PTs. As for the heat capacity and its first derivative with respect to the temperature, they turn out to be finite in the double CP, and only the second derivative of C with respect to T diverges (proportionally to $t^{-2\alpha}$).

The most complete experimental information about the behavior of various physical quantities in the area near the double CP is available at the present time only for Rochelle salt crystals, in which fluctuation effects are small and the Landau theory can be used up to PT points.^{7b} A discussion of corresponding experimental data is presented in the report of A. A. Volkov *et al.*

An increase of the width of the critical (fluctuation) region near the double CP could have been expected for liquid binary solutions; however, the careful experimental investigations of the properties of these systems (see the report of I. L. Fabelinskii *et al.*) indicate rather the opposite: as the double CP is approached the fluctuation region becomes narrower, and the values of the "critical exponents" correspond better and better to the predictions of the Landau theory for PTs.

There are no reasons, generally speaking, to expect a similar broad fluctuation region for the transitions "nematic-smectic A" in liquid crystals as in binary liquid solutions. However, in these solutions the experimental values of the

exponents γ and ν not only are closer to the values which follow from the fluctuation theory, but actually even exceed these values.⁴

In view of the mentioned discrepancies, further experimental studies of systems with a double CP are especially interesting.

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