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DILATOMETRIC INVESTIGATION OF THE FERROELECTRIC TRANSITION IN KH_2PO_4

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A detailed investigation of the ferroelectric transition in KH_2PO_4 (KDP) is carried out in a quartz dilatometer with a temperature resolution of ≈ 0.0005°. A volume discontinuity of $(6.0-10) \times 10^{-3}\%$ and expansion hysteresis are observed. The complex nature of the anomaly of the thermal expansion coefficient (α) and strong anisotropy of that part of α which arises in the immediate vicinity of the transition ($|T - T_{tr}| \lesssim 0.03$) are noted. The reliability of classification of transformations with a small latent transition heat and of comparison of the experimental data with the theoretical predictions are discussed for the transition in KDP when the measurements are performed with imperfect samples. The possibility of determining the slope (dP_c/dT_c) of the phase transformation line on the basis of the integral transition heats Q_{tot} and change of the volume $(\Delta V/V)_{tot}$ is discussed. For KDP this estimate yields $dP_c/dT_c = (2-3) \times 10^2$ atm/degree. The data on $(\Delta V/V)_{tot}$, Q_{tot} and $\delta(\Delta V/V)$ can also be employed for estimating the latent transition heat for the sample studied, $Q_{tot} \approx 8-20$ J/mole. The ferroelectric transition in the multidomain crystal KDP is classified as a transition of the first order which is close to the critical point of transitions of second order.

1. INTRODUCTION

THE anomalous properties of substances in the order-disorder transitions become manifest all the more clearly, the smaller the distance $\tau = (T - T_c)/T_c$ ahead of the transition (T—temperature). On the other hand, when $\tau \to 0$, the role of the inhomogeneity and of the impurities, as factors distorting the anomalies of the thermodynamic properties in the transition, increases. Consequently, in order to understand the gist of the "critical phenomena," it is necessary to find criteria that make it possible to judge the extent to which we can apply to anomalies in real materials abstract ideal concepts such as transition point T_c, the jump of the ordering parameter η, the δ-function of the specific heat C_p or of the coefficient of volume thermal expansion β, the logarithmic (power-law) singularity of C_p or β, and others. The absence of criteria leads to a situation wherein a prolonged dispute can arise even with respect to such a relatively simple question as the magnitude of the jump of η, although $\Delta\eta$ is the most stable and easily observable element of the anomaly. Recent communications report that certain universally known second-order transitions ($\Delta\eta = 0$) turned out to be of the first order ($\Delta\eta \neq 0$) upon further verification[1-5]. The present paper is devoted to the possibility of determining the character of the transition (observing the jump of η) from the temperature dependence of the volume V or of the entropy S near the transition point. Inasmuch as S(T) and V(T) are linearly related, it is possible to use in the evaluation of thermal-measurement data, which are more and more detailed than the available data of dilatometric investigations. In addition theoretical predictions also pertain directly to S(T).

It should be noted that the usual alternative—the transition, is either of first or second order—does in fact not exist, and the only alternative is whether we are dealing with a first-order transition or with the critical point of second-order transitions. According to Landau and Lifshitz[5], the point on the (P, T) plane (P—pressure) at which the line of the second-order transition goes over smoothly into the line of first-order transformations, is called the critical point of the second-order transitions (we shall henceforth call it simply the critical point). The transformation is characterized at this point by a more rapid variation of η ($\eta^2 \propto \tau^{1/2}$, and not $\eta^2 \propto \tau$ as in a second-order transition), and by the presence of an asymmetrical root singularity of C_p ($C_p \propto \tau^{-1/2}$ at $T < T_c$ and $C_p = \text{const}$ at $t > T_c$, Fig. 1b). Figure 1 shows schematically these cases. When $\Delta\eta \leq 0.3$, the latent heat of the transition Q_{lat} (the shaded region of Fig. 1a) may turn out to be much smaller than the total thermal effect ($Q_{tot} = Q_{lat}$ plus the energy of the ordering process), which is equal to the total area under the peak in Fig. 1a. A similar situation occurs also for the volume jump $\Delta V/V$, which may turn out to be many times smaller than $(\Delta V/V)_{tot}$ at small values of $\Delta\eta$.

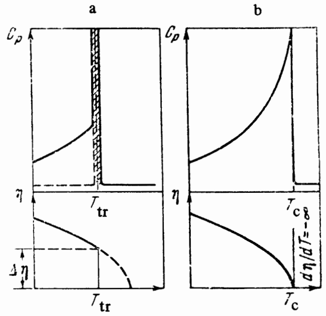

FIG. 1. Temperature dependences of the specific heat and of the ordering parameter for first-order transitions and for the critical point of second-order transitions: a) first-order transition, b) critical point. T_{tr}—temperature of first-order transition.

Nonetheless, for absolutely perfect samples it is possible to obtain exact data on the jumps of S and V, by using relatively simple apparatus, of the type described in[2,6] (calorimeters with loss $\sim 10^{-6}$ W and a dilatometer with sensitivity ~ 100 Å). Let us take, for example, the KDP crystal (KH_2PO_4). It has $Q_{tot} = 250-350$ J/mole[7]. Even if $Q_{lat} = Q_{tot}/100$, the thermogram plotted for a sample of only 1 cm^3 volume will have a temperature halt of duration exceeding one hour. Such an effect can be measured with accuracy $\sim 1\%$. A similar result is obtained also for $\Delta V/V$. However, as a rule, not only are there no exact data on Q_{lat} and $\Delta V/V$, when $\Delta\eta \leq 0.3$ ($Q_{lat}/Q_{tot} \lesssim 0.1$), but there is a debate concerning their presence or absence, and consequently, concerning whether the given transition is of the first or second order.

This is explained by the fact that the imperfections of the material (impurities, inhomogeneity), lead to a "smearing" of the jump of η, i.e., to a distortion of the corresponding thermograms[2] and specific-heat peaks[2,8-12]. It is easy to understand that when the $C_p(T)$ curve on Fig. 1a is slightly smeared out it becomes very similar to the curve on Fig. 1b. We are therefore unable to separate exactly the C_p (or β) δ-function and the excess part of C_p (or β) connected with the disordering process. In such cases it is very easy, depending on one's prejudice, to assign to Q_{lat} (or to $\Delta V/V$) the extreme values zero or Q_{tot} ($(\Delta V/V)_{tot}$). Moreover, if the anomalies of $C_p(T)$ on Fig. 1 are "smeared out" more strongly, then they become indistinguishable from the λ curve, which has a symmetrical singularity, since the perpendicular right-hand branch is transformed into an inclined curve, and the asymmetry typical of the critical point vanishes. In this case it becomes possible to mistake a first-order transition for a second-order transition having a weak (say logarithmic) singularity of C_p and β at the transition point.

The manner in which an inhomogeneity "spoils" the $\eta(T)$ dependence has been clearly demonstrated using the liquid-vapor critical point of benzene as an example[13]. The ordering parameter is in this case the deviation of the density from the critical value, and a measure of the inhomogeneity is the height of the liquid column, whose own weight causes the density gradient. It is proved in[14] that such an inhomogeneity distorts the anomaly of the specific heat so strongly that it remains finite, whereas in the experiment, where the gradient of η has been eliminated, $C_V \to \infty$ logarithmically. Similar effects were observed also in solids in first[8] and second[9,12,15-17] order phase transitions.

The individual properties of the sample affect particularly strongly the temperature dependence of η, S, and V near the transition point ($\tau \lesssim 10^{-2}$), i.e., precisely where we should seek an answer to the questions of the jumps of η, S, and V and of the analytic form of the singularity of the thermodynamic quantities. Taking into consideration the fact that in an imperfect material the jump of η cannot become steeper than in an ideal material[1)], we can make the following statements: 1) if the latent heat of the transition can be observed in at least one of a set of samples ($\Delta\eta$, ΔS, $\Delta V \neq 0$), then this result can be reliably reported as the property of an ideal system[2)]; 2) to the contrary, if we have $\Delta V/V \neq 0$ in an arbitrary large number of samples and Q_{lat} or $\Delta\eta$ has not been observed, but owing to the crudeness of the experiment or the imperfection of the samples it was impossible to come sufficiently close to the transition point[3)], then the general conclusion is that the transition must be classified as a second order transition in the given system (ideal substance).

An example of a correct generalization is the conclusion of the presence of a jump of η at the T_N point of chromium[1] and of latent heat of the orientation transition in NH_4Cl[2]. A classical example of an incorrect generalization is the ferroelectric transition in KDP.

The opinion that the transition in KDP is continuous and is of second order is based on the results of a number of investigations[7,19-23]. In[11,22], the hypothesis was advanced that this transition may be of the first order. However, in not one of the aforementioned experiments did the authors come sufficiently close to the transition point, either as a result of the crudeness of the temperature measurements (± 0.1 deg), or as a result of two rapid changes of the temperature of the sample ($dT/dt \geq 10^{-2}$ deg/min) or else owing to the insufficient perfection of the sample (polycrystal). Graig[4] considers the transition in KDP to be jumplike, since he observed a temperature hysteresis of the dielectric constant near T_c; the supercooling reached 0.05 deg. However, nothing is said in[4] concerning the rate of change of the sample temperature.

A special position in the investigation of the ferroelectric transition in KDP is occupied by the work of Reese and May[10], who made precision measurements of the specific heat near T_c. These authors have demonstrated in essence that their data satisfy practically any theory, depending on the choice of T_c, within the limits of the smearing of the peak, viz., a symmetrical logarithmic singularity and an asymmetrical power-law singularity are confirmed with sufficient accuracy. In our opinion, the asymmetrical power-law singularity ($C \propto \tau^{0.5}$ at $T < T_c$ and $C \propto \tau^{-1.0}$ at $T > T_c$) is not a fact

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[1)] According to [11, 13, 16] inhomogeneity always smears out the $\eta(T)$ dependence, but the influence of the absolutely uniformly distributed impurity on $\eta(T)$ of a multidomain system is still unclear. It is already known that it shifts and weakens the anomaly in "domainless" transitions, for example at the liquid-vapor critical point. Apparently, however, in real samples the impurity is always distributed unevenly, making it possible to state that the presence of the impurity (defects) smears $\eta(T)$ or $\Delta\eta$, ΔS, and ΔV.

[2)] It should be borne in mind that the result obtained for a multidomain sample can still not be generalized to include the properties of an ideal infinite system, since the process of the change of the separation boundaries between the domains may make its own contribution to the temperature dependence of the free energy of the crystal and the dependence $\eta(T)$.

[3)] On the basis of an analysis of our own and published data [4, 9-11, 13, 14] we have verified that even the properties having a stronger anomaly than C_p and β (for example, the magnetic permeability) are strongly subject to the influence of imperfections, and therefore, T_c of an ideal substance can be determined with the aid of measurements on a real sample only quite approximately. Therefore the problem of the behavior of various properties as functions of τ is very difficult to solve, since in most cases T_c is an arbitrary parameter even in the presence of the most careful measurements of the anomaly (see, for example, [10, 15, 18]).

that contradicts the classical theory. It is simply necessary to seek agreement not with the theory of Ornstein and Zernicke, as in[10], but with the critical point of second-order transitions[5]. The relation $C \infty \tau^{1.0}$ can then be interpreted as an infinite specific-heat jump that is smeared out by the inhomogeneity. It thus results that, owing to the lack of a criterion for an objective determination of T_c in a real material, the same data imply, with almost equal degree of reliability[4)], that the ferroelectric transition in KDP agrees with Landau's classical theory and with the two-dimensional Ising model. In addition, Reese and May also advanced the hypothesis that a small latent heat of the transition exists.

Such a wide range of contradictory fundamental results is explained by us as due to the fact that under the conditions realized in KDP there it is very difficult to obtain reliable information. The crystals as a rule are of exceedingly high perfection, and data of relatively rough measurements ($\tau \geq 10^{-3}$) made by various investigators are usually in perfect agreement with one another[19,20,23,24]. (The only exception is the discrepancy in the determination of T_c, but usually no importance is attached to this circumstance.) Moreover, under such approximations the transition is exceedingly distinct, reproducible, and has no hysteresis. This creates the erroneous impression that the result obtained with one crystal can be extended to KDP in general. It is therefore possible to mistakenly idealize the sample, as was done by Grindley[21], Teaney,[22], and in part by Reese and May[10], or to idealize the experiment, as was done by Cook[23]. Yet, inasmuch as the disorder in KDP sets in exceedingly rapidly, the answer to the question concerning the jumplike behavior of η must be sought in a region directly adjacent to T_c ($\tau \leq 10^{-3}$), and here the individual properties of even the better crystals come strongly into play.

In order to solve the problem of the character of the transition in KDP, we present in this paper a detailed investigation of the thermal expansion of an isolated KDP single crystal near its T_c. The dilatometric procedure is attractive also because it makes it possible to investigate the anisotropy of the anomaly of the thermal expansion. We shall describe and discuss below the procedure and the measurement results.

2. PROCEDURE AND MEASUREMENT TECHNIQUE

We had at our disposal a quartz optical-mechanical dilatometer, similar to that described in[25]. The measurements of the thermal expansion coefficients of the crystals of the KDP group have shown[24] that it is not suitable for subtle investigations near T_c not so much because of the sensitivity (≈ 170 Å) as because of the relatively rough resolution in temperature (± 0.005 deg). We were able to improve this instrument[26] (Fig. 2). This was effected by enclosing the quartz stage with the sample, 1, in an additional copper sheath 4, 5, and 6 and by placing copper plates 7 and 8 over the quartz rod 2, which transmitted the elongation. Five- and three-junction constantan-manganin vertical (11) and horizontal (10) thermocouples monitored the temperature drop inside the chamber 4–6; the drop did not exceed (2–3) $\times 10^{-3}$ deg, corresponding to 0.1 μV—the parasitic thermal emf of the conducting copper wires. Thus, equality of the temperatures of the thermometer and of the sample was maintained with accuracy ± (3–5) $\times 10^{-3}$ deg, and the time variation of the sample temperature could be traced with accuracy $\pm 7 \times 10^{-4}$ deg, corresponding to the accuracy with which the temperature can be measured with a 40-ohm platinum resistance thermometer 9[6] using an R-308 potentiometer.

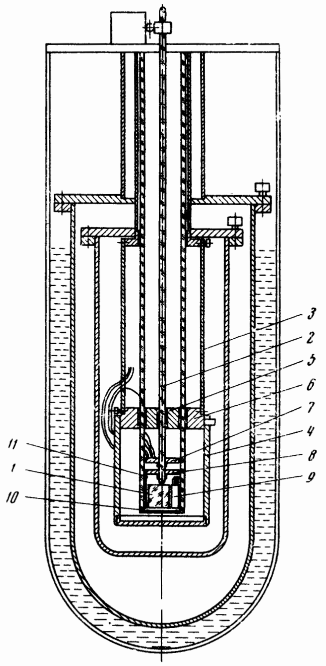

FIG. 2. Diagram of Strelkov dilatometer with improved thermostatic control: 1–sample, 2–quartz rod to transmit the elongation, 3–thin wall stainless-steel tube, 4–6–additional copper sheath, 7–8–copper plates; 9–thermometer, 10 and 11–horizontal and vertical gradient thermocouples.

The KDP single crystal was grown by I. V. Gavrilova (Crystallography Institute, USSR Acad. Sci.) and was used in[24]. It constituted a parallelepiped measuring 11.52 × 8.65 × (≈ 9) mm. The 8.65 and 9 mm edges were directed along the a_1 axes of the monoclinic unit cell[7]. The interference pattern in polarized light passing along the polar axis was a slightly diffuse cross. This made it possible to regard the homogeneity of the sample as fully satisfactory.

For a multidomain sample, the contribution of the shear component of the spontaneous deformation could not be taken into account, since this would require knowledge of the dimensions of the domains, their relative placements, and the configuration and dimensions of the voids that are possibly produced in the ferroelectric phase; to determine the volume expansion it is sufficient to measure only in two directions: along the polar axis ($n_{\parallel}$, Fig. 3; n—divisions of the dilatometer scale; each division equals ≈ 170 Å) and perpendicular to it ($n_{\perp}$, Fig. 4). The expansion was measured isothermally, point by point. The constancy of the temperature at each point reached $\pm (1-5) \times 10^{-3}$ deg/hr. For a more exact determination of the sample temperature,

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[4)] The preference given by Reese and May [10] to the logarithmic singularity seemed to us little founded, since in order to make it symmetrical they had to assume different values of T_c for the right and left branches.

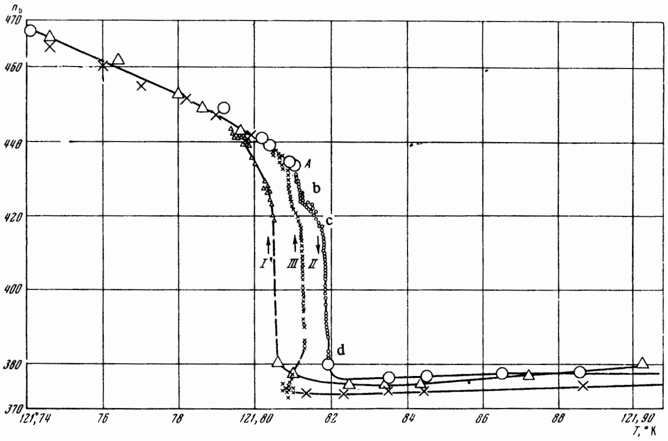

FIG. 3. Temperature dependence of the elongation along polar axis a_1 near the transition point.

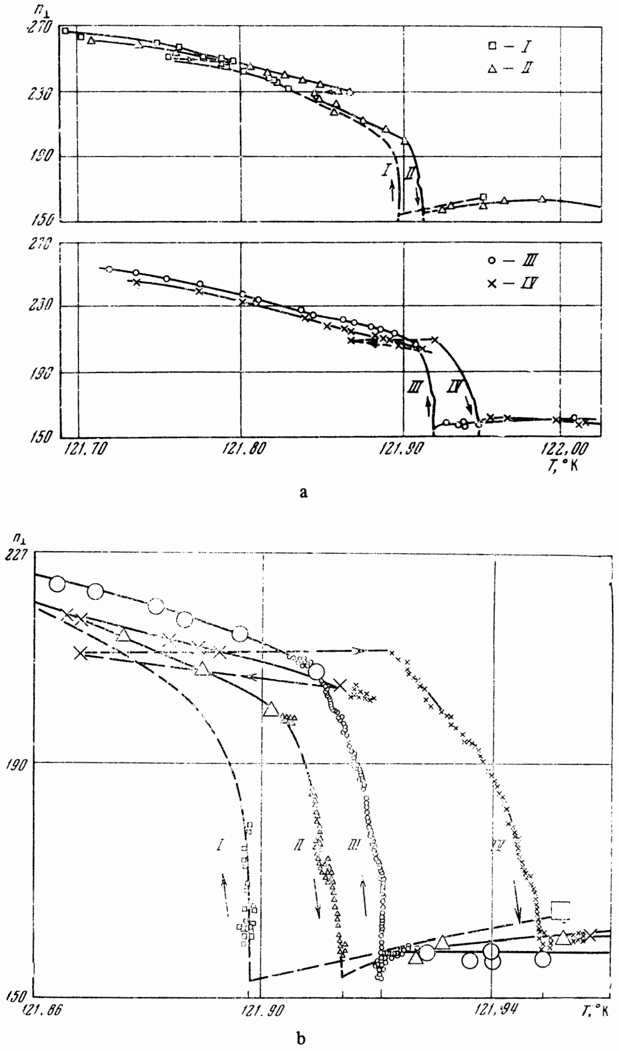

FIG. 4. Temperature dependence of elongation in a direction perpendicular to the polar axis near the transition point.

we measured the "course" of the temperature with time. The values of the elongation were plotted every 20–30 sec, on the same time scale as the temperature. The large number of expansion readings in each "course" has made it possible to get rid to a considerable degree of random scatter and to attain the most reliable values of the expansion with the maximum accuracy (≈ 170 Å). In these cases the equivalence of the result could be monitored by examining how the expansion "course" "followed" the variation of the temperature "course".

All the $n_{\parallel}(T)$ curves were obtained continuously one after the other without heating or cooling the sample by more than 0.3° from the transition point. The sample was then rotated 90° at room temperature, after which $n_{\perp}(T)$ was measured just as continuously as $n_{\parallel}(T)$.

3. MEASUREMENT RESULTS

The measurement results are shown in Figs. 3 and 4 and in Tables I–V.

Table I. Dependence of elongation* along the polar axis on the temperature**

$n_{\parallel}$	$T-121°K$	$n_{\parallel}$	$T-121°K$	$n_{\parallel}$	$T-121°K$	$n_{\parallel}$	$T-121°K$	$n_{\parallel}$	$T-121°K$	$n_{\parallel}$	$T-121°K$
469.5	7410	434.5	809_2	428	811_5	423	813_0	418	817_0	397	818_9
466.5	7460	433	810_0	427	811_6	425	813_1	417	817_1	393	819_0
461	7600	433	810_1	427	811_7	423	813_3	417	817_3	391	819_1
454.5	7700	433.5	810_3	427	811_9	422	813_4	416	817_6	389.5	819_2
452.5	7800	433	810_4	428	812_1	422	814_1	417	817_7	388	819_3
451	7820	433.5	810_5	423.5	813_0	422	814_3	416.5	817_8	382	819_5
449	7860	432	810_6	421.5	812_8	421	815_1	414	818_1	382.5	819_6
447	7900	432.5	810_7	425	812_6	423	815_2	411	818_2	381.5	819_7
449	7920	432	810_8	425	812_5	422	815_3	411	818_3	376	836_0
443	7947	430	811_0	424	812_4	420	816_1	409	818_4	377	846_0
442.5	7960	429	811_1	423	812_3	419	816_2	407	818_5	377.5	866_0
441.5	7990	428.5	811_2	425,5	812_2	421	816_3	405.5	818_6	377.5	887_0
441	8020	429.5	811_3	425	812_1	418	816_8	403	818_7	377.5	909_0
439	8040	428.5	811_4	426	812_0	417	816_9	398.5	818_8	377.5	955_0
										379	986_0
										373.5	985_0

*The values of $n_{\parallel}(T)$ near the hysteresis are given only for curve II of Fig. 3.

**The temperature column shows only the figures on the right of the decimal point, for example $T - 121°K = 0.741_0°K$.

The temperature dependence of the elongation is shown in Figs. 3 and 4; the directions of the measurements are indicated by the arrows. For curves II of Fig. 3 and curves III of Fig. 4, we present the values of the experimental points in Tables I and II respectively. These tables were used to plot the thermal expansion coefficients $\alpha_{\parallel}$ and $\alpha_{\perp}$ against the temperature (Table III). In Table IV it is possible to trace the shift of the transition point after the heating of the sample. The first value is taken from[24]. In Table V are given the values of the transition temperatures for each $n_{\perp}(T)$ and $n_{\parallel}(T)$ curve.

The obtained data can be briefly described as follows:

1. The curves of the longitudinal elongation $n_{\parallel}(T)$ (Fig. 3) show an abrupt break in the monotonicity of the elongation with change of temperature; this break occurs, so to speak, in two stages (segments AB and CD of curve II and the similar segments of curve III). Apparently such a segment, especially CD, can be treated as an elongation jump connected with the polarization jump. The elongation jump amounts to $\delta(\Delta l/l)_{\parallel} \approx (6\text{–}10) \times 10^{-3}\%$.

2. The behavior of the elongation in the longitudinal

Table II. Dependence of elongation* in the direction perpendicular to the polar axis on the temperature**

$n_\perp$	$T-121°K$	$n_\perp$	$T-121°K$	$n_\perp$	$T-121°K$	$n_\perp$	$T-121°K$	$n_\perp$	$T-121°K$	$n_\perp$	$T-121°K$
253	720_4	205	909_6	198	913_4	186	917_3	170	920_5	157	923_4
250.5	736_6	203.5	909_7	197	913_6	184	917_4	168	920_4	157.5	923_5
246.5	755_6	204	909_9	197	913_7	184	917_5	165	920_3	158	923_7
243.5	775_2	204	910_1	196	913_8	183	917_6	162	920_2	158	924_3
238.5	801_1	203.5	910_2	196	914_0	182.5	917_7	157	920_1	158.5	924_5
233.5	810_8	204	910_3	195	914_2	181.5	917_8	153.5	920_0	157	924_6
232	810_2	203	910_5	195	914_4	180.5	917_9	153	919_9	156	925_5
224	845_8	203	910_6	194	914_5	180	918_0	153.5	919_8	157	925_6
227	838_3	203	910_7	192,5	914_7	179	918_1	154	919_7	158	925_9
221	864_1	202	910_8	193	914_8	178,5	918_2	155	919_6	157	926_5
219.5	870_8	201	910_9	192	915_0	178	918_3	155	919_5	157.5	927_0
217	881_3	201	911_1	192	915_2	176.5	918_5	156.5	919_6	157	927_1
214.5	886_3	201.5	911_2	191.5	915_3	176	918_7	155	919_8	157	928_0
212,5	895_8	201	911_4	191	915_4	176,5	918_8	154	919_9	156	928_3
208.5	905_0	200.5	911_5	190.5	915_6	175.5	918_9	156	920_1	157	928_9
208	905_1	199.5	911_7	190	915_7	175	919_0	155	920_3	156	929_5
208.5	905_3	199	911_8	189.9	915_9	174	919_2	157	920_5	157	930_3
208	905_4	199	911_9	189	916_0	173.5	919_4	156	920_8	156,5	939_7
208	905_6	199	912_1	189	916_1	173	919_5	157	920_9	155,5	938_9
208	905_8	199	912_4	188,5	916_2	172.5	919_6	156	921_2	155,5	948_2
207	907_5	198.5	912_5	188,5	916_4	172,5	919_7	156	921_3	159.5	1.009_7
207.5	907_6	199	912_6	188	916_6	172	919_8	156	921_6	158,5	$1,035_3$
208	907_8	198.5	912_8	187.5	916_7	171,5	919_9	157	921_9	157.5	1.056_6
208	908_0	193	912_9	188	916_9	171	920_0	157	922_2		
207	908_3	198	913_1	187	917_0	170.5	920_1	157	922_7		
206	909_0	197.5	913_3	185,5	917_1	170.5	920_3	156.5	922_9		

*Curve III, Fig. 4.

**The temperature column shows only the figures on the right of the decimal point, for example T – 121° K = 0.741_0°K.

Table III. Dependence of the coefficient of thermal expansion on the temperature*

$-\alpha_\parallel \cdot 10^4$, deg^{-1}	$T-121$ °K	$\alpha_\parallel \cdot 10^4$, deg^{-1}	$T-121$ °K	$\alpha_\perp \cdot 10^4$, deg^{-1}	$T-121$ °K	$\alpha_\perp \cdot 10^4$, deg^{-1}	$T-121$ °K
5,8	752_5	28	816_0	—3.4	728_5	—550	920_1
9.3	772_0	125	817_8	—1.8	755_9	—480	920_3
9.1	785_0	500	818_6	—3.8	793_0	+30	920_5
8.3	796_0	330	819_2	—3.6	827_9	+17	921_1
15.0	805_6	31	820_8	—2.5	854_3	+17	921_5
35	810_0	0.60	829_0	—2.9	873_8	+6	922_3
83	811_0	0,66	851_0	—5.4	894_9	+3	923_9
50	811_9	0.40	876_5	—21	909_3	+0,5	927_6
28	813_6	0,05	920_0	—34	914_6	+0.2	939_8
				—96	917_5	+0.5	979_5
				—63	919_2	+0.6	1.033_1

*The temperature column shows only the figures on the right of the decimal point, for example t – 121° K = 0.741_0°K.

direction differs very strongly from the behavior in the transverse direction. First, accurate to 170 Å, it was impossible to observe the jump of $n_\parallel(T)$. The segment of 17 divisions on curve III of Fig. 4b, similar to segment CD of curve III of Fig. 3, is more likely to be connected with supercooling than with the jump of the expansion. Second, the hysteresis phenomena, although distinctly appearing in both cases, differ greatly in magnitude and character. The supercooling reaches 0.05 deg in case $n_\perp(T)$, and not more than 0.015 deg in the case $n_\parallel(T)$. In addition, all the hysteresis loops of the $n_\parallel(T)$ curves converge rapidly below the transition point, and above the transition point the ambiguity of the expansion extends beyond 0.1°. In the case of $n_\perp(T)$, to the contrary, there is practically no hysteresis above the transition point, and below T_{tr} it extends beyond 0.2°. Third, on the $n_\perp(T)$ curve (Fig. 4b, curve III) one can clearly see a characteristic "hook" at the transition point. The smeared "hook" can be discerned also on the non-equilibrium curve IV of Fig. 4b. However, as can be seen from curve III of Fig. 3, such a singularity of expansion is missing from $n_\parallel$. The "hook" appears on the $\alpha_\perp(T)$ dependence as a positive spike (Table III), and its height is almost 20 times larger than the peak of α in[24], which was interpreted there as going to infinity.

Table IV. Shift of transition temperature

Date (year, month)	History of sample	Direction of measurements relative to the polar axis	T_{tr} °K
1966, X	Initial sample	∥	121.3±0.4
1966, IX	Crystal cut in half. Section plane perpendicular to polar axis	⊥	121,3±0.3
1967, III — V	Heated to 190°C, and then cooled to 20°C within approximately one hour	∥	122,00±0,02
1967, V — VI	Heated to 20°C	∥	121,90±0.01
1967, VI	Heated to 20°C	∥	$121.80_5 \div 121{,}82_0$
1967, XI	Polished in the plane of the polar axis	⊥	121,90÷121,95
1967, XII	Heated to 20°C	∥	121.86÷121.91

Table V. Transition temperature for different measurement runs

$n_\parallel(T)$, fig. 3		$n_\perp(T)$, fig. 4	
Curve number	T_{tr} °K	Curve number	T_{tr} °K
I	$121.805_5 \pm 0.0005$	*I*	121.898±0.0002
		II	121.914±0.001
II	$121.818_5 \pm 0.0005$	*III*	$121.920_5 \pm 0.0005$
III	$121.812_5 \pm 0.0005$	*IV*	$121.948_5 \pm 0.0005$

The presence of the "hook" cannot be attributed to elastic indentation of the quartz rod 4 into the surface of the crystal (Fig. 2), if it is assumed that the stiffness of the isolated crystal has no anomaly at the Curie point[7]. In fact, according to[27], the indentation is determined by the relation

$$h = 0.75F^{2/3}\left(\frac{1-\sigma^2}{E}\right)^{2/3} R^{-1/3} \leqslant 0.75F^{2/3}E^{-2/3}R^{-1/3},$$

where h is the depth of indentation, F is the weight of the rod, σ is the Poisson coefficient, E is Young's modulus, and R is the radius of the surface of the rod at the point of contact with the surface of the crystal. For F = 10 g, R = 0.05 cm, and E ≈ 6×10^{11} dyne/cm^2, h amounts to 10–15 divisions and is practically independent of the temperature. The jumps of the Young's modulus at the point T_c[7] lead to a slight additional indentation amounting to 1–2 divisions. It can be assumed, however, that the stiffness may decrease by 40–50% directly at the transition point ($\tau < 10^{-3}$ deg), owing to the very rapid change of the polarization. In this case the presence of the "hook" can be attributed to reversible indentation.

3. The transition temperature is 121.80°K for $n_\parallel$

and 121.90°K for $n_{\perp}$. Inasmuch as the subsequent measurement of $n_{\parallel}$ yielded $T_c \approx 121.88°K$ (Table IV), it can be assumed that the transition temperature is actually the same for $n_{\parallel}$ and $n_{\perp}$.

4. Even relatively slow changes of the temperature have led to hysteresis phenomena. It can be verified that the temperature drift $dT/dt \approx 5 \times 10^{-4}$ deg/min, which is assumed in calorimetry, is frequently too rapid for KDP near the transition. Let us examine curve IV of Fig. 4 (the crosses). At a temperature 121.92°K, a random cooling of the sample by 5×10^{-2} deg took place, at a rate $dT/dt \approx -3.5 \times 10^{-3}$ deg/min, followed by heating to the previous temperature with $dT/dt \approx +4 \times 10^{-3}$ deg/min. The dashed line with the arrows shows the change of the dimension and of the temperature of the crystal. It is obvious that the drift $dT/dt \approx +4 \times 10^{-3}$ deg/min is infinitely rapid for the expansion of KDP in a direction perpendicular to the polar axis, since the dimensions of the crystal remain practically unchanged. Moreover, a temperature drift smaller by one order of magnitude also leads to a nonequilibrium result, wherein the transition (curve IV, Fig. 4, interval 121.9222–121.947°K), plotted at $dT/dt \approx +5 \times 10^{-4}$ deg/min, turns out to be strongly elongated compared with the transition plotted at a rate $dT/dt \approx +10^{-4}$ deg/min (curve II, Fig. 4b). Even relatively far from the transition, a change in the direction of the measurements of $n_{\perp}(T)$ always led to hysteresis of the elongation: on curve I of Fig. 4 at 121.765° (squares) and on curve II at 121.870°K (triangles).

4. DISCUSSION OF OBTAINED DATA

A. Jump of Volume

In spite of a certain slope of the $n_{\parallel}(T)$ curves in segments AB and CD of curve 1 of Fig. 3, these segments can be regarded as elongation jumps. In fact, there are a number of reasons for the smearing of the jump: inhomogeneity of the sample (distorted picture of the interference in polarized light), internal stresses (shift of the transition point, Table IV), possible lag of the sample temperature relative to the thermometer temperature owing to the latent heat. We know of no case in which the region of the smearing of the anomaly in the solid was smaller than 0.001°. We therefore assume that segments AB and particularly CD are elongation jumps stretched by ≈ 0.002°.

Attention is called to the stepwise character of the anomaly of $n_{\parallel}(T)$ (Fig. 3). Such an effect can be the result of the following causes.

First, the crystal consists of two unequal blocks. The smaller becomes depolarized in small sets, starting with the point A and ending with the point B, and the polarization of the larger block changes immediately over its entire volume (CD). Then

$$\Delta n \infty \Delta \mathcal{P}_s^2 = \int\limits_{T_{AB}}^{T_{CD}} \frac{\partial(\mathcal{P}_s^2)}{\partial T}\, dT$$

is a measure of the difference of the energies of activation of these processes. Here $\mathcal{P}_s$ is the spontaneous polarization and T_{AB} and T_{CD} are the temperatures of the left and right peaks of $\alpha_{\parallel}(T)$.

The segment AB corresponds to a continuation of the smooth depolarization process, wherein the disorder occurs inside the domains, but the interface between them remains constant; the segment corresponds to a jumplike vanishing of the spontaneous polarization, accompanied by the vanishing of the domain boundary. In this case Δn is a measure of the activation energy necessary in order for the process of the change in the area of the domain-wall surface to begin.

Third, the segment AB corresponds to the termination of the ferroelectric transition of the Landau critical-point type with $T_c = T_{AB}$, and the elongation jump is caused by some other factor changing the lattice parameter, but not by the change of polarization.

We consider the first of the foregoing causes to be the most probable and the third the least probable. Arx and Bantle[19], in measurements of the inverse piezoeffect, have noted that one of their crystals consisted of three approximately equal parts, which were deformed in succession as the crystal polarization was reversed. When the polarization of the crystal changed from $\mathcal{P}_s$ to zero in three jumps, each of these jumps corresponded to deformation of only one part of the crystal. They had, on the other hand, another crystal, which became repolarized without noticeable Barkhausen jumps, but its surface became hilly, in other words, the polarization jumps were very small, were effected in small volumes, and were well averaged over the entire crystal. Of course, when the field is applied, the domains always become larger and such a polarization-reversal process cannot be compared directly with the ordering process. However, the case described by Arx and Bantle[19] offers evidence that, depending on the individual properties of the sample, the ordering can occur either in large groups of domains that correlate with one another, or in small ones. It is not excluded that both these possibilities are combined in our crystal, and the segment AB corresponds to depolarization in small steps, while the depolarization in segment CD occurs immediately in a large volume. This does not contradict the fact that the segment AB has a smaller slope than CD (the left peak of $\alpha_{\parallel}(B)$ is approximately one-sixth as large as the right peak, see Table III).

Favoring the block structure is also the fact that supercooling causes the slope of the upper jump to become almost the same as that of the lower one, and the temperature difference of the jumps decreases strongly (by almost a factor of two). Incidentally, whereas one can attempt to explain the small difference $T_{CD} - T_{AB}$ itself as being due to the lag of the sample temperature relative to the thermometer temperature as a result of the latent heat of the transition, it is impossible to attribute the decrease of $T_{CD} - T_{AB}$ to such an effect, and all the more it is impossible to attribute to this lag the increase of the slopes of the jumps upon supercooling. Apparently, if the lag does exist, it acts only as one of the factors that smear out the jumps.

If the second cause is valid, then the steplike character of the anomaly is a property possessed by all the multidomain samples, but if the first cause is valid, then it is possessed only by few of them. Finally, this question can be solved only on the basis of experiments with the best crystals.

If the first cause is valid, then the jump in the expansion is the entire segment AD and $\delta(\Delta l/l)_{\parallel} \approx 1 \times 10^{-2}\%$. If the second cause is valid, then the jump must be identified with the segment CD, and $\delta(\Delta l/l)_{\parallel} \approx 6 \times 10^{-3}\%$. The accuracy with which the jump is determined under any of the assumptions is better than ±10%. However, recognizing that the jump AB can be the consequence of the joint action of both causes, we are justified only in stating that $6 \times 10^{-3}\% \leq \delta(\Delta l/l)_{\parallel} \leq 10 \times 10^{-3}\%$. Since no jumps were observed on the $n_{\perp}(T)$ curves, we assume that the $\delta(\Delta V/V) = \delta(\Delta l/l)_{\parallel}$.

Thus, the ferroelectric transition in a multidomain KDT crystal[5] is classified as a first-order transition close to the point of the second order transitions.

B. Latent Heat of Transition

It was noted in[2] that the applicability of the Clapeyron-Clausius equation to the experimentally determined slope of a phase-transition line is not an independent criterion for the classification of any particular order-disorder transition. In such a verification one usually determines $(\Delta V/V)_{\text{tot}}$ and Q_{tot}, integrating the peaks of the thermal expansion coefficient and of the specific heat, similar to those shown in Fig. 1. It is then assumed that these volume and thermal effects have occurred isothermally at T_{tr}. The accuracy with which these quantities are determined is not better than 10–50%, both as a result of the errors arising in the integration of the wings of the smeared peak, and as a result of the error arising in measuring the area near T_{tr} under the high and narrow part of the peak. The value of Q_{tot} obtained for KD_2PO_4[7] is almost half the value measured in[28], precisely because of the insufficiently detailed measurements[7] near T_{tr}. Within the limits of such an accuracy and the usual approximations to T_{tr}, it is possible to describe the ordering process by the Landau theory[5]. It will be shown with the aid of this theory that the Clapeyron-Clausius equation is automatically satisfied regardless of whether there exist or do not exist jumps of the entropy $(\Delta S)_{T_{\text{tr}}}$ and of the volume $(\Delta V)_{T_{\text{tr}}}$, provided Q_{tot} and $(\Delta V/V)_{\text{tot}}$ are referred to the transition point T_{tr} (or T_c).

According to[5], the anomalous part of the potential $\Phi(P, T)$ can be represented by an expansion in even powers of η:

$$\Phi - \Phi_0 = A(P, T)\eta^2 + B(P, T)\eta^4 + C(P, T)\eta^6 + \ldots \quad (1)$$

We differentiate (1) with respect to T and P, bearing in mind that $\partial(\Phi - \Phi_0)/\partial\eta = 0$, and then, neglecting the terms with η^4 and η^6, we obtain for the excess entropy $(S - S_0)$ and volume $(V - V_0)$ the expressions

$$\begin{aligned} -(S - S_0) &= (\partial A/\partial T)_P\eta^2 = a_P\eta^2, \\ V - V_0 &= (\partial A/\partial P)_T\eta^2 = a_T\eta^2, \end{aligned} \quad (2)$$

where a_P and a_T are constants determining the linear dependence of A on T and P. The phase-transition line is determined by the condition $A(P, T) = 0$, i.e., at the transition point $P_c = f(T_c)$, and consequently

$$(\partial A/\partial T)_{P_c} = (\partial A/\partial P)_{T_c} dP_c/dT_c,$$

i.e.,

$$a_{P_c} = a_{T_c} dP_c/dT_c. \quad (3)$$

Recognizing that Q_{tot} and $(\Delta V/V)_{\text{tot}}$ are defined in a rather narrow temperature interval (1–5°), where the transition line is straight in the first approximation, we can assume, accurate to 1–10%, that a_T is independent of the temperature and equals a_{T_c}. The question of the temperature dependence of a_{P_c} does not arise, since the process is isobaric. Thus, replacing a_T and a_P in (2) by a_{T_c} and a_{P_c}, we obtain

$$\frac{S - S_0}{V - V_0} = -\frac{a_{P_c}}{a_{T_c}} = -\frac{dP_c}{dT_c}, \quad (4)$$

meaning that

$$\left(\frac{\Delta S}{\Delta V}\right)_{T_{\text{tr}}} = \left(\frac{\partial S}{\partial V}\right)_{T_c\, P_c} = T_c V_c \frac{Q_{\text{tot}}}{(\Delta V/V)_{\text{tot}}}. \quad (5)$$

In other words, (5) is valid both for transitions with true jumps at T_{tr}, and for continuous transitions $(\partial S/\partial V)_{P_c T_c} = -dP_c/dT_c$. This conclusion holds to an equal degree for both second-order transitions (B > 0 in expansion (1)) and for the critical point of second-order transitions (B = 0), because only the first term of the series has been used for the determination of ΔS and ΔV.

Naturally, an attempt to verify the jump character of the transition with the aid of the Clapeyron-Clausius equation $\Delta S/\Delta V = -dP_c/dT_c$ is not productive. But we are attracted by the possibility of determining dP_c/dT_c from Q_{tot} and $(\Delta V/V)_{\text{tot}}$, which can be measured with an accuracy 2–5 times larger than the true jumps of T_{tr}. For example, for KDP there are data for ΔS_{tot}[7] and for $(\Delta V/V)_{\text{tot}}$[23]. Recognizing that in[7] are given two values of ΔS_{tot}, belonging to different authors (0.47 and 0.74 cal/mole-deg), we obtain

$$dP_c/dT_c = \frac{\Delta S_{\text{tot}}\, d}{(\Delta V/V)_{\text{tot}} M} \approx -(2-3)\cdot 10^2 \,\frac{\text{atm}}{\text{deg}},$$

where d is the density of the KDP and M is the molecular weight.

With the aid of (5) it is also possible to estimate Q_{lat} for our sample, using the value obtained here for the volume jump $\Delta V/V = \delta(\Delta l/l)_{\parallel} = (6-10) \times 10^{-5}$. We have

$$Q_{\text{lat}} = \left(\frac{\Delta l}{l}\right)_{\parallel} Q_{\text{tot}} \Big/ \left(\frac{\Delta V}{V}\right)_{\text{tot}}. \quad (6)$$

According to Bantle $Q_{\text{tot}} = 57$ cal/mole, and according to Stephenson and Hooley $Q_{\text{tot}} = 87$ cal/mole[7]. Substituting in (6) various values of Q_{tot} in $(\Delta l/l)_{\parallel}$, we find that

$$8\ \text{J/mole} \leqslant Q_{\text{lat}} \leqslant 20.5\ \text{J/mole}.$$

It must be borne in mind here that the value of Q_{lat} depends much more strongly on the individual properties of the sample, and therefore the numerical value of Q_{lat} pertains only to our sample, while the presence of latent heat is attributed to all multidomain samples.

Incidentally, the energy of the domain separation boundary, being proportional to η^2[29], is automatically taken into account by the coefficient A in the expansion (1).

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[5] We recall that there exists a certain probability that the jump is due to uniformly distributed impurity, which hinders the growth of the domains uniformly in the entire crystal.

We see that the accuracy with which Q_{lat} is determined with the aid of (5) is of the same order as in the direct measurement of Q_{lat}. For example, in[2] Q_{lat} has been determined accurate to ± 500%.

C. Ideal Sample

It is known[7,29] that the shear component of the spontaneous deformation causes the domains to be crystallographic twins. Since it is difficult to expect that the formation and growth of the twin structure can occur without an activation energy, it is probable that the step-like character of the anomaly of $n_{||}(T)$ and the hysteresis of n(T) are due precisely to the need for accumulating a certain electrostatic energy to overcome the activation energy of the domain growth. Thus, it can be assumed that the hysteresis of n(T) observed by us is due to the same causes as the Barkhausen jumps in[19]. Probably, if the domains could change their form independently of one another, then the transition in KDP would be of second order, or more readily a critical point. One can attempt to realize such a sample with the aid of a briquette of single-domain particles of KDP of "diameter" $\approx 10^{-5}$ cm[29]. The particles should be pressed in such a way that electrically they are equivalent to a multidomain sample, and mechanically to a free crystal. Since it is known that the maximum possible dislocation density is 10^{12} cm^{-3}, it can be readily understood that particles with "diameter" 10^{-8}—10^{-6} cm will have no dislocations, no matter how obtained. This leads to the paradoxical conclusion that the homogeneity of a briquette made of single-domain particles will be comparable with or even better than the homogeneity of perfect single crystals, and the results obtained with such a sample can be set in correspondence with theoretical calculations for an infinite system. The strongest stimulus for work in this direction is the fact that the Slater model corresponds to a two-dimensional Ising model[29].

5. BRIEF CONCLUSIONS

1. A volume jump of magnitude (6—10) × 10^{-3}% was observed at the point of the ferroelectric transition in an isolated KDP crystal.

2. Temperature hysteresis of elongation was observed. The known reproducibility of T_{tr} was ≈ 0.015 deg when $n_{||}(T)$ was measured, and approximately 0.05° when $n_{\perp}(T)$ was measured.

3. It is shown that near the transition point, $(T_{tr} - T) \approx 0.01°$, measurements performed at a temperature drift $\approx 5 \times 10^{-4}$ deg/min lead to non-equilibrium values of the measured quantity, particularly $n_{\perp}(T)$.

4. It was observed that in the case of rapid cooling (from 300 to 80°K within 2—3 hours), internal stresses are produced in the KDP sample, leading to shifts of the transition point.

5. The anisotropy of the anomalous part of the coefficient of linear expansion actually takes place only very close to the transition, $|T - T_{tr}| \lesssim 0.03°$.

6. It was shown that by means of integral thermal and volume effects it is possible to determine the slope of the line of the phase transitions independently of the presence of jumps of S and V at the transition point. The value of dP_c/dT_c estimated in this manner for KDP is $-(2-3) \times 10^{-2}$ atm/deg. With the aid of the same relations it is possible to determine the latent heat, if the volume jump is known. For our sample, an estimate yields $8 \leq Q_{lat} \leq 20.5$ J/mole.

7. Attention was called to the fact that in cases when doubts arise concerning the character of the transition, the alternative is a first-order transition or the critical point of second-order transitions, and not a first-order transition or a second-order transition.

8. It is concluded on the basis of an analysis of the published data that: a) if the presence of latent heat of the transition (the jump of η) is established at least in one of a set of samples, then the transition in the given substance if of first order; b) to the contrary, in order to state that there is no latent heat and to describe quantitatively the details of the anomaly in an ideal system, it is necessary to obtain experimental data in a sufficiently close vicinity of the transition point of the ideal substance, while data obtained for a sufficiently large set of samples of real materials, but not at T_{tr}, may turn out to be insufficiently reliable.

9. A special role in the process of ordering in KDP is played by the shear deformation, which causes differently-polarized domains to be crystallographic twins. The growth of the domains may be connected here with the presence of a certain activation energy, needed to change the separation boundary between them, as is frequently the case in the growth of an elastic twin. Apparently, the conclusions 1—4 are explained precisely by this circumstance.

10. The participation of the domain roles in the ordering process greatly limits the generality of the results obtained in concrete samples, and makes it practically impossible to compare the experimental and the theoretical results directly near T_c.

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223