Behavior of the specific heat of the ferroelectric phase of KH_2PO_4 near the transition temperature

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An investigation was made of the behavior of the anomalous component ΔC of the specific heat of the ferroelectric phase of KH_2PO_4 in the temperature range $0 \leq T_t - T \leq 30$ deg, where T_t is the temperature corresponding to the entropy discontinuity. An interpolation formula for $\Delta C(T)$ relating to the most reliable published data was calculated on a computer for the range $T_t - T > 0.02$ deg. In the immediate vicinity of the transition ($T_t - T < 0.01$ deg) the investigation was carried out by the method of differential quasistatic thermograms, using two KH_2PO_4 crystals. The experimental data were self-consistent provided it was assumed that only about 70 ± 10% of the enthalpy of transition was due to depolarization. One of the possible explanations of this observation could be the hypothesis that the polarization P was not the complete order parameter but only one of its components. The dependence $\Delta C(T)$ obtained experimentally in the range $T_t - T < 0.02$ deg was stronger than that extrapolated from temperatures further away from the transition point T_t. Obviously, the basic assumptions of the self-consistent field theory (Landau theory), which implied the spatial homogeneity of the order parameter and the additivity of the anomalous and normal components of the free energy, were not true close to T_t.

INTRODUCTION

The ferroelectric transition in KH_2PO_4 is usually described by a phenomenological theory in which the anomalous component of the free energy is represented by an expansion in even powers of the spontaneous polarization P. Since the coefficients of this expansion are determined experimentally, this approach automatically makes allowance for all the changes in the crystal (for example, shear deformation) which are directly related to changes in the polarization. However, Benepe and Reese[1] found that processes not related to the change in the polarization also contributed to the anomalous component of the free energy of KH_2PO_4. This was manifested by a discontinuity in the specific heat C_P (the subscript P refers to the polarization) at the transition point.

The present paper describes a further experimental study of the question of the applicability of the phenomenological Landau theory to the ferroelectric transition in KH_2PO_4. Near the transition point T_t the anomalies in the thermodynamic properties (for example, specific heat) are distorted by the imperfection of the crystals. Information free of these distortions can be obtained by carrying out measurements on crystals of different origin. Therefore, our investigations close to T_t were carried out by the method of quasistatic thermograms which allowed us to study simultaneously two crystals and which had a better temperature resolution than the controlled heating method. The question of the contribution of the change in the polarization to the total heat of transition could be resolved by an analysis of the published data on the specific heat at temperatures relatively far from T_t.

EXPERIMENTAL METHOD

The thermograms were recorded by placing the investigated samples in a fairly massive chamber in which the temperature was varied at a constant rate. The following relationships should be satisfied in the absence of temperature gradient in the chamber and samples:

$$Cu = W + k\Delta T, \tag{1}$$

where C is the specific heat of the crystal, $u = dT/dt$ is the rate of change of the temperature of the crystal, W is the power supply to the crystal, k is the coefficient of heat transfer between the crystal and the chamber, and ΔT is the difference between the temperatures of the chamber and the crystal.

It follows from the above relationship that the specific heat can be measured in two ways: 1) if the conditions are such that $\Delta T = 0$, the specific heat is proportional to the power W supplied to the crystal (the specific heat measured in this way is plotted in Fig. 1); 2) if no power is supplied to the crystal ($W = 0$), the specific heat is proportional to the lag of the crystal temperature behind the temperature of the chamber (Fig. 2). The cooling thermograms should be obtained by the second method. The latent heat of transition is found from the equation

$$Q_{\mathrm{la}} = \int_{t_1}^{t_2} W(t)\,dt + k\int_{t_1}^{t_2} \Delta T(t)\,dt, \tag{2}$$

where the subscripts 1 and 2 represent the beginning and end of the transition (the transition is identified with the "isothermal" entropy discontinuity).

According to the published data,[2] the dependence C(T) for KH_2PO_4 has a λ anomaly which transforms into a δ-like function C(T). This will simply be called the δ anomaly. Since the point at which the $\lambda \rightarrow \delta$ change takes place (beginning of the transition) is not accompanied by any physical changes, the limits of integration in Eq. (2) are somewhat arbitrary. The interval within which the beginning of the transition may be located is identified by the symbols A and B in Fig. 1. This indeterminacy gives rise to a ~20% error in the measurement of the latent heat of transition.

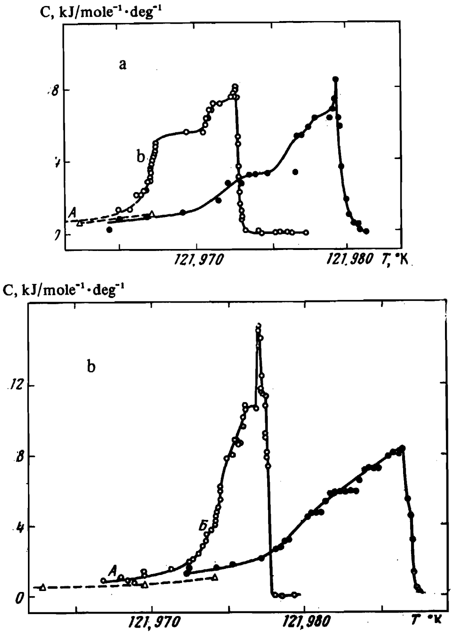

FIG. 1. Temperature dependences of the specific heat of KH_2PO_4. a—Crystal No. 1: ●—thermogram No. 4, $u = 6 \times 10^{-3}$ deg/h; ○—thermogram No. 6, $u = 3 \times 10^{-3}$ deg/h. b—Crystal No. 2: ○—thermogram No. 4, $u = 1 \times 10^{-2}$ deg/h; ●—thermogram No. 6, $u = 3 \times 10^{-3}$ deg/h; Δ—values of the specific heat calculated from the results given in [1]; the dashed curve represents the dependence C(T) obtained by extrapolation of Eq. (8). The points A and B represent the interval within which the beginning of the transition should be located.

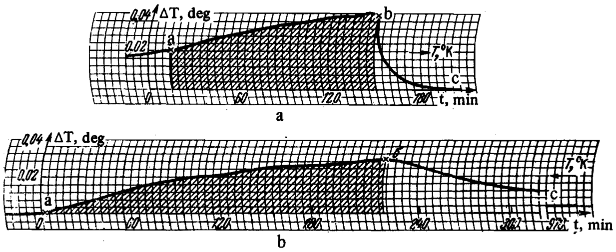

FIG. 2. Thermograms of the W = 0 type (crystal No. 1, $u = 2 \times 10^{-2}$ deg/h): a—heating (thermogram No. 3); b—cooling (thermogram No. 3′). The transition begins at the point a; between b and c the value of ΔT tends to its "equilibrium" value.

On approach to the transition point the weakly nonisothermal conditions (grad $T \sim 10^{-3}$ deg/cm) become important because of the rapid rise of the reduced derivative of the specific heat $\xi = C^{-1}dC/dT$. The condition (1) may thus be violated and the apparent specific heat may be much larger than the true value. Nevertheless, Eq. (2) still holds and we can obtain the correct value of Q_{lat} for a nonisothermal crystal if the limits of integration are known.

In the case of thermograms corresponding to W = 0, the steady-state condition of Eq. (1) is also violated on approach to the transition point because the rise of dC/dt to infinity ceases to correspond to the rise of the derivative d(ΔT)/dt, whose value cannot exceed the rate of drift of the temperature of the chamber. After the end of the transition the condition (1) holds again and ΔT tends to its "equilibrium" value in accordance with a nearly exponential law (Fig. 2, sections b and c). The latent heat of transition for W = 0 can also be determined correctly from Eq. (2).

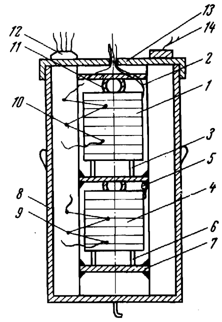

FIG. 3. Schematic representation of the chamber: 1, 4—two samples of KH_2PO_4; 2, 5—crystal heaters; 3, 6—quartz supports and thermal resistors; 7, 8, 13—chamber casing; 9, 10—thermocouples; 11—paper ring support; 12—thermometer; 14—chamber heater.

If Q_{lat} can be determined by both methods, the temperature of the ferroelectric transition should be found by the ΔT = 0 method because this approach eliminates the error in the calibration of the thermocouples. The precision of determination of the transition temperature is limited by the nonisothermal conditions and by the arbitrariness of the identification of the beginning of the transition.

A chamber containing two samples is shown schematically in Fig. 3. Two almost cubic samples of 2.30 and 1.59 g weight were placed inside the massive copper chamber (7,8,13) whose temperature varied with time. The chamber consisted of a can (8) closed by a sliding-fit cover (13). A set of "shelves" (7) was soldered to the cover. A platinum thermometer (12) and a heater were fitted into the supports of the shelves. The weight of the chamber was 66 g. The samples (1, 4) were supported by quartz rings (3, 6) which acted as the thermal resistances between the chamber and the crystals. The constancy of the properties of the crystal-chamber thermal contacts was ensured by smearing the ends of the rings (3, 6) with Ramsay grease. The same grease was used to attach heaters (2, 5) to the crystals. The temperature difference ΔT between the chamber and the crystals was measured with four-junction Chromel-constantan thermocouples (9, 10).

In recording the thermograms (W = 0) the thermocouple signal was applied to photoamplifiers F116/1, which differed from other photoamplifiers by the exceptional stability of its zero reading. The sensitivity of the F116/1 amplifiers was 2×10^{-8} V/div, and the linearity was within 5%. The signal from the F116/1 amplifiers was plotted automatically in synchronism with the temperature of the chamber (crystal). The stability of the zero reading of the F116/1 amplifiers was checked during measurements by reversing the polarity of the signal. The stray thermo-emf was deduced from the readings of the F116/1 amplifiers when the rate of drift of the temperature of the chamber u_0 was sufficiently small so that the lag ΔT of the crystal temperature behind the chamber temperature, calculated from Eq. (1), was less than the sensitivity of the F116/1 amplifiers of the thermocouple emf's; in the $T > T_t$ range the drift rate was $u_0 \sim 2 \times 10^{-4}$ deg/h.

The heat transfer coefficient of the chamber-crystal system k and the sensitivity of the thermocouples to ΔT were determined directly. A current I = 0.5 mA was passed through the heaters until the temperatures of the crystal reached a constant value. The heat transfer coefficient was that calculated from $K = I^2R/\Delta U$, where R is the resistance of the heater and ΔU the reading of the thermocouple. The value of k was similar for both crystals and equal to 3.5×10^{-5} W/μV. Next, we determined the sensitivity of the thermocouples. We compensated the reading ΔU by suitable heating of the chamber and the rise of the chamber temperature was measured with its own thermometer. In this way we found that the thermocouple sensitivity was about 50 μV/deg.

The temperature of the chamber was measured with a R308 potentiometer and recorded also with an ÉPP-09 recorder connected to the output of an F18 instrument, forming a diagonal of bridge in which the unknown arm R_x was a thermometer 12. This thermometer was connected by the three-wire method to reduce the influence of changes in the level of the liquid nitrogen in the cryostat. The bridge readings were calibrated before and after recording a thermogram. This was done to within ±0.003 deg using the R308 potentiometer. The total error in the automatic recording of the temperature was ~0.01 deg, whereas the error in personal readings was only 0.0003 deg.

In recording the thermograms of the $\Delta T = 0$ type, the signal from the output of the F116/1 amplifiers was applied to an integrodifferential regulator of the VRT-2 type. The output current from this regulator was supplied to the heater of the crystal and to a resistance box R33 from which the voltage was fed to the ÉPP-09 automatic potentiometer. The VRT-2 regulator, combined with the F116/1 amplifiers, ensured $\Delta T = 0$ to within $\sim 4 \times 10^{-4}$ deg ($\sim 2 \times 10^{-2}$ μV) for $q_{min} \leq 1$ μW. The corresponding threshold value of the specific heat was $C_{min} = q_{min}V_m/uV_{cr}$, where V_m is the molar volume and V_{cr} is the volume of the crystal. The threshold specific heat was $C_{min} \approx 60$ J.mole$^{-1}\cdot$deg^{-1} when the crystal temperature was varied at a rate $u \approx 3 \times 10^{-3}$ deg/h. Consequently, in the $C \lesssim 0.5$ kJ.mole$^{-1}\cdot$deg^{-1} range the error in the measurement of C resulting from heat exchange between the chamber and the crystal exceeded the error due to the inconstancy of the rate of drift of the temperature of the chamber. In fact, the dependences C(T) of Fig. 1 became definite only above $C \approx 0.6$–0.7 kJ.mole$^{-1}\cdot$deg^{-1}.

The chamber containing two crystals was suspended as a calorimeter, in a standard cryostat with two adiabatic screens.[3] The necessary rate of change of the temperature was set by heating the inner screen. This technique ensured a high degree of constancy of u and isothermal conditions in the chamber. The heater attached directly to the chamber was used only for fine regulation of the value of u. The power consumed by this heater did not exceed the power lost in the thermometer ($\sim 10^{-4}$ W).

EXPERIMENTAL RESULTS

1. Selection of samples

We had a batch of "perfect" KH_2PO_4 crystals at our disposal. We selected those crystals which differed strongly in respect of the growth conditions and optical properties. These crystals were grown in different laboratories. The infrared absorption coefficients ($\lambda = 1.06$ μ) of crystals Nos. 1 and 2 differed approximately by a factor of 1.5 and were, respectively, $\alpha_1 = 0.093$ cm^{-1} and $\alpha_2 = 0.057$ cm^{-1}. The interference pattern observed in polarized light passing along the polar axis was much clearer for crystal No. 1 than for crystal No. 2. Obviously, the macroscopic homogeneity (for example, the mosaic structure) was higher for crystal No. 1, whereas the microscopic homogeneity (for example, impurity distribution) was higher for crystal No. 2 ($\alpha_2 < \alpha_1$).[1)]

2. Behavior of specific heat near transition temperature

The specific heat was measured in a very narrow range of temperatures near the transition temperature T_t ($T_t - T \leq 0.01$ deg) because, in this range, the quasistatic thermogram method employed in the present study gave more reliable results than other methods[2,4] We recorded two slow thermograms in the $\Delta T = 0$ case (thermograms Nos. 4 and 6 in Fig. 1, Table I).

The correspondence between W(t) and C(T) was accurate to within the experimental error provided there was no gradient of the specific heat in the crystal and the rate of drift of the temperature of the crystal was equal to the rate of drift of the temperature of the chamber. According to Eq. (1), the precision of measurement of C was governed by the ratios $\delta W/W$ and $\delta u/u$. In the present experiments the error was mainly due to the indeterminacy of u, which was about 10% for $u \approx 3 \times 10^{-3}$ deg/h.[2)]

The monotonic rise of C(T) stopped near the point B (Fig. 1). It was natural to assume that the condition (1) was violated near the point B ($C \approx 4$ kJ.mole$^{-1}\cdot$deg^{-1}) because of the appearance of a temperature gradient in the crystal under investigation. The value of W became proportional to the average specific heat and the time t to the temperature of the surface part of the crystal but not to the temperature of the bulk. In this case, the isothermal variation of C(T) and, in particular, the δ-like singularity of the specific heat at the transition point would change to complex curves stretched by an interval Δt corresponding to the temperature drop $\circledcirc$ between the surface and the center of the crystal.

Let us now estimate $\circledcirc$. If $W \gg k\Delta T$, the heat is supplied to the lateral surface and the loss of heat from the ends can be ignored. It follows that, in the thermal

TABLE I. Latent heat of transition

No. of thermogram	Crystal No. 1				Crystal No. 2				Remarks
	u, deg/h	T_t, °K	Q_{lat}, J/mole	C_{max}, kJ/mole^{-1} $\cdot$ueg^{-1}	u, град/час	T_t, °K	Q_{lat}, J/mole	C_{max}, kJ/mole^{-1} $\cdot$deg^{-1}	
1	0,17	122,03	36	1	0,17	122,04	65	1.7	$\Delta T = 0$
2	0,047	122,05	43	2	0.045	122,03	70	3,6	$\Delta T = 0$
3	0,02	122,01	36	—	0.02	122.06	73	—	$W = 0$
3′	—0.021	122,00	44	—	—0.021	122.02	47	—	$W = 0$
4	0,006	121.98	45	8	0.01	121.98_7	59	8	$\Delta T = 0$
5	—	—	—	—	0,009	121.98_1	51	9	$\Delta T = 0$
6	0,003	121.97_3	45	8	0,003	121.97_8	46	16	$\Delta T = 0$

sense, the crystal represents an infinite cylinder with a radial heat flow. The regulator ensures that the surface of the crystal is heated at a constant rate (see Footnote 2). The "radius" of the crystal is ≈5 mm. If it is assumed that Θ is 4–5 times larger than the temperature drop in the surface layer 1 mm thick, the value of Θ should not be less than the true value. The power balance on the surface of the crystal is given by

$$W = C_s u + \lambda S \delta\Theta / \delta r, \tag{3}$$

where C_s is the specific heat of the surface layer; $C_s u$ is the power consumed to heat the surface layer; $\lambda = 1.5 \times 10^{-2}$ W.cm^{-1}·deg^{-1} is the thermal conductivity of the crystal;[6] S is the area of the surface layer (≈4 cm^2); $\lambda S \delta\Theta/\delta r$ is the power transmitted by the surface layer to the bulk of the crystal. A layer 0.5 mm thick can be regarded as sufficiently thin but, nevertheless, it represents about 10% of the volume of the crystal, so that $C_s = 0.1 C_{cr}$, where C_{cr} is the specific heat of the crystal. For the values of W employed in our experiments we can assume that $\delta r \approx 1$ mm. Then, the rise in the surface temperature $\delta\Theta$, deduced from Eq. (5) for $u = 0.003$ deg/h is $\sim 2 \times 10^{-5}$ deg at the point A and $\sim 10^{-4}$ deg at the point B. Consequently, the temperature drop between the surface and the interior of the crystal, $\Theta \leq 5\delta\Theta$, at the point B does not exceed 5×10^{-4} deg.

This very small temperature gradient between the surface and the bulk of the crystal can give rise to nonlinear effects only if the dependence C(T) is very strong. The nonisothermal criterion is obviously the quantity $\Delta C/C = \xi\Theta$, where ξ is the reduced derivative of the specific heat. In our experiments, $\Delta C/C \lesssim 0.1$, which can be regarded as sufficiently small. At the point A($(C \approx 0.7$ kJ.mole^{-1}·deg^{-1}) we find that $\Delta C/C < 0.1$ for both crystals. At the point B ($C \approx 4$ kJ.mole^{-1}·deg^{-1}) we find that $0.7 \lesssim \Delta C/C \leq 3$ for crystal No. 1 and $\Delta C/C \approx 0.4$ for crystal No. 2. It is worth noting that initially the reduced derivative ξ of both crystals increases approximately at the same rate and reaches ≈400 deg^{-1} when the specific heat becomes $C \approx 3.1$ kJ.mole^{-1}·deg^{-1}, which corresponds to $\Delta C/C \approx 0.1$–0.15. However, in the $C > 3.1$ kJ.mole^{-1}·deg^{-1} range the curves C(T) of the two crystals differ considerably.

We can show that the values $\xi \gtrsim 10^3$ deg^{-1}, sufficient for the violation of Eq. (1), can appear only near the beginning of the transition where the λ anomaly changes to a weakly broadened δ anomaly. In fact, the slope of C(T) in the region of the δ anomaly

$$\xi_\delta = \left(\frac{1}{C}\frac{dC}{dT}\right)_\delta$$

can be estimated knowing the latent heat of transformation $Q_{lat} = 45$ J.mole^{-1} (this value follows from[2] and the results obtained in the present study) and the width of the δ anomaly $d \lesssim 0.002$ deg.[1,5] Obviously, the smallest value of ξ_δ corresponds to a triangular δ anomaly. Then, $\xi_\delta = 4Q_{lat}/C_c d^2$, where C_c is the specific heat at the point of contact between the λ and δ anomalies. If we assume that $C_c = C_B \approx 4$ kJ.mole^{-1}·deg^{-1} we find that $\xi_\delta \gtrsim 10^4$, which gives $\Delta C/C \geq 5$. This value is close to $\Delta C/C$ at the point B for crystal No. 1. On the other hand, the upper limit of the slope of the λ curve

$$\xi_\lambda = \left(\frac{1}{C}\frac{dC}{dT}\right)_\lambda$$

fails to give values comparable with the experimental data. In fact, even if we assume an unrealistically rapid rise of the specific heat $C = A|\tau|^{-1}$, where $\tau = (T_c - T)/T_c$, we find that because the minimum possible value of τ is $\tau_{min} = (T_c - T_t)/T_c \sim 2 \times 10^{-4}$,[7] the steepness of the slope $\xi_\lambda = \tau^{-1}/T_c$ does not exceed 50. This corresponds to a negligible departure from isothermal conditions: $\Delta C/C \sim 0.03$.

Thus, in the immediate vicinity of T_t there is a range of temperatures in which the specific heat rises in accordance with an intermediate law which is stronger than that ruling in the λ-anomaly region but weaker than that in the δ-anomaly range: $\xi_\lambda < \xi < \xi_\delta$. This range of temperatures is denoted by AB in Fig. 1.

The intermediate law cannot be explained by the usual assumption of the distorting influence of imperfections in the crystals because we would then have to make the doubtful hypothesis that the broadening of the δ anomaly is asymmetric [it is evident from Fig. 2b that on the high-temperature side the front of C(T) is steeper than on the low-temperature side and, therefore, the kink at the point A is much sharper during cooling than during heating]. We can also assume that, under conditions closer to equilibrium, the range of the intermediate behavior of C(T) becomes narrower. However, it follows from Fig. 1 that such narrowing could hardly be significant because a reduction of u by a factor of 2–3 has practically no influence on the initial parts of the curves where $\xi \approx 200$ is much greater than the highest value of ξ_λ.

3. Transition temperature and latent heat of transition

The most reliable value of the transition temperature T_t can be obtained from the slow thermograms3) if the temperature T(t) is varied manually (thermograms Nos. 4, 5, 6, 8–13 in Tables I and II). The transition temperatures of the two crystals were practically identical and equal to 121.97 ± 0.01°K. This result was somewhat unexpected because, usually, the transition temperature varied from crystal to crystal.[2,4,5] Obviously, the crystals used in our study were very close in chemical composition. The mutual influence of the crystals was unlikely because the transitions always occurred at different times.

The hysteresis of T_t (Table II) was observed for all crystals but it did not exceed 0.01–0.02 deg. In the case of crystal No. 1, the differences between T_t during cooling and heating were random and depended weakly on u. On the other hand, crystal No. 2 exhibited a strong dependence of the hysteresis of T_t on u.

The methodological error in the determination of Q_{lat} from thermograms of the $\Delta T = 0$ type was dominated by the error in the measurement of u, whereas, in the case of the $W = 0$ thermograms, the error in Q_{lat} was mainly due to the indeterminacy in the heat exchange coefficient k. The values of Q_{lat} obtained in the present study were correct to within 10% for both types of thermogram. There was no point in trying to achieve a higher precision because it was, in fact, limited by the arbitrary nature of the selection of the beginning of the transition (Fig. 1). As expected, the values of Q_{lat} were the same for both crystals (within the limits of the experimental error). The assumption that the transition started at the point A yielded a

TABLE II. Hysteresis of transition temperature

	Heating				Cooling			
	No. of thermogram	u, deg/h	T_t, °K	Comments*	No. of thermogram	u, deg/h	T_t, °K	Comments*
Crystal No. 1	3	0.02	122.01	$W=0$, aut.*	3′	0.021	122.00	$W=0$, aut.
	4	0.006	121.98_0	$\Delta T=0$, man.*	4′	0.021	$121,99_6$	$W=0$, man.
	—	—	—	—	7	0.009	121.97	$W=0$, aut.
	8	0.005	121.98_0	$\Delta T=0$, man.	—	—	—	—
	6	0.003	121.97_3	$\Delta T=0$, man.	6′	0,006	121.97	$W=0$, aut.
	9	0.003	121.97_1	$\Delta T=0$, man.	—	—	—	—
Crystal No. 2	3	0,02	122.06	$W=0$, aut.	3′	0.021	122.02	$W=0$, aut.
	4	0.01	121.98_7	$\Delta T=0$, man.	4′	0.021	$121,97_3$	$W=0$, man.
	5	0.009	121.98_1	$\Delta T=0$, man.	—	—	—	—
	6	0.003	121.97_8	$\Delta T=0$, man.	6′	0.006	121.96	$W=0$, aut.
	10	0.006	$121,98_4$	$\Delta T=0$, man.	—	—	—	—
	11	—	—	—	11	0.004	121.96_9	$W=0$, man.
	12	0.003	121.98_4	$\Delta T=0$, man.	—	—	—	—
	13	0.003	121.96_8	$\Delta T=0$, man.	—	—	—	—

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*Here, "aut." and "man." denote the automatic and manual methods for measuring the rate of drift of the temperature.

latent heat of transition amounting to 45 ± 5 and 50 ± 5 J/mole for crystals Nos. 1 and 2, respectively. These values were in good agreement with the results given by Reese.[2]

In an earlier study,[5] whose purpose was to determine the nature of the transition, we assumed that the thermal expansion discontinuity occurred only along the polar axis because this seemed to be more reliable. The value of Q_{lat} calculated from the thermograms in[5] indicated that expansion discontinuities were comparable along the longitudinal and transverse directions.

4. Maintenance of thermodynamic equilibrium

It is evident from Table I that reproducible values of Q_{lat} were obtained for $u \leq 0.01$ deg/h. It was interesting to note that at higher rates u the value of Q_{lat} of crystal No. 1 decreased because of the "broadening" of the transition, whereas the value of Q_{lat} of crystal No. 2 increased. Obviously, the increase in Q_{lat} was due to the presence of metastable states, such as Barkhausen jumps (Tables I and II). The heat supplied during the "stoppage" of the transition simply raised the temperature of the crystal.

Since Reese[2] used rates $u \geq 0.1$ deg/h, it could be that the overheating and supercooling effects observed by him were not due to some features of the domain structure of Kh_2PO_4 but to nonequilibrium conditions.

In the earlier study[5] we found that the time needed to establish thermodynamic equilibrium increased strongly in the range $T_t - T = \pm 0.03$ deg. We found that in this range the rate of change of the temperature of the crystal $u \approx 0.01$ deg/h was not sufficiently slow. Investigation of this point was continued in the present study. The value of u was varied from 0.2 to 0.003 deg/h. We found (Fig. 1) that the dependences C(T) corresponding to $u \approx 0.01$ and 0.003 deg/h were quite different (thermograms Nos. 4 and 6).

DISCUSSION OF RESULTS

The results of calorimetric measurements on KH_2PO_4 are given in[2,4,8,9]. However, these results do not give a complete picture of the behavior of the specific heat in the temperature range $T_t - T \leq 30$ deg. We selected the most reliable results and were thus able to describe partially the dependence C(T). The lattice component of the specific heat was deduced from the results reported by Stephenson and Hooley,[9] who determined C(T) in the temperature range 12–300°C, and from the results of Benepe and Reese,[1] who determined the discontinuity ΔC_P at T_t (the subscript P refers to the polarization). The most reliable results in the temperature range 0.5 deg $\leq T_t - T \leq$ 10 deg were obtained by Strukov et al.[4] The value of C at T_t, amounting to 700 ± 50 $J.mole^{-1} \cdot deg^{-1}$, was obtained from the graph given by Reese.[2] 4)

In the present investigation, we determined the specific heat C(T) in the temperature range 0.001 deg $\leq T_t - T \leq$ 0.005 deg. This still left the gap 0.005 deg $\leq T_t - T \leq$ 1 deg. Consequently, the behavior of the specific heat in the range 0.005 deg $\leq T_t - T \leq$ 20 deg was found by interpolating all the available experimental results. Moreover, one could use information on the "electric" component of the specific heat using the data on the dependence of the polarization P on the temperature T.[1]

The results of Strukov et al.[4] were analyzed on a computer by a method similar to that described by Voronel' et al.[10] The approximating function was

$$\frac{C_{\text{exp}} - C_L}{RT} = \frac{\Delta C}{RT} = a\tau^{-n} - b, \tag{4}$$

where $\tau = (T_c - T)/T_c$; R is the gas constant; a and b are constants (b compensates for the anomalous component of the specific heat at high values of τ). In our case, b was such that $\Delta C/RT$ vanished at $\tau \approx 0.1$. The value of T_c was selected to be $T_t + (2-3) \times 10^{-2}$ deg because the dependence of the polarization on τ[1,7] was in the "one-index" form when T_c was assumed to have this value rather than T_t. In the Landau theory[11] the temperature T_c is, in contrast to T_t, a singular point of the state of matter because it represents the upper limit of metastability.

We selected parts of the dependence C(T)[4] corresponding to different values of τ. The most reliable part corresponded to τ from 0.08 to 0.005 because, in this interval, the error due to the broadening of the δ anomaly and the error in the determination of the lattice component C_L were smallest.

The results of Stevenson and Hooley[9] allowed us to separate graphically the lattice component of the specific heat because they extended over a wide range of temperatures (15–300°K). Several variants of the behavior of the lattice component of the specific heat

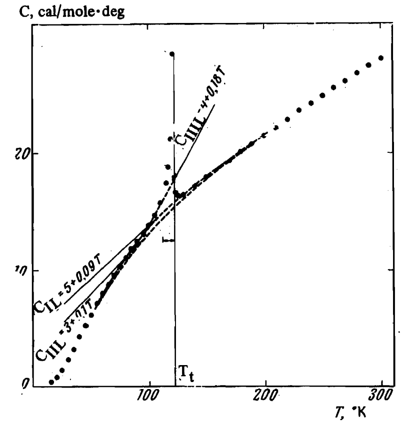

FIG. 4. Determination of the lattice component of the specific heat: ●—results taken from [9]; □—results taken from [1]. The arrows identify the range of temperatures in which C(T) was measured in [4]. Here, C_{IL}, C_{IIL} are the smooth dependences; C_{IIIL} is a dependence which includes a discontinuity in the lattice component of the specific heat at T_t. [1]

are plotted in Fig. 4. If we assume C_L to be a smooth function of the temperature, we find that its value in the transition region lies between the limits $C_{IL} \geq C_L \geq C_{IIL}$, where $C_{IL} = 5 + 0.09T$ cal.mole^{-1}·deg^{-1} and $C_{IIL} = 3 + 0.1T$ cal.mole^{-1}·deg^{-1}. If we allow for the discontinuity in C_P (P is the polarization) deduced from the electrocaloric measurements,[1] we obtain the third variant of the lattice specific heat (Fig. 4): $C_{IIIL} = -4 + 0.18T$ cal.mole^{-1}·deg^{-1}.

If C_L has no discontinuity at T_t, the function $\Delta C/RT = f(\tau)$ in the range $0.08 > \tau > 0.005$ has the form

$$\Delta C/RT = (6.8 \pm 0.5)\cdot 10^{-3}\tau^{-0.51\pm0.01} - (1.8 \pm 0.3)\cdot 10^{-2}. \quad (5)$$

However, if we assume the existence of a discontinuity in the lattice specific heat ($C_L = C_{IIIL}$), we find that the dependence C(T) in the same part of the curve is now described by the function

$$\Delta C/RT = 2.8_3\cdot 10^{-3}\tau^{-0,65} - 1,3\cdot 10^{-2}. \quad (6)$$

The rms error in $\Delta C/RT$ is governed not so much by the errors in the data given in[4] (about 2%) as by the indeterminacy in C_L. In Eq. (5) the error is practically all due to the difference between the variants C_{IL} and C_{IIL}, i.e., the error is about ±10%; for Eq. (6) the error amounts to ±12%.

The value of the specific heat at the transition temperature T_t extrapolated by means of Eq. (6), $C \approx 700$ J.mole^{-1}·deg^{-1}, is in better agreement with[2] than the value $C \approx 500$ J.mole^{-1}·deg^{-1} obtained from Eq. (5) using the first variant with C_{IL}.

As mentioned earlier, the temperature dependence of the specific heat can be obtained from the temperature dependence of the polarization if we apply the Landau theory.[11] However, if we follow[7] and use the electrostatic component of the free energy in the form

$$F_{el} = {}^1/_2\alpha(T - T_0)P^2 + {}^1/_4\beta P^4 + {}^1/_6\gamma P^6$$

($\alpha = 3.9 \times 10^{-3}$ deg^{-1}, $\beta = -1.9 \times 10^{-11}$ cgs esu, $\gamma = 6.3 \times 10^{-19}$ cgs esu, T_0 is the lower limit of metastability), the anomalous part of the specific heat can be represented by

$$\frac{\Delta C}{RT} = -\frac{\alpha}{R}P\frac{\partial P}{\partial T} = \frac{\alpha^{3/2}(\gamma T_c)^{-1/2}}{4R}\tau^{-0.5}. \quad (7)$$

Here, $\tau = (T_c - T)/T_c$; T_c is the upper limit of metastability, which—according to the Landau theory—can be expressed in terms of α, β, γ, and T_t; $T_c \approx T_t + 0.02$ deg.[7] The coefficient in front of $\tau^{-0.5}$ in Eq. (7) is $\sim 0.5 \times 10^{-3}$ deg^{-1}, which is ~1.5 times smaller than the value calculated using Eq. (5) and the calorimetric measurements.[4] Thus, the correct value of the specific heat at the point T_t is given neither by Eq. (5) nor by Eq. (7). Consequently, the dependence $\Delta C \propto \tau^{-0.5}$ is incorrect.

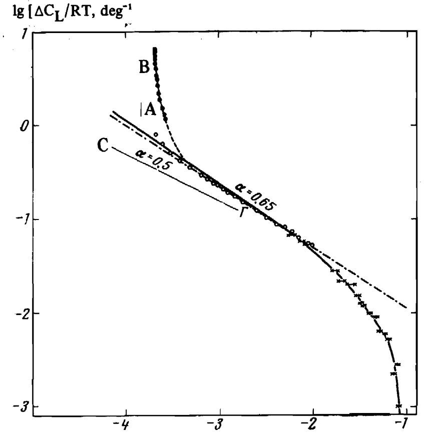

FIG. 5. Dependence of the anomalous component of the specific heat $\Delta C/RT$ of KH_2PO_4 crystals on $\tau = (T-T_C)/T_C$, plotted on double logarithmic scale. X—Results taken from [4], analyzed on a computer; O—values of the specific heat calculated using the Landau theory and the data given in [1]; O—our results. The continuous curve represents the dependence $\Delta C/RT - 2.8 \times 10^{-3}\tau^{-0.65} - 1.3 \times 10^{-2}$; the chain line is the dependence $\Delta C/RT = 2.5 \times 10^{-3}\tau^{-0.65}$. The segment CD shows the discrepancy between the dependences $\Delta C/RT \propto \tau^{-0.65}$ and $\Delta C/RT \propto \tau^{-0.5}$.

The dependences of the spontaneous polarization P and its derivative $\partial P/\partial T|_E$ on $T_t - T$ are tabulated in[1] for the interval $1 \text{ deg} \geq T_t - T \geq 0$ ($10^{-2} \geq \tau \geq 10^{-4}$).5) Then, using Eq. (7), we can calculate the anomalous component of the specific heat directly from the experimental values of P and dP/dT (Fig. 5).6) The dependence ΔC(T) obtained in this way can be described satisfactorily by the function

$$\Delta C/RT = 2.5\cdot 10^{-3}\tau^{-0.65}, \quad (8)$$

which is practically identical with Eq. (6). Nothing very definite can be deduced about the constant b from Eq. (6) because the contribution of b is negligible if $\tau \leq 10^{-2}$. Thus, the calorimetrically measured dependence of $\Delta C/RT$ on τ, given by Eq. (6), agrees within ≈10% with the dependence (8) calculated from the Landau theory (Fig. 5), which is quite satisfactory for such calculations.

Agreement of this kind is obtained only if the lattice component of the specific heat has a discontinuity at the transition point. At first sight, this condition seems to be unnatural. We may find that the anomalous part of the specific heat has two components which we shall call "electric" ($\Delta C_e/RT \propto \tau^{-0.65}$) and "nonelectric" ($\Delta C_{ne}/RT \propto \tau$).

This means that the order parameter is a complex quantity in which the electric polarization is only one of the components. The heat obtained by integrating the "electric" component of the specific heat $\Delta C \propto \tau^{-0.65}$ of Eq. (6) in the range $T < T_t$ amounts to ~230 J/mole. The energy corresponding to the polarization discontinuity $\Delta P \approx 5.7 \times 10^3$ cgs esu [1] can be calculated from the Landau theory: $Q_{lat.e} = T_t\alpha(\Delta P)^2$. This quantity is equal to ~45 J/mole, which is in good agreement with the calorimetrically measured heat of transition ([2] and results reported in the present paper). Thus, the total energy associated with the polarization is $Q_e \approx 270 \pm 15$ J/mole. The heat corresponding to the dependence $\Delta C \propto \tau$ is found by integrating, with respect to temperature, the difference between $C_{IIIL}(T)$ and $C_{IL}(T)$ or $C_{IIL}(T)$ from the point of their intersection (Fig. 4) to T_t. This heat is $Q_{ne} \approx 120 \pm 50$ J/mole, which is approximately 2—4 times smaller than Q_r. The The nature of the dependence of $\Delta C/RT$ on τ would lead us to expect the ratio Q_e/Q_{ne} to be much larger but it is found that these energies are expended at different temperatures. The contribution of Q_{ne} predominates far from the transition in the range 30 deg > $T_t - T$ > 10 deg, whereas Q_e is negligible at these temperatures. The "electric" and "nonelectric" specific heats become comparable only in the range $T_t - T \approx 5$ deg. The last 3—4 deg from the transition point are characterized by a rapid change in the polarization ($P^6 \propto \tau$[1]); in the last 0.01—0.02 deg before the transition point the additivity of the "electric" and "lattice" components of the energy is no longer true (region AB in Fig. 1) and, finally, at T_t the crystal goes over to the high-symmetry phase and the polarization changes discontinuously ($Q_{lat.e} = Q_{lat.tot}$). This gradual activation of the various mechanisms is not described by any of the current theories of the ferroelectric transition in KH_2PO_4.

Near T_t the measured values of $\Delta C/RT$ and those calculated from the Landau theory (open circles and black dots in Fig. 5) deviate from the power-law dependence at approximately the same values of τ ($\tau = 4 \times 10^{-4}$, i.e., $T_t - T = 0.02$ deg). There are several reasons why this deviation cannot be attributed to the broadening of the δ anomaly because of the imperfection of the crystals. These reasons are as follows.

1) The value of $T_t - T \approx 0.02$ deg is an order of magnitude greater than the width of the broadened polarization and volume discontinuities.[1,5] (We recall that the measurements reported in[5] were carried out on crystal No. 2, for which the value of $\Delta C/RT$ is given in Fig. 5).

2) It is difficult to see how the broadening of the δ anomaly can be asymmetric. Here, it is relevant to recall that the beginning of the transition on the high-temperature side, where $C \approx$ const changes to the δ function, can be determined with a precision better than 0.001 deg (cooling thermogram, point a in Fig. 2b).

These circumstances indicate that the observed deviations can be regarded as consequences of the physical processes which occur before the loss of the stability and not as a result of the influence of the imperfection of the crystals. It is worth noting that the values of $\Delta C/RT$ in the range $T_t - T < 0.02$ deg, calculated on the assumptions employed in the Landau theory[11] that the polarization P is homogeneous and the anomalous and lattice components of the free energy are additive, are almost an order of magnitude smaller than the values of $\Delta C/RT$ measured calorimetrically.

BRIEF CONCLUSIONS

1. The method of differential quasistatic thermograms was used to determine the behavior of the specific heat of KH_2PO_4 crystals as a function of temperature in the direct vicinity of the transition point: 8×10^{-3} deg $\gtrsim T_t - T \gtrsim 1 \times 10^{-3}$ deg. The limits of validity of this method in investigations of the specific heat anomalies and in the determination of the latent heat of transition were investigated.

2. The latent heats of transition Q_{lat} were determined for two crystals. The value of Q_{lat} was in agreement with the published data (within 10%) provided it was assumed that the heat of transition included the heat of the processes occurring in KH_2PO_4 in a relatively wide range of temperatures $0 < T_t - T \leq 0.02$ deg. The value of Q_{lat} determined in the range $T_t - T$ extending over the region of broadening of the polarization discontinuity was 20% smaller.

3. The temperature of the ferroelectric transition in both crystals was found to be the same to within 0.01 deg (121.97 ± 0.01°K). The hysteresis of T_t was observed for both crystals but it did not exceed 0.01—0.02 deg.

4. The establishment of thermodynamic equilibrium was also investigated. The rate of change of the temperature of the crystals was varied within the limits 0.2 deg/h $\geq u \geq$ 0.003 deg/h. It was found that the dependences C(T) obtained for $u \sim 0.01$ and $u \sim 0.003$ deg/h were quite different. Reproducible values of Q_{lat} were obtained only for $u \leq 0.01$ deg/h.

5. A comparison was made of the dependences of $\Delta C/RT$ on τ obtained relatively far from the transition temperature ($T_t - T \geq 10^{-2}$ deg) with the dependences in the direct vicinity of the transition temperature ($T_t - T \leq 10^{-2}$ deg). The anomalous specific heat was found to have two components: $\Delta C/RT \propto \tau^{-0.65}$, due to all the changes in the crystal associated with the change in the polarization P, and $\Delta C/RT \propto \tau$, which was not related to P. The corresponding heats of transition were $Q_e \approx 270 \pm 15$ J/mole and $Q_{ne} \approx 120 \pm 50$ J/mole. These heats were expended successively at different temperatures.

6. In the immediate vicinity of the transition point ($T_t - T \lesssim 0.02$ deg) the main assumptions of the Landau theory of the spatial homogeneity of the order parameter and the additivity of the anomalous and normal components of the free energy were not obeyed. In this region the measured dependence of the specific heat on τ was stronger than that calculated using the assumptions employed in the Landau theory and the experimental values of P(T).

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[1] Dilatograms, described in [5], were obtained for crystal No. 2.

[2] The experimentally observed dependences W(t) had a step-like structure due to the presence of a small lag of $\delta(T)$ of the temperature of the crystal behind the temperature of the chamber. This lag could not be distinguished by the regulator and, consequently, the output current of this instrument did not change until an error signal equal to δT was accumulated. One can show that the accumulation time of this signal, i.e., the width of the step in the W(t) diagram, is

$$\Delta t = \frac{\delta T}{u}\left(1 + \sqrt{\frac{C}{\Delta t}\frac{dt}{dC}}\right),$$

where C is the specific heat of the crystal in question. We used the actual values of the steps Δt in the interval between the points A and B and calculated the effective sensitivity of the regulator δT_0. The average value of this sensitivity was 5×10^{-5} deg, which was an order of magnitude better than the nominal sensitivity. Thus, the rate of drift of the temperature of the crystal could be assumed to be constant and equal to the rate of drift of the temperature of the chamber to within the value of the ratio $\delta T_0/\Delta t$, which gave rise to an error of the order of 10% in u for points between A and B.

3) In the heating thermograms T_t is assumed to be the temperature of the rapid fall in the specific heat, which exceeds the true value of T_t by not more than 0.01 deg.

4) The value of T_t deduced in [2] seems doubtful. According to Reese, $C_{T_t} = 620 \pm 10$ J/mole$^{-1}\cdot$deg^{-1}.

5) Benepe and Reese [1] do not distinguish between T_t and T_c but the dependence $P \propto \tau^{0.17}$ is correct if $T_c = T_t + 0.02_5$ deg. This is the value of T_c used in the present paper in the calculation of the dependence $\Delta C/RT(\tau)$.

6) The experimental value of α automatically allows for all the deformations associated with P so that the specific heat calculated from Eq. (7) includes the contributions not only of the electrostatic but also of the elastic energy. For the sake of simplicity, we shall refer to this anomalous specific heat as the "electric" component.

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