Acta Cryst. (1958). **11**, 575

On the Validity of the Classical Theory of Crystal Elasticity as Applied to Ammonium di-Hydrogen Phosphate

By N. Joel and W. A. Wooster

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

(*Received* 13 *December* 1957)

An elastogram of ammonium dihydrogen phosphate, obtained by Zwicker using the Bergmann–Schäfer method, has been re-analyzed. The ratio between the two elastic constants N_{44} and N_{55} was found to be 1·08±0·01. This difference cannot be explained by the classical theory of crystal elasticity but agrees with the theory of Laval.

1. Introduction and notation

The subject of crystal elasticity was very thoroughly studied by Voigt (1910), and all measurements of elastic constants have hitherto been interpreted in terms of his theory. No contradictions between theory and the experimental results were observed, within the limits of experimental errors. But in recent years there have been several contributions by Laval (1951*a*, *b*, 1957), Le Corre (1953, 1954, 1955), Viswanathan (1954, 1955), Raman & Viswanathan (1955), and Joel & Wooster (1957) putting forward a theory which is more general than Voigt's and which requires an increased number of elastic constants.

(In this note, the two theories will be referred to by the letters *V* and *L* respectively.)

In the *V*-theory, the 4th-order elastic tensor $c_{\alpha\beta\gamma\delta}$, relating strains, $S_{\gamma\delta}$, and stresses, $T_{\alpha\beta}$, and defined by

$$T_{\alpha\beta} = \sum_{\gamma\delta} c_{\alpha\beta\gamma\delta} S_{\gamma\delta} \quad (\alpha, \beta, \gamma, \delta = 1, 2, 3)\,, \quad (1)$$

has, in the most general case (crystals of classes 1 and $\bar{1}$), 21 independent components. This reduction from 81 to 21 is a consequence of the following relations:

(*a*) The stress tensor $T_{\alpha\beta}$ is symmetrical on account of equilibrium conditions; that is, $T_{\alpha\beta} = T_{\beta\alpha}$; therefore, it has only 6 independent components.

(*b*) The strain tensor $S_{\gamma\delta}$ is symmetrical because no net rotation is included in the deformation; that is, $S_{\gamma\delta} = S_{\delta\gamma}$; this leaves the strain tensor also with 6 independent components.

(*c*) The resulting 6×6 matrix is further reduced to 21 independent components owing to its own symmetry: $c_{\alpha\beta\gamma\delta} = c_{\gamma\delta\alpha\beta}$. This is due to the fact that the strain-energy function is single-valued.

By means of the abridged notation

$\alpha\beta$ or $\gamma\delta$	11	22	33	23 and 32	31 and 13	12 and 21
i or *j*	1	2	3	4	5	6

formula (1) can be written

$$T_i = \sum_j c_{ij} S_j \quad (i, j = 1, 2, \ldots, 6)\,, \quad (2)$$

keeping in mind that

$$c_{ij} = c_{ji}\,.$$

The number of non-vanishing and independent elastic constants decreases for crystal classes of higher symmetry. For instance, ADP (class $\bar{4}2m$) has 6 independent constants (see table, below).

In the *L*-theory, the elastic tensor $N_{\alpha\beta\gamma\delta}$ (in Laval's notation), defined by

$$T_{\alpha\beta} = \sum_{\gamma\delta} N_{\alpha\beta\gamma\delta} S_{\gamma\delta} \quad (\alpha, \beta, \gamma, \delta = 1, 2, 3)\,, \quad (3)$$

has in the most general case 45 independent components (as compared with the 21 in the *V*-theory).

The elastic tensor is still symmetrical, that is, $N_{\alpha\beta\gamma\delta} = N_{\gamma\delta\alpha\beta}$ (hence the reduction from 81 to 45), but permutations in $\alpha\beta$ or in $\gamma\delta$ are no longer permissible: the stress tensor is not symmetric ($T_{\alpha\beta} \neq T_{\beta\alpha}$), and the 9 components of strain have to be considered separately.

The abridged notation, following Laval, now runs as follows:*

$\alpha\beta$ or $\gamma\delta$	11	22	33	23	31	12	32	13	21
i or *j*	1	2	3	4	5	6	7	8	9

and formula (3) becomes

$$T_{ij} = \sum_j N_{ij} S_j \quad (i, j = 1, 2, \ldots, 9)\,, \quad (4)$$

with $N_{ij} = N_{ji}$.

Le Corre (1953) has tabulated the independent elastic constants for the 32 classes in the *L*-theory. In fact, the number of different tables is 11, one for each Laue group.

In the present paper special reference is made to ADP, $(NH_4)H_2PO_4$, whose elastic constants have been investigated by means of Bergman–Schäfer elastograms both before and after Laval's publications of 1951 (see § 3).

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* Raman & Viswanathan use a different notation: they write 4, 5, 6, 7, 8 and 9 for 23, 32, 31, 13, 12 and 21.

ADP belongs to the class $\bar{4}2m$, and has the following schemes of elastic constants in the V- and L-theories. The abridged notation is used, only the subscripts are indicated, and the vanishing components are represented by a dot.

V-theory

$$\begin{array}{cccccc}
11 & 12 & 13 & \cdot & \cdot & \cdot \\
12 & 11 & 13 & \cdot & \cdot & \cdot \\
13 & 13 & 33 & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & 44 & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & 44 & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & 66
\end{array}$$

L-theory

$$\begin{array}{ccccccccc}
11 & 12 & 13 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
12 & 11 & 13 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
13 & 13 & 33 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & 44 & \cdot & \cdot & 47 & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & 55 & \cdot & \cdot & 47 & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & 66 & \cdot & \cdot & 69 \\
\cdot & \cdot & \cdot & 47 & \cdot & \cdot & 55 & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & 47 & \cdot & \cdot & 44 & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & 69 & \cdot & \cdot & 66
\end{array}$$

The main difference between the two schemes, and the easiest to detect experimentally, is the following: L requires that $N_{44} \neq N_{55}$, while V requires $c_{44} = c_{55}$.

2. Calculation of the elastograms

This section contains a brief description of the elastograms and of the way in which they can be calculated.

Suppose that, in accordance with well established experimental methods (Schäfer & Bergmann, 1934, 1935; Bergmann, 1954, 1957; Zwicker, 1946; Jona, 1950) light is diffracted by the vibrating crystal and focused on to a plane perpendicular to the light beam at the image of the point source. Consider one point P of the diffraction pattern or elastogram (Fig. 1).

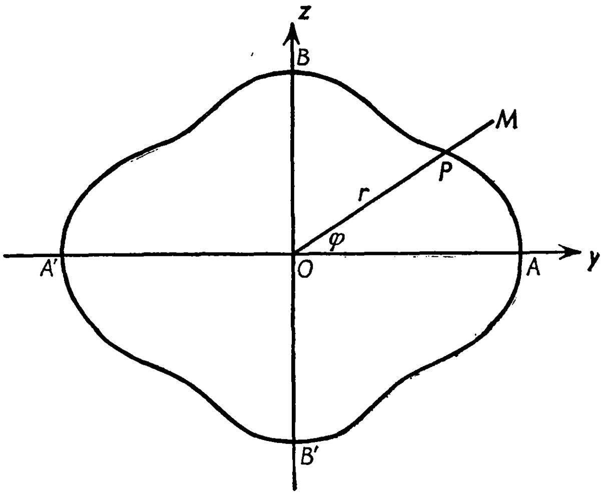

Fig. 1. Illustration of how an elastogram is generated (only part of it is shown).

It is produced by elastic waves travelling in the crystal in the direction OP. The length $OP = r$ is inversely proportional to the wavelength and hence to the velocity of the elastic wave.

Therefore, the calculation of an elastogram requires a knowledge of the velocity of propagation of elastic waves in all directions in a plane parallel to the elastogram (perpendicular to the direction of travel of the light in the crystal).

This requires the resolution of the Christoffel determinant:

$$\begin{vmatrix} A_{11}-Q & A_{12} & A_{13} \\ A_{12} & A_{22}-Q & A_{23} \\ A_{13} & A_{23} & A_{33}-Q \end{vmatrix} = 0\,, \qquad (5)$$

where

$$A_{\alpha\gamma} = \sum_{\beta\delta} N_{\alpha\beta\gamma\delta} q_\beta q_\delta \quad (\alpha, \beta, \gamma, \delta = 1, 2, 3)\,, \qquad (6)$$

$Q = \varrho v^2$,

ϱ is the density of the crystal, and

v is the velocity of the elastic wave in the direction defined by the unit vector $\mathbf{q}(q_1, q_2, q_3)$.

Equation (5) is in general of the third degree in Q (that is, in v^2); and if also the vibration directions of the three waves associated with each direction of propagation are required, then a set of linear equations has to be solved for each of the three roots of (5).

These calculations, in particular the resolution of the many equations of the third degree, may be lengthy, but this difficulty can be overcome by means of an electronic computer; EDSAC, the Cambridge University electronic computer, was used in the present study. The data were fed into the machine on the usual tape. The holes punched in it corresponded to the sets of $A_{\alpha\gamma}$ (formula (6)) belonging to each determinant. These $A_{\alpha\gamma}$ were calculated for directions such that each successive one differed from the previous one by 3°, using an ordinary desk calculating machine. It would also be possible, by means of more elaborate programming, to feed directly into the machine the values of $N_{\alpha\beta\gamma\delta}$ and a set of vectors $\mathbf{q}(q_1, q_2, q_3)$, and to use these directly in solving the determinant (5).

For the set of $A_{\alpha\gamma}$ corresponding to each propagation vector the results were printed, as shown in Table 1, in three horizontal rows of figures arranged in vertical columns corresponding to Q, $Q^{-\frac{1}{2}}$, u_1, u_2, u_3, respectively; the three last being the direction cosines of the vibration vector.

Table 1. *Presentation of the results, as printed by* EDSAC

Q	$Q^{-\frac{1}{2}}$	u_1	u_2	u_3
008630	107645	1·000000	0·000000	0·000000
010051	099747	0·000000	0·949397	−0·314079
033459	054669	0·000000	0·314079	0·949397

In drawing the elastograms we are interested only in $Q^{-\frac{1}{2}}$ (second column), which is proportional to r (Fig. 1). In this way, on any radial line OM there will be three points of the elastogram: one for each elastic wave. Experimental diffraction patterns show that this is in general the case, but in special cases only two curves are obtained. This actually happens with ADP in the orientation relevant to the work described.

The YZ elastogram of ADP, which gives information about N_{44} and N_{55}, is easily evaluated. The coefficients $A_{\alpha\gamma}$ reduce to:

$$\left.\begin{aligned} A_{11} &= N_{66}q_2^2+N_{44}q_3^2 &&= N_{44}+(N_{66}-N_{44})\cos^2\varphi\,, \\ A_{22} &= N_{11}q_2^2+N_{44}q_3^2 &&= N_{44}+(N_{11}-N_{44})\cos^2\varphi\,, \\ A_{33} &= N_{55}q_2^2+N_{33}q_3^2 &&= N_{33}+(N_{55}-N_{33})\cos^2\varphi\,, \\ A_{23} &= (N_{13}+N_{47})q_2q_3 &&= \tfrac{1}{2}(N_{13}+N_{47})\,\mathrm{sen}\,2\varphi\,, \\ A_{12} &= A_{13} = 0\,, \\ (\cos\varphi &= q_2)\,. \end{aligned}\right\} \quad (7)$$

The determinant is now factorized into the following two equations:

$$N_{66}q_2^2+N_{44}q_3^2-Q = 0 \quad (8)$$

and

$$(N_{11}q_2^2+N_{44}q_3^2-Q)(N_{55}q_2^2+N_{33}q_3^2-Q) - (N_{13}+N_{47})^2q_2^2q_3^2 = 0\,. \quad (9)$$

It is easy to show that equation (8) corresponds to a pure transverse wave vibrating along the X axis, which therefore does not contribute to the diffraction pattern as the crystal is observed along this X axis. Both vibrations corresponding to equation (9) can be shown to lie in the YZ plane: one is quasi-longitudinal and the other quasi-transverse. We are interested in the latter as it is more directly associated with the elastic constants N_{44} and N_{55}.

Equation (9) becomes, for waves travelling along the Y axis,

$$(N_{11}-Q)(N_{55}-Q) = 0\,, \quad (10)$$

and along the Z axis

$$(N_{33}-Q)(N_{44}-Q) = 0\,. \quad (11)$$

From these two equations it can be deduced that there is a transverse wave travelling along Y (vibrating along Z) with a velocity $(N_{55}/\varrho)^{\frac{1}{2}}$; and another transverse wave travelling along Z (vibrating along Y) with a velocity $(N_{44}/\varrho)^{\frac{1}{2}}$. These two waves correspond to the points A and B of Fig. 1. Therefore it is important to obtain a good value of the ratio $(\overline{AA'}/\overline{BB'})^2 = N_{44}/N_{55}$.

3. The elastic constants N_{44} and N_{55} of ADP

The elastic constants of ADP have been measured by several authors, and their results are reviewed by Hearmon (1952, 1956). Of these measurements, those of Zwicker (1946) and Le Corre (1954) were made using elastograms.* This method allows a direct comparison between N_{44} and N_{55}, on the same elastogram.

Le Corre did not publish a diffraction pattern photographed along [100], which is the setting required to show a difference between N_{44} and N_{55}. He made his measurements visually and reports the following results at 14° C.:

$$N_{44} = (10{\cdot}3\pm0{\cdot}6)\times10^{10}\ \text{dyne cm.}^{-2},$$
$$N_{55} = (7{\cdot}6\pm0{\cdot}5)\times10^{10}\ \text{dyne cm.}^{-2};$$

hence:

$$N_{44}/N_{55} = 1{\cdot}35\pm0{\cdot}16\,.$$

If the V-theory were valid this ratio would be unity.

Zwicker published, together with other elastograms, a diffraction pattern taken along [100]. At the time of his investigation, which was carried out several years before the publication of Laval's theory, Zwicker had to use the V-theory in interpreting his results. He chose the best mean value of c_{44} which he could obtain from his measurements: $c_{44} = (8{\cdot}5\pm0{\cdot}25)\times10^{10}$ dyne cm.$^{-2}$. His elastogram, however, shows that AA' and BB' (Fig. 1) are not equal. This was noted by Le Corre (1954, p. 1384) and by Hearmon (1956, p. 336). The latter estimated that the ratio AA'/BB' on Zwicker's elastogram was about 1·1.

We have studied this elastogram in great detail in order to obtain its ratio AA'/BB' as accurately as possible. The diffraction curve under consideration vanishes at the points where it would cross the Y and Z axes. Therefore it is not possible to locate accurately the points A, A', B and B' by mere inspection of the diffraction curve. The following system of extrapolation was devised to obtain the ratio AA'/BB' as accurately as possible.

Several elastograms of ADP along [100] were calculated by the method described in § 2, using for each of them values for the elastic constants of ADP as published by different authors.

These curves were first drawn on a large sheet of polar graph paper, and on the same sheet several experimental points taken from Zwicker's elastogram were inserted on the same scale as the calculated curves. The scale was adjusted so that the experimental points fitted as closely as possible on to the curve calculated with Zwicker's published constants in the region where the experimental curve is best defined.

From these curves and the experimental points it was possible to extrapolate the latter to the Y and Z axes and obtain for r the values 110·5 and 106·5 respectively. The scale is such that $Q = r^{-2}\times10^{15}$, and therefore we obtain for N_{44} and N_{55}:

$$N_{44} = 8{\cdot}8_2\times10^{10}\ \text{dyne cm.}^{-2},$$
$$N_{55} = 8{\cdot}1_9\times10^{10}\ \text{dyne cm.}^{-2},$$
$$N_{44}/N_{55} = 1{\cdot}08\,.$$

Fig. 2 shows, in orthogonal coordinates,* the ex-

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* Le Corre also used the Lucas–Biquard method, but the values of N_{44} and N_{55} were obtained by means of elastograms.

* The polar graph had to be drawn on a large scale to show clearly the differences in r and it is less suitable for publication than Fig. 2.

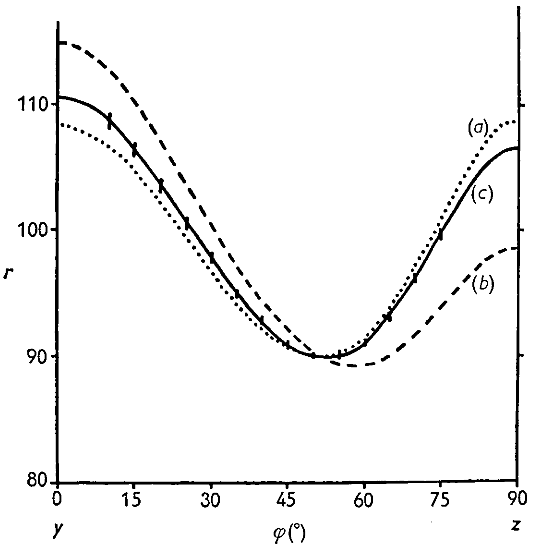

Fig. 2. Experimental points (their vertical length indicates the margin of error) taken from Zwicker's *YZ* elastogram of *ADP*, and three theoretical curves calculated with:

(*a*) Zwicker's published results, *V*-theory (dotted line).
b) Le Corre's published results, *L*-theory (broken line).
(*c*) The new values of N_{44} and N_{55} and all the other elastic constants as given by Zwicker, *L*-theory (full line).

perimental points taken from Zwicker's elastogram and two of the theoretical curves calculated for this extrapolation process; they are based on:

(*a*) Zwicker's published results, *V*-theory;
(*b*) Le Corre's published results, *L*-theory.

In the same graph is a third curve, (c), which was calculated using the two new constants N_{44} and N_{55} with all the others as given by Zwicker (*L*-theory). The agreement can be seen to be good.

Taking into account the finite width of the lines in the elastogram, and considering also a possible systematic error due to a wrong scaling factor, the individual values given for N_{44} and N_{55} have an uncertainty of about 3%. But owing to the character of the error mentioned, the ratio N_{44}/N_{55} is hardly affected at all by any small error in scale. The error in the ratio N_{44}/N_{55} is thus estimated as not more than 1%.

In conclusion, it must be said that the values of N_{44} and N_{55} given in this paper are not claimed to be the correct values for ADP. All that is claimed is that there is an elastogram published in 1946 from which it appears that there is a difference of 8%(±1%) between them. This difference cannot be explained by the classical theory.

It is a pleasure to acknowledge the kind interest of Dr. B. Zwicker, with whom we had some correspondence on the subject of this paper after the completion of the work.

We are indebted to Dr M. V. Wilkes, Director of the Mathematical Laboratory, Cambridge University, for making EDSAC available for the computations, and to Mr H. P. F. Swinnerton-Dyer for advice and help in the carrying out of these computations.

One of us (N. J.) gratefully acknowledges a research scholarship from the British Council, and wishes to thank Prof. N. F. Mott, F. R. S., and Dr W. H. Taylor for their interest in this work.

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