ARCHIVES OF ACOUSTICS
5, 2, 181-188 (1980)

MEASUREMENTS OF PROPAGATION VELOCITY OF ULTRASONIC WAVE AT A FREQUENCY OF 10 MHz IN PURE AND DEUTERATED KDP SINGLE CRYSTALS*

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The results of determination of all elastic constants of a KH_2PO_4 single crystal (KDP), and in the case of $KD_{2x}H_{2(1-x)}PO_4$ crystals (DKDP) of constants C_{66} i C_{11} and the temperature dependence of the constant C_{66} at a frequency of 10 MHz are reported.

The measurements showed an effect of deuteration on the constant C_{11} and on the change of the temperature dependence of C_{66} in the phase transition region.

1. Introduction

Ferroelectric crystals of the KDP group, both pure and deuterated, are interesting from the point of view of physics, due to the ferroelectric phase transition and the isotopic effect determined by a change of the physical properties of a pure single crystal after introduction of deuterium.

The investigation of dielectric and thermal properties of pure (KDP) and deuterated (DKDP) single crystals has been performed in detail in a wide approach, which is seen in the large number of the reported papers. The elastic properties of these crystals are less often investigated and are usually limited to the pure KDP single crystals or the crystals with special concentration of deuterium [1, 4] and to lower frequencies than those assumed in the overall range of the acoustic investigations in our work.

Information can be obtained from the acoustic investigations, based on the measurements of velocity and attenuation of the elastic wave, related to the static properties and the dynamics of the order parameter which describes the degree of order in a ferroelectric. The use of the acoustic methods for the investigation of ferroelectric phase transitions [8, 10] is particularly recom-

* Work supported by MR. I. 24.

mended when there is disagreement among data on the type of phase transition in the ferroelectric crystal, obtained on the basis of other independent investigations. They can be used in correlation with other experiments to verify the existent theoretical models of the mechanisms of phase transitions [8].

The purpose of this work is the use of the pulse-echo ultrasonic method to investigate the phase transitions in partially deuterated samples of DKDP crystals as a function of deuterium concentration and the frequencies of acoustic waves. The higher frequencies will be used in our further investigations.

The external elastic strain by the order process affects the order parameter. Strong fluctuations of the order parameter in the vicinity of the phase transition cause an increase in some effects connected with measured quantities, e.g. the ultrasonic wave velocity. A change in the ultrasonic wave propagation velocity is essentially determined by the form of coupling between the strain and the order parameter and thus it expresses the static properties of the order parameter. The type of coupling between these quantities is described by the function $F_c(Q_i, \varepsilon_k)$ which occurs in the expansion of the free-energy density in powers of the order parameter Q_i and the components of the strain tensor ε_k [10]. In the case of the KDP type ferroelectrics a linear coupling occurs between the strain and the order parameter,

$$F_c(Q_i, \varepsilon_k) = \beta_{ij} Q_i \varepsilon_j, \tag{1}$$

where Q_i are components of the order parameter, ε_j are the components of the strain tensor, β_{ij} is the coupling parameter.

2. The acoustic measurements of the KDP single crystals

Crystal KDP is a uniaxial ferroelectric with a phase transition temperature $T_c = 122$ K. It undergoes a ferroelectric phase transition from a tetragonal to an orthorombic structure. The order parameter is a spontaneous polarization P_3 directed along the tetragonal c axis. There is a linear coupling [10] between the spontaneous polarization P_3 and the strain ε_6 of the form

$$F_c(\varepsilon_i, P_k) = h_{36} P_3 \varepsilon_6, \tag{2}$$

where the coupling parameter is a relevant component of the piezoelectric stress constant h_{36} at a constant strain.

Only the shear strains are piezoelectrically coupled to the polarization along the c axis. Therefore, the elastic wave which gives information about the type of the phase transition in a KDP crystal is a transverse ultrasonic wave propagating in the (100) direction with its polarization in the (010) direction or a wave with the polarization in (100) propagating in the (010) direction.

Table 1. The elastic constants C_{ij} of a KDP crystal

C_{11}	C_{33}	C_{44}	C_{66}	C_{12}	C_{13}	
		$10^9 [Nm^{-2}]$				
80	80	12.8	6.1	34	41	W. P. Mason 1946 [7]
71.4	56.2	12.7	6.24	−4.9	12.9	W. I. Price 1950 [7]
71.65	56.40	12.48	6.21	−6.27	14.94	S. Haussühl 1964 [2]
71.57	56.61	12.86	6.23	−4.19	14.35	our measurements

The measurements of the ultrasonic wave propagation at a frequency of 10 MHz were performed by the echo-overlap method [9]. The X cut and Y cut quartz transducers were used for generation and detection of the ultrasonic wave. The method used here permits to measure the elastic constants of crystals with an error of less than 0.5 % and a sensitivity of 0.05 % for relative changes in them. This precision relates to the determination of only these elastic constants which are directly expressed through the mass density and the propagation velocity of a sufficient ultrasonic wave. The uncertainty increases respectively in the case of the elastic constants C_{12} and C_{13}, which are expressed not only by the above mentioned quantities, but also by other elastic constants.

The velocities of transverse and longitudinal ultrasonic waves propagating in the sufficiently oriented samples of a KDP single crystal were measured. The values obtained for the elastic constants of a KDP crystal are shown in Table 1 together with data from paper [3].

3. Measurements of the elastic constants C_{66} and C_{11} of DKDP crystals

Only the measurements of the velocity of transverse and longitudinal ultrasonic waves propagating in the (100) direction were performed and the elastic constants C_{66} and C_{11} measured.

The structure symmetry of the KDP type crystals determines that only the elastic constant C_{66} undergoes an anomalous change in the phase transition. The elastic constant C_{11}, however, seemed interesting because of the hydrogen bonds lying very close in the basal (xy) plane. The proton distribution is symmetrical and alongated along the bonds. Measurements of the velocities of the transverse ultrasonic wave V_{12} and the longitudinal ultrasonic wave V_{11} were carried out for three grown DKDP crystals with a different deuteration degree. The results obtained for the elastic constants C_{66} and C_{11} are shown in Table 2.

It should be noted that we observed a change of the elastic constant C_{11} with increasing deuteration in DKDP crystals. This variation of C_{11} is relatively large and exceeds the experimental error, and the investigations will be complemented when completely deuterated crystals have been grown.

Table 2. Phase transition temperatures, T_c, and the elastic constants C_{66} and C_{11} for KDP crystals with a varying deuterium concentration

Deuterium concentration in KDP crystal [mol %]	Phase transition temperature T_c [K]	C_{66} 10^9 [Nm^{-2}]	C_{11} 10^9 [Nm^{-2}]
0	122	6.23 ± 0.03	71.6 ± 0.4
41.4	166	6.21 ± 0.03	69.9 ± 0.3
57.3	183	6.23 ± 0.03	69.7 ± 0.3
70.4	197	6.20 ± 0.03	69.3 ± 0.3

In addition, measurements of the temperature dependence of the elastic constant C_{66} for three DKDP crystals with a different degree of deuteration were made. The experimental results for $C_{66}(T)$ are shown in Figs. 1, 2, and 3, respectively.

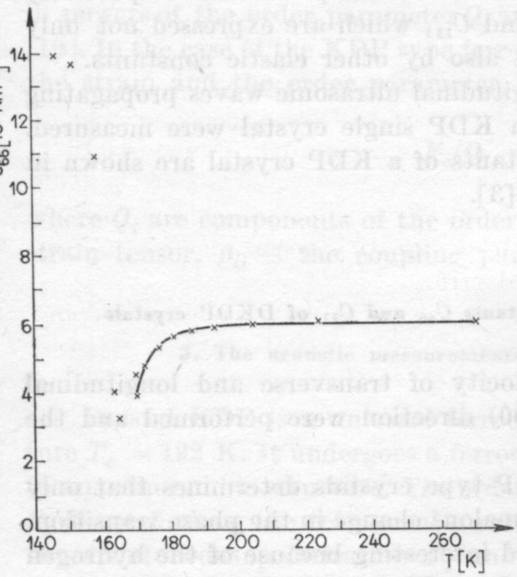

Fig. 1. Temperature dependence of the constant $C_{66}^{E=0}$ for a DKDP crystal with a deuterium concentration of 41.4 mol%

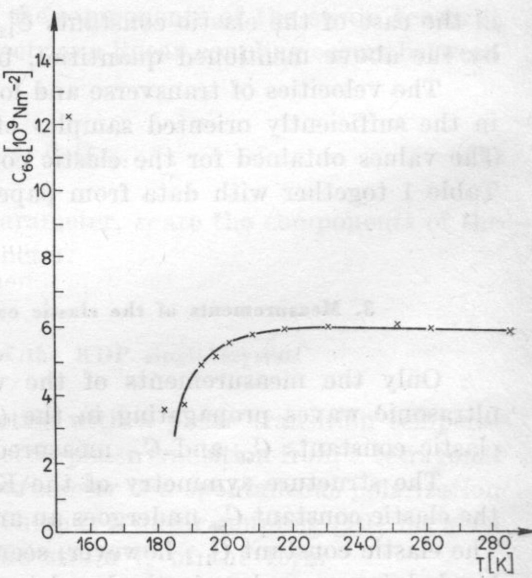

Fig. 2. Temperature dependence of C_{66}^{E} for a DKDP crystal with a deuterium concentration of 57.3 mol%

On the basis of the obtained plots of the dependence $C_{66}(T)$, the values of the phase transition temperatures, T_c, for each DKDP crystal were determined. From the linear dependence of the phase transition temperature T_c on the deuterium concentration in a crystal [5],

$$T_c = 121.7K + 1.07x, \tag{3}$$

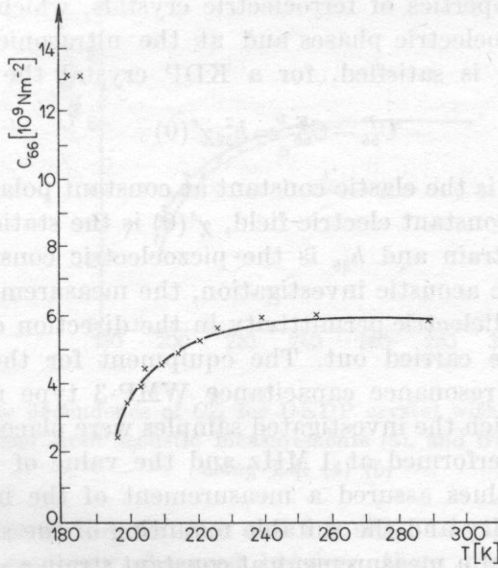

Fig. 3. Temperature dependence of C_{66}^E for a DKDP crystal with a deuterium concentration of 70.4 mol%

the deuteration degree of the crystals investigated was determined. Here x is the deuterium concentration in a DKDP crystal expressed in mol $^0/_0$. The results are given in Table 2. The linear dependence of $T_c(x)$ in the form of (3) is generally used and possible deviations from linearity according to [11] are small and do not exceed the experimental error.

In the first stage of the investigations, despite the use of the method recommended for growing DKDP crystals [2], no completely deuterated crystals were obtained.

4. Discussion of the experimental results

The disagreement occurring among the literature data with respect to the elastic constants C_{ij} of a KDP single crystal [3] required a determination of the elastic constants for the KDP crystals used in the investigations. The values obtained for C_{ij} were determined with an accuracy of more than 0.5 $^0/_0$. The values of C_{ij} for KDP, obtained in [3] previously, involve larger errors, and only the measurements of Haussühl and Price and Huntington [2], which were carried out with a similar accuracy, agree with the authors measurements.

The variation observed for the elastic constant C_{11} with an increasing deuteration in DKDP crystals suggests that the O–H–O bonds will become weaker upon the substitution of D for H. From the relation between the dielectric and elastic properties of ferroelectric crystals, which are piezoelectrics in the para- and ferroelectric phases and at the ultrasonic frequency, when the condition $\omega\tau \ll 1$ is satisfied, for a KDP crystal the relation

$$C_{66}^{P} - C_{66}^{E} = h_{36}^{2}\chi^{s}(0) \tag{4}$$

is valid [7], where C_{66}^{P} is the elastic constant at constant polarization, C_{66}^{E} is the elastic constant at a constant electric field, $\chi^{s}(0)$ is the static dielectric susceptibility at constant strain and h_{36} is the piezoelectric constant.

In addition to the acoustic investigation, the measurements of the temperature dependence of dielectric permittivity in the direction of the spontaneous polarization axis were carried out. The equipment for the measurement of $\varepsilon_{33}'(T)$ consisted of a resonance capacitance WMP-3 type meter and a measuring chamber, in which the investigated samples were placed. The capacitance measurements were performed at 1 MHz and the value of measuring voltage was 10 mV. These values assured a measurement of the nearly static value of dielectric permittivity and the suitable mounting of the sample in the measuring chamber assured a measurement at constant strain $s = 0$. Measurements of ε_{33}' were made with an accuracy of about 5 %. Temperature stability during the measurements was ± 0.01 K.

On the basis of measurements of $\varepsilon_{33}'(T)$, the variation in the elastic constant $C_{66}^{E}(T)$, according to Eq. (4), was calculated for a DKDP crystal with the highest deuteration degree ($x = 70.4$ mol %), in order to compare it with an experimentally obtained change in $C_{66}^{E}(T)$. The results obtained are shown in Fig. 4. Relevant values of h_{36} and C_{66}^{P}([5], p. 86 and 107] and of $\varepsilon_{33}'(T)$ and $C_{66}^{E=0}$, which were used in the calculations, are given in Table 3.

Table 3. Temperature dependencies of h_{36}, C_{66}^{P} and ε_{33} used for the calculation of $C_{66}^{E}(T)$ from Eq. (4)

Temperature [K]	h_{36}* 10^8[NC^{-1}]	C_{66}^{P}** 10^9[Nm^{-2}]	Temperature T[K]	ε_{33}***
373	6.48	5.9	255	80
313	7.05	6.0	238	125
293	7.32		226	184
273	7.50	6.2	220	236
253	7.74		213	303
233	7.98		210	371
213	8.19		205	411
193	8.37	6.5	203	452
173	8.43		199	596
123	9.21	7.0	196	707
			195	702
			193	664
			191	605

*[3], p. 86 **[3], p. 107 ***-our measurements

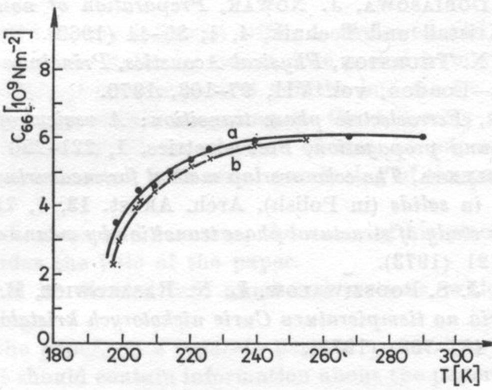

Fig. 4. Temperature dependence of C_{66}^E for DKDP crystal with a deuterium concentration of 70.4 mol% obtained from acoustic measurements (a), and from dielectric measurements using Eq. (4) (b)

The character of the curves *a* and *b* in Fig. 4 is analogous, and the stable quantitative discrepancy observed between them may suggest a systematic error between the experimental data and those calculated from Eq. (4). A source of the error may be the values of C_{66}^P and h_{36}, which were used in the calculations and were not measured for crystals investigated here.

Comparison of curves $C_{66}^E(T)$ from Figs. 1 and 3, obtained for two most differential deuterated samples, does not give an essential change of the character of dependence of $C_{66}(T)$ on increasing deuteration and only a well-known isotope effect on T_c is obtained.

An investigation of elastic constants in the region very close to T_c for DKDP crystals with a varying deuterium concentration seems more interesting on the low-temperature side of T_c, due to the possibility of other isotopic effects occurring and that of observing a possible change of the order phase transition due to deuteration.

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Received on October 12, 1978; revised version on May 25, 1979.