

electric arrangements of the crystal, since entropy may be gained from populating both types of levels. Although these suggestions are based on a model for the dihydrogen phosphates, it appears that they may also be important in the construction of model theories for other ferroelectric materials.

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## Elastic Constants of Ammonium Dihydrogen Phosphate (ADP) and the Laval Theory of Crystal Elasticity\*

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The acoustic shear wave velocities  $v_{yz}$  and  $v_{xy}$  have been measured in ADP by the direct method of piezoelectric resonances, and by the direct pulse-echo method. These velocities are found with each method to be equal within the experimental uncertainty. The resonance results have a probable error of 0.1% for the difference between the corresponding Laval elastic constants  $c_{44}$  and  $c_{77}$ . This experimental result disagrees with those previously obtained with ADP by indirect methods.

## INTRODUCTION

IN the established theory of crystal elasticity, the state of strain in a volume element is described by a symmetrical tensor. In terms of an orthogonal coordinate system there are three shear strain components<sup>1</sup>:

$$S_4 = \partial u_y / \partial z + \partial u_z / \partial y; \quad S_5 = \partial u_z / \partial x + \partial u_x / \partial z; \\ S_6 = \partial u_x / \partial y + \partial u_y / \partial x. \quad (1)$$

These strain components measure the change in angle between the vectors in the strained crystal medium which are parallel to the coordinate axes in the unstrained condition. The strain components are unaffected by a rotation of the volume element.

About ten years ago, J. Laval proposed a modified theory of crystal elasticity in which the strain and stress tensors may be unsymmetrical. This theory has been expounded in detail by LeCorre.<sup>2,3</sup> As a consequence, the number of independent elastic constants would be increased. For instance, LeCorre replaces the elastic shear constant  $c_{44}$  by two different constants  $c_{44}$  and  $c_{77}$  whenever the  $Y$  and  $Z$  directions in a crystal are not

equivalent. This would make the elastic energy dependent on rotation. One would hesitate to consider this theory seriously for static deformation, but there is some intuitive appeal in the concept that wave propagation in the  $Z$  direction with particle motion in the  $Y$  direction may be controlled by a different elastic constant from that involved in wave propagation parallel to  $Y$  and particle motion parallel to  $Z$ . The present authors have not found a theoretical foundation for this intuitive assumption as long as the elastic wavelength remains large compared to the lattice constants, and electric boundary conditions are taken into account for piezoelectric crystals. Nevertheless, some experimental work seemed called for in view of the serious consideration given the Laval theory<sup>4-6</sup> and the impact that its verification would have on the whole body of elastic constant measurements.

Experimental confirmation of deviation from classical elastic theory has rested largely on observation of light diffraction by ultrasonic waves in ammonium dihydrogen phosphate (ADP) which belongs to crystal class  $V_d=42m$ . For this crystal, LeCorre<sup>2</sup> claimed a value of  $1.36 \pm 0.11$  for the ratio  $c_{44}/c_{77}$ , while Joel and

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<sup>1</sup> For the nomenclature here used, see Institute of Radio Engineers, New York: Standards on Piezoelectric Crystals, 1949.

<sup>2</sup> Y. LeCorre, thesis, Paris, 1953; published in Bull. soc. franç. minéral. et crist. **77**, 1363 (1954), and **78**, 33 (1955).

<sup>3</sup> Y. LeCorre, J. phys. radium **17**, 934 (1956).

<sup>4</sup> N. Joel and W. A. Wooster, Acta Cryst. **11**, 575 (1958).

<sup>5</sup> H. Huntington, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, pp. 230-232.

<sup>6</sup> R. S. Krishnan, V. Chandrasekharan, and E. S. Rajagopal, *Indian Institute of Science, Golden Jubilee Research Volume* (1959), pp. 150-162.

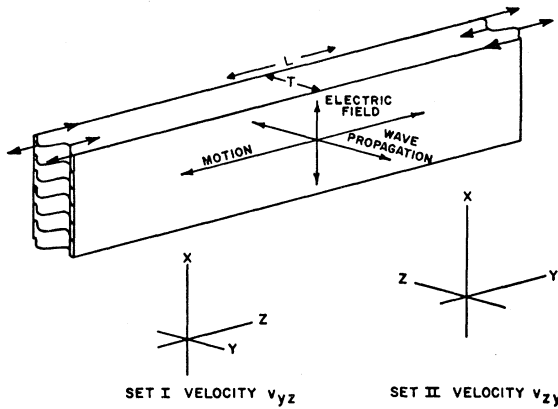


FIG. 1. ADP crystal bar in overtone resonance,  $n=3$ . The coordinate axes indicate the orientation of the two sets of plates used.

Wooster<sup>4,7</sup> derived  $1.08 \pm 0.01$  by analysis of an older "elastogram" of Zwicker.<sup>8</sup> Recently, Joel and Wooster<sup>9</sup> derived  $1.06 \pm 0.02$  from new painstaking measurements. Inspection of the photographed elastograms in this and Zwicker's papers shows how difficult it is to derive the elastic constants in question by this method. We have, therefore, undertaken new measurements by two methods which give the shear elastic constants directly.

#### MEASUREMENT OF PIEZOELECTRIC RESONANCES

In crystal class  $\bar{4}2m$ , an electric field parallel to any one of the crystal axes is coupled to shear strain between the other two axes, and to no other strain components. An electric field parallel to one of the sides of a plate having all edges parallel to crystal axes therefore can excite resonances of modes involving shear in the narrow face perpendicular to the field; among these, "thickness shear" modes with nodal planes parallel to the major face are prominent<sup>10</sup> (Fig. 1). The resonance frequencies of these modes approach for large values of  $l/tn$  the relation

$$f_n = nv/(2t) = n(c/\rho)^{1/2}/(2t); \quad n \text{ uneven}, \quad (2)$$

where  $n$  is the order of the mode,  $v$  the wave propagation velocity,  $l$  the length,  $t$  the thickness,  $\rho$  the density, and  $c$  the appropriate elastic constant. With electric field

<sup>7</sup> These authors as well as LeCorre refer to this ratio as  $N_{44}/N_{55}$  or  $c_{44}/c_{55}$ . Since the subscript 44 refers to shear in the plane perpendicular to  $X$  and the subscript 55 to shear perpendicular to  $Y$ , one of the present authors was led to the erroneous impression that the Laval theory claims a difference in elastic constants for these two planes which are transformed into each other by the symmetry plane of the ADP crystal [H. Jaffe, *Bull. Am. Phys. Soc.* 4, 427 (1959)]. In the nomenclature of LeCorre,  $c_{44}$  and  $c_{77}$  relate to the  $X$  plane and  $c_{55}$  and  $c_{88}$  to the  $Y$  plane; the symmetry of ADP gives  $c_{44}=c_{88}$  and  $c_{55}=c_{77}$ . We are obliged to Professor LeCorre for pointing out our misunderstanding.

<sup>8</sup> B. Zwicker, *Helv. Phys. Acta* 19, 523 (1946).

<sup>9</sup> N. Joel and W. A. Wooster, *Acta Cryst.* 13, 516 (1960).

<sup>10</sup> Excitation of thickness shear modes in quartz by field parallel to the major face was used by J. V. Atanasoff and P. J. Hart, *Phys. Rev.* 59, 85 (1941).

parallel to  $X$ , the Laval theory predicts different velocities  $v_{yz} = (c_{44}/\rho)^{1/2}$  for thickness (wave propagation) parallel to  $Y$ , and  $v_{zy} = (c_{77}/\rho)^{1/2}$  for thickness parallel to  $Z$ , while classical theory requires

$$v_{yz} = v_{zy} = (c_{44}^E/\rho)^{1/2}. \quad (3)$$

The superscript  $E$  indicates zero electric field strength, a condition closely approached at the resonance (minimum impedance) frequencies of crystal resonators having the wave normal perpendicular to the piezoelectric polarization.

The crystal specimens were ADP plates approximately 5 by 1.3 by 0.6 cm prepared by an industrial mill-cutting technique. One set of three plates had the length parallel to  $Z$  and another set had the thickness (0.6 cm) parallel to  $Z$ . Orientation was checked by x rays and found correct within  $\frac{1}{2}^\circ$ . Electrodes were applied to the 5- by 0.6-cm faces.

The piezoelectric constants of ADP are  $d_{14} = 1.3 \times 10^{-12}$ ,  $d_{36} = 48 \times 10^{-12}$  m/volt. The small value of  $d_{14}$  makes the electric impedance variation at the resonances excited by  $d_{14}$  rather weak, and stray field components parallel to  $Z$  may cause comparatively strong resonances by  $d_{36}$ . These stray fields were largely eliminated by the use of large shields extending beyond the electrodes. In the bars elongated along  $Z$  the remaining strain or misorientation field component along  $Z$  excites shear resonances of the face 1.3 by 0.6 cm whose controlling dimension is the same as for the desired mode. The velocity for shear waves in the  $XY$  plane excited by  $d_{36}$  is near 1800 m/sec, compared to about 2200 m/sec for the desired  $YZ$  mode. The two series of resonances are therefore easily separated.

Table I shows all recorded frequencies for one plate of each type. The fundamentals and third harmonics of the main series stand out in amplitude. The occurrence of many weak resonances due to complex modes near the fundamental is to be expected. Table II lists

TABLE I. Resonances of typical ADP bars.

$t=Y = 5.982 \text{ mm}$		$t=Z = 6.669 \text{ mm}$	
Freq. (kc/sec)	Assignment	Freq. (kc/sec)	Assignment
151.73	151.73 $\times 1$	168.80	168.80 $\times 1$
183.194	183.194 $\times 1$	180.25	
183.4		188.5	
191.4		190.5	
212.0		194.0	
215.9		206.6	
216.7		209.4	
218.0		226.4	
231.0		263.0	
237.2		327.2	
245.6		379.2	
452.7	150.9 $\times 3$	492.48	164.16 $\times 3$
536.1		820.13	164.03 $\times 5$
548.732	182.91 $\times 3$	1148.46	164.07 $\times 7$
754.746	150.95 $\times 5$	1478.39	164.27 $\times 9$
913.937	182.79 $\times 5$		
1281.3	183.04 $\times 7$		
1645.31	182.81 $\times 9$		

TABLE II. Main series resonances for two sets of ADP bars.

	$t=Y = 5.369$ mm		$t=Y = 5.982$ mm		$t=Y = 6.357$ mm	
	Freq. (kc/sec)	$v$ (m/sec)	Freq. (kc/sec)	$v$ (m/sec)	Freq. (kc/sec)	$v$ (m/sec)
Funda- mental	207.17		182.23		172.42	
3rd	611.90 } 612.69 }	2191.6	548.84	2188.4	516.37 } 516.74 } 517.09 } 517.58 }	2190.8
5th	1019.90 } 1020.65 }	2190.8	913.94	2186.8	858.08 } 861.31 }	2186.0
7th	1426.07	2187.6	1281.3	2190.0		
9th			1645.31	2187.2		
Over-all average $v_{yz} = 2188.8$ m/sec						
	$t=Z = 6.660$ mm		$t=Z = 6.669$ mm		$t=Z = 6.667$ mm	
	Freq. (kc/sec)	$v$ (m/sec)	Freq. (kc/sec)	$v$ (m/sec)	Freq. (kc/sec)	$v$ (m/sec)
Funda- mental	168.93		168.80		168.96	
3rd	489.84 } 492.51 } 494.95 }	2186.4	491.16 } 493.80 }	2189.6	491.70	2185.4
5th	822.76	2191.8	820.13	2187.8	822.26	2192.8
7th	1148.45	2185.2	1148.46	2188.2		
9th			1481.63 } 1475.16 }	2190.8		
Over-all average $v_{zy} = 2188.6$ m/sec						

the main series resonances for all six plates and the sound velocities derived from these by Eq. (2). The fundamentals were excluded because  $l/in$  for  $n=1$  is not sufficiently large. Average values were used for resonances which were multiple, probably due to coupling with bending modes. The value of velocity averaged over all overtones of all three bars in each set are

$$v_{yz} = 2188.8 \pm 0.64 \text{ m/sec,}$$

and

$$v_{zy} = 2188.6 \pm 0.83 \text{ m/sec;}$$

hence

$$v_{yz} - v_{zy} = 0.2 \pm 1.08 \text{ m/sec.}$$

The indicated error limits are the standard deviations of the measurements. Any systematic error in the measurements should not affect the velocity difference since identical data reduction methods were used for the two crystal sets.

Similar measurements were also carried out on the isomorphous potassium arsenate,  $\text{KH}_2\text{AsO}_4$ . For this crystal the piezoelectric constants  $d_{14}$  and  $d_{36}$  are about equal so that little difficulty with the interfering  $XY$  mode is experienced. Only one bar of each type about 2 cm in length was available. The velocities found were  $v_{yz} = 1978$  m/sec and  $v_{zy} = 1972$  m/sec. The difference is within the estimated limit of error.

#### SOUND VELOCITY MEASUREMENTS BY THE PULSE-ECHO METHOD

In the pulse-echo method<sup>11</sup> the acoustic wave velocities  $v_{yz}$  and  $v_{zy}$  are measured directly by determining

<sup>11</sup> See for example reference 5, pp. 267-269.

the transit time of an acoustic pulse and the length of the crystal. These are the acoustic velocities of transverse waves which travel in the direction of the first subscript, with particle motion in the directions of the second subscript.

The crystal specimens were one-inch cubes of ADP prepared with pairs of plane parallel faces perpendicular to the  $X$ ,  $Y$ , and  $Z$  axes within a maximum deviation of 2 degrees in all cases. A  $Y$ -cut ten megacycle per second quartz transducer was cemented by means of a salol first to a face perpendicular to the  $Y$  axis and then to a face perpendicular to the  $Z$  axis; in the former case, the direction of particle motion in the quartz plate (the  $X$  axis of quartz) is made parallel to the  $Z$  axis of the ADP crystal and in the latter, parallel to  $Y$  of ADP. Acoustic pulses approximately two microseconds long were generated by the quartz transducer. The pulse produced an oscilloscope display consisting in each case of four returning echoes at 23-microsecond intervals. The time delay between these echoes was measured with a least count of  $\pm 0.01$  microsecond. No attempt was made to attain high precision or to put the measurements on an absolute basis. The four velocity measurements which are reported were simply made with identical technique which was made possible by the uniform specimen size.

The results for two crystals are quoted in terms of the corresponding velocities in Table III. The velocities have been computed in all cases by subtracting the arrival time of the first echo from the arrival time of the fourth echo, dividing by three, and using this value as the transit time down and back. Much previous work in this laboratory has indicated that relative measure-

TABLE III. Velocities of 10-Mc/sec transverse acoustic waves in ADP (m/sec).

Crystal	$v_{xy}$	$v_{yz}$
A	2186	2185
B	2179	2184

ments made in this way have a standard deviation of 0.2%. It is seen that the velocities  $v_{yz}$  and  $v_{xy}$  agree in both crystals within this precision. The small variations in velocity shown in Table III are also comparable with the variations to be expected from the known angular deviations mentioned above, but no correlation could be obtained with the specific values of misorientation determined by x-ray diffraction.

The fact that the observed pulse velocities are 0.2% lower than the velocities from resonance is not significant because no attempt was made in either case to put the measurements on an absolute basis.

All measurements were made at  $25 \pm 2^\circ\text{C}$ .

## CONCLUSIONS

Measurements of shear wave velocities by each of two simple methods show these velocities for the two waves involving shear between the  $Y$  and  $Z$  axes to be equal well within the experimental error limits. For the resonance method, which was carried to higher accuracy than the pulse-echo method, the probable error in the velocity difference is 0.05% of the velocity which corresponds to 0.1% for the difference between the Laval elastic constants  $c_{44}$  and  $c_{77}$ . Reported differences of 6% or more between these elastic constants must therefore be regarded as erroneous, or possibly arising in phenomena other than elasticity affecting the ultrasonic light diffraction method.

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## Behavior of Excited Electrons and Holes in Zinc Sulfide Phosphors\*

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The luminescent properties of silver and copper activated ZnS phosphors have been investigated at room and liquid air temperatures using uv, blue light, and  $\beta$ -ray excitation. In many cases it was found that the deficiency area was considerably smaller than the glow curve area, especially for  $\beta$ -ray excitation of ZnS:Cu. This is explained by the hole production causing quenching during  $\beta$ -ray excitation, while during the glow curve the smaller amount of holes produced causes a much smaller amount of quenching. However, even with blue light where excitation does not directly produce holes, the deficiency area is smaller than the glow curve area. The effects of infrared radiation on the fluorescence, phosphorescence, and glow curve has been investigated, and the quenching and stimulation at room and liquid air temperature reported. For ZnS:Cu the long wavelength infrared band ( $\sim 12\,000\text{ \AA}$ ) produces quenching at room temperature but only stimulation at low temperature. A determination of trap density from the glow curves shows  $\sim 10^{17}/\text{cm}^3$  for ZnS:Cu and  $\sim 10^{16}/\text{cm}^3$  for ZnS:Ag at liquid air temperatures. Finally, a theoretical discussion of the possible transition mechanisms giving rise to these effects is given.

## 1. INTRODUCTION

LUMINESCENT properties of zinc sulfide type phosphors have been extensively investigated by many workers in the field of solid-state luminescence.<sup>1</sup> However, it is not yet possible to explain completely the

complicated phenomena associated with luminescence, that is, to describe the exact behavior of excited electrons and holes which participate in the excitation and emission processes in these phosphors. It is well known that the incorporation of small amounts of activators, especially copper and silver, into a zinc sulfide crystal creates impurity levels above the top of the valence band, although the exact nature of these levels is still under a discussion.<sup>2,3</sup> Luminescent emission has been attributed to an electron transition from the conduction band, or from an excited level located close to the

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<sup>1</sup> Latest review articles of this field are: C. C. Klick and J. H. Schulman, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1957), Vol. 5, p. 97; F. A. Kröger, *Ergeb. exakt. Naturw.* **24**, 61 (1956); W. W. Piper and F. E. Williams, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1958), Vol. 6, p. 95.

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