Field-dependent specific heats and soft modes in KTaO₃ and SrTiO₃ at low temperatures

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(Received 10 April 1978)

Measurements of the electric-field dependence of the specific heats of a $KTaO_3$ crystal (up to 16 kV/cm) and of a $SrTiO_3$ ceramic (up to 22 kV/cm) at temperatures below 10 K are reported. The specific heat of both materials decreases with applied field, and the data are analyzed assuming this decrease is due to the hardening and splitting of the soft TO mode frequency. The field dependence of the soft mode is described using a Lyddane-Sachs-Teller–Devonshire formalism, and the soft-mode contribution to the specific heat is described by appropriate Einstein terms. Good agreement with the experimental data is obtained.

Soft optical modes exist in the cubic perovskites $KTaO_3$ and $SrTiO_3$. The frequencies of these modes at low temperatures are in the range 10-20 cm^{-1}, and it is known from induced Raman scattering that an electric field has a dramatic effect in increasing and splitting the soft-mode frequency in these crystals.[1]

Low-lying modes below 100 cm^{-1} strongly influence (and often dominate) the low-temperature specific heats of ferroelectric,[2] superconducting,[3] superionic,[4] and amorphous[5] materials. Therefore, ferroelectrics with field-dependent low-lying modes will have associated field-dependent specific heats at low temperatures.[6] This paper reports the first measurements of this effect in $KTaO_3$ and $SrTiO_3$.

A single crystal of $KTaO_3$ [(100) major faces, 0.122 cm thick] and a carefully prepared and annealed ceramic sample of $SrTiO_3$ (0.055 cm thick) were gold electroded on the major faces and measured in the adiabatic calorimeter described elsewhere.[2] Isothermal data at three temperatures for each material are shown in Fig. 1, and the data were measured on decreasing the field strength from the maximum value.[7] The temperatures were maintained to within about ±0.5%, and the zero-field specific-heat values agree very well with previously reported zero-field data on the same $KTaO_3$ crystal[8] and the same $SrTiO_3$ ceramic.[9]

The Fig. 1 data show a decrease in the specific heats with applied field, as is expected from the field hardening of the soft-mode frequency. To interpret these data, we assume that the change in the specific heat is due entirely to the soft mode and adopt the combined Devonshire and Lyddane-Sachs-Teller (LST) formalism used to interpret the induced Raman scattering in $KTaO_3$ and $SrTiO_3$.[1]

An [001] field splits the TO mode into parallel and perpendicular components (corresponding to the zz and xx or yy components of the inverse di-

electric tensor, respectively) with frequencies given by[1]

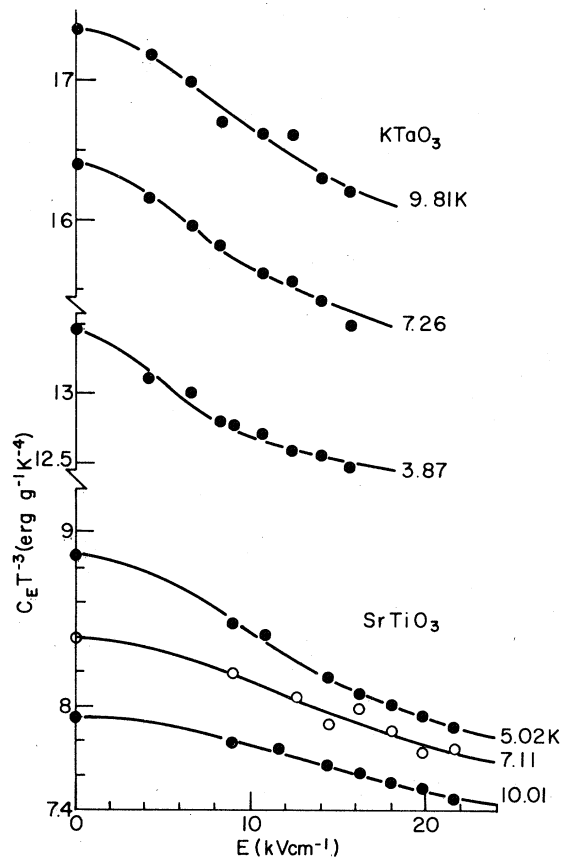$$(\omega_s^{\parallel})^2 = A\epsilon_0 (\chi + 3\xi P^2 + 5\zeta P^4) \qquad (1)$$

FIG. 1. Electric-field dependence of the low-temperature specific heat of $KTaO_3$ and $SrTiO_3$. During the course of a field sweep, isothermal conditions were maintained to ~ ± 0.5%. The curves through the points are theoretical curves based on the assumption that the field dependence of the specific heat is due entirely to the hardening and splitting of the soft-mode frequency.

and

$$(\omega_s^\perp)^2 = A\epsilon_0(\chi + \xi'P^2).\qquad(2)$$

The coefficient A is defined by the LST relation, $\omega_s^2\kappa = A$, and χ, ξ, ξ', and ζ are the Devonshire coefficients relating P and E,

$$E_z = \chi P_z + \xi P_z^3 + \xi'P_z(P_x^2 + P_y^2) + \zeta P_z^5 + \cdots.\qquad(3)$$

The specific heat is written as the sum of a field-independent term C' and the soft-mode term $C_s(E)$,

$$C_E = C' + C_s(E),\qquad(4)$$

where C_s can be written as two Einstein terms describing the soft-mode splitting,

$$C_s = 3Rr[\tfrac{1}{3}x^2e^x/(e^x-1)^2 + \tfrac{2}{3}y^2e^y/(e^y-1)^2],$$
$$x = \hbar\omega_s^\parallel/kT, \quad y = \hbar\omega_s^\perp/kT.\qquad(5)$$

In Eq. (5), R is the gas constant and r the zero-field mode strength. The field dependence of the frequencies in Eq. (5) are given by Eqs. (1) and (2). Finally, Eq. (4) is rewritten

$$C_E = C_0 - [C_s(0) - C_s(E)],\qquad(6)$$

to eliminate C'. The zero-field term $C_s(0)$ is just Eq. (5) with $\omega_s^\parallel = \omega_s^\perp = (A\epsilon_0\chi)^{1/2}$.

To compare Eq. (6) with the experimental data in Fig. 1 via Eqs. (1)–(3) and (5), the *only* fitting parameter is the mode strength r in Eq. (5), since everything else is known from previous studies: Dielectric data in the temperature range of interest were fitted to the Barrett model[10]

$$\chi = 4\pi[(\tfrac{1}{2}T_1)\coth(T_1/2T) - T_0]/B,\qquad(7)$$

with the results that B, T_1, and T_0 are 6.18×10^4, 48.3 K, and 8.02 K for $KTaO_3$,[8] and 1.041×10^5, 79.0 K, and 23.5 K for the $SrTiO_3$ ceramic,[9] respectively. The nonlinear coefficients were previously determined on the same samples from electrocaloric measurements: ξ and ζ are 0.98×10^{-11} and 0.62×10^{-19} (cgs) for $KTaO_3$,[8] 4.73×10^{-14} $(T+15.6)$ and 3.0×10^{-21} (cgs) for $SrTiO_3$,[9] respectively. Finally, the coefficient A in Eqs. (1) and (2) is evaluated from the zero-field frequencies using Eqs. (1), (2), and (7) and the literature values at 10 K: 22 cm^{-1} for $KTaO_3$,[11] and 11 cm^{-1} for $SrTiO_3$.[1] Following the Raman stud-

ies,[1] ξ' was set equal to ξ for both materials.

These equations were solved for the case of the field applied along [001], and the experimental C_E data in Fig. 1 were fitted to Eq. (6) with r of Eq. (5) being the only fitting parameter. The full curves in Fig. 1 are the results of these fittings, and the agreement with experimental data is very good. Note that the Einstein terms in Eq. (5) vary rapidly with temperature and are very sensitive to the ω_s values used.

The fitted r values for $KTaO_3$ show a slight temperature dependence ($r\times10^3 = 6.85$, 4.63, 5.19 at 9.81, 7.26, 3.87 K). This is probably due to uncertainties in the experimental data.

For the $SrTiO_3$ ceramic, the fitted r values show a more pronounced variation ($r\times10^3 = 3.48$, 1.37, 7.29 at 10.07, 7.11, 5.02 K). This variation is too large to be attributed to experimental uncertainties. There are two probable causes. First, the assumption of an [001] field is strictly valid only for the $KTaO_3$ crystal. And second, in contrast to $KTaO_3$, $SrTiO_3$ has two Raman-active modes at ~15 and ~50 cm^{-1} which are not components of the soft mode.[1] The contribution of the latter mode to $C_0 - C_E$, Eq. (6), is negligibly small. The frequency of the 15 cm^{-1} mode is field independent, but its amplitude may be field-dependent as suggested by the Raman data.[1] This mode would then contribute an additional term to $C_0 - C_E$.

In conclusion, we find that the measured decrease in the specific heat of $KTaO_3$ and $SrTiO_3$ with electric field at constant temperature can be satisfactorily explained as a soft-mode effect. These data demonstrate the dependence of thermal properties on a field-movable phonon mode which can be externally controlled. Similar phenomena are expected in the low-temperature thermal conductivity and thermal expansion of these materials,[12] due to interactions between the optical phonons and thermal acoustical phonons.

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