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Elastic Properties of Ammonium Oxalate Hydrate, Ammonium Hydrogen Oxalate Hemihydrate, and Ammonium Tetroxalate Dihydrate

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The elastic constants of the two orthorhombic crystals $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and $(\text{NH}_4)\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ were determined by diffraction of light by ultrasonic waves. These constants and those of the triclinic $(\text{NH}_4)\text{H}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ previously measured are correlated with the crystal structure. All three crystals show extreme elastic anisotropy which may be explained by the layer-like packing of the oxalate groups. The minimum elastic stiffness is observed normal to the C_2O_4 planes, whereas the direction of the maximum elastic stiffness may be correlated with the course of the periodic bond chains. It is shown that hydrogen bonds make a considerable contribution to the elastic properties of crystals. Correlations between elastic behaviour, morphology, and optical properties are discussed.

Introduction

In the present paper the elastic properties of three ammonium salts of oxalic acid are investigated: ammonium oxalate hydrate $[(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, point group 22], ammonium hydrogen oxalate hemihydrate $(\text{NH}_4\text{HC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, point group *mmm*), and ammonium tetroxalate dihydrate $[\text{NH}_4\text{H}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, point group $\bar{1}$], which for brevity will be referred to as AO, AHO and ATO respectively.

Because of its polar properties AO has attracted special attention. Vasilewskaya, Kuznetsova, Rez & Sonin (1968) have reported large electro-optical effects, Izraelenko, Orlov & Kopsik (1968) and Orlov (1969) have made use of AO in producing optical second-harmonic generation and, finally, Fournel & Vergnoux (1971) have performed infrared spectroscopic measurements. It seemed worthwhile to extend the measurements to the determination of the elastic constants of AO as these have not been measured previously.

There seem to be no reports on the physical properties of AHO in the literature.

The elastic constants of ATO have been measured by us (Küppers & Siegert, 1970). In the present paper an attempt will be made to give a structural interpretation of the anisotropic elastic properties of ATO as well as of the two other oxalates.

Methods

Single crystals of AO and AHO were grown from aqueous solutions at 35°C (Küppers, 1972a).

Sound velocities were measured by the Schaefer-Bergmann method as improved by Haussühl (1956): standing ultrasonic waves of about 15 Mc/s were excited in rectangular specimens (average dimension 1 cm, tolerance 1 μ). The ultrasonic wave causes the diffraction of a light beam from a mercury lamp ($\lambda = 546.07$ nm). The beam is focused through the crystal onto a film placed at a distance of about 2 m. Measurement of the distance between the diffracted light spots yields the sound velocity.

In order to determine the elastic constants of the two orthorhombic crystals, the velocities of the longitudinal waves propagating along [100], [010], and [001] were measured. Transverse waves in these directions produce no measurable diffraction of light because the elastic displacement in this case is parallel to one of the principal axes of the elliptical section of the indicatrix (Küppers, 1966). Furthermore, the velocities of the quasilongitudinal and quasitransverse waves in the directions [110]', [101]', and [011]' (as related to a Cartesian coordinate system with axes \mathbf{e}_i parallel to \mathbf{a}_i) were measured. The third wave in these directions is a purely transverse wave and is, for the same reasons

as above, not observable. The nine velocities measured in this way permit a direct determination of the nine elastic constants of orthorhombic crystals.

In birefringent crystals disturbing effects may arise if the ray does not coincide with the wave normal (Küppers, 1971). Measurements of sound velocities along $\langle 100 \rangle'$ with the light beam parallel to $\langle 011 \rangle'$ are not affected because the light component polarized parallel to $\langle 100 \rangle'$ does not undergo double refraction and the other component is refracted in a plane parallel to the wave fronts. In the course of measuring sound velocities along $\langle 110 \rangle'$ the entrance of the light beam was chosen perpendicular to faces $\langle 100 \rangle'$; in this direction no double refraction occurs.

All measurements were carried out at 20°C.

Results

The crystallographic axes a_1 , a_2 , and a_3 of AO and AHO were chosen according to Groth (1910).

The values of the 9 elastic constants (stiffnesses) c_{mn} of these two orthorhombic crystals are listed in Table 1. The relative errors are estimated to be smaller than 0.3% (for $m=n=1, 2, 3$), 1% (for $m=n=4, 5, 6$) and 2% (for $m \neq n$). Table 1 also contains the components of the tensor s_{mn} (elastic compliance) which are obtained from the c_{mn} by matrix inversion. It should be noted that, in the matrix notation, the values of the s_{mns} , for $m \geq 4$, differ from the values of s_{ijij} by a factor of 4.

The density for the determination of the constants c_{mn} was measured by flotation using large visually perfect crystals. The density of AO measured at 20°C was $\rho = 1.501 \text{ g.cm}^{-3}$, this is in good agreement with a value of $\rho_x = 1.500 \text{ g.cm}^{-3}$ as determined from X-ray measurements at room temperature (Robertson, 1965). The measured density of AHO at 20°C was $\rho = 1.6145 \text{ g.cm}^{-3}$, while the density as determined from our own X-ray measurements at 22°C (Küppers, 1972b) was $\rho_x = 1.6146 \text{ g.cm}^{-3}$.

The volume compressibilities, $K = -\partial \log V / \partial p = \sum_{ik} s_{iikk}$, are found to be $K_{AO} = 4.33$ and $K_{AHO} = 11.09 \text{ cm}^2 \cdot \text{dyne}^{-1}$.

Discussion

Anisotropy

A typical feature common to all three crystals under investigation is an extremely high elastic anisotropy. The ratio of maximal to minimal longitudinal stiffness, $c_{1111}^{\text{max}}/c_{1111}^{\text{min}}$, of ATO was previously reported as 4.67 (Küppers & Siegert, 1970). For AO and AHO the respective values are $c_{22}/c_{33} = 2.08$ and $c_{11}/c_{33} = 4.55$. It seems desirable, therefore, to give an interpretation of

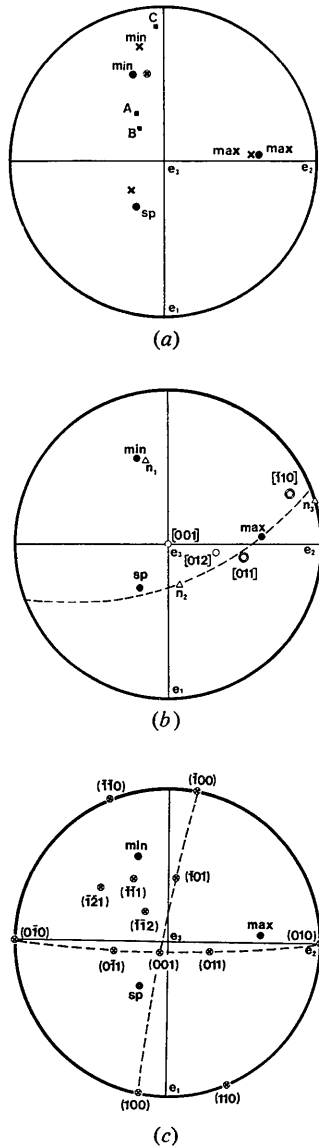


Fig. 1. Stereograms of ATO; closed circles: directions of c_{1111}^{max} , c_{1111}^{sp} , c_{1111}^{min} . (a) Directions of the normals of the oxalate residues A, B and C (squares) and average direction (en-circled square); directions of the principal axes of the tensor f'_{ij} (crosses); (b) directions of PBC vectors (circles) and refractive indices (triangles); (c) predominant faces of crystals grown from aqueous solution.

Table 1. Elastic stiffnesses c_{mn} ($\times 10^{11} \text{ dyne.cm}^{-2}$) and elastic compliances s_{mn} ($\times 10^{-12} \text{ cm}^2.\text{dyne}^{-1}$) of ammonium oxalate dihydrate (AO) and ammonium hydrogen oxalate hemihydrate (AHO) at 20°C

	<i>mn</i>	11	22	33	44	55	66	23	31	12
AO	<i>c_{mn}</i>	4.565	5.257	2.526	1.032	0.885	1.302	2.174	1.641	2.221
	<i>s_{mn}</i>	3.03	3.13	6.74	9.69	11.30	7.68	-2.22	-1.34	-0.723
AHO	<i>c_{mn}</i>	6.709	4.139	1.475	0.383	0.592	0.973	1.300	0.749	1.484
	<i>s_{mn}</i>	1.64	3.47	9.49	26.14	16.90	10.28	-2.83	-0.43	-0.45

this remarkable result with reference to the crystal structure. Since the potentials of the mutual interaction of the particles are not known with a sufficient accuracy, a rigorous theoretical derivation of the elastic behaviour is not yet possible. Therefore, in the following section simple models will be used to give a qualitative explanation of the observed anisotropy.

The six atoms constituting the oxalate ion, $C_2O_4^{2-}$, form a plane in nearly all oxalates whose structures have been explored so far. In AO, as an exception, the ion is twisted about the central C–C bond by only 26° , thus displaying a configuration that is still quasi-planar. In the crystals considered here the oxalate ions are packed in a layer-like fashion. Perpendicular to these layers only van der Waals forces are prevalent, whereas the planes are linked laterally by ionic or hydrogen bonds. These bonds extend preferentially in the planes which are defined by the oxalate ions. Since the elastic stiffness is essentially determined by the course of the principal bond chains, one should expect a rather low elastic constant in directions perpendicular to the C_2O_4 -residues, whereas in directions within these planes stronger forces should cause higher elastic constants.

Table 2. Direction cosines b_i for ATO

(a) Direction cosines of extrema of the longitudinal stiffnesses c'_{1111}

	b_1	b_2	b_3
c'_{1111}^{\max}	-0.0466	0.8898	0.4540
$c'_{1111}^{\text{saddlep.}}$	0.7142	-0.5580	0.4226
c'_{1111}^{\min}	-0.7994	-0.3813	0.4643

(b) Direction cosines to normals of the planes of the oxalate residues, A, B, C, and their weighted mean direction

	b_1	b_2	b_3
A	-0.5484	-0.3219	0.7713
B	-0.408	-0.2925	0.8644
C	-0.9882	-0.0652	0.1394
A+B+2C	-0.8191	-0.2080	0.5346

(c) Direction Cosines of N–O bonds and O–O hydrogen bonds

	b_1	b_2	b_3
N—O(1)	0.5278	0.7243	0.4437
N—O(4)	0.7143	-0.6995	0.0244
N—O(6)	-0.1389	0.5452	0.8266
N—O(8)	0.0021	-0.8709	0.4915
N—O(5)	0.0303	-0.1350	0.9905
O(2)—O(9)	0.5091	-0.8490	0.1418
O(3)—O(7)	0.1383	0.8162	0.5600
O(5)—O(10)	-0.1697	0.7730	0.6110
O(9)—O(8)	0.1028	0.4607	0.8809
O(9)—O(6)	-0.2507	-0.7983	0.5481
O(10)—O(4)	0.5480	0.7385	0.3932
O(10)—O(1)	0.7253	-0.6925	0.0434

(d) Principal components and direction cosines of the principal axes of the tensor f_{ij}

	b_1	b_2	b_3
$f'_{11} = 6.567$	-0.0596	0.9008	0.4302
$f'_{22} = 3.845$	0.3358	-0.3877	0.8584
$f'_{33} = 1.789$	-0.9400	-0.1956	0.2794

(e) Principal refractive indices and their direction cosines.

	b_1	b_2	b_3
$n_1 = 1.4237$	-0.8627	-0.0052	0.5057
$n_2 = 1.5500$	0.4905	0.1230	0.8626
$n_3 = 1.5687$	-0.2476	0.9688	0.0027

This concept will be tested by examination of the three ammonium oxalates.

(a) ATO

From the results previously published (Küppers & Siegert, 1970) only the position of the maximum, the minimum and the saddlepoint of the longitudinal stiffness c'_{1111} will be cited. Their direction cosines b_i , as related to a Cartesian coordinate system e_1, e_2 and e_3 [$e_2 \parallel a_2^*$, $e_3 \parallel a_3$, $e_1 = e_2 \wedge e_3$; a_i and a_i^* being the fundamental vectors of the crystal lattice and the reciprocal lattice, respectively, in Groth's (1910) mounting] are listed in Table 2(a). In the stereograms of Fig. 1(a), (b) and (c) these directions are marked by closed circles. The respective values of c'_{1111} are 5.89, 2.88, and 1.26 dyne.cm $^{-2}$.

The structure of ATO was explored by Currie, Speakman & Curry (1967). The space group is $P\bar{1}$. In order to clarify the spatial arrangement a perspective view of the structure is shown in Fig. 2, according to a drawing given in the paper of Currie *et al.* The unit cell contains two formula units, *i.e.* four oxalate residues. Two of them, designated as C, are connected by an inversion centre at $[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$; the planes built up

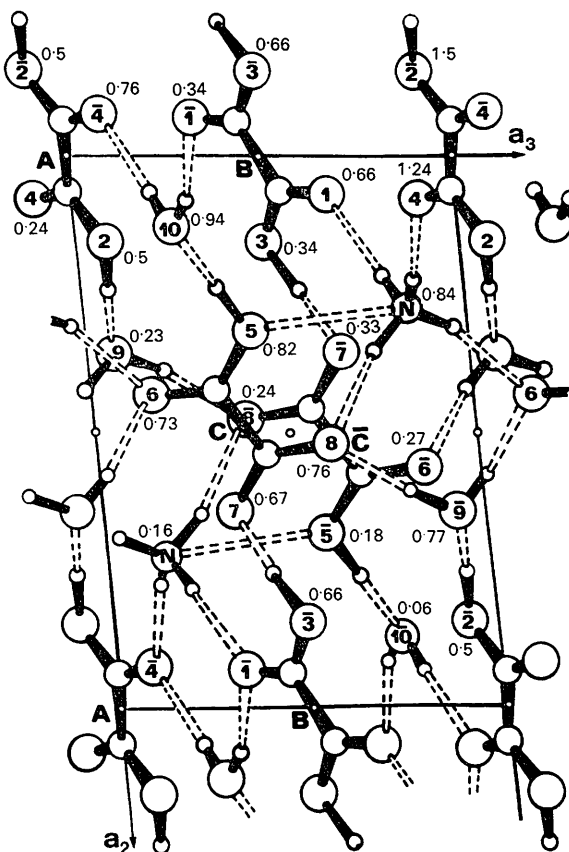


Fig. 2. Perspective view of the structure of ATO. Numbers inside the circles indicate the number of the oxygens; the corresponding equivalent point by inversion is indicated by a dash over the number; numbers beneath the atoms give the height in fractional coordinates. (From Currie *et al.*, 1967).

elastic stiffness more and larger faces will occur. This rule may suitably be proved on ATO because this crystal exhibits a relatively large number of faces. As was reported elsewhere (Küppers, 1972*a*), the prominent faces found on ATO crystals grown from aqueous solutions are (100), (010), (001), (110), (0 $\bar{1}$ 1), (011), (T01), (T11), (T2), and (T $\bar{2}$ 1). The directions for these planes are drawn in Fig. 1(c). It may be seen that the sector made up by the vectors $-\mathbf{a}_1^*$, $-\mathbf{a}_2^*$ and \mathbf{a}_3^* and including the direction of c_{111}^{\min} , also contains the majority of prominent faces. The only three faces (hkl) with h, k, l non-zero appear in this sector and group around the direction of c_{111}^{\min} .

(b) AHO and AO

In order to explain the elastic behaviour of AHO a structure analysis was performed; details will be published elsewhere (Küppers, 1972*b*). The main features to be considered here are as follows: space group $Pnma$; $Z=8$; $a_1=11.228$, $a_2=12.329$, $a_3=6.898$ Å; the oxalate group occupies a general position and is found to be planar; its normal is inclined with respect to the a_3 axis at an angle of 24° . By the action of the eight symmetry operations a symmetric distribution of the eight normals around \mathbf{a}_3 is achieved; thus, the average direction of the normals is the a_3 axis. Inspection of Table 1 reveals that \mathbf{a}_3 is also the direction of the minimum elastic stiffness, c_{33} , in accordance with the rule stated earlier. Fig. 3 shows a projection of half the unit cell of AHO; by the gliding-plane operation normal to \mathbf{a}_1 a similar arrangement is attained in the upper part of the unit cell. The oxalate ions are in between the mirror planes, m , whereas the nitrogen atoms and the water oxygens lie within these planes.

The structure of AO was refined by Robertson (1965). The space group is $P2_12_12$; $Z=2$; $a_1=8.035$, $a_2=10.309$, $a_3=3.795$ Å. The oxalate group occupies a special position: a twofold axis (parallel to \mathbf{a}_3) passes through the centre of the ion; thus, the C-C bond lies perpendicular to \mathbf{a}_3 ; the two COO planes are found to be twisted around the C-C bond forming an angle of 13° with the plane (001). An average plane drawn through the oxalate residue lies perpendicular to the a_3 axis which, again, is the direction of the minimal elastic stiffness, c_{33} . Both the ammonium ion and the water molecule are in tetrahedral environments. The configuration of the atoms in AO is shown in Fig. 4.

Thus, in the structures of both AHO and AO the oxalate residues are packed one upon the other in the \mathbf{a}_3 direction in a similar manner. The mutual van der Waals interaction would result in a very low elastic stiffness. In addition, however, the oxalate groups are linked sideways by the adjacent ammonium and water groups, forming zigzag chains in the \mathbf{a}_3 direction. The magnitude of the elastic stiffness c_{33} , therefore, is mainly determined by the density of such chains per area. When the unit cell of AO contains four NH_4 and two H_2O groups, which are distributed over an area of $a_1a_2=83$ Å², the density is 0.0724. In the AHO struc-

ture the numbers of NH_4 and H_2O groups in one layer (half the height of the unit cell) are also four and two respectively, $a_1a_2=138$ Å², the density being 0.0435. The chain-density ratio of AO to AHO is 1.67. On the other hand, the ratio of the experimentally determined elastic constants is $c_{33}^{\text{AO}}/c_{33}^{\text{AHO}}=1.71$, which is in reasonable agreement with the predicted value.

The elastic stiffness of AO in the \mathbf{a}_1 as well as in the \mathbf{a}_2 direction is obviously enlarged by the reinforcement of the rigid oxalate residues between the NH_4 and H_2O groups. On the same basis the value of c_{22} of AHO may be understood. This is of the same order as that of c_{11}^{AO} and c_{22}^{AO} . A surprisingly high elastic constant is observed in the \mathbf{a}_1 direction of AHO. Since the NH_4 and H_2O groups within the mirror planes do not seem to exhibit extraordinarily strong bonds this effect must be attributed to the hydrogen bond (bond distance = 2.56 Å) connecting the oxalate residues and forming an infinite chain in the \mathbf{a}_2 direction.

The consequence of this consideration is that a hydrogen bond may exhibit a stiffness similar to that of an ionic bond. This is an astonishing result, because the lattice energy contribution of a hydrogen bond is usually about an order of magnitude lower than the contribution of an ionic bond. However, the elastic behaviour is not determined by the amount of the potential minimum but by the curvature of the potential curve at the equilibrium point.

An examination of other crystals, those linked by hydrogen bonds forming straight continuous chains, confirms this result. In the crystal structure of tartaric acid the molecules are linked by strong (short) hydrogen bonds to linear chains extending in the \mathbf{a}_1 direction (Okaya, Stemple & Kay, 1966). These chains are then connected into two-dimensional layers by means of weaker (longer) lateral hydrogen bonds. Accordingly, c_{11} is found to have the relatively large value of

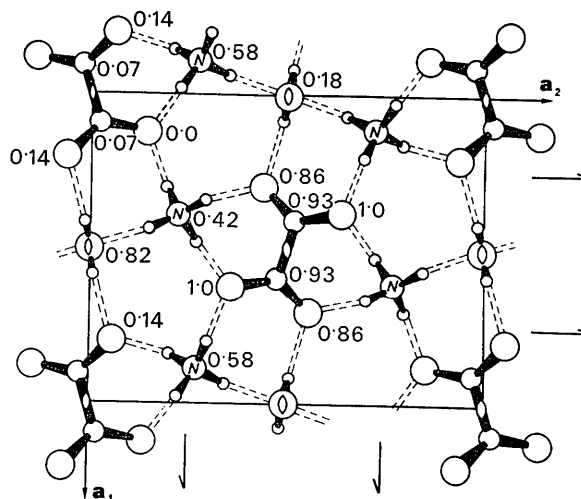


Fig. 4. Unit cell of AO; numbers indicate the height in fractional coordinates.

$9.8 \cdot 10^{11}$ dyne.cm⁻². This value is deduced by transforming the c_{mn} values given by Bechmann (1966) which in turn are calculated from the s_{mn} values measured by Mason (1950). On the other hand, c_{22} (normal to the layers) is only $1.9 \cdot 10^{11}$ dyne.cm⁻². Remarkably, the elastic constants of salts of tartaric acid, which contain ionic bonds, are much lower (in the range of $5 \cdot 10^{11}$ dyne.cm⁻²) (Bechmann, 1966). The potential functions deduced up to now for hydrogen bonds are too inaccurate to allow a theoretical comparison of the second derivatives with respect to the strains which are responsible for the elastic constants.

Cauchy relations

According to Haussühl (1967) the deviations from the Cauchy relations build a second-rank tensor, g_{rs} . Sign and magnitude of its components are determined by the type of bonding in the particular crystal. In the present case the components of the reduced tensor $g_{rs}^* = g_{rs} \cdot K$ (K = volume compressibility) have the following values for the two orthorhombic crystals:

$$\begin{aligned} \text{AO: } & g_{11}^* = 0.495; g_{22}^* = 0.328; g_{33}^* = 0.398, \\ \text{AHO: } & g_{11}^* = 1.017; g_{22}^* = 0.406; g_{33}^* = 0.566. \end{aligned}$$

These constants are positive as usually found in crystals bonded by ionic forces or hydrogen bonds. The g_{11}^* observed for AHO is extremely large. This result is in agreement with the rule stated by Haussühl (1967) that g^* should be large in crystals containing asymmetric constituent units such as the oxalate residues.

Optical properties

In ATO as well as in the two orthorhombic crystals there exists an interesting correlation between the elastic and the optical properties. As a consequence of the high polarizability within the plane of the oxalate residue, high refractive indices are found in directions within the plane (Hendricks & Deming, 1935). In contrast, the direction perpendicular to the oxalate planes should show the lowest refractive index because of the low polarizability normal to these planes. Therefore, the crystals considered here are found to be optically negative. Furthermore, the direction of the minimum refractive index, n_1 , of ATO (Porter, 1928), which is marked as a triangle in Fig. 1(b), is found just beneath the direction indicated by the encircled square, and so beneath the direction of c_{1111}^{min} .

In case of AO the refractive indices are reported to be: $n_1 = 1.547$, $n_2 = 1.595$, $n_3 = 1.438$ (indices are referred to the crystallographic axes) (Groth, 1910). The direction of minimum refractive index coincides with the direction of the minimum elastic constant.

The refractive indices of AHO were not determined hitherto. They were measured by us using the prism method, their values being listed in Table 4 for five different wavelengths. In this case also a close correlation between optical and elastic constants is indicated.

Table 4. *Refractive indices of AHO for various wavelengths*

λ [nm]	n_1	n_2	n_3
632	1.5619	1.5652	1.4331
589	1.5641	1.5676	1.4346
546	1.5668	1.5711	1.4367
488	1.5720	1.5766	1.4401
436	1.5790	1.5846	1.4449

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