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Third-Order Elastic Constants of Orthorhombic Calcium Formate

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Abstract

All 20 independent third-order elastic constants (TOEC) of orthorhombic calcium formate, $Ca(HCOO)_2$, $Ca^{2+}.C_2H_2O_4^{2-}$, space group *Pcab*, have been determined with the aid of stress-induced shifts of ultrasonic resonance frequencies. Longitudinal and transverse effects possess negative values indicating the high stability of calcium formate over a wide pressure range. The anisotropy of TOEC, characterized by $-c_{111} > -c_{333} > -c_{222}$, corresponds with the anisotropy of second-order elastic constants ($c_{11} > c_{33} > c_{22}$). The value 5·22 for the pressure derivative of the inverse bulk compressibility coincides with the quasi-invariant value of *ca* 5 observed in most stable cubic crystals so far investigated. There exists a pronounced departure from third-order Cauchy relations: the 'transverse' constants exceed the corresponding 'shear' components considerably in absolute magnitude in accordance with the behaviour of the second-order Cauchy relations. These effects are explained as originating from the non-centrosymmetric formate ions. A comparison of TOEC of calcium formate and cubic calcium fluoride confirms the typical contribution of the formate ions to the third-order elastic behaviour.

Introduction

The deviation from Hooke's law, represented by the third-order elastic constants, offers the most informative manifestation of anharmonic behaviour of solids. Thermal expansion, another property originating from anharmonic interactions, though much more easily accessible to experimental determination than TOEC, permits only a very rough knowledge of anharmonic behaviour. In the last two decades TOEC of more than 100 cubic crystals have been reported in the literature. However, only a few materials with non-cubic symmetry like quartz, calcite, Al_2O_3 and $LiNbO_3$ have been investigated hitherto. Therefore, it was hardly possible to establish general relations between second- and third-order elastic constants and other properties on the basis of experimental data. In this paper we report the determination of the complete TOEC tensor of orthorhombic calcium formate, a material which belongs to the best known crystals with respect to higher-order tensor properties (Haussühl, 1963*a*; Haussühl & Hesse, 1966; Bach, Haussühl & Weber, 1977; Bohatý & Haussühl, 1977).

Experimental

The method employed for the measurement of TOEC is based on stress-induced shifts of resonance frequencies of thick plates. Details have been outlined recently (Haussühl & Preu, 1978). Resonance frequencies are detected by diffraction of light by ultrasonic waves which are transmitted into the specimen with the aid of *X*- and *Y*-cut quartz generators at frequencies between 14 and 30 MHz.

The basic equations for the determination of non-linear acoustic properties of crystals, primarily derived by Seeger & Buck (1960) and by Thurston & Brugger (1964), are used in the notation given by Wallace (1970) in his review article. The following equation combines the unknown TOEC c_{ijklmn} with observable quantities:

$$\partial(\rho_0 W^2)/\partial\sigma_{pq} = k_p k_q + 2\rho_0 W^2 s^T_{ijpq} w_i w_j + c_{ijklmn} s^T_{mnpq} k_j k_l w_i w_k.$$

All quantities are taken at zero stress. W is the 'natural velocity' of a sound wave defined by $W = (l_0/l_1)\,v$, where l_0 and l_1 denote the length of the specimen in the direction of the propagation vector without and with applied stress respectively. v is the measured wave velocity of plane elastic waves, ρ_0 the density. σ_{ij}, s^T_{ijkl}, k_i and w_i are the components of the isothermal static stress tensor, the elasticity **s** tensor (inverse **c** tensor), the components of the propagation vector and the displacement vector respectively. The TOEC are defined as

$$c_{ijklmn} = \rho_0(\partial^3 U/\partial\eta_{ij}\,\partial\eta_{kl}\,\partial\eta_{mn}),$$

where U is the internal energy per unit mass and η_{ij} are the components of the Lagrangian deformation tensor.

The relation between measured quantities $\partial f/\partial\sigma_{pq}$ and the left-hand side of the basic equation is

$$\partial(\rho_0 W^2)/\partial\sigma_{pq} = 2\rho_0 W^2(1/f)\,(\partial f/\partial\sigma_{pq}),$$

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where f is the relevant resonance frequency (Wallace, 1970, p. 370).

Each experimental arrangement for different sets of directions of stress, propagation and displacement vectors yields one linear equation containing the unknown TOEC. After collecting a sufficient number of such equations the evaluation of the TOEC should be possible.

Table 1. *Selected arrangements for the determination of TOEC for crystals of symmetry group mmm*

Number	Wave type*	Direction of stress	Propagation vector $\mathbf{k}\parallel$	Displacement vector $\mathbf{w}\parallel$	TOEC involved
1	l	hydrostatic	[100]	[100]	$c_{111}, c_{112}, c_{113}$
2–4	l	[100], [010], [001]	[100]	[100]	
5	l	hydrostatic	[010]	[010]	$c_{122}, c_{222}, c_{223}$
6–8	l	[100], [010], [001]	[010]	[010]	
9	l	hydrostatic	[001]	[001]	$c_{133}, c_{233}, c_{333}$
10–12	l	[100], [010], [001]	[001]	[001]	
13	t	hydrostatic	[100]	[010]	$c_{166}, c_{266}, c_{366}$
14–15	t	[100], [010]	[100]	[010]	
16	t	hydrostatic	[100]	[001]	$c_{155}, c_{255}, c_{355}$
17–18	t	[100], [001]	[100]	[001]	
19	t	hydrostatic	[010]	[100]	$c_{166}, c_{266}, c_{366}$
20–21	t	[100], [010]	[010]	[100]	
22	t	hydrostatic	[010]	[001]	$c_{144}, c_{244}, c_{344}$
23–24	t	[010], [001]	[010]	[001]	
25	t	hydrostatic	[001]	[100]	$c_{155}, c_{255}, c_{355}$
26–27	t	[100], [001]	[001]	[100]	
28	t	hydrostatic	[001]	[010]	$c_{144}, c_{244}, c_{344}$
29–30	t	[010], [001]	[001]	[010]	
31	ql	hydrostatic	[101]′	~[101]′†	$c_{111}, c_{112}, c_{113}, c_{155}, c_{255}, c_{355}, c_{133}, c_{233}, c_{333}, c_{123}$
32–34	ql	[101]′, [010], $[\bar{1}01]'$	[101]′	~[101]′†	
35	t	hydrostatic	[101]′	[010]	$c_{144}, c_{244}, c_{344}, c_{166}, c_{266}, c_{366}, c_{456}$
36–37	t	[101]′, [010]	[101]′	[010]	
38	qt	hydrostatic	[101]′	~$[\bar{1}01]'$†	$c_{111}, c_{112}, c_{113}, c_{155}, c_{255}, c_{355}, c_{133}, c_{233}, c_{333}, c_{123}$
39–40	qt	[101]′, $[\bar{1}01]'$	[101]′	~$[\bar{1}01]'$†	
41	l	[101]′	[010]	[010]	$c_{122}, c_{222}, c_{223}$

* l = longitudinal; t = transverse; ql = quasi-longitudinal; qt = quasi-transverse.

† The exact displacement vector is calculated from second-order elastic constants.

Table 2. *TOEC of calcium formate at* 295 *K in* 10^{10} Nm^{-2}

Limits of error: c_{ijj} $(i,j \le 3)$ 5%; c_{ijj} $(i \le 3; j = 4, 6)$ 10%; c_{123}, c_{456}, c_{i55} $(i \le 3)$ 15%.

c_{111}	−41·9	c_{144}	−6·5
c_{112}	−26·4	c_{244}	−5·8
c_{113}	−31·1	c_{344}	−6·2
c_{122}	−17·6	c_{155}	−3·0
c_{222}	−29·8	c_{255}	−3·0
c_{223}	−10·2	c_{355}	−3·8
c_{133}	−24·6	c_{166}	−10·8
c_{233}	−13·8	c_{266}	−4·0
c_{333}	−38·0	c_{366}	−11·1
c_{123}	−27·7	c_{456}	−5·4

In orthorhombic crystals with point symmetry group *mmm*, 20 independent TOEC exist in all. In Voigt notation (index pair $ii \to i$, index pair $ij \to 9-i-j$) these are: c_{111}, c_{112}, c_{113}, c_{122}, c_{222}, c_{223}, c_{133}, c_{233}, c_{333}, c_{123}, c_{144}, c_{244}, c_{344}, c_{155}, c_{255}, c_{355}, c_{166}, c_{266}, c_{366}, c_{456}. Differences between adiabatic, isothermal and 'mixed' TOEC are neglected due to their smallness (Guinan & Ritchie, 1970).

Single crystals of calcium formate with dimensions of more than 20 mm in all directions have been grown from aqueous solution in optical quality by temperature-controlled evaporation (Haussühl, 1963*a*).

The measurements were performed on two specimens of rectangular shape with the orientation $(100)' \times (010)' \times (001)'$ and $(101)' \times (010)' \times (\bar{1}01)'$ respectively. The dashed symbols refer to the Cartesian reference system with its axes $\mathbf{e}_i$ parallel to the crystallographic axes $\mathbf{a}_i$ in the setting given by Groth (1910). The dimensions of these plane-parallel plates ranged between 11 and 16 mm. Uniaxial stresses had to be confined to 2×10^6 Pa in order to avoid mechanical damage of the specimens. Hydrostatic pressures applied were limited to $1{\cdot}5 \times 10^8$ Pa. The resonance frequencies connected with elasto-optically inactive transverse modes were detected with the aid of an auxiliary crystal of RbI mounted on the vibrating specimen (Haussühl & Scholz, 1975). All frequency shifts observed gave a linear dependence on stress. In all 32 different and not symmetrically equivalent measurements under different experimental arrangements could be collected (Table 1). For control, several measurements were repeated in symmetrically equivalent arrangements.

All further data necessary for the evaluation of the auxiliary quantities s^T_{ijkl}, ρ_0, *etc.* were taken from an earlier paper (Haussühl, 1963*a*). A least-squares method for the solution of overdetermined systems of linear equations was employed utilizing the complete set of equations for all 32 types of measurements available. The weight of each mode was chosen in inverse proportion to the statistical error of the measured quantities. The values obtained for 295 K are listed in Table 2.

Discussion

For simplification we distinguish four types of TOEC in orthorhombic crystals:

(I) pure longitudinal effects c_{iii}, $i \le 3$;

(II) transverse effects $c_{ijk}, j \ne k, i,j,k \le 3$;

(III) shear effects of the first kind c_{ijj}, $i \ne j$, $i \le 3$, $j > 3$;

(IV) shear effects of the second kind c_{ijk}, $i,j,k > 3$.

The normal behaviour of stable crystals (no phase transition with strong second-order component in a neighbouring temperature or pressure range) is characterized by negative values of type (I) and (II) TOEC. TOEC of type (I) are considerably larger in absolute magnitude than those of type (II). Further relations may be derived from the stability criteria of the second-order elastic constants and their pressure and stress derivatives. Calcium formate shows a normal behaviour in that sense.

The anisotropy is characterized by $-c_{111} > -c_{333} > -c_{222}$. A corresponding relation holds for the elastic constants $c_{11} > c_{33} > c_{22}$ (see Table 3). Owing to the scarceness of corresponding data for other crystals we cannot decide whether a general rule for the relation between principal third- and second-order elastic constants exists, stating that both are in the same sequence of magnitude if the anisotropy is sufficiently strong. It should be mentioned that a related rule is observed in cubic isotypic groups where the ratios c_{111}/c_{11} vary only slightly and are therefore characteristic for a certain structure type.

Another point of view is the departure from Cauchy relations, which express the total commutability of indices in the components c_{ijklmn}. Cauchy relations are expected to be fulfilled under very restrictive conditions only (centrosymmetric potential of the lattice particle interactions, zero temperature, no primary stress). In orthorhombic crystals, the following ten relations have to be considered:

$$c_{112} = c_{166}, c_{122} = c_{266}, c_{133} = c_{355}$$
$$c_{113} = c_{155}, c_{223} = c_{244}, c_{233} = c_{344}$$
$$c_{123} = c_{144} = c_{255} = c_{366} = c_{456}.$$

In all cases the 'transverse' components c_{ijk} with $i, j, k \leq 3$ exceed the corresponding 'shear' components in magnitude considerably. The same is valid for the second-order elastic constants (Haussühl, 1963*a*). Such behaviour is typical for structures which are built up by asymmetric constituents like formate ions (Haussühl, 1967).

The pressure derivatives dc_{ij}/dp represent the non-linear elastic properties in a simpler form. Their determination follows directly from measurements under hydrostatic pressure or by the evaluation from TOEC. Both sets of values agree fully within the limits of error. They are listed in Table 3. All elastic constants increase with higher pressure, quite normal behaviour for stable crystals. The dimensionless quantity $d(K^{-1})/dp$, the pressure derivative of the inverse bulk compressibility K, has been recognized to be a quasi-invariant quantity for most stable cubic crystals hitherto investigated. Employing a simple model, Slater (1940) derived that $d(K^{-1})/dp$ should equal *ca* $2(\gamma + \frac{2}{3}) \simeq 5$, where γ denotes the quasi-invariant Grüneisen parameter. Calcium formate yields the value 5·22 confirming its normal behaviour. $d(K^{-1})/dp$ is easily derived from the presentation of K as a function of the c_{ij}. Another quantity to be obtained from dc_{ij}/dp is the pressure dependence of Poisson's ratio $Q_{ij} = s_{ij}/s_{jj}$ $(i, j \leq 3)$ which expresses the ratio of longitudinal deformations perpendicular and parallel to a uniaxial stress applied in direction $\mathbf{e}_j$. s_{ij} are elastic compliances. These values exhibit a strong anisotropy (Table 4), characterized by negative values for dQ_{13}/dp and dQ_{31}/dp and positive values for dQ_{23}/dp and dQ_{32}/dp, underlining again the existence of minimum and maximum values for properties assigned to the directions $\mathbf{e}_1$ and $\mathbf{e}_2$ [*e.g.* the pairs (c_{11}, c_{22}), (c_{111}, c_{222}), $(dc_{11}/dp, dc_{22}/dp)$, $(dc_{13}/dp, dc_{23}/dp)$, *etc.*].

Finally, we compare the TOEC of calcium formate and cubic calcium fluoride. The structure types of both crystals are quite different; however their chemical composition and bond type are comparable. In order to effect the comparison, we have to provide average values for the TOEC of calcium formate which comply with point symmetry group $m3m$ of calcium fluoride. The relations yielding these values c'_{ijk} are given in Table 5 together with the TOEC of calcium fluoride. Further, some typical ratios like c_{111}/c_{11}, c_{112}/c_{11}, c_{123}/c_{11} and the corresponding averaged values are included. We recognize that there exists a certain agreement between c'_{111}/c'_{11} and c_{111}/c_{11} but a strong difference between c'_{112}/c'_{11} or c'_{123}/c'_{11} and the corresponding values for calcium fluoride (Alterovitz & Gerlich, 1969; Haussühl, 1963*b*). Here again we find a confirmation for the rule already mentioned in connection with the departure from Cauchy relations stating that the replacement of a symmetrical ion by another ion of lower symmetry is accompanied by a strong increase of all transverse effects.

Further investigations on other crystals with low symmetry will prove whether the features of the third-order elastic behaviour observed on calcium

Table 4. *Poisson ratios* $Q_{ij} = s_{ij}/s_{jj}$ (*dimensionless*) (*uniaxial stress parallel to* $\mathbf{e}_j$, *transverse longitudinal deformation parallel to* $\mathbf{e}_i$) *and their pressure derivatives* (*in* 10^{-10} N^{-1} m^2) *for calcium formate at* 295 K

ij	12	21	13	31	23	32
Q_{ij}	−0·457	−0·803	−0·407	−0·366	−0·172	−0·088
dQ_{ij}/dp	−0·95	0·94	−5·18	−2·42	3·37	1·46

Table 3. *Elastic constants* c_{ij} (*adiabatic*) (*in* 10^{10} Nm^{-2}) *and pressure derivatives* dc_{ij}/dp (*dimensionless*) *of calcium formate at* 295 K

ij	11	22	33	12	13	23	44	55	66
c_{ij}	4·923	2·441	3·539	2·483	2·452	1·450	1·050	1·212	2·822
dc_{ij}/dp	15·66	8·47	8·49	9·54	13·68	4·22	1·19	0·97	1·38

Table 5. *Averaged values* c'_{ij} *and* c'_{ijk} (*in* 10^{10} $\mathrm{Nm^{-2}}$) *of calcium formate complying with symmetry group m*3*m and TOEC of cubic calcium fluoride*

	$Ca(HCOO)_2$	CaF_2
$c'_{11} = (c_{11} + c_{22} + c_{33})/3$	3·634	16·357
$c'_{12} = (c_{12} + c_{13} + c_{23})/3$	2·128	4·401
$c'_{44} = (c_{44} + c_{55} + c_{66})/3$	1·695	3·392
$c'_{111} = (c_{111} + c_{222} + c_{333})/3$	−36·6	−124·6
$c'_{111} = (c_{112} + c_{223} + c_{133} + c_{113} + c_{122} + c_{233})/6$	−20·4	−40·0
$c'_{123} = c_{123}$	−27·7	−25·4
$c'_{144} = (c_{144} + c_{255} + c_{366})/3$	−6·9	−12·4
$c'_{166} = (c_{244} + c_{355} + c_{166} + c_{344} + c_{155} + c_{266})/6$	−4·4	−21·4
$c'_{456} = c_{456}$	−5·4	−7·5
c'_{111}/c'_{11}	−10·07	−7·62
c'_{112}/c'_{11}	−5·61	−2·45
c'_{123}/c'_{11}	−7·62	−1·55

formate reflect the existence of general rules valid for any type of stable crystals.

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The Influence of In-Plane Collimation on the Precision and Accuracy of Lattice-Constant Determination by the Bond Method.
I. A Mathematical Model. Statistical Errors

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Abstract

A mathematical model based on a convolution formula has been derived which shows the effect of in-plane (horizontal) collimation on the shape of a measured profile $h(\omega)$ in the Bond method. With simplifying assumptions the profile has been presented in an analytical form. The effect of the width of collimator slits d_1, d_2 on the variance $\sigma^2\omega_0$ of the peak position ω_0 was considered based on the model. From the method of analysis used by Wilson [*Br. J. Appl. Phys.* (1965), **16**, 665–674], the variance $\sigma^2\omega_0$ was estimated for the profile approximated by a least-squares parabola. It has been found that for certain collimation parameters a minimal value of $\sigma^2\omega_0$ is obtained, and the conditions of the optimal choice of collimator slit widths from the point of view of statistical errors have been given. An example of the application of such conditions has been presented.

1. Introduction

A new design of Bond diffractometer constructed in this institute (Łukaszewicz, Kucharczyk, Malinowski & Pietraszko, 1978) is used more for investigations of the relative changes of lattice constants (for example as a result of changing temperature to investigate phase transitions) than for measuring their absolute values. In such measurements there are no high requirements regarding systematic errors and accuracy, $\Delta d/d$, analysed in part II (Urbanowicz, 1981), but they

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