PHYSICAL REVIEW B VOLUME 9, NUMBER 1 1 JANUARY 1974

Brillouin-scattering study of the elastic anomaly in ferroelectric KH_2PO_4[†][*]

Edward M. Brody
Institute of Optics, Materials Science Program, University of Rochester, Rochester, New York 14627

H. Z. Cummins[‡]
Department of Physics, New York University, New York, New York 10003

(Received 11 May 1973)

Brillouin-scattering measurements have been performed on potassium dihydrogen phosphate (KDP) in the temperature range $113 < T < 291$ °K with electric fields between 0 and 3937 V/cm. Values of the adiabatic x-y shear elastic constant $c_{66}^{E,S}$ deduced from the experiment are presented in tabular form. The data are compared with the predictions of several free-energy expressions. The Slater-SUS (Silsbee, Uehling, and Schmidt) theory is shown to predict values of the elastic constant in reasonable agreement with the experimental values, but the SUS parameters which provide the best fit to the elastic-constant data are somewhat different from those which give a best fit to spontaneous-polarization data. The data are also compared to the predictions of three phenomenological free-energy expressions which are all variants of the Landau-Devonshire power-series expansion. The simple molecular-field expression is shown to give poor agreement with the $c_{66}^{E,S}$ data, and to require parameter values for even a poor fit which then predict unreasonably large values for the spontaneous polarization. Two other phenomenological free energies are considered, one having a tenth-power nonlinear polarization term and predicting a second-order transition, and another, proposed by Benepe and Reese, having fourth- and eighth-power nonlinear polarization terms and predicting a slightly first-order transition. These two phenomenological free energies have previously been utilized in the analysis of various thermodynamic properties of KDP, and it is found that both are able to predict values for the elastic constant $c_{66}^{E,S}$ in reasonable agreement with experiment while providing adequate predictions for the spontaneous polarization with the same parameters. The behavior of $c_{66}^{E,S}$ within 0.1 °K of the transition, however, favors the Benepe-Reese free energy.

I. INTRODUCTION

The ferroelectric phase transition in potassium dihydrogen phosphate (KDP) has been studied extensively in recent years, and the paraelectric phase has by now been quite thoroughly characterized. There is still considerable uncertainty surrounding the properties of the ferroelectric phase, however, largely due to the very rapid increase of spontaneous polarization below the transition temperature $T_c = 122.00$ °K[1] and to the tendency of the crystal to form many small ferroelectric domains, which makes the interpretation of spontaneous-polarization and dielectric constant measurements extremely difficult.

Since KDP is piezoelectric in both the paraelectric and ferroelectric phases, the dielectric anomaly produces anomalous behavior in the elastic constant c_{66}^E, and accurate measurements of this constant can be used to improve understanding of the transition. The critical anomaly in c_{66}^E was first observed in the paraelectric phase by Mason in 1946.[2] It has subsequently been studied in detail with ultrasonic techniques in both the paraelectric and ferroelectric phases.[3] However, in the ferroelectric phase the scattering of ultrasound by the domains is so severe that measurements must be made in the presence of sizeable biasing fields which seriously distort the transition.

Brillouin scattering is a particularly suitable technique for studying the soft x-y shear acoustic mode (whose velocity is determined by c_{66}^E) in the ferroelectric phase since the scattering volume is very small (typically $1\times0.1\times0.1$ mm) and can be located anywhere within the crystal, while the results are relatively insensitive to the presence of domains. We have performed Brillouin-scattering measurements on KDP in the temperature range 113–291 °K, with electric fields of between 0 and 3937 V/cm applied along the ferroelectric axis. Preliminary results of the zero-field measurements were reported previously.[4] In this paper we present our data graphically and give the velocity and elastic constant results in tabular form.

We discuss the experiment and present the results in Sec. II. In Sec. III, we use our elastic constant data to test the predictions of several free-energy expressions. The Slater–Silsbee-Uehling-Schmidt free energy is considered first, and the Silsbee-Uehling-Schmidt (SUS) parameters which fit our data are given and compared with fits to polarization data.[5] We also consider three phenomenological expressions for the free energy, all of which are variants of the Landau-Devonshire power-series expansion. We find the parameters which produce best fits to our elastic constant data and compare with predictions for the spontaneous polarization. In particular, w show that the free-energy expression employed by Benepe and Reese to fit their recent spontaneous-polarization data predicts values for the elastic constant in reasonable agreement with our data.[6]

The principal thermodynamic relations used in the presentation of Sec. III are derived in the Appendix.

II. EXPERIMENT

Brillouin-scattering measurements were performed with a conventional 90° spectrometer consisting of a Spectra-Physics model No. 125 He-Ne laser producing 60 mW of 6328-Å multimode output, a pressure-scanned plane Fabry-Perot interferometer with mirror separations of 3, 10, 13, or 15 mm, pulse electronics, and a strip-chart recorder.[7]

A. Sample preparation

The scattering geometry was chosen to obtain spectra exhibiting only the x-y shear acoustic mode for which $v=(c_{66}/\rho)^{1/2}$. Since the phonon propagation vector q must lie along the x axis (or along the tetragonally equivalent y axis), the incident and scattered wave vectors $\vec{k}_0$ and $\vec{k}_s$ can lie either in the xy or xz plane. For 90° scattering, the appropriate choices for $\vec{k}_0$, $\vec{k}_s$ are either $[110], [\bar{1}10]$ or $[101], [\bar{1}01]$. Examination of the Brillouin tensors for this $\bar{4}2$-m crystal class shows that with the first choice the x-y shear mode is not active for any of the four polarization choices available, while for the second choice the x-y shear mode occurs alone in either H_V or V_H polarization.[8]

High-purity single crystals of KDP were obtained from Isomet[9] in the form of face-cut cubes approximately 1.25 cm on a side. Samples were prepared for use in the second geometry by grinding and polishing the four $\{101\}$ edges to make flat faces 3 mm wide and 1.25 cm high through which the laser beam and the scattered light could pass at normal incidence.

The shape of the samples viewed perpendicular to the y axis is shown in Fig. 1 along with Brillouin spectra obtained with the four polarization combinations V_V, V_H, H_V, and H_H. For the V_H polarization (which was the polarization actually used in the experiment), the spectrum shows only the x-y shear mode Brillouin doublet as predicted.

In order to maintain constant electrical boundary conditions, gold electrodes were applied to all z faces including the small $\{101\}$ faces through which the light passed. Eight windows were provided by placing circular masks 2.8 mm in diameter about $\frac{1}{3}$ and $\frac{2}{3}$ of the way up each (101) face before vacuum evaporation of the gold. Either the upper or lower set of windows could be used in an experiment which allowed us to check for vertical temperature gradients. The final configuration of the KDP samples is shown in Fig. 2.

This elaborate plating procedure was necessary for accurate measurements in the ferroelectric phase since spontaneous polarization causes a surface charge to accumulate on the z faces. If this charge is not eliminated by shorting, the electrical boundary conditions are unknown and not reproducible. Before the crystals were prepared with the gold electrodes, the acoustic-velocity measurement showed large hysteresis effects for a few degrees above T_c. When the crystals were plated, the hysteresis disappeared and the results were reproducible to ±0.01 °K, the reproducibility of our temperature measurement. It is inferred that the surface charge produced in the ferroelectric region persisted for a few minutes at temperatures greater than T_c.

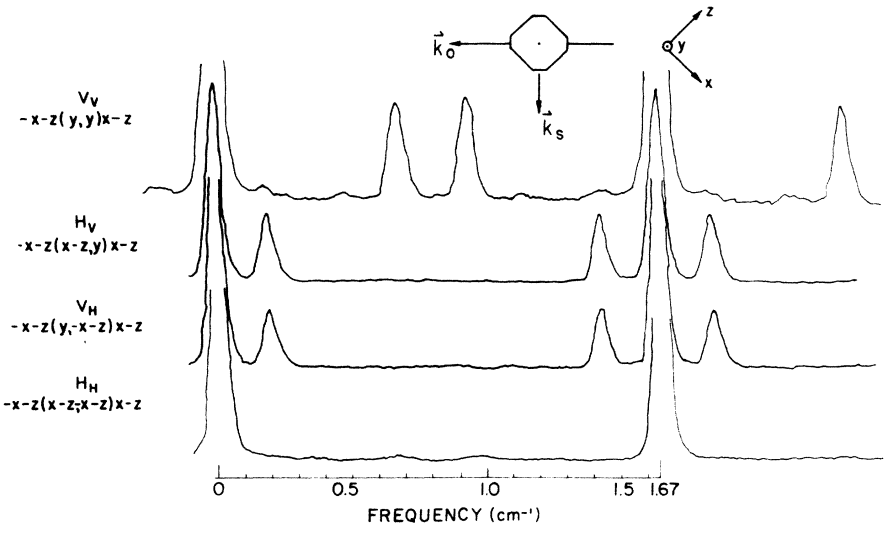

FIG. 1. Polarized Brillouin spectra of KDP at $T=300$ °K. Inset: view of crystal along the y axis showing orientation of $\vec{k}_0$ and $\vec{k}_s$. The xyz axes correspond to the crystallographic a, b, c axes.

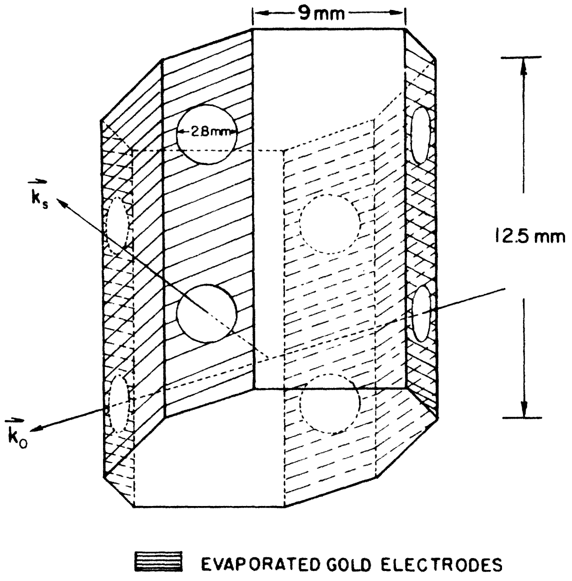

FIG. 2. KDP sample preparation for Brillouin-scattering experiment.

B. Temperature control and measurement

The sample temperature was controlled by a specially constructed Dewar shown in Fig. 3. The sample was placed in a cavity within a solid copper cylinder which was surrounded by polyurethane insulation and cooled by liquid nitrogen. The measured time constant for the cooling of the sample was 3.3 h. The sample space was filled with 2-methyl butane which served as a thermostating fluid, provided partial refractive index matching, and protected the surfaces of the water-soluble crystal from condensation. 2-methyl butane freezes at 110 °K, setting the lower limit to obtainable temperatures.

The sample temperature was controlled by a Fisher proportional temperature control with a thermistor sensor. The controller output, approximately 11 W at 122 °K, was applied to carbon resistors fixed into vertical columns with epoxy and distributed symmetrically about the axis of the copper cylinder.

The temperature was measured using two independently calibrated platinum resistance thermometers supplied and calibrated by the Rosemont Engineering Co. (model No. 118L).[10] Their resistance was measured with a dc Wheatstone bridge. One thermometer was placed in the fluid surrounding the KDP, 1 cm above the scattering volume. The readings from this thermometer were the source for all quoted temperatures. Corrections were made for lead resistance of the thermometer and for the temperature gradients in the sample cavity to deduce the absolute temperature at the scattering volume. It is estimated that the absolute temperature was precise to ± 0.1 °K, and that the precision relative to T_c was ± 0.01 °K.

A second thermometer was placed in the wall of the copper cylinder. When controlling temperatures near T_c, the two thermometers agreed to ± 0.03 °K, which shows that the temperature gradients in the sample volume were small.

Temperature gradients in the vicinity of T_c were measured by watching the motion of the interface between ferroelectric and paraelectric regions in several small plates of KDP, $3\times3\times1$ mm, cut from a single sample. The ferroelectric z axis was parallel to the 1 mm dimension. All plates were oriented in the sample volume with z axes in the $\vec{k}_0$ direction, which is shown in Fig. 3. By viewing in white light between crossed polarizers, the ferroelectric domain structure was easily seen and the interface, which is an isotherm at T_c, could be followed as a function of temperature. The gradients thus measured were

$$\Delta T_{\text{horizontal}} = \pm 0.002 \text{ °K/mm} ,$$

$$\Delta T_{\text{vertical}} = \pm 0.004 \text{ °K/mm} .$$

Since the scattering volume was a horizontal cylinder 1 mm long and 0.1 mm in diameter the maximum gradient in the scattering volume was ± 0.002 °K.

C. Measurement procedure and data reduction

In order to obtain reproducible spectra in the ferroelectric phase, it was necessary to follow a careful cooling procedure which minimized the possibility of damaging the crystal. The temperature was lowered slowly through T_c with an applied electric field of several kV/cm. For the zero-field measurements the field was reduced slowly to zero, allowing the temperature to equilibrate, and measurements were begun. The temperature was raised for each succeeding measurement. A sequence of readings was made over a period of several days so that there was no doubt that the temperature had equilibrated. The crystal was extremely sensitive during the temperature reduction through T_c. Unless the laser was attenuated by at least a factor of 10, the crystal cracked along the beam direction as the temperature was lowered through T_c.[11] The lowest temperature for which the Brillouin shifts could be measured with zero field was 118.72 °K. Below this temperature, the attenuation of the incoming beam, caused by domain scattering, reduced the scattered signal to a value too small to be accurately measured.

The temperature lowering procedure was repeated many times. The measured Brillouin shifts were reproducible with temperature and small excursions about T_c showed no hysteresis.

Examples of the spectra obtained are shown in Fig. 4. The Brillouin shifts decrease as T_c is approached from above or below. The increase of the Brillouin intensity which accompanies the decrease in the Brillouin shift has been discussed by Brody and Cummins and by Fritz *et al.*[12]

The sound velocity v was deduced from the measured Brillouin shifts $\Delta\nu_B$ from the relation[13]

$$\Delta\nu_B = vq/2\pi = v\,|\vec{k}_s - \vec{k}_0|/2\pi \xrightarrow[\theta\to 90^\circ]{} v(n_s^2+n_0^2)^{1/2}/\lambda_0\ , \quad (1)$$

where λ_0 is the vacuum wavelength of the incident light and n_s and n_0 are the refractive indices for the scattered and incident light. The adiabatic elastic constant $c_{66}^{E,S}$ was then deduced from the sound velocity v since $c_{66}^{E,S} = \rho v^2$.[14]

For our geometry $n_s = n_y$, and n_0 is calculated considering the anisotropy of the crystal.[15] It is an excellent approximation to let $n_0 = \frac{1}{2}(n_x + n_z)$. The values $n_x = n_y = 1.51$, $n_z = 1.47$, and $n_0 = 1.49$ were used. They have been extrapolated to T_c for $\lambda_0 = 6328$ Å from literature values.[16] The value of the density $\rho = 2.38$ gm/cm^3 was extrapolated to T_c also. The change in the value of n and ρ over the temperature range 112–122 °K was estimated to change the multiplicative factor which converts frequency shifts to velocities by less than 0.1% and this temperature dependence was not included in the calculations in Table I. For the paraelectric data in Table II, the temperature dependence of n and ρ is slightly greater due to the larger temperature range and has been included in the analysis.

The elastic constant $c_{66}^{E,S}$ as a function of tem-

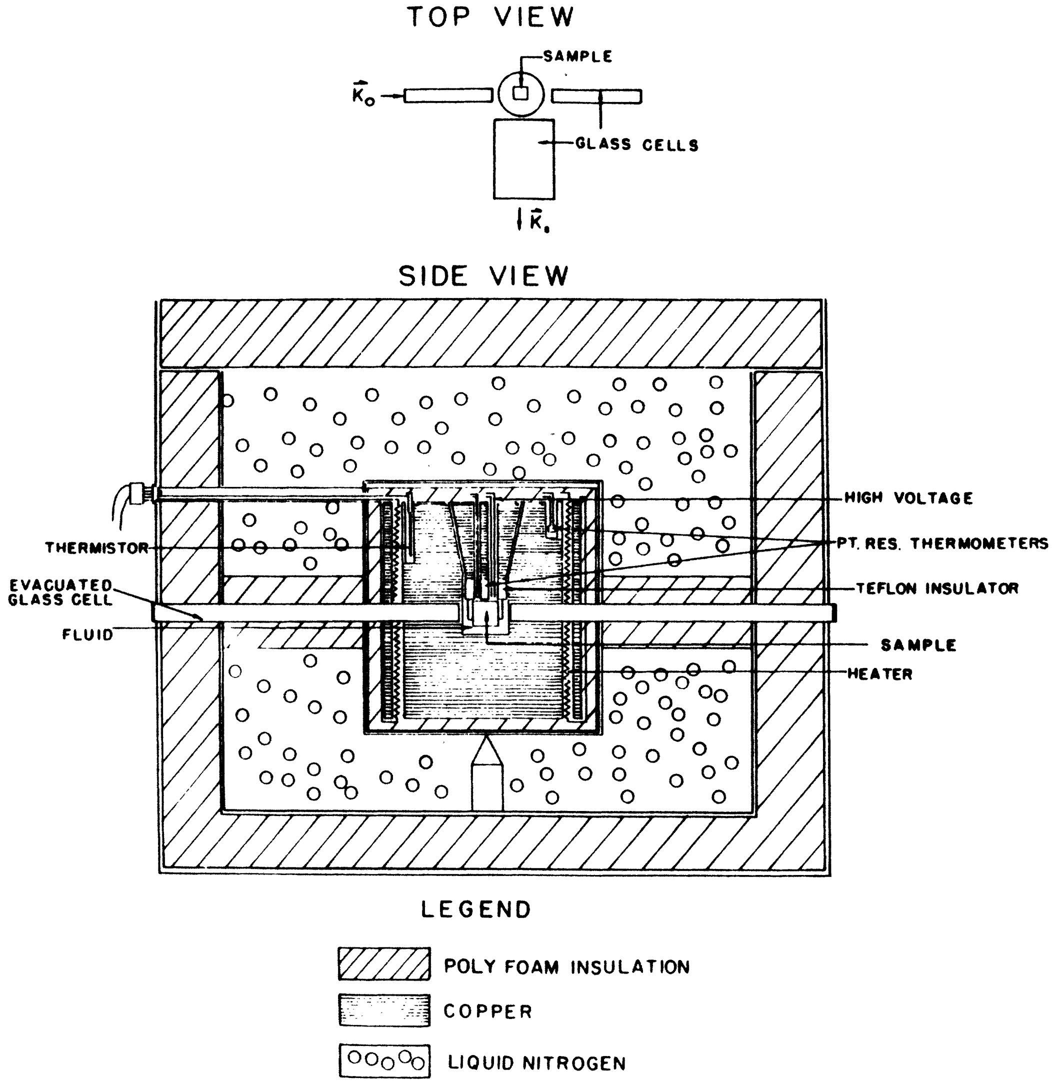

FIG. 3. Schematic diagram of Dewar construction. Inset: top view showing optical access to the sample.

perature is plotted in Fig. 5 for electric fields of 0, 500, 787, and 3937 V/cm. Note that increasing the electric field always increases the elastic constant at any temperature, and that the general effect of a nonzero field is to smooth out the transition. Similar rounding was observed when samples without electrodes were used, showing that the buildup of surface charge due to spontaneous polarization produces depolarizing fields large enough to significantly distort the phase transition.

Brillouin shifts for the $E=0$ data below T_c are listed in Table I along with the sound velocity and elastic constant derived from the experiment. There has been no attempt to smooth the data, and in some cases there is a small departure from monotonic temperature dependence, for instance, at 120.86 °K. For the least favorable measurements, close to T_c, the errors in $c_{66}^{E,S}$ may be large as 5%. Data for $E=0$ measurements above T_c are given in Table II, and $E\neq 0$ data are given in Table III.

Where errors are quoted in the Tables they represent the maximum excursion from the average value for several measurements made on the same sample. The measurements were made at different times and the past history of the sample was different for each measurement. The rather large errors from 121.97 through 122.00 °K are due to the fact that the slope of c_{66}^{E} with temperature is large and the 0.01 °K uncertainty in reproducing the temperature causes comparably large variations in the elastic constant. For temperature less than 121.97 °K it is estimated that the velocities were reproducible to ± 1% and $c_{66}^{E,S}$ to ± 2%. These errors are greater than the uncertainty in the value of n and ρ which were used to calculate v and $c_{66}^{E,S}$.

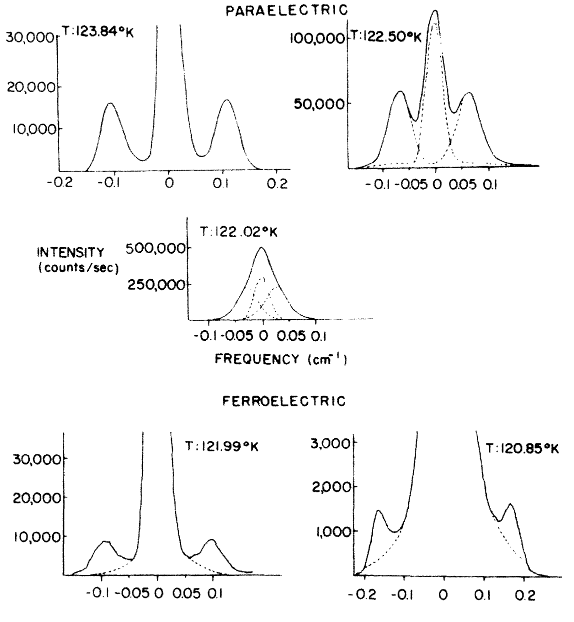

FIG. 4. H_V polarized Brillouin spectra of KDP with $E=0$ at five temperatures in the vicinity of the transition temperature T_c.

The sharp rise in the elastic constant below T_c could be discontinuous. The most successful phenomenological free energy in fitting our data predicts a discontinuous rise to 1.60×10^{10} dyn/cm^2 at T_c.[17] It is possible that the measurements made within 0.01 °K below T_c, which show a value as small as 0.45×10^{10} dyn/cm^2, indicate superheating since the value was not stable. It decreased from 1.60×10^{10} to 0.45×10^{10} dyn/cm^2 (the smallest resolvable value in the ferroelectric phase) over a period of 15 min, and the crystal became paraelectric.

The free energy predicting this discontinuous transition, called G_3 in Sec. III, also predicts that the transition occurs 0.012 °K above the Curie temperature. This means that c_{66}^{E} never reaches zero in the paraelectric phase. The prediction, using Eq. (8), is that in the paraelectric phase $c_{66}^{E}|_{T_c^+} = 0.021\times 10^{10}$ dyn/cm^2, $v|_{T_c^+} = 0.094\times 10^5$ cm/sec, and $\nu|_{T_c^+} = 0.31\times 10^9$ Hz (0.01 cm^{-1}). This frequency shift is not resolvable with the multimode laser we were using since it had a half-width at half-maximum of 0.02 cm^{-1}.

The Brillouin experiment should be repeated in the vicinity of T_c with a single frequency laser to look for discontinuities and hysteresis effects in $c_{66}^{E,S}$.

III. ANALYSIS

The temperature dependence of the soft acoustic mode in KDP can be discussed within the framework of a dynamical theory of piezoelectrically coupled acoustic and optic modes where the optic mode is the ferroelectric soft mode associated with the spontaneous polarization P_3.[4,12,18]

For KDP, however, the long-wavelength acoustic-mode frequency is so much lower than the characteristic frequencies of the polarization dynamics that the acoustic modes may be described thermodynamically in terms of an elastic constant c_{66}.[2] Empirical justification for this approach is found in the agreement between elastic constants obtained from Brillouin scattering and those obtained from ultrasonic experiments at much lower frequencies.[3]

The thermodynamic analysis proceeds from a free energy constructed from some combination of statistical mechanics and phenomenology. For example, Slater's statistical theory may be used to specify $A_0(P,T)$, the free energy of the polarization P in a rigid lattice, and the elastic and piezoelectric energy can then be added phenomenologi-

TABLE I. Temperature dependence of the Brillouin shift frequency ν_B, sound velocity v, and adiabatic elastic constant $c_{66}^{E,S}$ at zero electric field for ferroelectric KDP ($T < T_c$).

T (°K)	ν_B (10^9 Hz)	v (10^5 cm/sec)	$c_{66}^{E=0,S}$ (10^{10} dyn/cm^2)
122.00	1.46–2.78	0.44–0.83	0.45–1.6
121.99	$3.15^{+0.21}_{-0.48}$	$0.94^{+0.06}_{-0.15}$	$2.10^{+0.28}_{-0.60}$
121.98	$3.42^{+0.22}_{-0.18}$	$1.02^{+0.06}_{-0.05}$	$2.47^{+0.32}_{-0.26}$
121.97	$3.16^{+0.33}_{-0.43}$	$0.94^{+0.10}_{-0.13}$	$2.11^{+0.46}_{-0.54}$
121.96	3.63 ± 0.12	1.08 ± 0.05	2.78 ± 0.17
121.95	3.85	1.15	3.12
121.94	3.90	1.16	3.21
121.93	3.89	1.16	3.19
121.92	3.74	1.12	2.96
121.91	3.80	1.13	3.04
121.88	3.98	1.19	3.34
121.87	3.98	1.19	3.35
121.83	4.03	1.20	3.43
121.81	4.18	1.25	3.69
121.78	4.27	1.27	3.84
121.77	4.45	1.33	4.19
121.71	4.35	1.30	4.00
121.49	4.62	1.38	4.51
121.37	4.71	1.40	4.69
121.34	4.66	1.39	4.59
121.08	4.99	1.49	5.25
121.06	4.92	1.47	5.11
120.86	5.17	1.54	5.64
120.79	5.09	1.52	5.46
120.74	5.01	1.49	5.30
120.46	5.26	1.57	5.85
120.11	5.23	1.59 ± 0.01	5.99 ± 0.04
120.04	5.32	1.59	5.98
119.36	5.30	1.58	5.94
118.72	5.49	1.64	6.37

cally to yield the Helmholtz free energy $A(x, P, T)$ where x is the x-y shear strain. The Slater free energy may be further modified to allow for long-range interactions and for polarization configurations not included in the Slater $A_0(P, T)$, leading to the SUS form of the free energy A_{SUS}.[5]

Alternatively, one may construct a free energy phenomenologically as a power series in the appropriate thermodynamic variables following Landau and Devonshire.[19,20] We will consider the Slater-SUS theory first, and then turn to phenomenological free-energy expressions.

A. Slater model

In 1941 Slater proposed a statistical model for KDP.[5] He assumed that each proton had two equilibrium positions along the O-O bond and that at any temperature there were two and only two protons "close" to a PO_4 tetrahedron. (This last restriction is called the "ice rule.") The ordered orientation of protons which would give a dipole moment along the z axis is called a Slater group and its energy is taken as the ground-state energy. All other proton configurations, with respect to a PO_4

group which satisfy the ice rule, have energy ϵ_0. The transition temperature is related to ϵ_0 by

$$T_0 = \epsilon_0 / k \ln 2 \ . \tag{2}$$

The Slater model enables one to compute the Helmholtz free energy of the clamped crystal, $A_0(P_3, T)$. Since this free energy refers to constant strain conditions, the transition temperature is T_0, the "clamped" Curie temperature, which is 4 °K lower than the "free" Curie temperature T_Θ.[21] The phase transition temperature T_c occurs at T_Θ for a second-order transition or above T_Θ for a first-order transition.[22]

The Slater A_0 describes paraelectric KDP well but is less successful for the ferroelectric phase predicting that for $T < T_0$, $P = P_{\max}$ and $c_{66}^{E,S} = c_{66}^{P,T}$, and that the dielectric susceptibility reverts to its nonanomalous value.[5] The Slater transition is curious in that all orders of the derivative of the free energy with respect to polarization are zero at T_0, so that the usual Ehrenfest classification of phase transition as first or second order is inapplicable

TABLE II. Temperature dependence of the Brillouin shift frequency ν_B, sound velocity v, and adiabatic elastic constant $c_{66}^{E,S}$ at zero field for paraelectric KDP ($T > T_c$).

T (°K)	ν_B (10^9 Hz)	v (10^5 cm/sec)	$c_{66}^{E=0,S}$ (10^{10} dyn/cm^2)
122.00	0.59	0.17	0.07
122.03	0.90	0.27	0.17
122.11	1.20	0.357	0.303
122.16	1.17	0.349	0.289
122.20	1.38	0.408	0.395
122.25	1.54	0.460	0.502
122.33	1.76	0.523	0.651
122.38	1.69	0.504	0.604
122.51	1.95	0.582	0.804
122.68	2.18	0.652	1.01
122.86	2.39	0.713	1.21
123.04	2.59	0.773	1.42
123.19	2.76	0.823	1.61
123.38	2.92	0.870	1.80
123.56	3.05	0.910	1.97
123.64	3.12	0.929	2.05
123.77	3.08	0.917	2.00
123.84	3.21	0.958	2.18
124.31	3.45	1.03	2.50
124.79	3.66	1.09	2.82
125.33	3.84	1.14	3.11
125.86	3.97	1.18	3.33
126.38	4.13	1.23	3.61
127.36	4.34	1.29	3.98
128.52	4.55	1.35	4.35
129.95	4.70	1.40	4.65
131.20	4.83	1.44	4.92
132.54	4.92	1.46	5.09
134.00	5.02	1.49	5.30
135.65	5.08	1.51	5.44
137.43	5.12	1.52	5.52
139.43	5.23	1.56	5.76
141.57	5.23	1.56	5.76
145.28	5.28	1.57	5.87
146.86	5.36	1.60	6.04
157.69	5.41	1.61	6.15
158.57	5.48	1.63	6.32
177.41	5.57	1.66	6.52
199.01	5.55	1.65	6.45
236.54	5.50	1.64	6.33
247.13	5.49	1.64	6.29
256.87	5.46	1.63	6.23
269.02	5.42	1.62	6.15
284.24	5.40	1.61	6.07
291.56	5.46	1.63	6.22
295	5.46	1.63	6.22

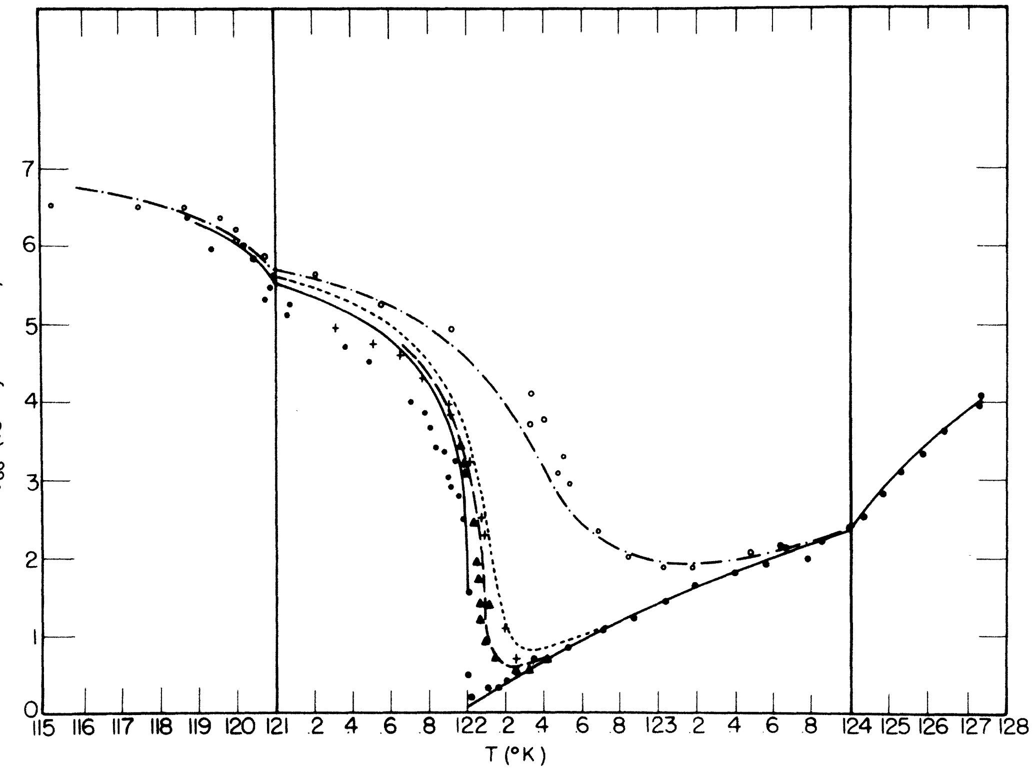

FIG. 5. Temperature and electric field dependence of the elastic constant $c_{66}^{E,S}$ deduced from Brillouin shift measurements. ●: $E=0$; ▲: $E=500$ V/cm; +: $E=787$ V/cm; ○: $E=3937$ V/cm. The lines are predictions of the SUS theory with $\epsilon_0/k=61.78$ °K, $\beta/k=14.7$ °K, $\epsilon_1/k=475.0$ °K. —($E=0$); ---($E=500$ V/cm); -----($E=787$ V/cm); —•—•— ($E=3937$ V/cm).

In order to improve agreement with experiment in the ferroelectric region, the Slater free energy has been modified by the inclusion of two additional energy parameters, ϵ_1 and β. ϵ_1 is the energy of a configuration having one or three protons "close" to a PO_4 group, a relaxation of the ice rule. It is assumed that the contribution from zero or four "close" protons is negligible. β is an energy which takes account of the long-range Coulomb forces which arise when $P \neq 0$. This modified Slater free energy, $A_0(P, T)$, has been investigated by SUS.[5] We shall explore the success of the SUS equations in describing $c_{66}^{E,S}$ and other experimental quantities.

The SUS equations describe a very general type of transition which can be either first or second order depending on the values of the parameters used. In the limit $\beta \rightarrow 0$, $\epsilon_1 \rightarrow \infty$, the original Slater free energy is recovered.

The SUS free energy $A_0(P, T)$ is determined once ϵ_0, β, and ϵ_1 are specified. $A_0(P, T)$ can be connected to experimental quantities as shown in the Appendix. However, since the SUS equations are expressed in terms of a dimensionless polarization $p = P/P_{\max}$, there is a fourth parameter $P_{\max}$ which must be specified.

We choose $P_{\max}$ in the following manner: The inverse dielectric susceptibility $\partial^2 A_0/\partial P^2 = (1/P_{\max})^2 \partial^2 A_0/\partial p^2$ is found experimentally to be linear with temperature in the paraelectric phase. For paraelectric temperatures all combinations of ϵ_1, ϵ_0, and β we explored gave a nearly linear temperature dependence for the predicted inverse susceptibility. We chose a value of $P_{\max}$ so that the slope of $\partial^2 A/\partial p^2$ would agree with the observed Curie constant $C = 3250$ °K,[23] thereby letting the Curie constant, ϵ_1, ϵ_0, and β determine $P_{\max}$. We used the value of the inverse susceptibility as 0 at T_0 and $\alpha_0 \times 10$ °K at $T_0 + 10$ °K to determine the slope. This method uses paraelectric zero-field dielectric measurements to choose $P_{\max}$, once ϵ_1, ϵ_0, and β have been specified ($\alpha_0 = 4\pi/C$).

It should be pointed out that for $C = 3250$ °K, the Slater free energy predicts $P_{\max} = 5.38$ μC/cm^2, in reasonable agreement with the largest experimental value of 5.12 μC/cm^2 at 93 °K.[24] In the SUS equations, as ϵ_1 is decreased and β is increased giving transitions farther from the Slater limit, the prediction for $P_{\max}$ increases. Thus, while the SUS modifications to the Slater theory round off the temperature dependence of the polarization in

TABLE III. Temperature dependence of the Brillouin shift frequency ν_B, sound velocity v, and adiabatic elastic constant $c_{66}^{E,S}$ of KDP with electric fields.

T (°K)	ν_B (10^9 Hz)	v (10^5 cm/sec)	$c_{66}^{E,S}$ (10^{10} dyn/cm^2)	E (V/cm)
121.99	3.21	0.956	2.17	51
121.98	3.50	1.04	2.59	157
121.99	3.71	1.11	2.91	315
122.25	1.17	0.510	0.619	472
122.16	1.84	0.549	0.716	500
122.11	2.59	0.773	1.42	500
122.10	2.3 ± 0.2	0.69 ± 0.07	1.1 ± 0.2	500
122.09	2.87	0.854	1.74	500
122.07	3.03	0.904	1.94	500
122.04	3.42	1.02	2.47	500
122.01	3.84	1.14	3.12	500
122.00	3.90	1.16	3.22	496
121.97	4.06	1.21	3.48	500
123.87	3.10	0.924	2.03	787
123.77	3.04	0.906	1.95	787
123.56	2.87	0.856	1.74	787
123.28	2.79	0.830	1.64	787
123.09	2.62	0.781	1.45	787
122.93	2.46	0.734	1.28	787
122.75	2.26	0.673	1.08	787
122.57	2.03	0.606	0.874	787
122.42	1.88	0.559	0.743	787
122.25	1.9 ± 0.1	0.58 ± 0.03	0.79 ± 0.08	787
122.20	2.24	0.667	1.06	787
122.16	2.78	0.828	1.63	787
122.13	3.08	0.916	2.00	787
122.10	3.33	0.993	2.35	787
122.09	3.27	0.974	2.26	787
122.08	3.77	1.13	3.01	787
122.06	3.84	1.14	3.11	787
122.02	4.03	1.20	3.43	787
121.94	4.28	1.28	3.87	787
121.91	4.26	1.27	3.83	787
121.90	4.34	1.29	3.97	787
121.76	4.53	1.35	4.34	787
121.65	4.64	1.38	4.54	787
121.51	4.74	1.41	4.75	787
121.31	4.84	1.44	4.94	787
127.19	4.32	1.29	3.94	3937
126.09	4.08	1.22	3.51	3937
125.07	3.77	1.12	3.00	3937
124.13	3.39	1.01	2.42	3937
123.73	3.16	0.940	2.10	3937
123.50	3.12	0.931	2.06	3937
123.18	2.98	0.887	1.87	3937
123.04	2.99	0.890	1.88	3937
122.86	3.07	0.915	1.99	3937
122.69	3.33	0.993	2.35	3937
122.54	3.74	1.11	2.95	3937
122.51	3.94	1.18	3.28	3937
122.48	3.83	1.14	3.10	3937
122.40	4.23	1.26	3.79	3937
122.33	4.20	1.25	3.73	3937
122.27	4.39	1.31	4.06	3937
121.92	4.82	1.44	4.92	3937
121.55	5.00	1.49	5.27	3937
121.22	5.16	1.54	5.62	3937
120.75	5.27	1.57	5.88	3937
120.00	5.34	1.59	6.02	3937
119.99	5.43	1.62	6.24	3937
119.61	5.49	1.64	6.37	3937

TABLE III. (*Continued*)

T (°K)	ν_B (10^9 Hz)	v (10^5 cm/sec)	$c_{66}^{E,S}$ (10^{10} dyn/cm^2)	E (V/cm)
118.76	5.57	1.66	6.56	3937
117.51	5.57	1.66	6.54	3937
115.24	5.56	1.66	6.52	3937
112.89	5.67	1.69	6.78	3937

agreement with experiment, they also predict absolute values for the polarization at low temperatures which exceed measured values. We shall discuss this point later.

We explored the predictions of the SUS theory for $c_{66}^{E,S}$ for various parameter combinations ϵ_1, ϵ_0, and β. One of these three parameters can be eliminated by using the measured $T_0 = 118$ °K.

In practice it makes little difference in the choice of parameters whether we consider the SUS equations as giving the free energy at constant strain or constant stress, i.e., as giving the Helmholtz or Gibbs free energies. In the latter case one would use Eq. (A7b) instead of (A5b) of the Appendix to connect with $c_{66}^{E,S}$ and one would make $\partial^2 G/\partial p^2 \to 0$ at the measured T_Θ which is 122 °K. The parameters ϵ_0, ϵ_1 and β would then pertain to a "free" ($\sigma_6 = 0$) crystal. We have followed this procedure and our final choice of parameters is for the free crystal. The change in parameters which results is small, basically because the percentage change in temperature from 118 to 122 °K is only 3%.

The ferroelectric elastic constant data cannot uniquely determine the SUS parameters because $c_{66}^{E,S}$ depends on both the second derivative of the free energy with respect to polarization (the inverse susceptibility) and the polarization itself through the adiabatic correction [see Eq. (A4c)]. However, it was observed that the best agreement occurred for those values of the parameters which predict a transition near the boundary between first- and second-order transitions.[25] We varied ϵ_1 and β, always adjusting ϵ_0 to give the proper transition temperature. The range of parameters giving a reasonable correspondence is within the following limits: (i) $\epsilon_1/k = 350$ °K, $\epsilon_0/k = 56.1$ °K, and $\beta/k = 22.0$ °K (continuous transition); (ii) $\epsilon_1/k = 350$ °K, $\epsilon_0/k = 49.9$ °K, and $\beta/k = 23.0$ °K (first-order transition: $c_{66}^{E,S}|_{T\to T_c^-} = 2.1\times 10^{10}$ dyn/cm^2; $T_c - T_\Theta = 0.03$ °K); (iii) $\epsilon_1/k = 525$ °K, $\epsilon_0/k = 67.0$ °K, and $\beta/k = 9.00$ °K (continuous transition).

From our elastic constant measurements we can limit ϵ_1/k to the range 350–525 °K, ϵ_0/k from 50 °K to 67 °K, and β/k from 9 °K to 22 °K with the proviso that the actual parameter combination chosen must give the proper transition temperature $T_c = 122$ °K.

The SUS parameters can be chosen uniquely if we assume a first-order transition in the elastic constants since $c_{66}^{E,S}|_{T\to T_c^-}$ and $T_c - T_\Theta$ determine ϵ_1 and β. Using $c_{66}^{E,S}(T_c^-) = 1.54\times 10^{10}$ dyn/cm^2 (the smallest stabilized value we observed in the ferroelectric region) and $T_c - T_\Theta = 0.012$ °K (as found by Benepe and Reese)[6] we find

$$\epsilon_1/k = 475\text{ °K}, \quad \epsilon_0/k = 61.78\text{ °K}, \quad \beta/k = 14.7\text{ °K}, \quad P_{\max} = 6.48\ \mu\text{C/cm}^2 \tag{3a}$$

(free crystal: the transition occurs at T_Θ) or

$$\epsilon_1/k = 475\text{ °K}, \quad \epsilon_0/k = 61-63\text{ °K}, \quad \beta/k = 12-13\text{ °K}, \quad P_{\max} = 6.2\ \mu\text{C/cm}^2 \tag{3b}$$

(clamped crystal: the transition occurs at T_0).[26]

This comparison shows that the common neglect of the distinction between T_0 and T_Θ (i.e., between the Helmholtz-Gibbs free energies) in using the SUS equations does not give serious changes in the parameters.

For the parameter combination (3a), with $a_{36}^T = 3.3\times 10^4$ esu/cm^2 and $\tilde{C}^{P,\sigma} = 1.12\times 10^7$ erg/°K cm^3, the mean-fitting error for the elastic constant $c_{66}^{E,S}$ at various electric fields had the following values[27]: With $E = 0$, the mean error was 0.37×10^{10} dyn/cm^2 for all data in the ferroelectric phase. With $E = 500$, 787, and 3937 V/cm, the mean errors were 0.14, 0.25, and 0.20×10^{10} dyn/cm^2, respectively, for data points at temperatures low enough to exhibit departures from the zero-field values. (These fitting errors should be compared with the experimental accuracy which is about 0 1×10^{10} dyn/cm^2.)

To check the consistency of the SUS equations we examined the parameters which gave a reasonable description of the spontaneous polarization as measured by Benepe and Reese. The parameters giving a good fit were

$$\epsilon_1/k = 350\text{ °K}, \quad \epsilon_0/k = 56.1\text{ °K}, \quad \beta/k = 22.0\text{ °K}, \quad P_{\max} = 6.8\ \mu\text{C/cm}^2. \tag{4}$$

The predictions of the SUS equations for $c_{66}^{E,S}$ and P with the parameter combinations (3a) and (4) are shown in Figs. 6 and 7. For the range $0 < T_c - T < 1$ °K the mean-fitting error for $c_{66}^{E,S}$ was 0.45×10^{10} dyn/cm^2 for parameter combination (3a) and 0.53×10^{10} dyn/cm^2 for combination (4). The mean-fitting error for the polarization in the same tem-

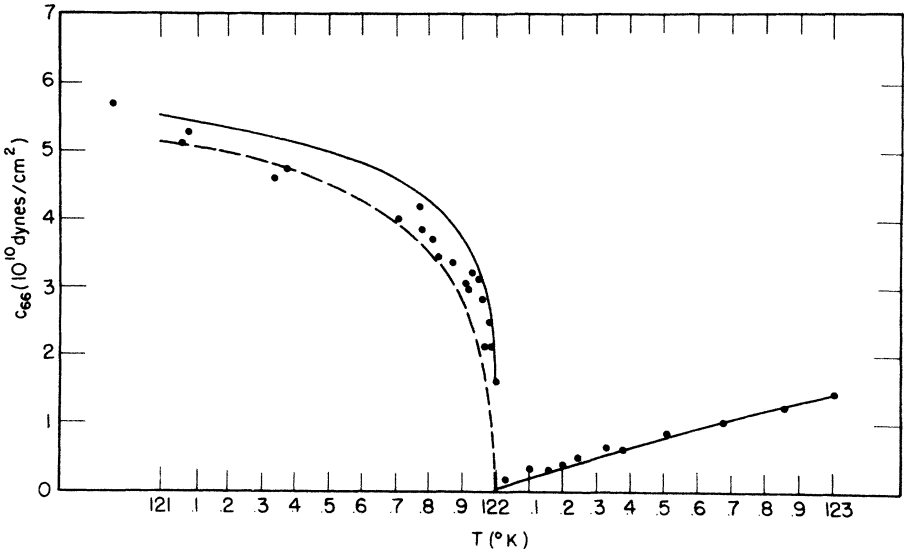

FIG. 6. Comparison of SUS theory to the experimentally determined elastic constant $c_{66}^{E,S}$ at $E=0$. Solid line, [(SUS prediction (3)]: $\epsilon_1/k=475$ °K, $\epsilon_0/k=61.78$ °K, $\beta/k=14.7$ °K; dashed line [(SUS prediction (4)]: $\epsilon_1/k=350$ °K, $\epsilon_0/k=56.1$ °K, $\beta/k=22.0$ °K.

perature range, using the data of Benepe and Reese, was 0.82 μC/cm^2 for parameter combination (3a) and 0.52 μC/cm^2 for combination (4). The improved fit to the polarization data which results from using combination (4) in place of (3a) leads to degradation of the fit to the elastic constant data.

As an aside we note that ϵ_0 has been measured in a series of compounds isomorphous to KDP although not in KDP itself.[28] The measured values are lower than the original Slater model would predict, but do increase with increasing T_0. Using ϵ_0/k of 54 °K, measured for KH_2AsO_4, and multiplying by the ratio of the transition temperatures for the two compounds, 122 °K/96 °K, we would predict $\epsilon_0/k=69$ °K for KDP, a value in reasonable agreement with our parameter choice (3a).

The success of the SUS equations can be summarized as follows.

(i) The maximum spontaneous polarization is connected to the Curie constant and ϵ_1, ϵ_0, and β. Using $C=3250$ °K, the predictions range from 5.38 (for $\epsilon_1\rightarrow\infty$, $\beta\rightarrow 0$) to 6.8 μC/cm^2 for parameters (4). These numbers are to be compared with the largest experimental measurement of 5.12 μC/cm^2. The theory can take paraelectric data, i.e., the Curie constant, and deduce the maximum spontaneous polarization, agreeing with experiment within 30%.

(ii) The theory can predict the rapid increase of $c_{66}^{E,S}$ and P near T_c in the ferroelectric phase, either as a second- or first-order transition.

The failure of the SUS equations is that one set of parameters cannot give an equally good fit to both the elastic constant data and the spontaneous-polarization data.

Blinc and Svetina have suggested that a quantum-mechanical term Γ representing the proton tunneling energy should be included in the free energy.[29] In the limit $\Gamma=0$, their expressions reduce to the SUS form. When $\Gamma\neq 0$, their equations are difficult to solve and we have not tried to adjust the Blinc-Svetina parameters to fit our data.

B. Phenomenological free energies

As an alternative approach to the thermodynamic properties of KDP, one can construct a free energy phenomenologically without appeal to any specific microscopic model. Following Landau and Devonshire,[19,20] the free energy can be expanded in a power series in P, and the elastic and piezoelectric energies added in as in the Slater-SUS analysis.

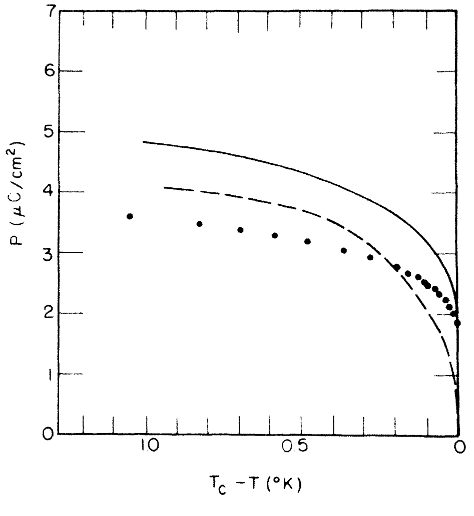

FIG. 7. Comparison of SUS theory to spontaneous-polarization data of Benepe and Reese (Ref. 6). Solid line [SUS prediction (3)]: $\epsilon_1/k=475$ °K, $\epsilon_0/k=61.78$ °K, $\beta/k=14.7$ °K; dashed line [SUS prediction 4]; $\epsilon_1/k=350$ °K, $\epsilon_0/k=56.1$ °K, $\beta/k=22.0$ °K.

Since we will be interested in the properties of the unstressed crystal, it will be most convenient to work with the Gibbs free energy $G(\sigma, P, T)$ with the stress $\sigma = 0$.

As we show in the Appendix, the isothermal and adiabatic elastic constants $c_{66}^{E,T}$ and $c_{66}^{E,S}$ are related to the Gibbs free energy of the unstressed crystal $G(P, T)_{\sigma=0}$ through expressions (A7a) and (A7b). The last term in the denominator of (A7b) for $c_{66}^{E,S}$ is the "adiabatic correction."[30] Its physical origin is in the temperature variation accompanying an adiabatic sound wave which the spontaneous polarization $P(T)$ must follow. The additional work increases the "stiffness" raising the value of the adiabatic elastic constant above that of the isothermal one. (In the paraelectric phase where $P = 0$, this term is identically zero and the two elastic constants are indistinguishable.)

We consider the following three phenomenological expressions for the Gibbs free energy $G(P, T)_{\sigma=0}$: (i) the simplest "molecular-field" form of the Landau-Devonshire expression,

$$G_1(P, T) = \tfrac{1}{2}\alpha P^2 + \tfrac{1}{4}b_2 P^4 \; ; \tag{5}$$

(ii) a modified Landau form which we have previously used in analyzing Brillouin, Raman, and dielectric data,[31]

$$G_2(P, T) = \tfrac{1}{2}\alpha P^2 + (1/n) b_n P^n ; \tag{6}$$

(iii) a form proposed recently by Benepe and Reese on the basis of their polarization measurements,

$$G_3(P, T) = \tfrac{1}{2}\alpha P^2 + \tfrac{1}{4} b P^4 + \tfrac{1}{8}\delta P^8 \; . \tag{7}$$

All three free energies are of the form $G(P, T) = \frac{1}{2}\alpha P^2 + \phi(P)$, where $\phi(P)$ is a "saturation function" assumed to be temperature independent. For $T > T_c$, the observed temperature dependence of the dielectric constant at zero stress, $\epsilon^{\sigma,T} = C/(T - T_\Theta)$ with Curie constant $C = 3250$ °K, determines $\alpha = \alpha_0 (T - T_\Theta)$ with $\alpha_0 = 4\pi/C = 3.867 \times 10^{-3}/$°K.

For G_1 and G_2, the saturation function $\phi(P)$ is positive definite so the transition is continuous (second order) and $T_\Theta \equiv T_c$. For G_3 with Benepe and Reese's values [$b = -4.4 \times 10^{-12}$ cm^4/esu^2 and $\delta = 2.96 \times 10^{-27}$ cm^{12}/esu^6] the transition is slightly first order, with $T_\Theta = T_c - 0.012$ °K.

G_1 and G_2 give identical predictions for all thermodynamic properties in the paraelectric phase. Below T_c, however, the molecular-field form G_1 predicts that the spontaneous polarization $P(T) = P_0 (T_0 - T)^\beta$ with $\beta = \frac{1}{2}$, while G_2 predicts $\beta = 1/(n-2)$. G_2 has been previously found to describe many of the known properties of the ferroelectric phase of KDP at least qualitatively with $n \sim 10$ or 12.[31] The resultant small value of the critical exponent $\beta \simeq \frac{1}{8}$ or $\frac{1}{10}$ is surprising at first since for most three-dimensional critical systems $\frac{1}{3} \leq \beta \leq \frac{1}{2}$. Its origin is related to the constraint on polarization configuration (the ice rule) proposed by Slater.[5] In fact, in the limit $n \to \infty$, G_2 reproduces Slater's results exactly.[32]

For $T > T_c$, all three forms of G predict

$$c_{66}^{E} = c_{66}^{P,T} - \frac{(a_{36}^T)^2}{\alpha_0 (T - T_\Theta) + (a_{36}^T)^2 / c_{66}^{P,T}} \; . \tag{8}$$

The value $c_{66}^{P,T} = 7.0 \times 10^{10}$ dyn/cm^2 is known from direct measurements[2,30]; however, a_{36}^T has only been measured indirectly, with reported values ranging from 3.0×10^4 to 3.5×10^4 esu/cm^2 in the paraelectric region, while no reliable values exist in the ferroelectric region.[33] We therefore deduce a_{36}^T from fitting (8) to our data for $T > T_c$, letting $T_\Theta = 122$ °K, which gives $a_{36}^T = 3.3 \times 10^4$ esu/cm^2.[34] The fit is shown in Fig. 8. (The possible difference of ~ 0.01 °K between T_Θ and T_c predicted by G_3 is too small to affect this fit.)

C. Phenomenological fits of data for $T < T_c$

The adiabatic correction term in $c_{66}^{E,S}$ is shown in the Appendix [Eq. (A12)] to be given by

$$-\frac{\partial^2 G}{\partial P \partial T} \Big/ \frac{\partial^2 G}{\partial T^2} = \frac{\alpha_0^2}{\tilde{C}^{P\sigma}} T P^2(T) \; , \tag{9}$$

where $\tilde{C}^{P\sigma}$ is the specific heat at constant stress and polarization. Thus the predictions for $c_{66}^{E,S}$ and for $P(T)$ cannot be disentangled, and these predictions must be considered together in analyzing the data for $T < T_c$.

a. G_1 (molecular field). With the free energy of Eq. (5), the spontaneous polarization is given by

$$P(T) = p_0 (T_c - T)^{1/2} \tag{10}$$

and the isothermal and adiabatic elastic constants are

$$c_{66}^{E,T} = c_{66}^{P,T} - \frac{(a_{36}^T)^2}{2\alpha_0 (T_c - T) + (a_{36}^T)^2 / c_{66}^{P,T}} \; , \tag{11}$$

$$c_{66}^{E,S} = c_{66}^{P,T} - (a_{36}^T)^2 [2\alpha_0 (T_c - T) + (a_{36}^T)^2 / c_{66}^{P,T} + \{(\alpha_0^2 / \tilde{C}^{P\sigma}) T P^2(T)\}]^{-1} \; . \tag{12}$$

Taking $\tilde{C}^{P,\sigma} = 1.12 \times 10^7$ ergs/°K cm^3 (63.77 J/mole °K) from its value ~ T_c, the only remaining free parameter is p_0.[35]

Figure 9 shows the isothermal and adiabatic elastic constants predicted by Eqs. (11) and (12) with two choices of p_0. The upper curve ($p_0 = 5.5$ μC/cm^2) gives a "best fit" to the data *neglecting* the range $0 < T_c - T < 0.25$ °K with mean error of 0.16×10^{10} dyn/cm^2 but if all the data are included, the mean error is 0.82.

In Fig. 10 we show the 1944 spontaneous-polarization data of von Arx and Bantle[36] (+) and the recent data of Benepe and Reese[6] (●).[37] For molecu-

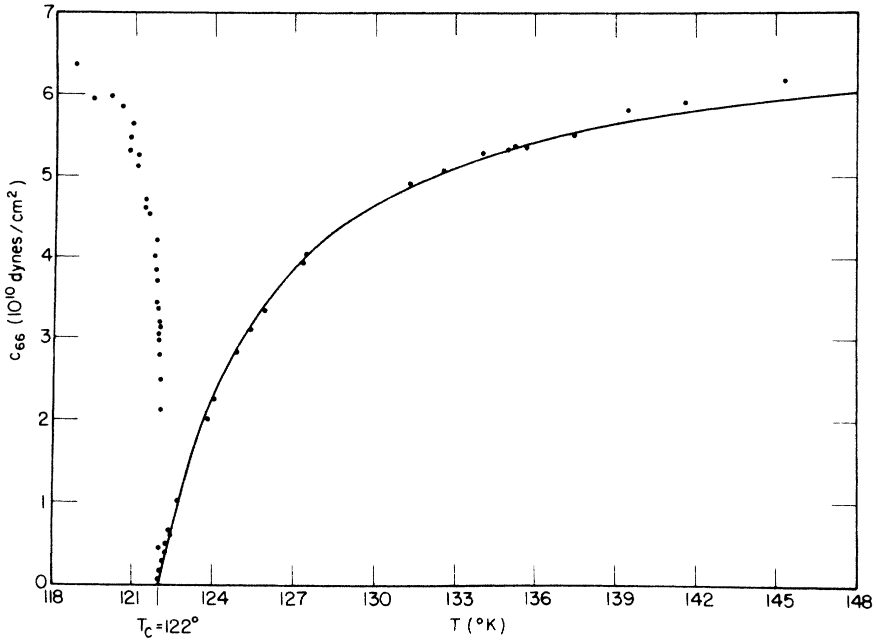

FIG. 8. Fit of elastic constant data for $T > T_c$ to Eq. (8) with $c_{66}^{P,T} = 7\times10^{10}$ dyn/cm^2, $\alpha_0 = 3.867\times10^{-3}$ °K^{-1}, and $T_\theta = 122.0$ °K. The solid curve, with $a_{36}^T = 3.3\times10^4$ esu/cm^2, gave the best fit.

lar field ($\beta = \frac{1}{2}$), the best fit (which is very poor) to the older polarization data is shown in curve *A*, with $p_0 = 1.7$, while in curve *B* the value $p_0 = 5.5$ (which gives the best fit to the elastic constant data in Fig. 9) is seen to predict completely unreasonable values for $P(T)$.

b. G_2 (Modified Landau).

$$c_{66}^{E,T} = c_{66}^{P,T} - (a_{36}^T)^2 \times [(n-2)\alpha_0(T_c - T) + (a_{36}^T)^2/c_{66}^{P,T}]^{-1}\,, \tag{13}$$

$$c_{66}^{E,S} = c_{66}^{P,T} - (a_{36}^T)^2[(n-2)\alpha_0(T_c - T) + (a_{36}^T)^2/c_{66}^{P,T} + (\alpha_0^2/\bar{C}^{P,\sigma})TP^2(T)]^{-1}\,, \tag{14}$$

$$P(T) = p_0(T_c - T)^{1/(n-2)}\,. \tag{15}$$

We use the same values for $c_{66}^{P,T}$, a_{36}^T, T_c, and $\bar{C}^{P\sigma}$ as in G_1, so that p_0 and n are now the free parameters.

In Fig. 10 we show two theoretical polarization curves for $n = 10$ and $p_0 = 3.16$, and 3.5; $p_0 = 3.16$

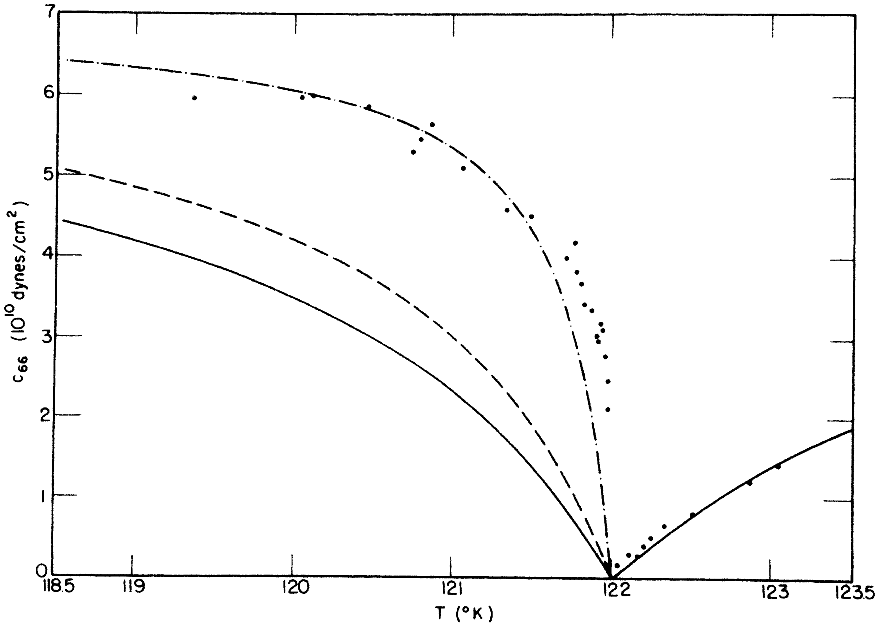

FIG. 9. Isothermal and adiabatic elastic constants predicted by G_1 (molecular field). Solid line: isothermal $c_{66}^{E,T}$; dashed line: adiabatic $c_{66}^{E,S}$ with $p_0 = 1.7$ μC/cm^2; dashed-dot line: $c_{66}^{E,S}$ with $p_0 = 5.5$ μC/cm^2.

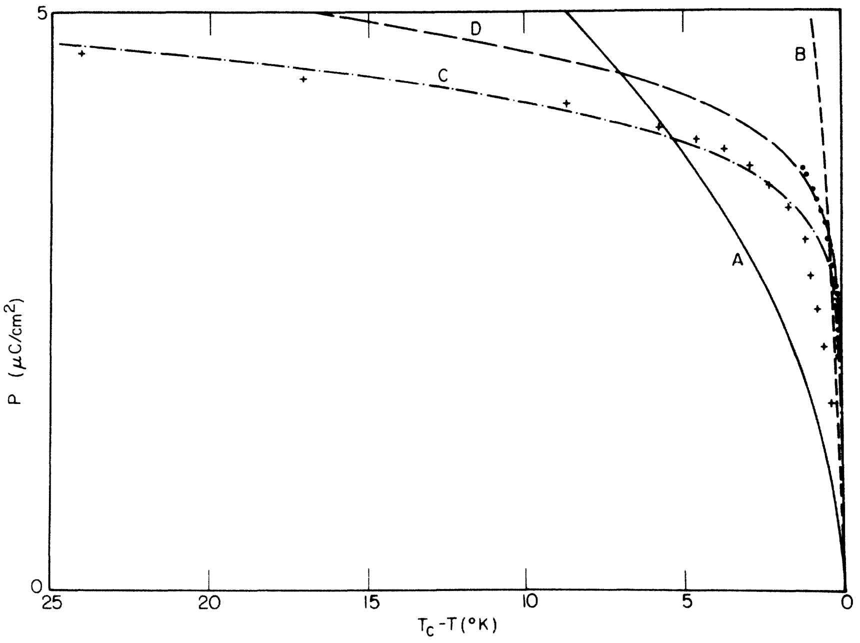

FIG. 10. Comparison of spontaneous-polarization data with predictions of G_1 (molecular field) and G_2 (modified Landau). +: data of Von Arx and Bantle (Ref. 36); ●: data of Benepe and Reese (Ref. 6). (a) —: G_1 (molecular field) with $p_0 = 1.7$ μC/cm^2; (b) - -: G_1 (molecular field) with $p_0 = 5.5$ μC/cm^2; (c) -•-: G_2 (modified Landau) with $N = 10$, $p_0 = 3.16$ μC/cm^2; (d) — —: G_2 (modified Landau) with $N=10$, $p_0=3.5$ μC/cm^2.

(curve C) gives a best fit to the von Arx and Bantle polarization data, while $p_0 = 3.5$ (curve D) gives a somewhat better fit to the combined polarization data.

The elastic constant fits for G_2 are shown in Fig. 11. The best fit, obtained with $p_0 = 3.5$, gives a mean error of 0.17. For $p_0 = 3.16$, the mean error is 0.24.

c. G_3 (Benepe and Reese). Benepe and Reese have recently redetermined the spontaneous polarization $P(T)$ of KDP using a "polaroelectrocaloric" technique based on measurement of the temperature changes produced by adiabatic changes in polarization.[6]

They found that the polarization jumps discontinuously at the transition to 1.87 μC/cm^2 and that $\beta \simeq \frac{1}{6}$.

The validity of their technique rests on the assumption that the saturation function $\phi(P)$ depends on neither temperature nor electric field, and that temperature changes produced by the adiabatic conversion of the multidomain crystal at $E = 0$ to the presumably single-domain state at high fields can be neglected. Although these assumptions have yet to be completely tested, we believe that these polarization measurements are the most reliable to date, and that other consequences of the Benepe-Reese free energy G_3 should be critically tested.

With the free energy G_3 given by Eq. (7), the isothermal and adiabatic elastic constants are

$$c_{66}^{E,T} = c_{66}^{P,T} - (a_{36}^T)^2[\alpha_0(T - T_\Theta) + (a_{36}^T)^2/c_{66}^{P,T} + 3bP^2 + 7\delta P^6]^{-1}, \qquad (16)$$

$$c_{66}^{E,S} = c_{66}^{P,T} - (a_{36}^T)^2[\alpha_0(T - T_\Theta) + (a_{36}^T)^2/c_{66}^{P,T} + 3bP^2 + 7\delta P^6 + (\alpha_0^2/\tilde{C}^{P,\sigma})TP^2(T)]^{-1}, \qquad (17)$$

while $P(T)$ is found from

$$P^6(T) - \tfrac{3}{4}P_0^4P^2(T) + \frac{P_0^6(T - T_\Theta)}{2(T_c - T_\Theta)} = 0, \qquad (18)$$

where $P_0 = 1.872$ μC/cm^2 and $T_c - T_\Theta = 0.012$ °K. The Benepe-Reese $P(T)$ data are very well described by

$$P(T) = 3.54(T_c - T + 0.026)^{1/6} \ \mu\text{C/cm}^2 . \qquad (19)$$

Taking the same values of a_{36}^T and $\tilde{C}^{P\sigma}$ used in fitting G_1 and G_2, Eq. (17) predicts $c_{66}^{E,S}$ as shown by the dashed curve in Fig. 12 which gives a mean error of 0.28 with no adjustable parameters.

Benepe and Reese, however, find that for $T < T_c$, $\tilde{C}^{P,\sigma}$ increases to 1.37×10^7 erg/°K cm^3 ($9.39R$).[38] Since such a change in $\tilde{C}^{P,\sigma}$ might well be accompanied by a change in a_{36}^T, we again fit our data to (17) with $\tilde{C}^{P,\sigma} = 1.37\times10^7$ letting a_{36}^T be a free parameter. The best fit was obtained with $a_{36}^T = 2.95 \times 10^4$, with a mean error of ~0.26 and is shown by the upper curve in Fig. 12. Such a large change in a_{36}^T from morphic effects seems unlikely, however, especially when compared with the slight change at T_c in $c_{66}^{P,T}$ and the other nonanomalous elastic constants. It would be valuable to have values for $\tilde{C}^{P,\sigma}$ and a_{36}^T in the ferroelectric phase determined by methods independent of the polarization.

The phenomenological fitting procedure thus shows that one can construct a free energy (G_2 or G_3) which gives reasonable fits to both the elastic

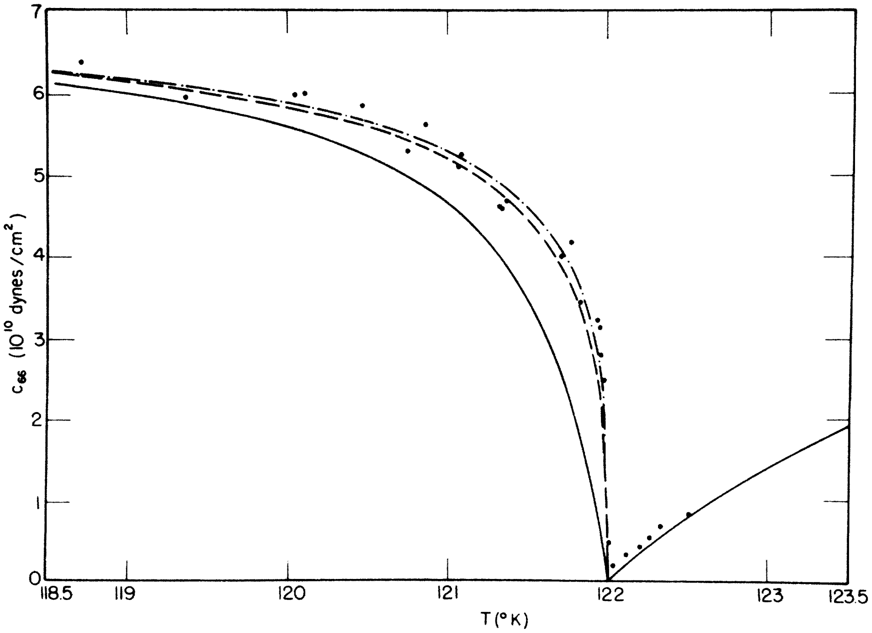

FIG. 11. Isothermal and adiabatic elastic constants predicted by G_2 (modified Landau) with $N = 10$. Solid line: isothermal $c_{66}^{E,T}$; dashed line: adiabatic $c_{66}^{E,S}$ with $p_0 = 3.16\ \mu C/cm^2$; dash-dot line: $c_{66}^{E,S}$ with $p = 3.5\ \mu C/cm^2$.

constant and polarization data, while the mean-field free energy G_1 can only be brought into agreement with either the elastic constant or polarization data, but not with both. Our elastic constant data appear to be slightly closer to the over-all predictions of G_2 than of G_3, although the experimental accuracy is not good enough to permit a definitive choice based on fitting errors alone. Qualitatively, the data appear to support a small discontinuity at the transition as predicted by G_3.

IV. CONCLUSIONS

We have presented our Brillouin-scattering results for $c_{66}^{E,S}$ and used the $E = 0$ data for $T < T_c$ to test several expressions for the free energy.

The Slater-SUS free energy can successfully account for the major features of the measured elastic constants giving good agreement in the paraelectric phase and moderately good agreement in the ferroelectric phase. There is no unique choice

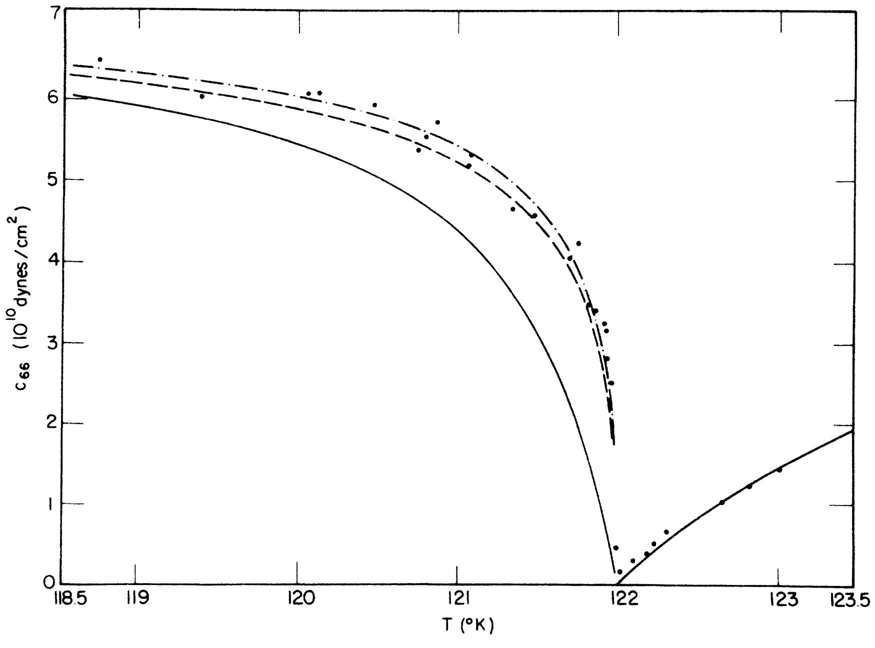

FIG. 12. Isothermal and adiabatic elastic constants predicted by G_3 (Benepe and Reese). Solid line: isothermal $c_{66}^{E,T}$; dashed line: adiabatic $c_{66}^{E,S}$ with $\bar{C}^{P,\sigma} = 1.12 \times 10^7$ ergs/°K cm^3 and $a_{36}^T = 3.3 \times 10^4$ esu/cm^2; dash-dot line: $c_{66}^{E,S}$ with $\bar{C}^{P,\sigma} = 1.37 \times 10^7$ ergs/°K cm^3; and $a_{36}^T = 2.95 \times 10^4$ esu/cm^2.

of the SUS parameters that fits both the elastic constant data and polarization data; however, the agreement is best in the immediate vicinity of T_c for the choice

$$\epsilon_1/k = 475\ ^\circ\mathrm{K}\ ,\quad \epsilon_0/k = 61.78\ ^\circ\mathrm{K}\ ,\quad \beta/k = 14.7\ ^\circ\mathrm{K}$$

$$P_{\max} = 6.48\ \mu\mathrm{C/cm}^2\ (T_\Theta = 121.99\ ^\circ\mathrm{K})\ .$$

It would seem worthwhile to attempt an expansion of the SUS free energy in terms of powers of the polarization. Such an expansion would have to be valid in the limit of large ϵ_1 and small β to correspond with the above choice of parameters. This would allow one to connect ϵ_1, ϵ_0, β, and $P_{\max}$ to the parameters of the phenomenological free-energy expressions.

We have also considered three phenomenological expressions for the free energy, all of which are variants of the Landau-Devonshire power-series expansion. The molecular-field form for the free energy $G_1(P,T)$ is found to be unsatisfactory, an inevitable consequence of its failure to conform with the rapid increase and subsequent saturation of the polarization below T_c. Although a qualitative fit to our data for $T_c - T > 0.5\ ^\circ$K could be achieved by treating the magnitude of the polarization as an adjustable parameter, the fit obtained requires an unreasonably large value of p_0 and, in any case, fails to produce even qualitative agreement with our data for $T_c - T < 0.5\ ^\circ$K. We note that Elliott, Smith, and Young have found that the KDP elastic constant data apparently agree with a theory they have formulated for a related coupled-mode problem.[39] Although their free-energy function differs considerably from our $G_1(P,T)$, it does employ a molecular-field approximation, and the choice of parameters which they made gave a reasonable fit to the elastic constant data only if the region within $\sim 0.25\ ^\circ$K of the transition was neglected, and the resulting predictions for the polarization and other thermodynamic properties were then found to be rather poor.

Either the modified Landau free energy G_2 with $n = 10$ or the Benepe-Reese free energy G_3 appear to provide consistent descriptions of the transition in that both the elastic constant and spontaneous-polarization predictions can be made to fit the data reasonably well with a unique choice of parameters. Within 0.10 °K of the transition, however, our data conform more closely with G_3, indicating a small discontinuity in the transition as reported by Benepe and Reese.

Finally, it is interesting to note that the ferroelectric transition in KDP is very close to the "Curie critical point" in Landau's theory where the line of first-order transitions goes over into a line of second-order transitions.[40] This is the point at which the coefficients of the terms in G which are quadratic and quartic in the order parameter vanish simultaneously, hence the saturation function should be dominated by terms higher than quartic, as indeed appears to be the case. The marked differences in critical exponents in this case are very likely related to the changes in critical exponents which occur at the tricritical point.[41]

ACKNOWLEDGMENTS

We wish to thank Professor Robert W. Gammon who participated in the early stages of this experiment and with whom we explored the consequences of various modifications to the Landau-Devonshire free energy. We also thank Professor Roger Elliott for several helpful discussions on the connection between microscopic Hamiltonians and thermodynamic free-energy expressions.

APPENDIX: THERMODYNAMIC RELATIONS FOR KDP

The thermodynamic analysis of KDP begins with $A_0(P,T)$, the Helmholtz free energy for the polarization in a rigid lattice. $A_0(P,T)$ may either be derived from a statistical theory such as Slater's, or represented phenomenologically as a power-series expansion in the polarization. To complete the Helmholtz free energy $A(x,P,T)$, the elastic energy and piezoelectric coupling energy must be added to $A_0(P,T)$.[20]

Neglecting all strains except x_6 and all polarization except P_3 and retaining only the leading terms in x_6, we have

$$A(x_6, P_3, T) = \tfrac{1}{2} c_{66}^{P,T} x_6^2 - a_{36}^T x_6 P_3 + A_0(P_3, T) \qquad \text{(A1)}$$

from which we find (with subscripts omitted)

$$\sigma = \frac{\partial A}{\partial x} = c^{P,T} x - a^T P\ , \qquad \text{(A2a)}$$

$$E = \frac{\partial A}{\partial P} = -a^T x + \frac{\partial A_0}{\partial P}\ , \qquad \text{(A2b)}$$

$$S = -\frac{\partial A}{\partial T} = -\frac{\partial A_0}{\partial T}\ , \qquad \text{(A2c)}$$

where $\sigma = \sigma_6$ and $E = E_3$ are the stress and electric field and S is the entropy.

For small departures from equilibrium,

$$\delta\sigma = c^{P,T}\,\delta x - a^T\,\delta P\ , \qquad \text{(A3a)}$$

$$\delta E = a^T\,\delta x + \frac{\partial^2 A_0}{\partial P^2}\,\delta P + \frac{\partial^2 A_0}{\partial P\,\partial T}\,\delta T\ , \qquad \text{(A3b)}$$

$$\delta S = -\frac{\partial^2 A_0}{\partial P\,\partial T}\,\delta P - \frac{\partial^2 A_0}{\partial T^2}\,\delta T\ . \qquad \text{(A3c)}$$

The elastic constants $\delta\sigma/\delta x$ with various constraints follow from Eqs. (A3).

a. Constant P and T.

$$\left(\frac{\delta\sigma}{\delta x}\right)^{P,T} = c_{66}^{P,T} = \frac{\partial^2 A}{\partial x^2}\ . \qquad \text{(A4a)}$$

b. Constant E and T.

$$\left(\frac{\delta\sigma}{\sigma x}\right)^{E,T} = c_{66}^{E,T} = c_{66}^{P,T} - (a_{36}^{T})^2 \Big/ \frac{\partial^2 A_0}{\partial P^2} \,. \tag{A4b}$$

c. Constant E and S.

$$\left(\frac{\delta\sigma}{\delta x}\right)^{E,S} = c_{66}^{E,S} = c_{66}^{P,T} - (a_{36}^{T})^2 \times\left[\frac{\partial^2 A_0}{\partial P^2} - \left(\frac{\partial^2 A_0}{\partial P\partial T}\right)^2 \Big/ \frac{\partial^2 A_0}{\partial T^2}\right]^{-1} . \tag{A4c}$$

The term $-(\partial^2 A_0/\partial P\partial T)^2/(\partial^2 A_0/\partial T^2)$ which appears in $c_{66}^{E,S}$ but not in $c_{66}^{E,T}$ is designated the "adiabatic correction" in the text.

Equations (A4b) and (A4c) can be written entirely in terms of derivatives of $A(x, P, T)$ as follows:

$$c_{66}^{E,T} = \frac{\partial^2 A}{\partial x^2} - (a_{36}^{T})^2 \Big/ \frac{\partial^2 A}{\partial P^2} \,, \tag{A5a}$$

$$c_{66}^{E,S} = \frac{\partial^2 A}{\partial x^2} - (a_{36}^{T})^2 \Big/ \left[\frac{\partial^2 A}{\partial P^2} - \left(\frac{\partial^2 A}{\partial P\partial T}\right)^2 \Big/ \frac{\partial^2 A}{\partial T^2}\right] . \tag{A5b}$$

For a free crystal ($\sigma_6 = 0$) it is often more convenient to work with the elastic Gibb's function

$$G(\sigma, P, T) = A(x, P, T) - x\sigma \,.$$

From (A2a) with $\sigma = 0$ we find $x = a^T P/c^{P,T}$, whence from (A1),

$$G(0, P, T) = \tfrac{1}{2} c^{P,T}(a^T P/c^{P,T})^2 - a^T(a^T/c^{P,T})P^2 + A_0(P, T) \,, \tag{A6}$$

$$G(P, T)_{\sigma=0} = A_0(P, T) - \tfrac{1}{2}(a^T P)^2/c^{P,T} \,.$$

In terms of $G(P, T)$, Eqs. (A4b) and (A4c) for the adiabatic and isothermal elastic constants become

$$c_{66}^{E,T} = c_{66}^{P,T} - (a_{36}^{T})^2 \Big/ \left(\frac{\partial^2 G}{\partial P^2} + \frac{(a_{36}^{T})^2}{c_{66}^{P,T}}\right) , \tag{A7a}$$

$$c_{66}^{E,S} = c_{66}^{P,T} - (a_{36}^{T})^2 \Big/ \left[\frac{\partial^2 G}{\partial P^2} + \frac{(a_{36}^{T})^2}{c_{66}^{P,T}} - \left(\frac{\partial^2 G}{\partial P\partial T}\right)^2 \Big/ \frac{\partial^2 G}{\partial T^2}\right] . \tag{A7b}$$

The clamped and free isothermal dielectric constants $\epsilon^{x,T}$ and $\epsilon^{\sigma,T}$ can be found from (A1) and (A6). Experimentally, for $T > T_\Theta$, both are of the Curie form:

$$\frac{4\pi}{\epsilon^{x,T}} \equiv \frac{\partial^2 A}{\partial P^2} = \frac{\partial^2 A_0}{\partial P^2} = \frac{4\pi}{C}(T - T_0) \,, \tag{A8}$$

$$\frac{4\pi}{\epsilon^{\sigma,T}} \equiv \frac{\partial^2 G}{\partial P^2} = \frac{\partial^2 A_0}{\partial P^2} - \frac{(a^T)^2}{c^{P,T}} = \frac{4\pi}{C}(T - T_\Theta) \,. \tag{A9}$$

Equations (A8) and (A9) show that T_0, the Curie temperature of the clamped crystal, should be lower than T_Θ, the Curie temperature of the free crystal, by

$$T_\Theta - T_0 = (C/4\pi)(a^T)^2/c^{P,T} \,. \tag{A10}$$

Equation (A9) also shows that the form of G should be

$$G(P, T) = G_0(T) + \alpha_0(T - T_\Theta)P^2 + \phi(P) \,, \tag{A11}$$

where G_0 contains all contributions to G from other nonanomalous degrees of freedom, $\alpha_0 = 4\pi/C$, and $\phi(P)$ is a "saturation function" representing all higher-order terms in P.

From (A11), with the assumptions that G_0 is independent of polarization and $\phi(P)$ is temperature independent, the form of the adiabatic correction term to the elastic constant $c^{E,S}$ in Eq. (A7b) becomes

$$-\left(\frac{\partial^2 G}{\partial P\partial T}\right)^2 \Big/ \frac{\partial^2 G}{\partial T^2} = \frac{\alpha_0^2 P^2 T}{\tilde{C}^{P,\sigma}} \,, \tag{A12}$$

where $\tilde{C}^{P,\sigma}$ is the specific heat at zero stress and polarization.

[†] Based in part on the Ph.D. thesis of Edward M. Brody, The Johns Hopkins University, Baltimore, Md., 1969 (unpublished).

[*] The experimental results reported here were obtained while the authors were at The Johns Hopkins University, Baltimore, Md., and were part of a program supported by The U.S. Army Research Office, Durham.

[‡] Alfred P. Sloan Research Fellow.

[1] This was our measurement. Published values of T_c range from 121.97 to 122.06 °K.

[2] W. P. Mason, Phys. Rev. **69**, 173 (1946); also, see F. Jona and G. Shirane, *Ferroelectric Crystals* (MacMillan, New York, 1962), Chap. 3.

[3] C. W. Garland and D. B. Novotny, Phys. Rev. **177**, 971 (1969); E. Litov and C. W. Garland, Phys. Rev. B **2**, 4597 (1970).

[4] E. M. Brody and H. Z. Cummins, Phys. Rev. Lett. **21**, 1263 (1968).

[5] J. C. Slater, J. Chem. Phys. **9**, 16 (1941); H. B. Silsbee *et al.*, Phys. Rev. **133**, A165 (1964).

[6] J. W. Benepe and W. Reese, Phys. Rev. B **3**, 3032 (1971).

[7] H. Z. Cummins, in *Light Scattering in Solids*, edited by M. Balkansi (Flammarion, Paris, 1971), p. 3.

[8] H. Z. Cummins and P. E. Schoen, *Laser Handbook* (North-Holland, Amsterdam, 1972), p. 1056.

[9] Isomet Corp., 103 Bauer Dr., Oakland, N. J. 07436.

[10] Rosemont Engineering, 4900 W. 78th St., Minneapolis, Minn. 55424.

[11] Presumably because of temperature gradients resulting from local heating by the laser beam.

[12] E. M. Brody and H. Z. Cummins, Phys. Rev. Lett. **23**, 1039 (1969); I. J. Fritz, R. L. Reese, E. M. Brody, C. M. Wilson, and H. Z. Cummins, Ref. 7, p. 415.

[13] L. Brillouin, Ann. Phys. (Leipz.) **17**, 88 (1922).

[14] The measured elastic constant will be adiabatic if the period of the elastic wave is short compared to the time required for relaxation by heat conduction. [See discussion in K. F. Herzfeld and T. Litovitz, *Absorption and Dispersion of Ultrasonic Waves* (Academic, New York, 1959), p. 45.] The necessary inequality [cf. M. W. Zemansky, *Heat and Thermodynamics* (McGraw-Hill, New York, 1957), p. 133] can

be written $\nu < \nu_c$, where the "crossover" frequency $\nu_c = v^2 \rho \tilde{C}_v / 2\Lambda$. ($v$ is the sound velocity and ρ, $\tilde{C}_v$, and Λ are the density, specific heat, and thermal conductivity of the crystal, respectively.) At $T = 300\,°\mathrm{K}$, $v = 1.63 \times 10^5$ cm/sec, $\tilde{C}^{E,x} = 2.1 \times 10^7$ erg/cm^3 °K and $\Lambda = 2 \times 10^5$ erg/cm sec °K so that $\nu_c \simeq 10^{12}$ Hz. Close to T_c, the crossover frequency ν_c decreases, but is always far above the Brillouin-shift frequencies which we observe, so that our elastic constants are all adiabatic.

[15] M. Born and E. Wolf, *Principles of Optics* (Pergamon, New York, 1964), p. 665ff. Also see D. F. Nelson *et al.*, Phys. Rev. B **6**, 3109 (1972).

[16] V. N. Vishnevskii and I. V. Stefanskii, Opt. Spektrosk. **20**, 357 (1966) [Opt. Spectrosc. **20**, 195 (1966)].

[17] To calculate this result, use Eq. (17) with $T = T_c$, $T_c - T_\theta = 0.012\,°\mathrm{K}$, $\tilde{C}^{P,\sigma} = 1.12 \times 10^7$ erg/°K cm^3, $P = 1.872\ \mu\mathrm{C/cm}^2$, $\alpha_0 = 3.87 \times 10^{-3}/°\mathrm{K}$, $a^T_{36} = 3.3 \times 10^4$ esu/cm^2, and $c^{P,T} = 7 \times 10^{10}$ dyn/cm^2. ($b = -4.4 \times 10^{-12}$ cm^4/esu^2, $\delta = 2.96 \times 10^{27}$ cm^{12}/esu^6).

[18] R. L. Reese, I. J. Fritz and H. Z. Cummins, Phys. Rev. B 7, 4165 (1973).

[19] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, Mass., 1958), p. 430; A. F. Devonshire, Adv. Phys. **3**, 86 (1954).

[20] F. Jona and G. Shirane, Ref. 2, p. 15ff.

[21] H. Baumgartner, Helv. Phys. Acta **24**, 326 (1951).

[22] The calculation of $T_\theta - T_0$ and the procedure for relating A_0 to various experimentally observable properties of the crystal are discussed in the Appendix.

[23] P. Craig, Phys. Lett. **20**, 140 (1966). This is the value used in Ref. 6. Our own dielectric constant measurements gave $C = 3050\,°\mathrm{K}$; however, we have chosen to use the larger value to facilitate comparison with Ref. 6.

[24] J. Azoulay, Y. Grinberg, I. Pelah, and E. Wiener, J. Phys. Chem. Solids **29**, 843 (1968).

[25] Extensive discussion of the SUS fitting procedures are presented by E. M. Brody, in Ph.D. thesis (Johns Hopkins University, 1969) (unpublished).

[26] The calculations for parameter choices (3b) were not as accurate as those for (3a); that is why there is a 2 °K uncertainty in ϵ_0/k and a 1 °K uncertainty in ϵ_1/k.

[27] The choice of the thermodynamic parameters is discussed in the following section on phenomenological free energies.

[28] J. L. Bjorkstam, J. Phys. Soc. Jap. Suppl. **28**, 101 (1970).

[29] P. Blinc and S. Svetina, Phys. Rev. **147**, 430 (1966).

[30] H. Baumgartner, Helv. Phys. Acta **23**, 651 (1950).

[31] H. Z. Cummins, Bull. Am. Phys. Soc. **13**, 354 (1968); in *Proceedings of the International School of Physics "Enrico Fermi", Course LI*, edited by M. S. Green (Academic, New York, 1971), p. 439; E. M. Brody, Ref. 25.

[32] The result $\beta \backsim 1/8$ resembles the prediction of the two-dimensional Ising model and could be related to the planar ordering of the hydrogen bonds. However, it seems far more likely that the small β value is due to the three- and four-body forces underlying Slater's "ice rule", since exact solutions of the Slater model in two dimensions reproduce the Slater result $\beta = 0$. [E. H. Lieb, Phys. Rev. Lett. **19**, 108 (1967).]

[33] T. Mitsui *et al., Landolt-Börnstein-Numerical Data and Functional Relationships in Science and Technology 3* (Springer-Verlag, Berlin, 1969), p. 134ff.

[34] The "best fit" value of a^T_{36} also depends on the choice of the Curie constant C which we take as 3250 °K (see Ref. 23). In Ref. 4, we used a smaller value for C (3050 °K) which led to $a^T_{36} = 3.5 \times 10^4$ esu/cm^2.

[35] W. Reese and L. F. May, Phys. Rev. **162**, 515 (1967).

[36] A. von Arx and W. Bantle, Helv. Phys. Acta **17**, 298 (1944).

[37] Additional spontaneous-polarization data determined from hysteresis-loop measurements were reported by I. Nazario and J. A. Gonzalo, Solid State Commun. **7**, 1305 (1969). Their results, which indicate a second-order molecular-field-type transition, differ so drastically from other data that we have chosen not to include them in this analysis. (See discussion in Ref. 6.)

[38] An alternate conclusion, which Benepe and Reese reject, is that α_0 decreases in the ferroelectric region. We have not explored the consequences of a decreasing α_0.

[39] R. J. Elliott *et al.*, J. Phys. C **4**, L179 (1971); J. Phys. C **4**, L317 (1971); J. R. Sandercock *et al.*, J. Phys. C **5**, 3126 (1972).

[40] L. D. Landau and E. M. Lifshitz, Ref. 19, p. 452.

[41] R. B. Griffiths, Phys. Rev. Lett. **24**, 715 (1970); A. Hankey *et al.*, Phys. Rev. Lett. **29**, 278 (1972).