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# ELASTIC PROPERTIES OF AMMONIUM DIHYDROGEN PHOSPHATE AND THE LAVAL-RAMAN THEORY OF ELASTICITY

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Laval (**1**) and Raman (**2, 3**) proposed a new theory of the elasticity of crystals. The basic premise of this theory is the rejection of the well-known proposition of the classical theory of elasticity, which asserts the symmetry of the stress and strain tensors in the general case of an anisotropic elastic medium. This increases the number of independent elastic constants in a triclinic crystal from 21 to 45. In recent years a considerable number of papers have appeared in the literature whose authors support the new theory and, on the other hand, a large number of high-precision measurements have been published in which no deviation from the classical theory of elasticity was found in those classes of crystals where such a deviation ought to have appeared (see the review papers (**4-6**)).

The most important experimental confirmation of the theory is considered to be the results of measurements of the elastic constants of the ammonium dihydrogen phosphate crystal, $NH_4H_2PO_4$, belonging to the symmetry class $\bar{4} \cdot m$. Before the measurements by Le Corre (**7**) no deviations from the classical theory had been found in this crystal, despite the fact that the investigations of Zwicker (**8**), as well as of Price and Huntington (**9**), had been carried out with high accuracy. From the data of paper (**7**) it followed that the ratio of the shear moduli $N_{44}/N_{55}$ is equal to $1.36 \pm 0.16$, whereas according to the classical theory it should be equal to $c_{44}/C_{44} = 1$. Later, Joël and Wooster (**10**), after carrying out a detailed analysis of Zwicker' s experimental data (**8**), found that $N_{44}/N_{55} = 1.08 \pm 0.01$. Finally, recently the same authors (**11**) repeated the measurements and reduced this ratio to $1.06 \pm 0.02$.

**Fig. 1.** Block diagram of the apparatus. *1* –heterodyne wavemeter, *2* –continuous-oscillation generator, *3* –modulator, *4* –piezoelectric transducers, *5* –fused-quartz rods, *6* –intermediate bonding layers, *7* –specimen, *8* –broad-band amplifier, *9* –detector, *10* –video amplifier, *11* –cathode-ray tube

The value of this ratio can easily be checked by the pulsed ultrasonic method.

Using the equations for the propagation of elastic waves in crystals in the notation of the new theory (**3**), it is easy to show that the velocity of a purely shear elastic wave propagating along the $Z$ axis of the crystal with displacement along $X$ ($V_{xz}$) is determined by the modulus $N_{55}$, while the velocity of a wave propagating along $X$ with displacement along $Z$ ($V_{zx}$) is determined by the elastic modulus $N_{44}$. From the literature data (**11**) it could be expected that

$$N_{44}/N_{55} = \rho V_{xz}^2/\rho V_{zx}^2 \geq 1.06$$

and

$$V_{xz} \geq 1.03\, V_{zx},$$

whereas according to the classical theory of elasticity the relations

$$c_{44}/C_{44} = \rho V_{xz}^2/\rho V_{zx}^2 = 1.00$$

and

$$V_{xz} = V_{zx},$$

where $\rho$ is the density of the crystal, should hold.

For the measurements we used an apparatus constructed by the authors and operating according to the principle proposed by McSkimin (**12**), in the frequency range 10-100 MHz (see Fig. 1). The voltage of the continuous-oscillation generator 2 is modulated by -shaped pulses of duration 1-10 $\mu$sec and is fed to the piezoelectric transducer of an $X$- or $Y$-cut quartz 4.

An ultrasonic pulse passes through a fused-quartz rod 5 and, after multiple reflections in the specimen 7, reaches the receiving plate 4. After amplification 8 and detection 9, the video signal is fed to the cathode-ray tube 11. On the tube screen one sees overlapping pulses of successive reflections in the specimen, having the form of a "staircase," if all signals arriving at the receiver are in phase. By measuring, with the wavemeter 1, the values of the frequencies at which the "in-phase" condition is realized, one can determine the number of half-waves $n_0$ fitting into a specimen of length $l$ at a given frequency $f_0$, and the velocity of ultrasound in the specimen $V$, from the relation

$$V = \frac{2lf_0}{n_0 - \varphi_0/\pi},$$

where $\varphi_0$ is the phase angle of the wave reflected from the interface specimen—7 intermediate layer 6—fused quartz 5 ($^{12}$).

Thanks to the use of optimum transition layers between the transducers and the fused quartz ($^{13}$), it was possible to ensure a sufficiently broad pass band of the acoustic system, which made it possible to perform measurements at higher harmonics without regluing the transducers, whose natural frequency was 10 MHz.

The measurements were made on two pairs of $X$- and $Z$-cut specimens of ammonium dihydrogen phosphate, oriented with different accuracy. The first pair of specimens, oriented with respect to $X$ and $Z$ to an accuracy of $\pm 1^\circ$, was used by us for preliminary measurements of $V_{xz}$, $V_{zx}$, and for determining the elastic moduli $c_{11}$, $c_{33}$, and $c_{66}$. The second pair of specimens was made from blocks oriented to an accuracy of $\pm 2$–$3'$, in order to eliminate a possible error caused by inaccurate orientation. The specimens for accurate measurements had dimensions $l_x = 2.362 \pm 0.0005$ mm, $l_z = 3.868 \pm 0.0005$ mm, and were glued between fused-quartz rods with an epoxy resin, followed by heating of the entire measuring device at $80^\circ$ for 30 min, in order to reduce the thickness of the resin layer under the specimen.

**Table 1**

Measurement errors, %

| Sources of errors | $X$-cut specimen, $l_x = 2.362 \pm 0.0005$ mm | $Z$-cut specimen, $l_z = 3.868 \pm 0.0005$ mm |
|---|---:|---:|
| Inaccuracy of orientation | $10^{-5}$ | $10^{-5}$ |
| Measurement of dimension | $2 \cdot 10^{-2}$ | $1.3 \cdot 10^{-2}$ |
| Measurement of frequency | $0.1 \cdot 10^{-2}$ | $0.1 \cdot 10^{-2}$ |
| Setting of the “in-phase” condition | $< 0.3 \cdot 10^{-2}$ | $< 0.3 \cdot 10^{-2}$ |
| Phase angle $\varphi_0$ at a frequency of 90 MHz | $< 1.5 \cdot 10^{-2}$ | $< 1.5 \cdot 10^{-2}$ |
| Total error | $< 4 \cdot 10^{-2}$ | $< 3 \cdot 10^{-2}$ |

Possible errors in measuring the velocity of ultrasound, caused by various reasons, are given in Table 1 for these two specimens of the crystal.

The elastic moduli $c_{11}$, $c_{33}$, $c_{44}$, and $c_{66}$, measured on the first pair of crystal specimens, proved to be equal (in $10^{11}$ dyn/cm$^2$): $c_{11} = 6.80 \pm 0.02$, $c_{33} = 3.42 \pm 0.01$, $c_{44} = 0.862 \pm 0.001$, $c_{66} = 0.602 \pm 0.001$, which agrees well with the known literature data ($^{8,9,11}$).

The results of several measurements of the ultrasonic velocities $V_{xz}$ and $V_{zx}$ in the frequency range 30–90 MHz at a temperature of $25.5 \pm 0.5^\circ$ are presented

Fig. 2. Results of measuring the ultrasound velocities $V_{xz}$ (a) and $V_{zx}$ (b) in an ammonium dihydrogen phosphate crystal at various frequencies

Figure 1: Fig. 2. Results of measuring the ultrasound velocities $V_{xz}$ (a) and $V_{zx}$ (b) in an ammonium dihydrogen phosphate crystal at various frequencies

in Fig. 2. Small changes in temperature led to changes in the measured velocities by an amount of order $10^{-4}$ $\deg^{-1}$. The figure gives the results of several independent measurements of these velocities on the same specimens, but with complete regluing and repeated heating of the measuring device. For each of these measurements all points lie on a smooth curve with a scatter of no more than 0.02%. This curve:

tends to a definite limit with increasing ultrasound frequency owing to the approximation of the front of the propagating elastic wave to an ideal plane wave and the decrease in divergence of the ultrasonic beam with increasing frequency.

The small scatter between the measurements, which appears in the low-frequency region, is evidently due to the different thickness of the layer between the fused quartz and the specimen. However, in all measurements these variations are smoothed out as the frequency increases, where the film thickness approaches $\lambda/4$ and the phase angle upon reflection of the pulse approaches zero (12). This is also indicated by the fact that the values of the velocities measured at frequencies of 70 and 90 MHz prove to be practically identical and, in all measurements, tend to one and the same limit, equal to $(2.1857 \pm 0.0007) \cdot 10^5$ cm/sec.

Fig. 2. Results of measurements of the ultrasound velocities $V_{xz}$ (a) and $V_{zx}$ (b) in an ammonium dihydrogen phosphate crystal at various frequencies

Thus, the data presented in Fig. 2 show that the expected difference between $V_{xz}$ and $V_{zx}$ of about 3% was not found. The velocities of elastic shear waves, measured on strictly oriented specimens, prove to be equal to one another with an accuracy of ±0.05%, and, consequently, the ratio of the moduli $N_{44}/N_{55} = 1.000 \pm 0.002$, at least in the region of room temperatures. These data contradict the known optical measurements (7,10,11), which served as confirmation of the Laval–Raman theory of elasticity. Without doubting the accuracy of these measurements, it remains to suppose that the deviations from the classical theory of elasticity observed by the authors are due to causes inherent in the very method of measuring the elastic constants of transparent crystals by studying the diffraction of light by ultrasonic waves.

In work (6) the suggestion was already expressed that such causes may be phenomena produced by strong second-order effects in the ammonium dihydrogen phosphate crystal. In favor of such a supposition is the large scatter in the results of works (7,8,10,11), which were carried out at different amplitudes of oscillation of the specimens and by different methods of exciting oscillations in the specimen.

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*Note: Figure translations are in progress. See original paper for figures.*