SOVIET PHYSICS JETP VOLUME 25, NUMBER 6 DECEMBER, 1967

ON THE NATURE OF THE ORDER-DISORDER TRANSITION IN AMMONIUM CHLORIDE

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Submitted to JETP editor December 21, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) 52, 1464–1471 (June, 1967)

Hysteresis of the temperature dependence of specific heat near the order-disorder transition temperature is found in NH_4Cl. The most reproducible supercooling was ~0.3 degrees. The heat of transition Q_{tot} is measured. Since the discontinuity $\Delta\eta$ of the ordering parameter apparently occurs at small values of η when intense ordering fluctuations occur, the fluctuation energy probably comprises a significant part of Q_{tot}. Impurities and structural imperfections of a sample smear out the specific heat peak and thus make it difficult to determine the contribution of the latent heat to the total heat of transition. Only the upper and lower limits of the specific heat are given. On the basis of the measurements it is concluded that the order-disorder transition in NH_4Cl is a transition of the first order.

1. INTRODUCTION

We are often in doubt whether a particular phase transition is of the first or second order. There exists a belief that such doubt cannot be resolved on the basis of calorimetric measurements alone. We shall show that this is an unjustified prejudice when the experimental work is performed with sufficiently high accuracy. Our result is of great general importance because many doubtful cases exist. When we cannot clearly distinguish between first order and second order transitions we are unable to determine unambiguously the nature of the specific heat anomaly at a second order transition point.

There has hitherto been no uncertainty regarding the classification of the order-disorder transition in NH_4Cl, which is customarily considered to be of the second order.[1-5] However, Ubellohde[6] has classified this as a first order transition after observing discontinuities of the volume, thermal-expansion hysteresis, and the coexistence of phases. Hysteresis of Young's modulus in a polycrystalline sample of NH_4Cl has been noted by Lawson.[7]

Urbach[8] has attempted to solve the difficulty by means of the Clapeyron-Clausius equation

$$(dT/dp)_\lambda = T_\lambda \Delta V / Q_{lat}, \qquad (1)$$

which describes first order transition curves, and the Ehrenfest relation

$$(dT/dp)_\lambda = T_\lambda V_\lambda \Delta\beta / \Delta C_p, \qquad (2)$$

which nolds true for second order transitions. Here $(dT/dp)_\lambda$ is the slope of the phase transformation curve in a p-T diagram; T_λ is the transition temperature; V_λ is the volume of 1 mole of NH_4Cl at T_λ; Q_{lat} is the latent heat of transition; ΔV is the volume discontinuity at the transition point; ΔC_p and $\Delta\beta$ are the jumps in the molar specific heat and thermal coefficient of volume expansion. From his treatment of the experimental data in [9] Urbach concluded that the order-disorder transition in NH_4Cl is a first order transition, because the value of $(dT/dp)_\lambda$ obtained by means of (1) agrees very much better with experiment[5] than the value calculated from (2).

It must be mentioned that the applicability of either (1) or (2) is not an independent criterion for distinguishing between first order and second order transitions in doubtful cases. Indeed, if sufficiently accurate and detailed experimental information is available regarding the temperature dependences of C_p and β in the transition region, then the presence or absence of a δ-like singularity of C_p and β can be determined directly from such data. Otherwise no treatment, even by means of (1) and (2), will yield the desired result, since the possibility of correctly determining ΔC_p, $\Delta\beta$, Q_{lat}, and ΔV objectively is excluded. On the basis of data from several investigations[5, 7, 10] and Eq. (2) we easily obtained any value of $(dT/dp)_\lambda$ in the range $(0.6-1.9) \times 10^{-2}$ deg/atm, whereas the experimental value is 0.92×10^{-2} deg/atm.[5] Different methods have been used to calculate the discontinuities of C_p and β: a) graphic extrapolation to T_λ of the $C_p(T)$ and $\beta(T)$ values far from T_λ; b) definition of the discontinuities of the thermodynamic quantities as

$$\Delta C_p = \lim_{t\to 0}[C_p(-t) - C_p(t)], \quad \Delta\beta = \lim_{t\to 0}[\beta(-t) - \beta(t)],$$

where $t = |T - T_\lambda|$.[11] Calculations by the second of these methods are apparently more objective, because we then assume only the symmetry of the singularity in the immediate vicinity of T_λ (as $t \to 0$), whereas the first method assumes the complete absence of any characteristics besides the jump. However, even the second method is arbitrary to a considerable degree, because the selected value of T_λ lies between certain nearest experimental points for the peak.

Garland and Jones[4] recently reported a number of facts that support the classification of the NH_4Cl transition at 242.6 °K as of the second order: No hysteresis of elastic properties was observed in the transition region, and a broad (238–248 °K) ultrasound absorption peak was observed. We undertook direct measurements of the heat of transition in order to determine the nature of the order-disorder transition in NH_4Cl. We shall now present a description of the experimental work, our results, and a discussion.

2. EXPERIMENTAL TECHNIQUE AND RESULTS

We measured the specific heat and latent heat of transition of a powdered NH_4Cl sample ("OSCh" brand) weighing 28.1 g in an adiabatic calorimeter of the type constructed by Strelkov et al.[12] The heat-exchanger gas in the calorimeter ampoule was helium at ~300 mm Torr. The heat capacity of the calorimeter was 5.65 cal/deg at $T \approx T_\lambda$. Adiabatic conditions were maintained to within $\pm 1.0 \times 10^{-3}$ deg using a semiautomatic attachment on an F-16 photocompensated galvanometer.[13] The coolant was liquid nitrogen at atmospheric pressure.

The error in heat capacity measurements depends on the temperature rise ΔT induced by the introduction of measuring heat. When $0.2 \text{ deg} \le \Delta T \le 2$ the error (~1%) is practically independent of ΔT, but increases for $\Delta T < 0.2$ deg and reaches 10–15% for $\Delta T \sim 0.02$ deg. Consequently the measurements are more accurate on the wings than at the peak of the $C_p(T)$ curve (Fig. 1). For points that are ~0.1 deg distant from the temperature at the curve maximum, the error of the heat capacity is under 1–2%.

Since we were interested in the possibility that hysteresis of sample properties exists we performed measurements during both the heating and cooling runs. Figure 1 shows the temperature dependence of C_p for a filled calorimeter in the transition region. The data given in [10] are shown for comparison. Hysteresis of the heat capacity is manifested by the presence of two peaks; the maximum $T_{max} = 242.58$ °K represents the customary technique of measurements obtained with a rising temperature (⊙); the maximum $T_{max} = 242.25$ °K represents measurements taken in the reverse direction, i.e., during cooling (○).

The measurements of C_p during the cooling process were performed as follows. The calorimeter run was "reversed"; during slow adiabatic cooling heat was supplied at a rate that elevated the temperature by amounts (0.02–0.2 deg) lower than the drop effected by cooling. In this way the left-hand peak was traced below its maximum (i.e., up to ~242.1°K). Above this point the metastable

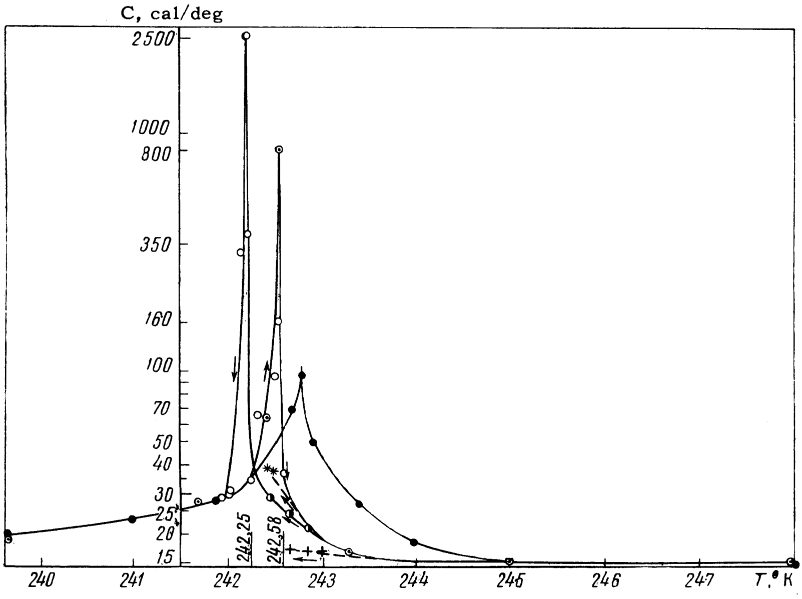

FIG. 1. Temperature dependence of the heat capacity of a calorimeter filled with NH_4Cl in the transition region. ⊙ – during heating of the calorimeter; + – first supercooling; ○ – complete cycle (second supercooling and heating); * – third supercooling; ◑ – fourth supercooling; ● – data from [10].

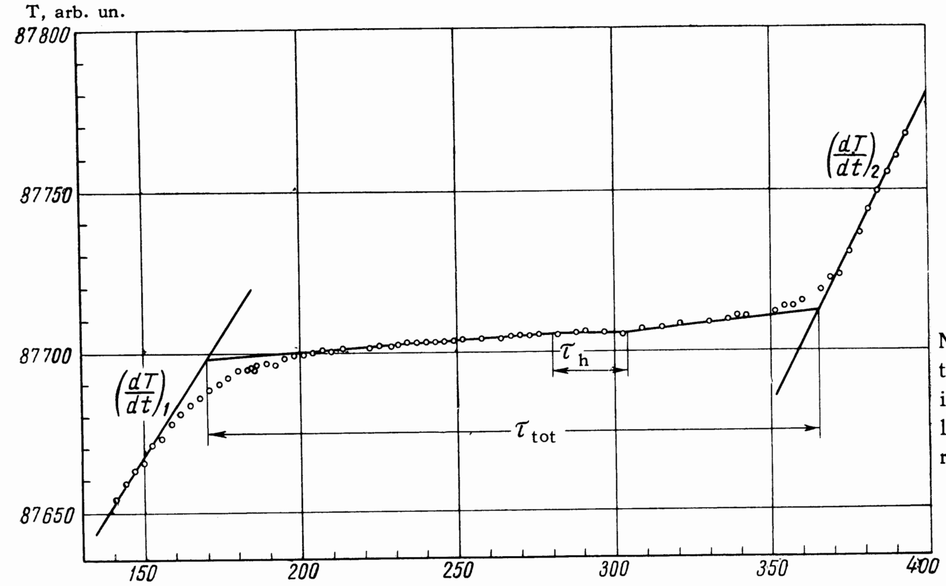

FIG. 2. Thermogram of heating run No. 1 close to the transition temperature. The unit of the temperature scale is ~2 × 10^{-3} deg. τ_h represents the lower limit of the latent heat; τ_{tot} represents the total heat transition.

state broke down; increased heat was supplied to induce temperature rises (0.3–0.5 deg) that exceeded the cooling-induced decreases, and the measurement run was reversed to the usual direction of increase. The measurements obtained in this way coincided well with those recorded previously in the customary upward run exhibiting a peak at 242.58° K.

We have thus observed an appreciable supercooling effect amounting to 0.33 deg, which is 15 times larger than the uncertainty in the position of the peak maximum. The other series of measurements (*, ◑, +) show that the supercooling can vary in magnitude for accidental reasons. It should also be noted that the heat capacity clearly tends to infinity at T_λ. In a ~0.15-deg temperature interval it increases 30 times at 242.58°K and ≈ 100 times at 242.25°K.

Both the supercooling and the rapid rise of the heat capacity toward infinity indicate that the order-disorder transition in NH_4Cl involves the surmounting of an energy barrier, which is reflected in the presence of latent heat. The latter was measured in five thermograms, during two heating runs (Nos. 1 and 2) and three supercooling runs (Nos. 3, 4, 5). These thermograms were recorded as follows. The adiabatic jacket was overheated (or overcooled) relative to the calorimeter by a fixed temperature difference that was maintained constant within 1×10^{-3} deg during the entire experiment. Figure 2 shows a typical thermogram.

The thermogram exhibits the following characteristics: 1) regions of constant drift rate $dT/dt = \text{const}$ corresponding to slight variation of the heat capacity outside of the peak; 2) a thermal plateau τ_{tot} where dT/dt is small but does not vanish entirely; 3) a region τ_h where $dT/dt = 0$; 4) rounding between the regions No. 1 and No. 2 that corresponds to the wings of the peaks. The latent heat was evaluated from each thermogram by measuring the rate of heat loss or gain by the calorimeter, using the drift rate and previously measured heat capacity:

$$\frac{dQ}{dt} = C_p(T_1)\left(\frac{dT}{dt}\right)_1 = C_p(T_2)\left(\frac{dT}{dt}\right)_2, \qquad (3)$$

where dQ/dt is the heat flow from (or into) the calorimeter; $C_p(T_1)$ and $C_p(T_2)$ are the heat capacities at T_1 and T_2, which are respectively above and below the temperature interval for τ_{tot}; $(dT/dt)_1$ and $(dT/dt)_2$ are the drift rates (slopes of the thermogram) at T_1 and T_2. The process represented by (3) was actually stationary within ~10%. The results obtained from the thermograms are summarized in the accompanying table, where Q_{tot} is the total heat of transition per g-mole of NH_4Cl, q is the heat of transition corresponding to the interval τ_h, T_0 is the temperature during τ_h, $(dT/dt)_{tot}$ is the mean rate of drift during the time τ_{tot}. Most of the error (10–25%) in determining the heat of transition comes from uncertainty regarding the length of the temperature plateau τ_{tot} resulting from the temperature spread of the anomaly.1)

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1)In the cases of rapid cooling (thermograms 3 and 4) we have $(dQ/dt)_1 > (dQ/dt)_2$ by 15–20%. This appears to be accounted for by the fact that during the time $\tau_{tot} < 60$ min the entire heat of transition could not be generated; this was manifested in an excessive reduction of $(dT/dt)_2$. A corroborating result is the fact that Q_{tot} measured in experiments 3 and 4 was about 20% smaller than in thermogram 5, which we can confidently consider to represent an equilibrium regime.

	Heating		Supercooling		
	1	2	3	4	5
T_1, °K	241.95	242.21	242.75	243.08	242.58
T_2, °K	242.34	—	240.22	241.00	240.04
T_0, °K	242,57	242.58	242.28	242.18	242.22
τ_h, min	21	—	—	6	50
τ_{tot}, min	185±10	170±15	22±5	54±6	620±25
$(dT/dt)_1$, deg/min	0.0075	0.0083	0.125	0.057	0.00423
$(dT/dt)_2$, deg/min	0.0051	—	0.115	0.037	0.00282
$(dT/dt)_{tot}$, deg/min	0.0002	0.00025	0.006	0.001	0.0001
$(dQ/dt)_1$, cal/min	0.21	0.28	3.3	1.04	0.107
$(dQ/dt)_2$, cal/min	0.224	—	2.8	0.84	0.114
Q_{tot}, cal/mole	76±6	84—10	107±20	97±20	125±10
q, cal/mole	9.5±1.5	±	—	11±3	11.5±1.5

The thermograms confirmed the existence of the hysteresis that was observed in the heat capacity measurements. The table shows that during the heating process T_0 is about 0.35 deg higher than during cooling. (The closeness of T_0, during cooling, to the temperature maximum of the left-hand peak in Fig. 1 permitted us in calculating dQ/dt to use the values of the heat capacity that were determined from the curve of this peak.) The supercooling effect is almost six times greater than the maximum nonreproducibility of T_0 (0.06 deg in thermograms 3 and 5) and is actually independent of the cooling rate (the values of dT/dt that were used varied by a factor of 25); this excludes the possibility of accounting for the hysteresis by a temperature gradient in the sample.

The total heat of transition was computed from the formula $Q_{tot} = (dQ/dt)\,\tau_{tot}$; we here neglected the drift rate $(dT/dt)_{tot}$, which was 20–25 times smaller than dT/dt outside of the plateau. In the normal state (during heating) $Q_{tot} \approx 80$ cal/mole, while in the supercooled state $Q_{tot} \approx 125$ cal/mole. However, the thermograms in Fig. 2 clearly show a strictly horizontal interval τ_h where the temperature drift is smaller than the sensitivity of the thermometer ($\sim 1 \times 10^{-3}$ deg).

Figure 3 shows a portion of the cooling thermogram No. 5 including the interval τ_h. The error of temperature measurements ($\pm\, 1 \times 10^{-3}$ deg) corresponds to the diameters of the points. From Fig. 3 we have $(dT/dt)_{t < 355\ \mathrm{min}} > (dT/dt)_{t > 450\ \mathrm{min}}$, which shows that the interval 355–450 min corresponds to the vertex of the λ-type peak of heat capacity (where the high-temperature branch is below the low-temperature branch). An additional plateau of the thermogram at t ~ 425 min shows that not all of the latent heat was released in the interval τ_h. However, since we are endeavoring to determine only the lower limit of the latent heat q we can confine ourselves to τ_h in our calculations. This interval comprises $^1/_8 - ^1/_{11}$ of τ_{tot} and evidently corresponds to the lowest possible limit of the true heat of transition. In the table this quantity, denoted by q, equals ≈9.5 cal/mole in the ordinary state and ≈ 11 cal/mole in the metastable state.

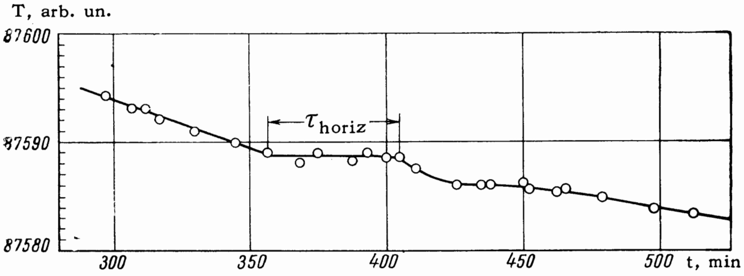

FIG. 3. A section of the cooling thermogram No. 5 about τ_h.

3. DISCUSSION OF RESULTS

The presence of latent heat and the establishment of a metastable state during an order-disorder transition in NH_4Cl permits us to classify this transition confidently as of the first order. It should be noted, however, that strong fluctuations of the ordering parameter (the ultrasound absorption peak is located somewhere in the interval 238–248°K[4]) complicates the picture of the transition. We here apparently have a first order phase transition, which in the P-T phase diagram lies quite close to the so-called critical point of second-order phase transitions, i.e., to the point where the first-order transition line passes over into the second-order transition line.[14] Then to a considerable degree conditions are generated that lead to a sharp increase of fluctuations in the system. As a result the heat capacity anomaly that is charac-

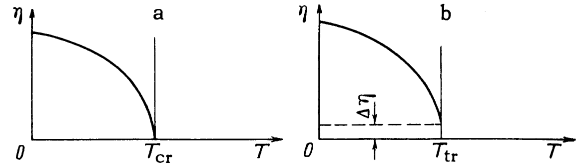

FIG. 4. Ordering parameter versus temperature. a – second-order transition; b – first-order transition.

teristic of second order transitions is combined with δ-like curve that typifies first order transitions.

Figure 4a shows schematically the case of a second order transition in which the ordering parameter η [14] smoothly approaches the vanishing point at T_{cr} where $d\eta/dT \rightarrow 0$. In the case of a first-order transition the ordering parameter drops to zero abruptly at a point T_{tr} (Fig. 4b) which is the temperature of the phase transformation. When the jump Δη of the ordering parameter is sufficiently small (the transition is close to the critical point of second-order transitions), $d\eta/dT$ is very large in the vicinity of T_{tr}, so that it becomes quite difficult to distinguish the two cases experimentally.

Under the foregoing conditions the fluctuation process is strongly developed, since it depends on the magnitude of $d\eta/dT$. It is therefore obvious that the total heat of transition Q_{tot} cannot be regarded as latent heat; a considerable portion is expended as fluctuation energy. It is also obvious that the true latent heat exceeds $Q_{tot}/8 = q$, because our powdered OSCh sample was very much different from a perfect crystal and should exhibit a smearing of the δ-like heat capacity anomaly; this effect is the so-called "premelting,"[15, 6] which does not enter into q.

We have verified that latent heat exists in the order-disorder transition in NH_4Cl, although its magnitude has still not been determined precisely: $q < Q_{lat} < Q_{tot}$. It is entirely unclear how much of the spread of the peak in Fig. 1 resulted from imperfections of the sample and how much resulted from proximity to the critical point. A more precise determination of Q_{lat} in this case would be possible only for a crystal having a "premelting" region that is clearly smaller than the sensitivity of the thermometer ($\sim 1 \times 10^{-3}$ deg).

Both the δ-type anomaly and the ordering-fluctuation-induced characteristic of the heat capacity are greatly distorted by the imperfections of the sample.[15, 16] Therefore in the cases of not very pure materials it is practically impossible to distinguish by means of the heat capacity curve the regions dominated by the different smearing mechanisms and to integrate the latent heat correctly.

In Fig. 1 our results are compared with those in [10]. The peak has been so much distorted that it has completely lost its λ-type shape and has a right-hand branch that is wider than its left-hand branch. Of course, the integration of this peak yields an incorrect result, $Q_{lat} \approx 155$ cal/deg. The latent heat derived from the Clapeyron-Clausius equation (1) at $T_\lambda = 242.6°K$, together with $\Delta V = 0.15$ cm^3/mole from [6] and $(dT/dp)_\lambda = 0.92 \times 10^{-2}$ deg/atm from [5], yields $Q_{lat} \approx 93$ cal/mole, which is quite close to the value $Q_{tot} = 84 \pm 10$ cal/mole that we have obtained in the present work. This does not indicate that our measured value of Q_{tot} consists entirely of latent heat, but rather that the contribution of fluctuations to the thermal expansion comprises approximately the same fraction of the total volume change ΔV as the fraction that the fluctuation energy comprises of the total heat of transition.

In conclusion the authors wish to thank R. S. Aristova for assistance with the measurements.

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Translated by I. Emin
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