crement is given by (32), with the substitution (38) necessary in the region $\varphi_f \gg \varphi_W$. A strong resonance is described in a somewhat more complicated manner. Outside the narrow resonance region, the resonance is weak as before. In the immediate vicinity of the resonance, however, where the condition (26) is satisfied, it is necessary to use Eqs. (34) and (35).

We note in conclusion that the study of the anomalous skin effect in a magnetic field has been shown here to be a most effective method of investigating the surface scattering of conduction electrons. The calculations presented apply to an isotropic metal. This restriction, however, is not essential, since the current is determined by a narrow "strip" on the Fermi surface, where $v_x = 0$. The specularity of reflection of such electrons and the vanishing of the diffuseness coefficient in accord with Eq. (4) are simple consequences of the indistinguishability of the electronic states near this strip. In the other limiting case ($\varphi_f \gg \varphi_W$) we used in general form only the sharp directivity of the scattering indicatrix.

I take the opportunity to thank sincerely V.G. Peschanskiĭ for a discussion of the work.

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Orientational phase transitions in ammonium bromide at high pressures

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The phase diagram and isobaric heat capacity of NH_4Br are investigated up to 2.65 kbar using an improved adiabatic calorimetric technique. The pressure is maintained constant to within 10^{-2} bar. The coordinates of the triple point are $T_{tr} = 203.35 \pm 0.15$ °K and $P_{tr} = 1730 \pm 20$ bar. The coordinates of the tricritical point on the δ–β transition line are $T_{tc} = 207.9 \pm 0.3$ °K and $P_{tc} = 2250 \pm 35$ bar. The heat of the δ–γ transition is found to vanish in the vicinity of the triple point, which can thus be regarded as a "distorted" bicritical point.

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I. INTRODUCTION

A large number of experimental[1-13] and theoretical[14-18] papers are devoted to the study of the phase transitions in ammonium halides. Ammonium halides are of interest because of the nature of the phase transitions in these compounds changes with pressure. Ammonium halides have all important advantage over ferroelectrics and magnets: they have no depolarizing and demagnetizing fields complicating the interpretation of the experimental data. Ammonium bromide is especially attractive; in this compound, there are three types of orientational phase transitions in a relatively accessible pressure range.

Two orientations of the NH_4^+ tetrahedron are possible within the crystal lattice. On the NH_4 phase diagram (Fig. 1) there are the orientationally disordered β phase, the δ phase with parallel ordering of the ammonium ions, and the γ phase with antiparallel ordering. As has been shown[14-18] both types of ordering are due to the ammonium octupole interaction: direct interaction leads to parallel ordering, and indirect interaction (through the hydrogen-halogen dipole) leads to antiparallel ordering. The interaction potentials depend primarily on the polarizability of the halide ion, which is a strong function of pressure.

Previously available data on the NH_4Br phase diagram have been very crude. Thus, in Ref. 6 the pressure at the tricritical point[1)] on the δ–β transition line is indicated to be in the interval 2.5–3.65 kbar, and the uncertainty in the triple point coordinates amounted to several hundreds of bars. We have set ourselves the task of significantly refining the nature of the phase diagram and investigating the isobaric heat capacity of NH_4Br up to pressures of 2.6 kbar with an accuracy that is no

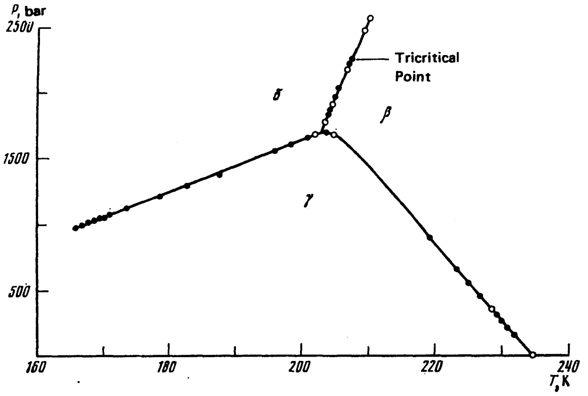

FIG. 1. Phase diagram of NH_4Br. ○ - point of the maximum of $C_P(T)$, ● - point of inflection of the adiabat. Tricritical point coordinates: $P_{tc} = 2.25 \pm 0.035$ kbar, $T_{tc} = 207.9 \pm 0.3$ °K.

worse than that attainable in calorimetric measurements at low pressures.[21]

II. EXPERIMENTAL TECHNIQUE

The calorimetric investigation of critical phenomena at high pressures requires fundamentally new techniques, in which the isobaric heat capacity is a directly determinable quantity. With this goal, an apparatus was designed and constructed for the measurement of C_P at pressures up to 2.5 kbar.[22,23] In such an apparatus, an additional source of uncontrolled energy flow may arise—as a result of pressure fluctuations. Minimization of these flows required construction of a system for pressure stabilization.

The piston manometer MP-2500 used to maintain the pressure in the system has an accuracy rating of 0.05. However, leakage of fluid into the gap between the piston pair causes the piston to drop to the stop after a time on the order of 10–100 sec, and its operating lifetime ends. Attempts to correct this deficiency by means of a relay regulator were not successful, since pulsations arose which were connected with the finite accelerations of the piston. At a pressure of ~2 kbar in the system, the pressure oscillations amounted to about 1 bar. This, in turn, led to error in the heat-capacity determination. Indeed, in the vicinity of the transition a strong $C_P(P)$ dependence developed. Investigations of ammonium bromide showed that on going a distance $\delta T = 0.1$ °K from the transition, a change in pressure of 1 bar changes the heat capacity by 8%. In turn, an adiabatic pressure change of 1 bar induced a temperature change of 0.01 °K. If the width of the calorimetric step is 0.05 °K, this leads to an error of 20% in the determination of C_p, which is two orders of magnitude poorer than the present capabilities of calorimetry in this temperature range. Therefore we took on the task of improving the pressure stability by two orders of magnitude. It turned out to be possible to solve this problem by obtaining stability of the piston position at a fixed height as a result of including a thermocompressor in the stabilization system.[24]

The stabilizer works as follows: when, as a result of fluid leakage, the manometer piston is displaced, a photoelectric sensor of the piston position gives a signal; under the action of this signal, the power released by the heater of the thermocompressor increases. The volume of fluid increases, and as a result the manometer piston returns to its original level. Experiments showed that the vertical position of the piston is stabilized by such a method to within 0.1 mm. As a result, the absolute stability of the pressure amounts to 10^{-2} bar.

The contribution of temperature-drift oscillations to the error in determination of the calorimetric step was thus diminished to $2 \cdot 10^{-5}$ °K, while the total error amounted to $1 \cdot 10^{-4}$ °K. The hydraulic system of the apparatus is shown schematically on Fig. 2. A bellows divider separated two loops—pentane and oil. Pentane has a low freezing point and therefore is used as the hydrostatic compression medium for the test sample at relatively low temperatures—up from 150 °K. But a very viscous fluid must be used as the working medium in the piston manometer. For this reason, the hydraulic system was separated into two loops.

The method of vacuum adiabatic calorimetry is used in the apparatus. Steps were taken to reduce the gradients along the calorimeter and the shields, and also for adiabatic support of the capillary relative to the calorimeter.[25]

In the critical region, the form of the anomaly in the heat capacity depends strongly on the impurities. Therefore special attention was paid to purification of the material. A powdered sample of "very pure" grade was subjected to repeated sublimation from its solution in tridistillate. After this, it was dried under vacuum in the presence of zeolite, and the latter was itself previously calcined under vacuum. Spectral analysis revealed no traces of alkali and alkaline earth ions—except for potassium ions, the content of which amounted to less than 0.002%.

The specifies of the given method result in a variable mass of pentane entering into the calorimeter. In order to eliminate the error due to the fact that the mass of pentane is not constant, a calibration experiment is performed with a copper sample which has the

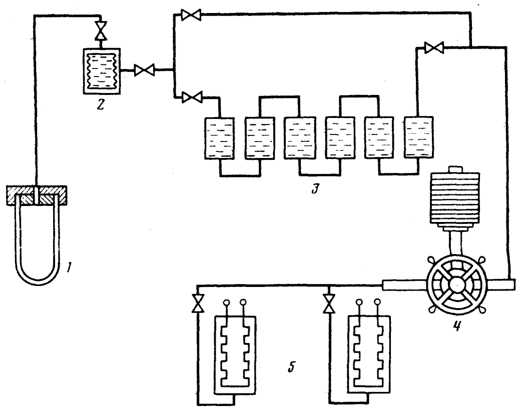

FIG. 2. Hydraulic system of the apparatus: 1) high-pressure calorimeter; 2) bellows divider; 3) pulsation filter; 4) piston manometer; 5) thermocompressors.

same volume as the investigated sample. In the pressure range under consideration, copper has no phase transitions; its heat capacity is practically independent of pressure and is tabulated in detail. Calculation of the heat capacity of the test sample is reduced to this procedure: $C_P = C_1 + C_2 - C_3$, where C_1 is the total heat capacity of the calorimeter, the test sample, and pentane; C_2 is the heat capacity of the copper sample; C_3 is the total heat capacity of the calorimeter, the copper sample, and pentane.

The calibration experiment does not completely eliminate the ballast heat capacity of the calorimeter and of the variable-mass pentane. In order to take into account the difference between the compressibility coefficients of the test sample and copper as well as the difference between their thermal expansions, we must introduce corrections. The systematic errors are primarily due to the inaccuracy of these corrections. Far from the phase transition point, they amount to 0.1% of the regular part of the heat capacity of the test material. At the transition point, an additional error appears in connection with the jump in volume; the upper limit of the error is equal to 0.12% of the regular part of C_P. The mean square deviation of the experimental C_P values from the smoothed curves amounts to 0.15–0.3% for the sample.

The apparatus described allows us to obtain the adiabats, i.e., the pressure dependence of the temperature for constant entropy. The measurement technique is as follows: At zero isobaric temperature drift, the load on the piston manometer is varied in rather small steps, waiting at each pressure value until temperature equilibrium is established. The nonadiabaticity of the calorimeter is estimated as $2 \cdot 10^{-2}$ J/hr. The $T(P)_S$ dependences obtained are adiabatic for the complex system composed of the tested material, the calorimeter, and the pressure-transmission medium. Due to the monotonic character of the thermodynamic properties of the calorimeter and the transmission medium, singular points on the adiabats correspond to singular points of the phase diagram.

III. PHASE DIAGRAM OF AMMONIUM BROMIDE

The $P-T$ diagram of NH_4Br plotted from our results is presented in Fig. 1. The triple point has the coordinates $T_{tr} = 203.35 \pm 0.15$ °K and $P_{tr} = 1730 \pm 20$ bar. The slopes of the phase-transition lines are described by the following values: for the $\gamma-\beta$ transition line, $dP/dT = -56$ bar/°K; for the $\delta-\beta$ line, this value is equal to 117 bar/°K; for the $\delta-\gamma$ line it is equal to 19 bar/°K. These phase-diagram parameters differ significantly from the results of other authors.[2,3,6,13] In all these papers, the accuracy in the pressure determination is low (the error reaches several hundred bar); the differences between triple-point coordinates obtained by various authors reach 30° and 300 bar.

The adiabat method allows us to investigate hysteresis phenomena on the phase-transition lines. The calorimetric methods are poorly adapted to this goal, since in this case it is difficult to realize the cooling regime.

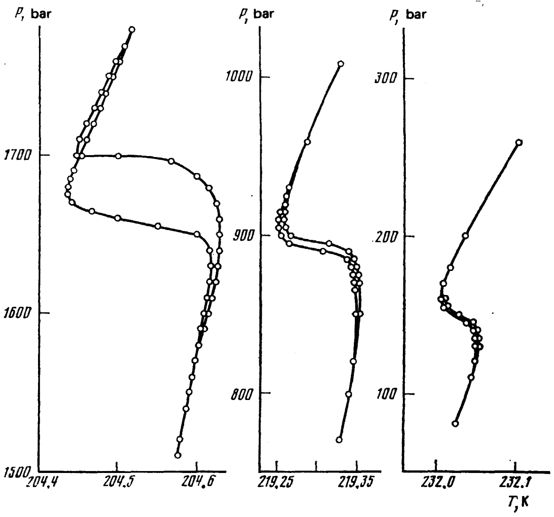

FIG. 3. Adiabats in the vicinity of the γ-β transitions: temperature hysteresis decreases with decrease in pressure.

The adiabats $T = f(P)_S$ form in the vicinity of the $\gamma-\beta$ transition hysteresis loops which are characteristic for first-order transitions. The sizes of the loops vary markedly along this transition line, as is evident from Fig. 3. At high pressures, close to the vicinity of the triple point, this loop is large; at $P = 1.67$ kbar, the temperature hysteresis amounts to 0.2 °K and the pressure hysteresis is equal to 42 bar. On lowering the pressure, these dimensions monotonically decrease and at $P = 0.15$ kbar they amount to 0.044 °K and 2.4 bar, respectively. At $P < 0.9$ kbar, the temperature hysteresis of the adiabats is practically linearly dependent on the pressure, as Fig. 4 demonstrates. Extrapolating the hysteresis size to zero, we may assume that the heat of transition will disappear on the continuation of the $\gamma-\beta$ transition line to the negative pressure region (at $P \approx -0.5$ kbar). Press *et al.*,[6] studying the integrated intensity of neutron scattering by an NH_4Br single crystal as a function of temperature at different pressures, also observed hysteresis in the corresponding curves. These authors indicate that the hysteresis is minimized in the region $P = 0.4$ kbar; however, our data have not confirmed this.

On the $\delta-\beta$ transition line, the temperature hysteresis on the adiabats is also maximum in the vicinity of the triple point, decreases with increasing distance

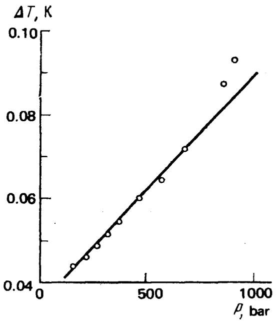

FIG. 4. Pressure dependence of the width of the hysteresis loop on the γ-β line.

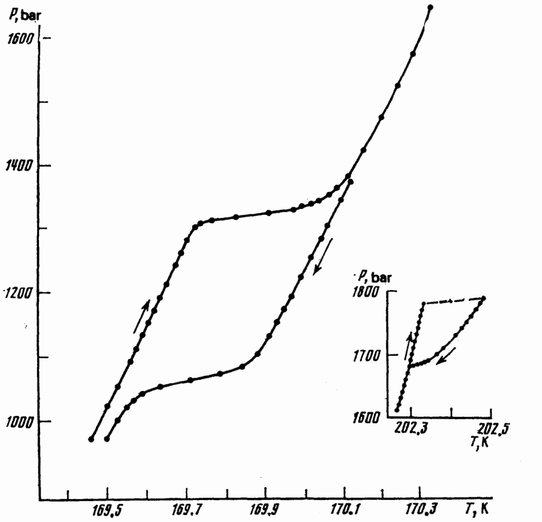

FIG. 5. Adiabats in the vicinity of the δ-γ transitions: temperature hysteresis decreases with approach to the triple point.

from the triple point, and finally disappears at pressures of ≈2.2 kbar—i.e., at the tricritical point. The hysteresis of the δ-γ transition line behaves differently: its magnitude tends toward zero as the triple point is approached (see Fig. 5). This shows that the triple point in NH_4Br is not an accidental point of intersection of three first-order transition lines. We should point out that the hysteresis loop on a given transition line in the 173 °K region changes size discontinuously. Furthermore, the transition line itself has here a slight break.

In Refs. 2 and 13, a new phase was observed at $P \gtrsim 4$ kbar in NH_4Br. The continuation of the transition line from this phase to the δ phase ends up approximately at the same place on the δ-γ transition line where we observed the anomaly. However, at pressures less than 4 kbar, the authors of Refs. 6 and 17 did not observe a new phase. Our data are only an indirect indication of the possibility of the existence of such a phase, so that additional investigations are necessary for the ultimate resolution of this question.

IV. NATURE OF THE HEAT-CAVITY SINGULARITY CLOSE TO THE PHASE TRANSITION LINES

We studied the anomaly in the heat capacity on the orientational ordering lines. The measurement results[2)] are approximated by a formula with a singular and a regular part:

$$C_P=A_1T|\tau|^{-\alpha}+T_c(A_2+A_3\tau),\ \tau=(T-T_c)/T_c, \tag{1}$$

T_c is the fitting parameter, the extrapolated temperature of the divergence in the heat capacity, which does not coincide with the first-order-transition temperature. The statistical analysis method used is described in detail in Ref. 26. The unbiased estimates of the parameters α, A_1, A_2, A_3, and T_c are given by minimization with respect to the parametric sum of the weighted square deviations. However, due to the possible inadequacy of the model, a biased estimate may be obtained for the confidence intervals ΔA_i of the parameters A_i. Therefore the adequacy of the model was tested for each variant of the calculation.

In the statistical analysis program, a limiting parameter $|\log|\tau||_{\max}$ is introduced to compare computational variants of different proximity to the transition. If, beginning with a certain variant, further narrowing of the treated temperature interval does not lead to a significant change in the parameters (primarily, the critical exponent), then this choice of computational variant must be considered satisfactory.

Transitions on the δ-β line

The $C_P(T)$ dependence was studied on four isobars: at $P=1.9$, 2.17, 2.47, and 2.57 kbar; and furthermore the neighborhood close to the transition at $P=1.77$ kbar was studied. It is found that close to the triple point on this transition line, the power-law divergence is characterized by an exponent close to the tricritical value $\alpha=0.5$. Thus, on the $P=1.9$ kbar isobar, α is found to equal 0.533 ± 0.016 at $T<T_c$ (see Fig. 6) for 95% confidence probability. On Fig. 7 is presented the 95% confidence region for the model of the approximation in Eq. (1), and the same region for the extended model, comparison with which allows us to judge the adequacy of Eq. (1). All five parameters are varied: α, A_1, A_2, A_3, and T_c. The confidence corridor has a form typical also of our other measurements: for values of $|\tau|$ from 10^{-1} to $2.5\cdot10^{-2}$, the corridor half-width is 0.04–0.05%; upon decrease of $|\tau|$ to 10^{-2}, the half-width increases to 0.12%; and at $|\tau|=5\cdot10^{-3}$ the corridor half-width increases up to 0.25%. At the same time, the confidence corridor of the approximation to the experimental data in the extended model fluctuates about the axis of the confidence corridor of the basic model in Eq. (1), for the most part overlapping it, which means that the model used is adequate.

In order to study the close vicinity of the phase transition, we need to decrease the width ΔT of the calorimetric step. The absolute error in the determination of ΔT in our experiments is about 10^{-4} °K. Far from

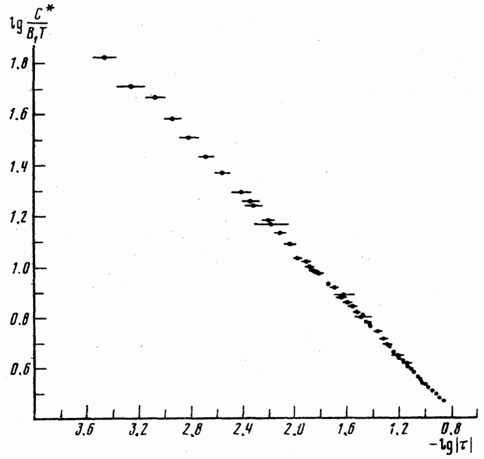

FIG. 6. Dependence of the excess heat capacity on the relative temperature for $P=1.9$ kbar. The slope of the straight line corresponds to the value $\alpha=0.533\pm0.016$. The horizontal bars give the width of the calorimetric step.

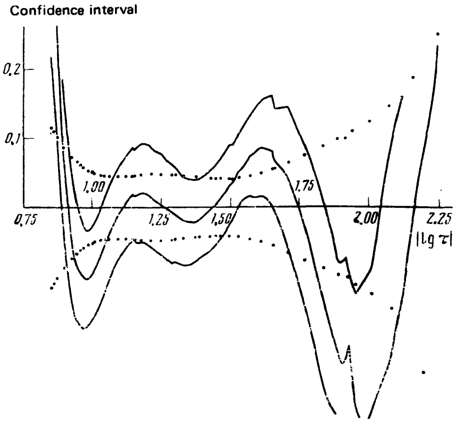

FIG. 7. Confidence corridors for approximation model for the heat capacity at $P=1.9$ kbar (dotted lines) and for the extended model (solid lines) for confidence probability of 0.95.

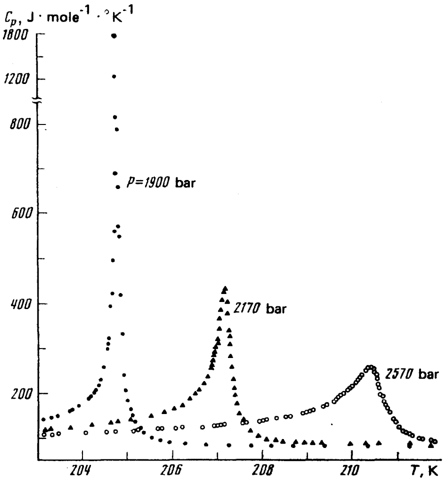

FIG. 8. Disappearance of the δ function on the $C_P(T)$ curves for pressures higher than the tricritical pressure .

the transition, where $\Delta T\approx 1$ °K, this contributes ~0.01% to the error of the heat capacity. Close to the transition, the width of the experimental points decreases to 0.013 °K (see Table 2 in Ref. 27). At the same time, the increase in the equalization time in this region increases the error in the determination of the step width to 10^{-3} °K—i.e., to 3%. This explains the increase in the scatter of the experimental data at the peak of the curve, when the values of the heat capacity exceed 400 J/mole · °K.

The presence of "frozen" impurities in the solid explains why the sample "remembers" its previous history, and in different series of measurements several differing (by an amount on the order of 10^{-2} °K) values of the transition temperature are obtained. This compelled us to include in the statistical reduction the points of both measurement series only up to $|\tau|=4\cdot 10^{-3}$ and to restrict ourselves to only the points of the second series for the close vicinity of the transition.

Despite the indicated difficulties, the power-law divergence was traced up to very close to the transition point ($|\tau|\approx 2\cdot 10^{-4}$, i.e., $T_{\text{trans}}-T\approx 0.04$ °K), which could not be obtained in other solid-state systems in which the tricritical point was observed.

Despite the fact that the power-law divergence is traced practically to the very transition temperature, the transition itself at $P=1.9$ kbar must be classified as first-order, since a heat $Q_{\text{trans}}=95\pm 8$ J/mole is absorbed in the disordering process. It is well known that this leads to the appearance of a δ function in the $C_P(T)$ plot. Due to the "frozen" impurities, the δ function is broadened. The region of broadening of the δ function practically coincides with the steep portion of the high-temperature branch of the heat capacity distorts the power-law characteristic dependence at $T>T_c$ and does not make it possible to determine the exponent by statistical reduction of this branch.

An analogous pattern is observed at the pressure of $P=2.17$ kbar. The power-law for the divergence is adequate up to $|\tau|\approx 2\cdot 10^{-3}$ for $T<T_c$. The heat of transition is $Q_{\text{trans}}=21\pm 5$ J/mole. The heat of transition disappears at $P=2250\pm 35$ bar, $T=207.9\pm 0.3$ °K. Of course, this point is taken as the tricritical point.

In this region of temperature and pressure, the hysteresis of the adiabats and the δ function (Fig. 8) disappears.

Disappearance of the signs of the first-order transition (the δ function and the region of its broadening, within which a transition heat is released) contributes to the fact that at higher isobars, an adequate description of the high-temperature branch by a power law for the divergence seems possible. Thus, for $P=2.57$ kbar, at $T>T_c$ and $|\tau|>4\cdot 10^{-3}$ we have $\alpha=0.483\pm 0.053$. Regarding the low-temperature branch, a lowering of the effective exponent is observed here: $\alpha=0.37$ at $P=2.57$ kbar. This apparently means that the system is in a region of transition from tricritical behavior to critical behavior, although the available experimental data is not sufficient to confirm this unambiguously.

At pressures lower than tricritical the values obtained for the heat of transition and for the difference between the transition temperature and the divergence temperature T_c agree within the framework of the Landau theory[20,28] (see Table I).

Transitions on the γ-β line

The results of the investigation of the heat capacity at normal pressure and at $P=0.35$ kbar were published previously.[28,29] We repeated the statistical analysis of these papers. Furthermore, measurements were carried out on the $P=1.67$ kbar isobar (see Fig. 9). The experimental data, approximated by Eq. (1), are de-

TABLE I.

T_{trans}, °K	P, kbar	Q_{trans}, J/mole	$(T_c-T_{\text{trans}})_{\text{exp}}$	$(T_c-T_{\text{trans}})^*_{\text{calc.}}$
207.17	2.17	21	0.005	0.0016
204.72	1.9	95	0.02	0.037
203.58	1.77	142	–	–

*According to the Landau theory.

scribed adequately by the exponent $\alpha = 0.32 \pm 0.07$ at normal pressure and $\alpha = 0.30 \pm 0.03$ at $P = 1.67$ kbar. It is essential that in this case all five parameters of the model in Eq. (1) were free. Heat capacities on the $\gamma-\beta$ transition line at atmospheric pressure which are close to our results are obtained by Lushington and Garland,[30] who varied only the critical exponent α and obtained $\alpha = 0.2$ for an inadequate description. They extracted the regular part of the heat capacity from the experimental data by resorting to additional assumptions.

The value $\alpha = 0.3$ does not follow from the familiar theoretical models usually used to describe the orientational transitions in NH_4Br. There may be two causes for this value of the exponent. First of all, it could be due to the crossover from tricritical behavior to critical behavior. [Thus, data on the heat capacity of liquid crystals[31] (exponent $\alpha = 0.33$) could be interpreted using the interpolation crossover mode.] Secondly, such an exponent could be due to broadening of the δ function. Although the narrow neighborhood of the transition point was excluded in the statistical treatment of the data, it may turn out that the broadening of the δ function at the $\gamma-\beta$ transition can occur also at larger distances from the transition point.

The reduction at the crossover was carried out, as in Ref. 31, according to the model

$$C_P = \frac{T}{B_1|\tau|^{0.5} + B_2|\tau|^{\alpha}} + T_c(B_3 + B_4\tau).$$

An adequate description is achieved for $0 < \alpha < 0.15$. In all cases, the ratio of the constants $B_1/B_2 \approx 10$—i.e., critical behavior appears in the immediate vicinity of the transition line ($|\tau| < 3 \cdot 10^{-3}$). On approaching the tricritical point from the first-order transition side, there can be no crossover to critical behavior. Apparently, the break from the second-order transitions to those of first order occurs for a reason not associated with the tricritical point.

The value of the heat of transition, determined from the calorimetric experiment, was equal at normal pressure to 72 ± 9 J/mole, and at $P = 1.67$ kbar it increased to 153 ± 19 J/mole.

V. ANOMALOUS CHARACTER OF THE δ-γ TRANSITION IN THE VICINITY OF THE TRIPLE POINT

On the $P = 1.67$ kbar isobar, we observed two peaks (Fig. 9). The low-temperature $\delta-\gamma$ transition was found only after painstaking searches by means of successive narrowing of the calorimetric steps. The difficulty in detection of this peak is associated with the fact that it arises without any pretransitional phenomena as a very narrow (less than 0.05 °K) almost unbroadened δ function (see Fig. 10) with an unusually low heat of transition, which does not exceed 0.9 J/mole ($Q/RT \approx 5 \cdot 10^{-4}$). Such an anomalous absence of heat of transition is at first glance unexpected, since from symmetry considerations it follows that the transition itself is of first order. The vanishingly small value of the heat of transition in this case is confirmed by the fact that the heats of the $\delta-\beta$ and $\gamma-\beta$ transitions close to the triple point are practically equal, 142 ± 16 J/mole at 1.77 kbar, and 153 ± 19 J/mole at 1.67 kbar, i.e., their algebraic sum, equal to the heat of the $\delta-\gamma$ transition, is insignificantly different from zero. The absence of heat in the $\delta-\gamma$ transition close to the triple point would be reasonable if this point were a bicritical point. A bicritical point arises on interaction of two order parameters φ and η. In our case, φ may be correlated with the parallel ordering of the ammonium tetrahedra, and η with the antiparallel ordering. Knowing the symmetry of the NH_4Br phase ($\beta - O_h^1$, $\delta - T_d^1$, $\gamma - D_{4h}^7$), we may find the invariant combinations of order parameters that enter in the thermodynamic potential. The parameter of the $\beta-\delta$ transition transforms in accordance with a one-dimensional irreducible representation of the group O_h^1. The corresponding invariants are φ^2, φ^4, etc. The parameter of the $\beta-\gamma$ transition transforms in accordance with an irreducible three-dimensional representation belonging to the star K $= (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The corresponding invariants are: $\eta_1^2 + \eta_2^2 + \eta_3^2$, $(\eta_1^2 + \eta_2^2 + \eta_3^2)^2$, $\eta_1^4 + \eta^4 + \eta_3^4$ etc. The mixed invariant of lowest order has the form $\varphi^2(\eta_1^2 + \eta_2^2 + \eta_3^2)$, since in fact the three-component order parameter has only one independent component, we obtain as a result the thermodynamic potential[3]:

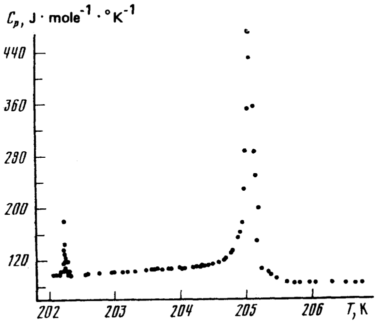

FIG. 9. General form of the $C_P(T)$ dependence for $P = 1.67$ kbar.

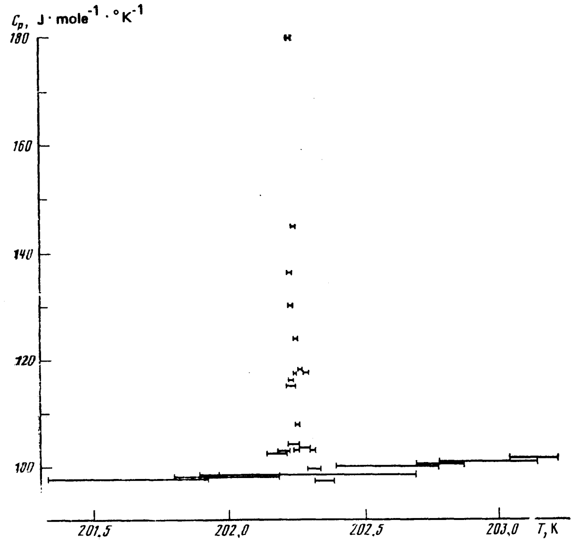

FIG. 10. Anomalies in the heat capacity for the first-order δ-γ transition: $Q_{trans} < 0.9$ J/mole. The bars indicate the width of the calorimetric step.

$$\Phi=\Phi_0+{}^1/_2\tau_1\varphi^2+{}^1/_4u_1\varphi^4+{}^1/_2\tau_2\eta^2+{}^1/_4u_2\eta^4+{}^1/_2v\varphi^2\eta^2, \qquad (2)$$

where $\tau_1=T-T_{c1}$, $\tau_2=T-T_{c2}$; $T_{c1}(P)$ and $T_{c2}(P)$ are the temperatures of the second-order transitions from a disordered phase to ordered phases. Minimization of this potential with respect to φ and η gives four possible phases[32]: 1) $\varphi=\eta=0$ (β phase); 2) $\varphi=0, \eta\neq 0$ (γ phase); 3) $\varphi\neq 0, \eta=0$ (δ phase), 4) $\varphi\neq 0, \eta\neq 0$. Phase 4) is unstable under the condition $u_1u_2<v^2$, which in our case should be satisfied since this phase is absent in NH_4Br. In this case, at the bicritical point—the coordinates of which are determined by the expressions $T_{bi}=T_{c1}(P_{bi})=T_{c2}(P_{bi})$—according to theory, the two second-order transition lines ($\gamma-\beta$ and $\delta-\beta$) and the one first-order transition line ($\delta-\gamma$) should converge. The entropy discontinuities ΔS on the $\delta-\gamma$ line are equal to $\Delta S=T_{c1}-T_{c2}/2(u_1u_2)^{1/2}$—i.e., as the bicritical point is approached, the heat of the $\delta-\gamma$ transition tends toward zero.

The triple point of the $P-T$ diagram of NH_4Br is in fact not bicritical, since on the ordering lines ($\delta-\beta$ and $\gamma-\beta$) second-order transitions do not occur, and they break away to first order. However, the closeness of these transitions to a second-order transition ($Q/RT\lesssim 10^{-1}$) makes it possible to consider the triple point in NH_4Br as a "distorted" bicritical point.

VI. CONCLUSIONS

The investigation of the phase diagram and of the heat capacity of ammonium bromide left unanswered several questions. Primarily: the existence of an additional phase at low temperature, the value of the critical exponent of the heat capacity in the region of the $\delta-\beta$ second-order transitions, and the nature of the change in the heat of transition. From a theoretical point of view, the mechanism by which the tricritical point arises on the $\delta-\beta$ transition line remains unclear. A universal approach to polycritical phenomena, based on consideration of interactions of several order parameters,[32] may prove to be effective in this case. For this, it is necessary to understand the nature of such additional order parameters, the interaction with which determines the nature of the transitions. We can note here the substantial role of phonons[16] and of polarized dipoles.[33]

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[1)] The point at which the line for second-order phase transition changes into a line for a first-order transition.[19, 20]

[2)] Tables of experimental data are given in Ref. 27.

[3)] We carry out the examination within the framework of the Landau theory; for a quantitative investigation, the fluctuations must be taken into account.[32]

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