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RAYLEIGH SCATTERING NEAR THE PARAELECTRIC-FERROELECTRIC PHASE TRANSITION IN $BaTiO_3$

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In $BaTiO_3$ strong Rayleigh scattering near the paraelectric to ferroelectric phase transition was observed for (z,y) geometry. In a static external electric field this peak strongly increases in intensity and shifts to higher temperatures as well. These results can in principle be explained by the Ginzburg theory. However, other scattering mechanisms can not be excluded.

As outlined by Ginzburg in 1955[1] additional light scattering should be observed in solids near second order phase transitions and, in particular, near critical Curie points. This scattering is due to fluctuations in the order parameter. In the last years extensive experimental and theoretical work was performed in connection with critical phenomena near phase transitions in solids[2].

In this note we report on some preliminary light scattering experiments near the paraelectric to ferroelectric phase transition in $BaTiO_3$. This phase transition is known to be of first order. Consequently, in the region of the transition temperature, no additional light scattering due to fluctuations is expected. However, as shown by Meyerhofer[4] and DeBretteville[5] the first order paraelectric to ferroelectric phase transition nearly becomes second order under the influence of an external static electric field. Furthermore, for many years $BaTiO_3$ served as a "model" ferroelectric, and therefore many independent experimental data are available[3].

For the light scattering experiments, single crystals grown from the KF flux by the Remeika[6] method were prefered to the available melt grown crystals, because of their better optical quality and poling properties. These crystals were selected for minimum internal strain and an optical axis could be definitively determined using conoscopical microscopy. Care was taken that only a single domain was passed by the light. The temperature of the symple was varied linearly by 1 K/minute. All experiments were performed in back-scattering or forward-scattering geometry.

Fig. 1 shows typical results for x(z,y)x geometry. The electric field was applied parallel to the ferroelectric axis (z-axis) of the crystal. The most remarkable feature is a strong peak in the integrated scattering intensity, shich shifts to higher temperatures and increases in intensity with increasing field strength. Qualitatively, such a behaviour was found as well by Romanovskis and Zvirgzde[7]. In Figs. 2 a and 2 b the temperature at which the peak occurs, and the peak height normalized to the height at zero field, respectively, are plotted as a function of field strength.

Similar results were obtained in z(x,y)z geometry, while for z(x,x)z only a steep rise in the scattering intensity occurred at the phase transition. Such a behaviour was expected from the selection rules.

In spite of the fact that we can not definitively exclude that inhomogeneities, e.g. phase boundaries,

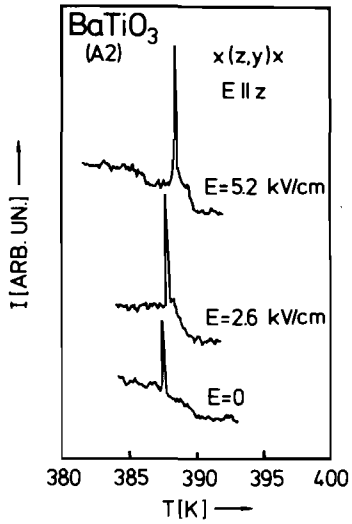

Figure 1: Temperature dependence of integrated rayleigh scattering intensity in $BaTiO_3$ near the paraelectric-ferroelectric phase-transition.

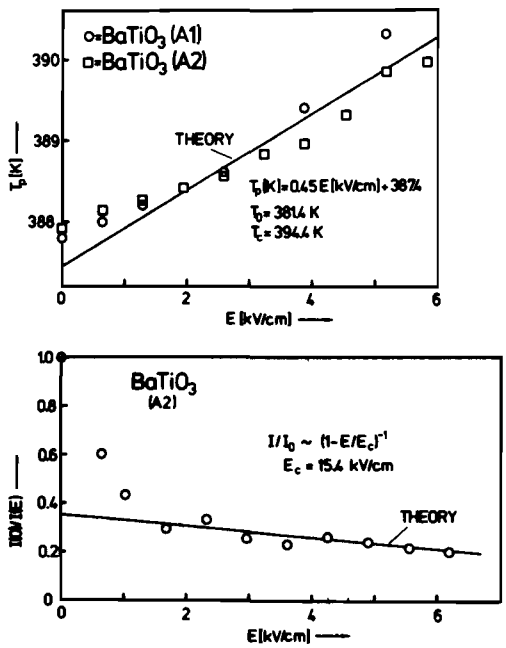

Figure 2: a) Shift of peak position T_p as function of electric field.
b) Inverse of maximum scattering intensity as function of electric field.

internal strain, domain or defect rearrangements etc., are responsible for the "anomalous" scattering near the phase transition, we now try to compare these results with the predictions based on the theory by Ginzburg[1] and Krivoglaz and Rybak[8]. The reduced equation of state can be written in the form

$$8\,e = 15\,tp - 10p^3 + 3p^5 \qquad (1)$$

with $e = E/E_c$, $p = P/P_c$,

$$t = (T-T_o)/(T_c-T_o) \qquad (2)$$

where T_c, P_c and E_c are the critical values for temperature, polarization and electric field. A plot of equation (1) is shown in Fig. 3 in order to illustrate the strong analogy to a van der Waals equation. From this diagram

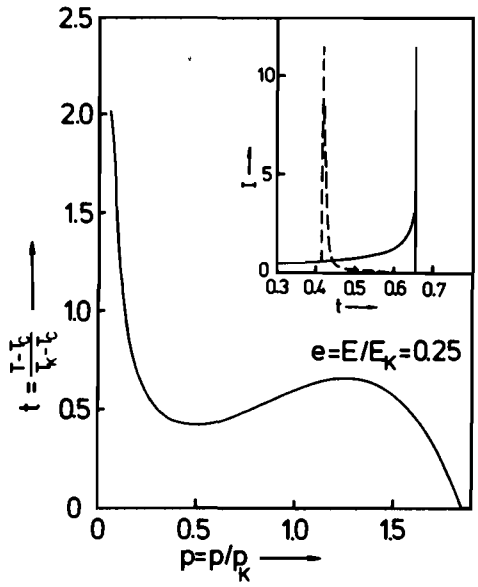

Figure 3: Temperature dependence of the polarization in an electric field according to equation (1). t = 0 corresponds to the supercooling temperature for zero field case, t = 1 corresponds to critical temperature.

the transition temperature can be calculated. This temperature can, within 0.05 reduced temperature units, be approximated by

$$t_p \approx \frac{8}{15}e + \frac{7}{15} \qquad (3)$$

Equation (3) can be derived for the limiting case e, p, $t \longrightarrow 1$ (second order transition). It should be pointed out that equation (1) reflects Pytte's[9] self-consistent calculations for the case of zero field. Following Ginzburg[1] and Krivoglaz and Rybak[8],

and neglecting supercooling or superheating effects (the extremal cases for the light scattering intensity are indicated in the inset of Fig. 3), the maximum scattering intensity at the phase transition is given by

$$I(E)/I(0) = (1-e)^{-1} \qquad (4)$$

From Fig. 2 b together with equation (4) we can estimate the critical field to $E_c \approx 15.4$ kV/cm. In analogy, from Fig. 2 a and equation (3) we obtain for the critical temperature $T_c \approx 394.4$ K and for the Curie temperature $T_o \approx 381.4$ K. These data are in reasonable agreement with the data derived from the birefringence measurements of Meyerhofer[4], the measurements of polarization by DeBretteville[5], and the calculations by Kulwicki[10] which are based on dielectric data.

The systematic deviation of our experimental results at low field strength i.e. below the coercitive field strenth of about 1 kV/cm (see Fig. 3) may be either due to hysteresis effects or due to inhomogeneities as mentioned above.

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