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THE TEMPERATURE DEPENDENCE OF THE NONLINEAR PIEZOELECTRIC COEFFICIENT e_{345} OF KDP[1]

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The results of the measurement of the temperature dependence of the nonlinear piezoelectric effect in potassium dihydrogen phosphate (KDP) are presented. The used ultrasonic method operates with a low frequency ac field and is well suited for measurements near phase transitions.

I. INTRODUCTION

Potassium-dihydrogen-phosphate KH_2PO_4-KDP-shows a first order phase transition from a paraelectric high temperature tetragonal phase (point group $\bar{4}2$ m) to a ferroelectric orthorhombic phase (point group mm) at 123 K [1]. A great number of publications concerning linear elastic and electromechanic properties is already known, e.g. [2, 3, 4]. Room temperature measurements of nonlinear elastic and nonlinear piezoelectric coefficients were carried out by Korobov [5] and Petrakov et al. [6]. The temperature dependence of the nonlinear piezoelectric coefficient d_{316} of KDP was published by Sysoev et al. [7].

II. EXPERIMENTAL

We applied an ultrasonic method developed by Korobov et al. [8] to investigate the temperature dependence of the nonlinear piezomodul e_{345} of KDP. A conventional stable phase rf generator excites a quartz transducer with short pulses. This transducer also receives the echo impulse series. A sampling oscilloscope converts the transit time variation introduced by an alternating electric field of low frequency via the slope of a delayed rf echo cycle into a voltage that is further processed in a lock in an amplifier. Transit time variations $\Delta\tau/\tau$ of $10^{-6} \dots 10^{-7}$ can be detected if low sample attenuation is provided.

The initial sound velocity W_0 at a given temperature is calculated from the sound path length divided by the transit time τ_0. An electric field E_0 causes a transit time variation $\Delta\tau$ of a corresponding sound velocity variation ΔW. According to Ljamov [9] we define the quantity γ in the form:

$$\gamma = \frac{\Delta W}{W_0 E_0} = -\frac{\Delta\tau}{\tau_0 E_0} = \frac{1}{2\varrho_0 W_0^2}(2F\varrho_0 W_0^2 - E + G) . \tag{1}$$

The material density is denoted by ϱ_0, F, E and G represent the linear piezoelectric, the nonlinear piezoelectric and the combination of the third order elastic with the linear piezoelectric effects, respectively.

All nonlinear piezoelectric coefficients can be measured in principle, provided all linear piezoelectric, stiffness and all third order stiffness coefficients are given. Seven independent piezoelectric coefficients must be taken into account for the paraelectric phase of KDP ($\bar{4}2$ m) [9, 10].

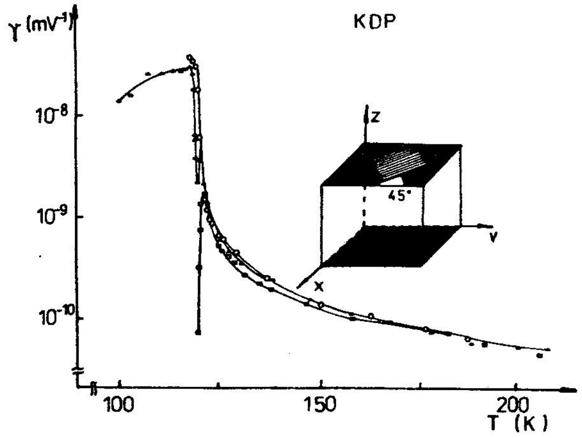

Fig. 1. Arrangement of transducer, sample and electric field. Specific sound velocity variation γ on the temperature T. The sound wave propagates in the z-direction, which is also the direction of the electric field. The particle displacement is chosen along the [110] — direction. Static electric field: ○ ... 0 kV/cm, △ ... 0.7 kV/cm and □ ... 4 kV/cm. Ultrasound frequency: 30 MHz.

The coefficient e_{345} can be determined with a geometry shown in fig. 1. (We use the matrix notation for the coefficients). The excited wave is a pure wave in the z-direction. F, E and G are reduced to the following relations in this case:

$$F = d_{36} \tag{2}$$

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$$E = e_{345} \tag{3}$$

$$G = d_{36}\, c_{456}\,. \tag{4}$$

The other six nonlinear piezoelectric coefficients cannot be found with sound wave propagation in the axes directions. Several combinations of directions of the sound wave and the electric field would be necessary to measure and to compute the other coefficients.

III. RESULTS AND DISCUSSION

The results of the investigations are plotted in fig. 1. The sample was cooled and its temperature was stabilized at each measuring point within 0.1 K. The absolute values of γ were checked using transit time variations introduced by a static electric field far above the transition. The absolute error lies in the order of magnitude of 5 %.

The transit time variation in dependence of the applied electric field was exact linear, no harmonics of the modulation frequency could be detected even, near the phase transition. The modulation voltage was varied and measured during the experiment in such a manner that the output of the lock in the amplifier and hence the transit time variation remained constant. Attenuation and velocity showed no remarkable temperature dependence. The velocity corresponds to the c_{44} stiffness coefficient and its increase with decreasing temperature is less than 2 % over a region of 100 K.

Measurements below the phase transition were impossible without a static electric field because the signal amplitude became field dependent. If a small static field of 0.7 kV/cm was superimposed, this effect vanished and the γ-value remained at a high level after a short decay in the transition region. The high voltage constant field curve shows a rapid decrease just below the transition temperature. Varying the static electric field no intermediate case could be found between these two kinds of behaviour. The critical field strength dividing these two cases was estimated to be about 1.5 kV/cm.

Fig. 2 shows a log—log plot of the γ-values without a static field above the transition. The phase transition temperature was determined from the Curie—Weiss law of the dielectric permittivity ε_{33}. Additional measurements of the linear piezoelectric coefficient d_{31} with the resonance-antiresonance method [11] were also performed with samples cut from the same crystal. These results are plotted in fig. 2 too. Both γ and d_{31} have critical exponents of -1 ± 0.03. The nonlinear piezomodul e_{345} may be calculated from equations (1) to (4):

$$e_{345} = d_{36}\, c_{456} - 2\varrho_0\, W_0^2\, (d_{36} - \gamma)\,. \tag{5}$$

The factor $2\varrho_0\, W_0^2$ is nearly constant. The theoretical critical exponent of d_{36} od

-1 coincides with the measured one. Applying the theory of Beige [12] e_{345} has a critical exponent of -1 too. The third order elastic coefficient c_{456} should have also an anomaly following this theory. But this anomaly would be very low if the validity of equation (5) were provided. Unfortunately we could not find any measurements of the temperature dependence of the third order elastic stiffnesses of KDP.

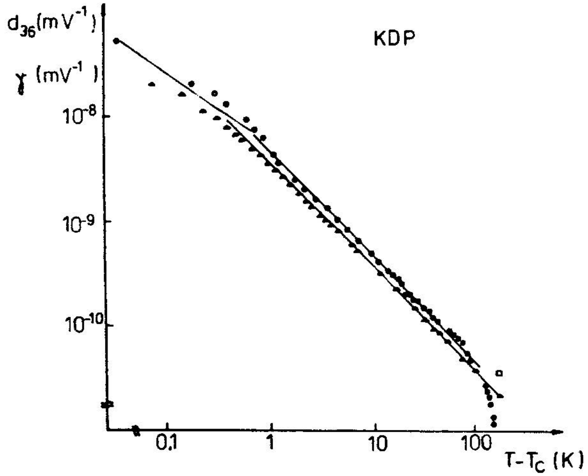

Fig. 2. Log—log plot of the sound velocity variation γ vithout the static electric field (○) and the piezoelectric coefficient d_{31} (△) versus temperature difference $(T - T_c)$ above the transition temperature T_c. The point □ is taken from [6].

The following values at room temperature are known:

$$\begin{aligned} W_0 &= 2340 \text{ m/s},\\ \varrho_0 &= 2338 \text{ kg/m}^3,\\ c_{456} &= (0.08 \pm 0.02 \times 10^{11} \text{ Pa } [5],\\ d_{36} &= 2.75 \times 10^{-11} \text{ m/V},\\ \gamma &= 2.75 \times 10^{-11}, \end{aligned}$$

with γ extrapolated from low temperature values. Using formula (5) we get for the room temperature value of the nonlinear piezoelectric coefficient

$$e_{345} = 0.07 \text{ N/Vm}\,.$$

A definite uncertainty of this value should be noted.

The measurements showed clearly that the used method is well suited for measurements of temperature dependencies of nonlinear piezoelectric coefficients in ferroelectrics. Further investigations of the nonlinear elastic and nonlinear electromechanic behaviour of KDP with the aid of utrasound are planned.

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ТЕМПЕРАТУРНАЯ ЗАВИСИМОСТЬ НЕЛИНЕЙНОГО ПЬЕЗОЭЛЕКТРИЧЕСКОГО КОЭФФИЦИЕНТА e_{345} В КРИСТАЛЛЕ KDP

Показаны результаты измерений температурной зависимости нелинейного пьезоэлектрического эффекта в кристалле KDP. Примененный метод работает переменным электрическим полем низкой частоты и является выгодным для измерений недалеко фазовых переходов.