The influence of an electric field on the latent heat of the ferroelectric phase transition in KDP

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Abstract
The specific heat, heat flux (DTA trace) and dielectric constant of KDP ferroelectric crystal have been measured simultaneously for various electric fields with a conduction calorimeter. The specific heat presents a strong anomaly, but these simultaneous measurements allow us to evaluate the latent heat accurately. The latent heat decreases with field, and the value of the critical electric field—that where the latent heat disappears—is estimated to be $(0.44 \pm 0.03)$ kV cm\textsuperscript{-1}. Incidentally, we have measured simultaneously the dielectric permittivity, which suggests that latent heat is developed as domains are growing.

1. Introduction

The KDP family is one of the most extensively studied [1, 2] hydrogen-bonded ferroelectric crystals. The potassium dihydrogen phosphate KH\textsubscript{2}PO\textsubscript{4} crystal exhibits a discontinuous phase transition at $T_0 = 121$ K from a tetragonal paraelectric phase to an orthorhombic ferroelectric phase. The specific heat anomaly at the transition temperature shows [3–5] a strong $\lambda$-type anomaly; perhaps that is why the transition was initially considered continuous. However, Reese [4] showed that the transition is discontinuous by measuring its latent heat, which was evaluated to be 46.1 J mol\textsuperscript{-1}. It was shown that the discontinuity disappears under the influence of pressure or electric field.

The value of the critical electric field $E_c$ for which the discontinuity disappears is a subject of discussion. Reese et al [6] also carried out a measurement of the specific heat with an applied field of 294 V cm\textsuperscript{-1}, finding controversial evidence of latent heat. Above $E = 785$ V cm\textsuperscript{-1} they found no evidence of latent heat and suggested $E_c = 300$ V cm\textsuperscript{-1} from the shift of the maximum of the specific heat as function of the electric field. Measurements of specific heat under electric fields higher than 360 V cm\textsuperscript{-1} were carried out by Sandvold and Fossheim [7]
and the authors suggest that Landau theory for continuous transitions with 2-4-6 potential was appropriate to describe the shape of the specific heat curves.

Other works have led to estimations of the critical field. For instance, Strukov et al. [8] evaluated \( E_c = 124 \text{ V cm}^{-1} \) from electrocaloric experiments. Sidnenko and Gladki [9] found \( E_c = 370 \text{ V cm}^{-1} \) while Okada and Sugie [10] obtained 160 V cm\(^{-1}\) for \( E_c \). Vallade [11] deduced a value of 254 V cm\(^{-1}\) from birefringence measurements. In contrast to these values, Kobayashi et al. [12] found, by x-ray measurements, 8000 V cm\(^{-1}\); Eberhard and Horn [13] derived a value of 6500 V cm\(^{-1}\) from dielectric susceptibility.

In this frame it would be interesting to evaluate the latent heat as a function of the electric field to determine the value of the critical electric field \( E_c \) for which the latent heat becomes null.

The difficulty of an accurate determination of \( E_c \) from calorimetric measurements in standard equipment—such as differential thermal analysis DTA and differential scanning calorimeter DSC—is that these systems really measure changes of enthalpy, which has two contributions near the transition: one due to the latent heat and the other due to the variation of specific heat with temperature. In the case of phase transitions near a tricritical point or a discontinuous ferroelectric phase transition under an electric field close to the critical field, the specific heat presents a strong anomaly and the latent heat becomes very small. This fact makes it difficult to separate both contributions and to distinguish the temperature interval where the latent heat is present. This may explain the lack of study of the influence of electric field, smaller than \( E_c \), on the specific heat and latent heat of KDP after Reese [6].

Our group has developed a method, named square modulated differential thermal analysis SMDTA [14–16], based on conduction calorimetry, which is able to measure absolute values of specific heat and the heat flux exchanged by the sample when its temperature is changed at a rate as low as 0.1 K h\(^{-1}\). The comparison of the data allows us to separate the above two contributions to the total enthalpy and to evaluate the latent heat, in case there were any.

This technique has been successfully applied to the study of the almost tricritical phase transition of KMnF\(_3\) [14], whose latent heat was first measured with this technique. Furthermore, the effect of the substitution of Mn by Ca was also investigated by measuring the latent heat [15], which showed that the doping makes the transition become continuous [17]. The method of SMDTA has been also applied to show that the phase transition in CoO [18], whose character was also controversial, is continuous.

In this paper we have applied this method to study a KDP single crystal. We have measured the specific heat and the heat flux exchanged by the sample in the neighbourhood of the ferroelectric phase transition. The measurements have been carried out at four values of \( E: 0, 100, 400, 1000 \text{ V cm}^{-1} \).

Simultaneously to these measurements, the dielectric susceptibility of the sample has also been measured, and we have related its behaviour around the transition temperature with the temperature interval where the latent heat is produced. Dielectric measurements provide information about the mechanism of the ferroelectric phase transition of KDP crystal [19, 20] and the simultaneous measurement of thermal and dielectric properties would be worthy.

2. Experimental details

The measurements were performed in a high resolution conduction calorimeter which has been described in detail previously [21–23]. The sensor is formed by two identical heat fluxmeters, each one having 48 chromel–constantan thermocouples connected electrically in series but thermally in parallel. The sample is pressed between both fluxmeters whose signal is measured by a Keithley 182 nanovoltmeter. Two electrodes and two heaters are placed between the sample and the fluxmeters.
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The sensor is placed inside a calorimeter block which is suspended within two cylindrical radiation shields. The whole assembly is then placed in a hermetic outer case at a high vacuum. The device is then surrounded by a coiled tube and placed in an alcohol bath. Liquid N₂ circulates through the coil and regulates the temperature of the bath with a good thermal stabilization. As a result, it is possible to change the temperature of the sample smoothly (at a rate of about 0.1 K h⁻¹) without observing significant temperature fluctuations (always less than 10⁻⁶ K) in the block temperature.

The specific heat is measured using the method previously described [16]. The same constant power $W$ is dissipated in both heaters (dissipation branch) for 12 min, and a steady state characterized by a constant temperature difference between the sample and the calorimeter block is reached. The power is then cut off until a new steady state is reached 12 min later (relaxation branch). Then, the power is again switched on and the sequence is continuously repeated while the temperature of the assembly is changed at a low constant rate. That is, a long-periodic serial of square thermal pulses is superposed to a heating or cooling ramp. The temperature increase of the sample due to the thermal pulse of 12 min (about $50 \times 10^{-3}$ K) is higher than the temperature variation of the sample produced by the rate of change of temperature in these 12 min (about $\pm 20 \times 10^{-3}$ K). Hence, the sample is being cooled and heated alternatively during a run.

The integration of the electromotive force given by the fluxmeter between every pair of steady states allows us to determine the sample’s thermal capacity. Hence, the method is able to determine two data of heat capacity in each cycle. The first one is calculated from the dissipation branch $C_d$, and the second one from the relaxation branch $C_r$. The heat capacity obtained in either branch shows a regular behaviour if there is no phase transition or if it is continuous. When a discontinuous phase transition occurs, both data become different, showing an anomalous behaviour in the temperature interval where the latent heat is produced as a result of the thermal hysteresis and transition kinetics. That behaviour is an evidence of the discontinuous character of the transition [16]. Incidentally, we must point out that specific heat data are not reliable when this behaviour is observed.

On the other hand, the DTA trace is continuously measured in a second run without dissipation in the sample and using the same temperature scanning rate used to measure the specific heat. Due to the high number of thermocouples and the good thermal stability of the sample, the equipment works like a very sensitive DTA device. The electromotive force given by the fluxmeters is proportional to the heat flux, $\phi_d$, exchanged between the sample and the calorimeter block.

From the specific heat data obtained in the first run and using a method previously described [14–16], we calculate the heat flux $\phi_c$ which would have been due exclusively to the behaviour of the thermal capacity of the sample around the transition temperature. Comparing the measured $\phi_d$ and the calculated $\phi_c$, we deduce that only in the temperature range $(T_f, T_p)$ where both data do not coincide is there an effect from the latent heat. Its value is determined by integrating $\phi_d/v$, where $v$ is the rate of temperature change, between $(T_f, T_p)$ and using the straight line $\phi_d/v(T_f) - \phi_d/v(T_p)$ as a baseline [15]. The sensitivity of the method is estimated to be better than 5 mJ.

The single crystal of KH₂PO₄ was grown at the Institute of Physics of Poznan University (Poland). The sample has 0.3857 g mass, with a thickness of 2.16 mm along the ferroelectric axis and electrodes with circular faces of 78.5 mm² surface area. Gold electrodes were evaporated of the surface of the sample; those electrodes were connected to a capacitance bridge ESI-SP 5400 which has allowed us to measure the dielectric permittivity of the sample, simultaneously to the heat flux, with an imposed external bias field of 0, 100, 400 and 1000 V cm⁻¹.
3. Results

3.1. Calorimetric measurements

The temperature dependence of the specific heat $c_p$ of a sample of KDP was measured on cooling, with quasistatic conditions at a scanning temperature rate of about $v \sim 0.1 \text{ K h}^{-1}$ using the method described in section 2 for different applied electric fields. In figure 1, the specific heat data in a wide temperature interval for different applied electric fields (a) $E = 0 \text{ V cm}^{-1}$, (b) $E = 100 \text{ V cm}^{-1}$, (c) $E = 400 \text{ V cm}^{-1}$ and (d) $E = 1000 \text{ V cm}^{-1}$ are shown.
These specific heat data show a linear temperature dependence in the paraelectric phase and for 0, 100 and 400 V cm\(^{-1}\) a sharp \(\lambda\)-type anomaly in a narrow temperature interval is observed. For 1000 V cm\(^{-1}\) the maximum is more rounded and the transition is smeared. The shape of the specific heat curve for high electric field tends to be almost symmetric; such behaviour was also suggested by Reese [6]. The maximum value of \(c\) initially increases with increasing field but decreases for sufficiently high values. As expected, the specific heat tail in the paraelectric phase increases with field as a consequence of the coupling of the order parameter to the field.

In figure 2, we have plotted the specific heat excess obtained in the dissipation branch (\(c_d\)) and in the relaxation branch (\(c_r\)) in a narrow temperature interval, 1 K, for each electric field. We observed that for 0, 100 and 400 V cm\(^{-1}\), \(c_d\) and \(c_r\) data do not coincide around the...
transition temperature while for 1000 V cm$^{-1}$ both series of data almost coincide in the whole range of temperature. As we have stated above, the temperature variation of the sample due to the thermal pulses is slightly higher than the variation due to the temperature ramp. This means that in every period the temperature of the sample increases and decreases consecutively. Due to thermal hysteresis, to kinetics of the phase transition, etc, the process of heating and cooling when two phases coexist is different, and consequently data obtained in the dissipation branch and relaxation branch become different under these conditions. We have reported previously that the difference is very significant even in systems near the tricritical point, where the latent heat is very small ($L = 0.13$ J g$^{-1}$ for KMnF$_3$, $L = 0.010$ J g$^{-1}$ for KMn$_{0.997}$Ca$_{0.003}$F$_3$) [16].

Hence, in the case of KDP, it is clear from figure 2 that for 0, 100 and 400 V cm$^{-1}$ the phase transition is discontinuous. In contrast, the similar behaviour of $c_d$ and $c_r$ for 1000 V cm$^{-1}$, figure 2(d), indicates that no trace of latent heat is present, so we can deduce that for 1000 V cm$^{-1}$ the phase transition is continuous. Hence the critical field lies between 400 and 1000 V cm$^{-1}$.

On the other hand, the baseline with respect to which the fluxmeter emf is integrated in order to calculate the specific heat is the underlying signal due to the temperature ramp imposed on the calorimeter. This signal changes very slowly and it does not affect the specific heat measurement except when a latent heat effect occurs. It produces a nonlinear variation of the baseline and consequently erroneous data of specific heat may appear. Keeping in mind that the measurements have been carried out in a cooling ramp, in figure 2(a) the first $c_r$ at the beginning of the transition which does not coincide with the corresponding $c_d$ data is lower than the regular contribution to the specific heat. In figure 2(b) we can also observe a similar point, but this effect is smeared. Finally, in figure 2(c) we cannot observe any decrease in $c_r$. Nevertheless, $c_r$ deviates from $c_d$ in a small range of temperature as in the two previous figures. Hence, we can deduce that the latent heat decreases with field and should be very small for 400 V cm$^{-1}$.

To confirm this suggestion and to calculate the latent heat, we measured the DTA trace in a second run, changing the temperature of the sample at the same constant rate as that used in the specific heat measurements to make both sets of data comparable. We must point out that the rate of change of temperature is about two orders of magnitude lower than the minimum value achieved in conventional DTA equipment. In figure 3, we represent the heat flux given by the fluxmeters $\phi_d/v$ (DTA trace) and the heat flux $\phi_c/v$ calculated from the specific heat data, using the method previously described, for the fields 0 V cm$^{-1}$ (a), 100 V cm$^{-1}$ (b), 400 V cm$^{-1}$ (c).

For 0 and 100 V cm$^{-1}$, $\phi_d/v$ is higher than $\phi_c/v$ in a very small temperature interval of about 0.05 K, showing the effect of latent heat. For 400 V cm$^{-1}$, $\phi_d/v$ is also higher than $\phi_c/v$, but the difference between them is smaller, indicating a very small latent heat.

The choosing of the baseline to determine the latent heat value for 0 V cm$^{-1}$ in graph figure 3(a(i)) is difficult due to the very small temperature interval where the latent heat is present and, consequently, the few data recorded inside that interval. However, by considering as a baseline the straight line between the extreme temperatures where $\phi_d/v$ and $\phi_c/v$ coincide, we obtain a value of 43 J mol$^{-1}$. This line is also represented in figure 3(a). The value obtained for KDP deuterated at 80% using the same set-up and procedure was 317 J mol$^{-1}$ [24].

To confirm the validity of that choice of baseline we again measured the heat flux exchanged by the sample in identical conditions. Those heat flux data are also plotted in figure 3(a(ii)). The figure shows that both heat flux data coincide with $\phi_c$ (stars) in the same range of temperature, thus supporting the baseline used for the determination of the latent heat. In fact, the latent heat for the second run is 45 J mol$^{-1}$, in good agreement with that of the first one. On the other hand, these values of the latent heat are in agreement with Reese [6].
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It is noteworthy that the peak area—i.e. latent heat—is quite reproducible despite the kinetic effects that occurred in each experiment. In contrast, the difference observed in $\phi/v$ during the phase transitions suggests the existence of a non-equilibrium kinetic process such as those expected for a discontinuous phase transition—for instance phase front generation—which, as a general fact, are non-reproducible.

For $E = 100$ and $400$ V cm$^{-1}$ we decreased the scanning rate of the temperature when measuring the specific heat so as to get a higher number of data points in the neighbourhood of the phase transition. Hence, the determination of the baseline becomes easier, as shown in figure 3. The integration of the peaks gives 35 and $4.2$ J mol$^{-1}$ respectively.

The results obtained confirm that the latent heat diminishes with electric field (see figure 4). At $400$ V cm$^{-1}$ the latent heat is reduced by an order of magnitude with respect to that of zero field, and it is close to the critical field. Assuming a linear behaviour of the latent heat with the field we deduce that the critical field is $(0.44 \pm 0.03)$ kV cm$^{-1}$.

3.2. Dielectric measurements

In order to relate the calorimetric and dielectric behaviour the dielectric permittivity along the ferroelectric axis has been measured simultaneously with the heat flux.

In figure 5 we represent $\varepsilon(T)$ for the different electric fields. The dielectric permittivity increases in all cases during the phase transition following the Curie law. In the ferroelectric phase the dielectric permittivity remains in a plateau, indicating also the large domain wall contribution to the dielectric permittivity, but the maximum of permittivity decreases with the applied electric field. It has been previously reported that the maximum value of dielectric permittivity is due to the contribution of the domain wall [25]; under an electric field the sample becomes close to a monodomain state, so the number of domain walls decreases, and also the
Figure 4. Plot of the latent heat $\Delta h$ at various electric fields. The critical field is found to be $(0.44 \pm 0.03)$ kV cm$^{-1}$.

Figure 5. Plot of the dielectric permittivity at various electric fields. Permittivity data were measured simultaneously with the heat flux data of figure 3.

dielectric permittivity. Nevertheless, the behaviour at the transition temperature is different for 0 and 100 V cm$^{-1}$—discontinuous transition—than for 400 V cm$^{-1}$—close-to-critical-point transition—and 1000 V cm$^{-1}$—continuous transition. We show in figure 6 the shape of the dielectric permittivity for 0 and 400 V cm$^{-1}$. 
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Figure 6. (a) Plot of the inverse of the dielectric permittivity (right axis) and $\phi v^{-1}$ (left axis) for $E = 0 \text{ V cm}^{-1}$. (b) Plot of the dielectric permittivity (right axis) and $\phi v^{-1}$ (left axis) for $E = 400 \text{ V cm}^{-1}$.

The heat flux and the inverse of the dielectric permittivity versus temperature for $E = 0 \text{ V cm}^{-1}$ are represented in figure 6(a). Three regions may be distinguished in this figure: (i) the paraelectric phase where the permittivity follows the Curie law, (ii) the phase transformation interval where the permittivity slightly deviates from the previous behaviour, and (iii) the ferroelectric phase where the permittivity shows a plateau. We must point out that the maximum of the permittivity matches with the end of the phase transformation.

For $400 \text{ V cm}^{-1}$, $\varepsilon(T)$ shows a different behaviour—see figure 6(b). At the transition temperature there is a minimum. This has been observed by Bornarel [19] in crystals of KDP for higher values of electric field (about 1 kV cm$^{-1}$). In that work Bornarel explains this behaviour in terms of some domain arrangements during the phase transition; $\varepsilon(T)$ is described as the sum of the behaviour of the $\varepsilon_1(T)$ contribution that corresponds to the behaviour of a monodomain sample, and the corresponding $\varepsilon_2(T)$ due to the contributions of domains. Moreover, $\varepsilon_1(T)$ increases from the paraelectric phase and after the maximum at the transition temperature decreases to zero in the ferroelectric phase; $\varepsilon_2(T)$ increases from zero at the transition temperature and remains in a plateau in the ferroelectric phase. The sum of both contributions gives the appearance of $\varepsilon(T)$ in figure 6(b).

It may also be seen from the results presented in figure 6 that the peak of the heat flux at the transition temperature appears at the temperature where the production of domains become dominant.

4. Conclusions

The thermal and dielectric behaviour of KDP crystal near the temperature of its ferro–paraelectric phase transition have been simultaneously studied under the influence of electric
field. For 0 V cm$^{-1}$ the latent heat has been measured twice. Although both measurements show a different kinetic, their results are similar and in good agreement with those obtained by Reese [6]. Despite the high increase of the specific heat around the transition temperature, the very small values of the latent heat and the narrow temperature range—about 0.1 K—where the transition is developed, we have been able to ascertain the contribution of the latent heat to the total change of enthalpy. Finally, simultaneous measurements of the heat flux and dielectric susceptibility suggest that the effect of latent heat appears in a temperatures range where domains are growing. The maximum dielectric permittivity was observed at the temperature where the phase transition ends.

It was established that the latent heat decreases with the field, and the critical electric field is estimated to be $(0.44 \pm 0.03)$ kV cm$^{-1}$.

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