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The Electron Density of α-Oxalic Acid Dihydrate at 100 K by X-ray Diffraction: a Contribution to the IUCr Commission on Charge, Spin and Momentum Densities Project on the Accurate Determination of Electron Densities*

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Abstract

The results of the determination of the electron density of α-oxalic acid dihydrate at 100 K by means of X-ray diffraction are reported as part of the project on the accurate determination of electron densities which was initiated by the International Union of Crystallography. An extensive data set, consisting of all reflexions in the whole reciprocal sphere up to $\sin\theta/\lambda = 1{\cdot}3$ Å^{-1}, was measured. Most of the structural parameters and experimental deformation densities compare well with the findings of an earlier published study [Stevens & Coppens (1980). *Acta Cryst.* B**36**, 1864–1876]; thermal parameters, however, differ significantly. Application of a correction for thermal diffuse scattering increased the vibrational parameters by 12%. The polarization of the water O lone-pair density, found by Stevens & Coppens (1980), is firmly confirmed by this study.

1. Introduction

A quantitative interpretation of electron densities, as obtained from X-ray diffraction experiments, is generally of limited value due to the fact that it is hardly feasible to perform a diffraction experiment under a variety of conditions in order to assess the errors in the observed electron densities, which may be the result of the particular choices made for the experimental setup, treatment of the data, refinement techniques *etc.* In order to facilitate such an error assessment, the IUCr initiated a project in which researchers were invited to perform experiments and/or calculations aiming at an accurate determination of the electron density distribution of a single substance: α-oxalic acid dihydrate. Some studies on this subject have already appeared in the literature (Johansen, 1979; Stevens & Coppens, 1980; Stevens, 1980) and this determination of the

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electron density of α-oxalic acid dihydrate at 100 K by means of X-ray diffraction is presented in order to contribute to the project.

2. Experimental

2.1. *General*

Diffracted intensities were collected on a PW 1100 automated four-circle diffractometer (Mo $K\alpha$ radiation) which was equipped with a pyrolitic-graphite monochromator. The diffraction geometry and details about the homogeneity of the primary beam have been described by Harkema, Dam, van Hummel & Reuvers (1980). A crystal of dimensions 0·46 × 0·30 × 0·37 mm, grown from an aqueous solution, was mounted in an arbitrary orientation on a glass fiber with silicone vacuum grease, the b axis making an angle of about 20° with the φ axis of the diffractometer.

The crystal was cooled by means of a nitrogen gas stream, the outer part of which was heated in order to prevent icing of the crystal. The temperature of the cold nitrogen gas stream was monitored during the experiment by means of a copper–constantan thermocouple, which was placed in the cold gas tube. During the experiment the temperature remained stable within 1 K.

A small KH_2PO_4 crystal, mounted on the diffractometer in a similar way as described above, served to calibrate the sample temperature. The intensities of reflexions of this crystal are known to change rapidly at a temperature of 122 K (Frazer & Pepinsky, 1953) because of a phase transition. In view of the uncertainty in the determination of the transition point and the fluctuation in sample temperature, we estimate the temperature of our oxalic acid crystal to have been 100 ± 2 K.

Cell dimensions of α-oxalic acid dihydrate at 100 K were obtained by a least-squares refinement (using a wavelength of 0·70930 Å) of 38 setting angles of $K\alpha_1$ reflexions at high Bragg angles. The cell parameters are: a = 6·0986 (5), b = 3·4981 (3), c = 11·952 (1) Å and β = 105·777 (8)°.

2.2. *Data collection*

Horizontal and vertical detector apertures were determined from low-angle reflexions by seeking the smallest apertures which would allow all intensity to be recorded, resulting in horizontal and vertical apertures of 3·0 and 1·5° respectively. The scan range used during the measurements was taken according to the formula $\Delta\omega = A + B\text{tg}\theta$, in which $\Delta\omega$ is the scan range in θ. A is a term determined by the mosaic spread of the crystal, the size of the crystal and the divergence of the primary beam, while B depends on the spectral band of the incoming radiation (Alexander & Smith, 1962, 1964).

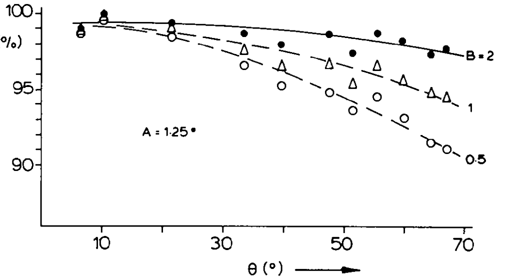


Fig. 1. The ratio $I_r = I(\Delta\omega)/I(\Delta\omega_{\max})$ *versus* the Bragg angle θ for different values of B in the formula $\Delta\omega = A + B \tan\theta$ with A fixed at 1·25°, from reflexion profiles from a small CaF_2 crystal.

Prior to the actual measurement the values of A and B were coarsely determined by examination of peak shapes in different ranges of $\sin\theta/\lambda$. A and B values of 2·3 and 0·5°, respectively, seemed to allow for an accurate background determination.

Peak profiles were measured with the $\omega/2\theta$ step-scan technique with a step size of 0·02° and a scan speed of 0·08°/s.

For peak definition more accurate values of A and B are needed. The factor B was determined with the aid of a small CaF_2 crystal exhibiting intense high-order scattering, small mosaic spread and a minimal amount of peak broadening due to thermal diffuse scattering. From low-angle reflexions A was determined so as to include at least 99% of the intensity. Using this value of A the intensities of reflexions at various values of θ were determined using a number of B values. The results are shown in Fig. 1. From this figure we see that large scan ranges are needed to measure all integrated intensity. We have chosen a B value of 0·75°, risking underestimation of integrated intensities at high Bragg angles by an amount of at most 6%. For oxalic acid the same procedure was applied to determine A, resulting in a value of 1·25°. No significant anisotropic character for A was detected. The remaining parts of the measured profile were used to determine the background.

All reflexions in the whole reciprocal sphere up to $\sin\theta/\lambda = 1\cdot3$ Å^{-1} were collected. Each reflexion was measured for (at most) five different orientations of the crystal obtained by rotation about the scattering vector by an amount of 22°. This procedure resulted in a total of 46 994 scan profiles, collected in five weeks.

2.3. *Corrections on and treatment of net intensities*

During data acquisition three standard reflexions were recorded every 60 min. The results are shown in Fig. 2. In this figure we observe a decrease in intensity of about 4% over the period of measurement. The net intensities were corrected for this long-term instability by applying a scale factor $K(t)$, determined as follows.

The intensities $S_j(t_l)$ of each standard reflexion j as a function of time were fitted by means of a cubic spline function $f_j(t)$. The scaling functions $K_j(t)$ are defined by $K_j(t) = \bar{S}_j/f_j(t)$ with j = 1,2,3 and $\bar{S}_j = 1/N \times \sum_{l=1}^{N} S_j(t_l)$. The average of the three scaling functions

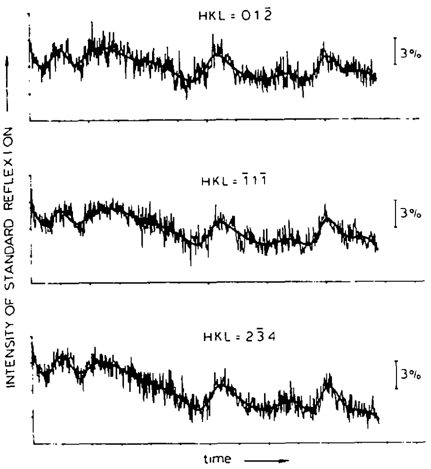


Fig. 2. The intensities of three standard reflexions measured at regular times during the data acquisition which lasted about 5 weeks.

at time $t, K(t)$, was used to correct the measured intensities. Its value ranged from 0·98 to 1·02.

A combined absorption (μ = 0·170 mm^{-1}) and beam-inhomogeneity correction was performed according to Harkema *et al.* (1980). The correction factors ranged from 0·927 to 0·909. Symmetry-equivalent intensities were averaged leading to a set of 3304 independent observed reflexions.* A reflexion was regarded to be observed when $I/\sigma_{\text{ex}}(I) > 3{\cdot}0$, in which I is the average net intensity and $\sigma_{\text{ex}}(I)$ the standard deviation in I as estimated from the spread in intensities belonging to a set of symmetry-related reflexions (see § 2.4). Finally, a Lorentz–polarization monochromator correction was applied (Azaroff, 1955), assuming the monochromator to be of the ideally mosaic type; see also Kerr & Ashmore (1974).

2.4. *Estimation of the accuracy in the intensity measurements*

The variance to be assigned to an experimentally determined integrated intensity is known to consist not only of a contribution due to Poisson statistics. Rees (1977) has enumerated several other sources of error, many of which are proportional to the integrated intensity. McCandlish, Stout & Andrews (1975) have given a procedure to estimate the variance from repeatedly measured standard reflexions. Another method which may be followed is to estimate the variance from the data in the case where each reflexion has been measured a sufficient number of times. In this case the variance will also contain contributions due to systematic errors present in the data for which no correction was applied (Schulz, 1971). Both approaches will be considered here.

Apart from our choice of scaling function we have used the same expressions as given by McCandlish *et al.* (1975) to derive the variance in an integrated intensity. In their paper McCandlish *et al.* (1975) observed that the variance of the scale factor, var$[K(t)]$, usually increases with increasing time. It should be noted, however, that this is inevitable when linear-fit functions are chosen which are set to unity at the start of the experiment. Since the time dependence of the variance of the factor $K(t)$ is dependent on the definition of the scaling function and therefore rather arbitrary we have taken the maximum value for var $[K(t)]$. So the variance in a single integrated intensity becomes:

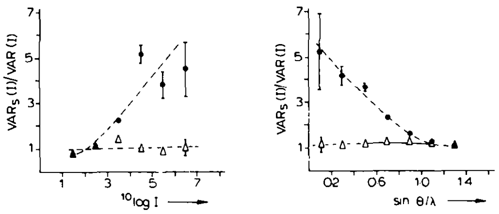
$$\begin{aligned}\text{var}(I) &= K_t^2\,\text{var}(I)_{\text{counting}} + K(t)^2\,\overline{c^2}\,I^2 \\ &\quad + \text{var}[K(t)]_{\max}\,I^2 \\ &\equiv K(t)^2\,\text{var}(I)_{\text{counting}} + d^2\,I^2, \end{aligned} \tag{1}$$

where we have taken $\overline{c^2}$ to be the average of the c^2 values as determined from the standard reflexions. For this experiment we found for the three standards: $c_1^2 = 36 \times 10^{-6}$, $c_2^2 = 45 \times 10^{-6}$ and $c_3^2 = 41 \times 10^{-6}$. The value for var$[K(t)]_{\max}$ was found to be $2{\cdot}1 \times 10^{-4}$. The values $K(t)^2\,\overline{c^2}$ + var$[K(t)]_{\max}$ are combined in $d_s^2 = 2{\cdot}5 \times 10^{-4}$.

Subsequently the variance was estimated from the spread in intensity for the various sets of symmetry-related or multiply measured reflexions.

For most reflexions the resulting sample variances could be approximated by expression (1), assuming $d \equiv d_r = 3 \times 10^{-2}$. For about 2% of the reflexions the sample variance exceeded three times the value calculated with d_s and a value of $d_r = 6 \times 10^{-2}$ was adopted.

To test the results the reflexions were divided in groups according to intensity and to sin θ/λ. For each reflexion the ratio of the sample variance and var(I) was calculated, using either d_s or d_r. These ratios were averaged over the members of the group. The result is shown in Fig. 3. Clearly the variance is well described with (1) using d_r.



(*a*) (*b*)

Fig. 3. Average ratio of the sample variances var$_s(I)$ over var(I), *versus* (*a*) intensity and (*b*) sin θ/λ (Å^{-1}). Bars indicate 2σ in the calculated averages. ● corresponds to var(I) calculated from the standard reflexions. △ corresponds to var(I) calculated with the procedure described in the text.

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* Internal agreement factor $R(I) = 3{\cdot}1\%$. Of course, it would be more elegant to average after corrections for anisotropic effects like extinction and thermal diffuse scattering had been performed. In this case, however, *a posteriori* justification was given as extinction was found to be small (§3) as well as anisotropy in thermal diffuse scattering for reflexions measured at different ψ angles (§ 4).

3. Refinements and calculation of difference densities

Least-squares refinements have been carried out by minimizing the objective function $\Delta = \sum_{\mathbf{H}} w[F_o(\mathbf{H}) - k|F_c(\mathbf{H})|]^2$ with $F_o(\mathbf{H})$ the experimentally determined (observed) structure factor for reflexion **H**, $F_c(\mathbf{H})$ the calculated structure factor, k the scale factor and $w = 1/\sigma^2(F)$, in which $\sigma(F)$ was calculated from var(I) according to Hamilton (1964). Atomic scattering factors for C and O were taken from *International Tables for X-ray Crystallography* (1974). H scattering factors were chosen according to Stewart, Davidson & Simpson (1965). For C and O the anomalous-scattering factors of Cromer & Liberman (1970) were used. An isotropic-extinction parameter was included in the refinement as described by Larson (1970). Only a very small number of reflexions appeared to be affected by extinction. The largest extinction correction (13% on the intensity) was found for the 110 reflexion. Positional and thermal parameters of the H atoms were kept fixed at the values from the neutron study of Koetzle & McMullan (1980).

The results of a conventional full-angle refinement in which the scale factor, isotropic-extinction parameter and positional and anisotropic thermal parameters of non-hydrogen atoms were varied are listed in Table 1.

It is well known that parameters determined by means of a full-angle refinement may be biased by bonding features for which the applied model (spherical atoms) does not account. A way to overcome this bias is to determine positional and thermal parameters from reflexions at high values of sin θ/λ (HO refinement), where the influence of bonding effects should be minimal (Stewart, 1968). A practical problem is then to determine the value of sin θ/λ below which the data should be discarded. Several refinements with increasing values of the sin θ/λ threshold value revealed that no significant shifts in parameters occurred above sin $\theta/\lambda = 1\cdot0$ Å^{-1}. The results of a refinement with this sin θ/λ threshold value are summarized in Table 2.* Corresponding interatomic distances and bond angles are shown in Table 3.

Table 1. *Discrepancy indices, scale factor, fractional atomic coordinates* ($\times 10^5$) *and thermal parameters* (Å^2 × 10^5) *resulting from a full-angle refinement*

$R = 0\cdot031$; $R_w = 0\cdot035$; $N_o = 3304$; sin θ/λ range 0·0–1·3 Å^{-1}; goodness of fit 3·49; scale 16·60 (2).

	x	y	z
C(1)	−4500 (5)	5870 (8)	5193 (2)
O(1)	8534 (4)	−5612 (7)	15017 (2)
O(2)	−22143 (4)	24255 (7)	3631 (2)
O(3)	−45143 (4)	63108 (7)	17869 (2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
C(1)	932 (8)	1036 (8)	767 (7)	113 (7)	−1 (7)	256 (6)
O(1)	1285 (8)	1869 (9)	707 (6)	501 (7)	84 (7)	215 (6)
O(2)	1169 (8)	1713 (9)	958 (7)	541 (7)	68 (7)	373 (6)
O(3)	1147 (8)	1805 (9)	881 (7)	297 (7)	106 (7)	375 (6)

The deformations of the free-atom electron densities that result from chemical bonding, smeared by thermal motion, are approximately displayed by the dynamic difference density $\Delta\rho(\mathbf{r})$ obtained from X-ray diffraction measurements:

$$\Delta\rho(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{H}}\left[\frac{F_o(\mathbf{H})}{K} - F_c(\mathbf{H})\right] e^{-2\pi i\mathbf{H}.\mathbf{r}}$$

in which V is the volume of the unit cell, F_o and F_c are the observed and calculated structure factors re-

Table 2. *Discrepancy indices, scale factors, fractional atomic coordinates* ($\times 10^5$) *and thermal parameters* (Å^2 × 10^5) *resulting from high-order* (*HO*) *refinement and a subsequent full-angle* (*FA*) *refinement of the scale factor*

$R = 0\cdot040$; $R_w = 0\cdot027$; $N_o = 1479$; sin θ/λ range 1·0–1·3 Å^{-1}; goodness of fit 1·28; HO scale 16·53 (8); FA scale 16·57 (1).

	x	y	z
C(1)	−4495 (5)	5879 (11)	5194 (2)
O(1)	8500 (5)	−5605 (13)	15007 (2)
O(2)	−22121 (5)	24236 (12)	3629 (2)
O(3)	−45150 (5)	63088 (12)	17858 (2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
C(1)	924 (8)	1065 (10)	746 (7)	169 (6)	−4 (6)	253 (4)
O(1)	1265 (8)	1858 (12)	729 (6)	505 (7)	78 (6)	228 (4)
O(2)	1162 (8)	1750 (11)	920 (6)	585 (7)	74 (6)	356 (4)
O(3)	1166 (8)	1774 (11)	877 (6)	288 (6)	111 (6)	387 (4)

Table 3. *Bond lengths* (Å) *and angles* (°) *for* α-*oxalic acid dihydrate at* 100 K *derived from an HO refinement* (*sin* θ/λ > 1·0 Å^{-1}) [H *positions from Koetzle & McMullan* (1980)]

C(1)–C(1′)	1·5432 (4)	O(1)–C(1)–O(2)	126·94 (4)
C(1)–O(1)	1·2882 (4)	O(1)–C(1)–C(1′)	112·59 (3)
C(1)–O(2)	1·2221 (5)	O(2)–C(1)–C(1′)	120·46 (3)
O(1)–H(1)	1·0696 (7)	C(1)–O(1)–H(1)	113·25 (5)
O(3)–H(2)	0·9698 (8)	H(2)–O(3)–H(3)	106·10 (7)
O(3)–H(3)	0·9662 (9)	O(1)–H(1)···O(3′)	177·5 (1)
H(1)···O(3′)	1·4192 (7)	H(1)···O(3′)–H(2′)	112·39 (7)
H(2)···O(2″)	1·8780 (7)	H(1)···O(3′)–H(3′)	118·17 (9)
H(3)···O(2)	1·9217 (8)	O(3)–H(2)···O(2″)	165·1 (2)
O(1)···O(3′)	2·4883 (4)	H(2)···O(2″)–C(1″)	121·54 (5)
O(3)···O(2″)	2·8264 (4)	O(3)–H(3)···O(2)	155·7 (1)
O(3)···O(2)	2·8303 (4)	H(3)···O(2)–C(1)	128·90 (5)

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* A list of structure factors has been deposited with the British Library Lending Division, as Supplementary Publication No. SUP 38752 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

spectively and K is the scale factor. For calculation purposes the effects of extinction and anomalous dispersion are absorbed in $F_0(\mathbf{H})$. The positional and thermal parameters, required to calculate the structure factors $F_c(\mathbf{H})$ corresponding to the free-atom densities, were taken from the HO refinement. The scale factor, K, was determined from a full-angle refinement in which all parameters except the scale factor were kept fixed (van der Wal, de Boer & Vos, 1979). The deformation densities have been calculated* to a resolution of $\sin\theta/\lambda = 1{\cdot}05$ Å^{-1}, as inclusion of the numerous high-order reflexions added only noise. Experimental deformation maps for several cross sections are shown in Figs. 4–8.

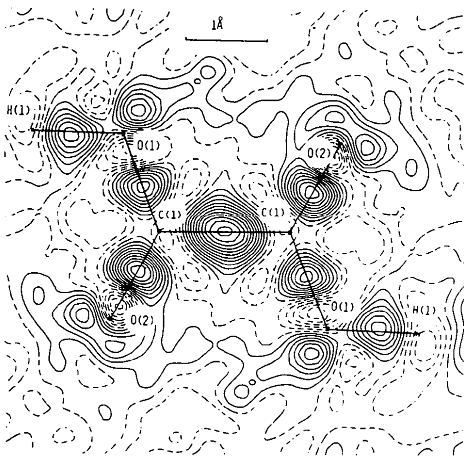

Fig. 4. Experimental difference electron density in the plane of the oxalic acid molecule. Contours are drawn at intervals of 0·05 e Å^{-3}; zero and negative contours dashed.

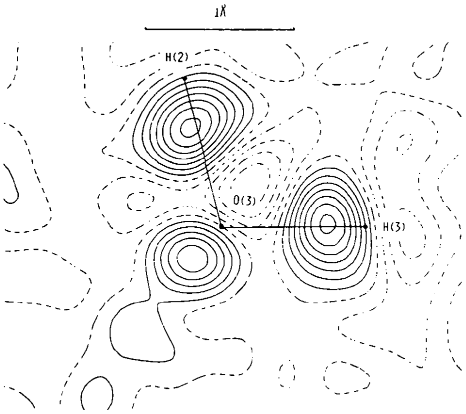

Fig. 5. Experimental difference electron density in the plane of the water molecule. Contours as in Fig. 4.

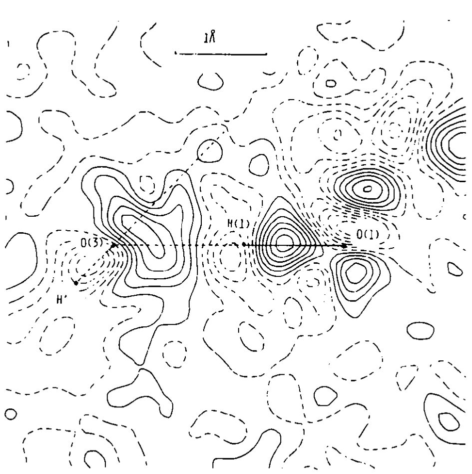

Fig. 6. Experimental difference electron density of the short O(1)—H(1)···O(3) hydrogen bond in the plane perpendicular to the water molecule, bisecting the HOH angle. H' is the projection of H(2) and H(3) on this plane. The lone-pair density near O(3) is clearly asymmetric with respect to the line H'—O(3).

4. Discussion

With respect to the positional parameters we arrive at basically the same conclusions as Stevens & Coppens (1980): the largest asphericity shift as found by comparing the positions of the full-angle and HO refinement (Tables 1 and 2 respectively) is only 0·002 Å for O(1). Furthermore, there are no significant differences between our HO positional parameters and those of Stevens & Coppens (1980); our heavy-atom coordinates agree with the values as found from two published neutron studies of Feld (1980) and Koetzle & McMullan (1980) within 0·002 Å.

A more extensive comparison of crystallographic parameters of α-oxalic acid dihydrate as found by participants of the oxalic acid project will be published elsewhere under the auspices of the IUCr Commission on Charge, Spin and Momentum Densities (Coppens *et al.*, 1984).

A comparison of temperature factors shows a less optimistic picture, as is evident from Table 4 where equivalent isotropic temperature factors for the several studies are compared. From this table we see that there are large differences (up to 15%) in the vibrational parameters of the heavy atoms. The observed discrepancies may be caused by such factors as differences in sample temperature, in methods for determination of integrated intensities from peak profiles and in scan procedures. Owing to these different procedures different corrections for truncation and TDS correction should be applied.

Qualitatively, the bonding features as displayed in the deformation density maps (Figs. 4–8) agree rather well with the corresponding figures of Stevens & Coppens (1980). A quantitative comparison is given in Table 5. In view of the estimated errors (Stevens &

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* Calculations were performed with the program *SPFT* (van de Waal, 1975).

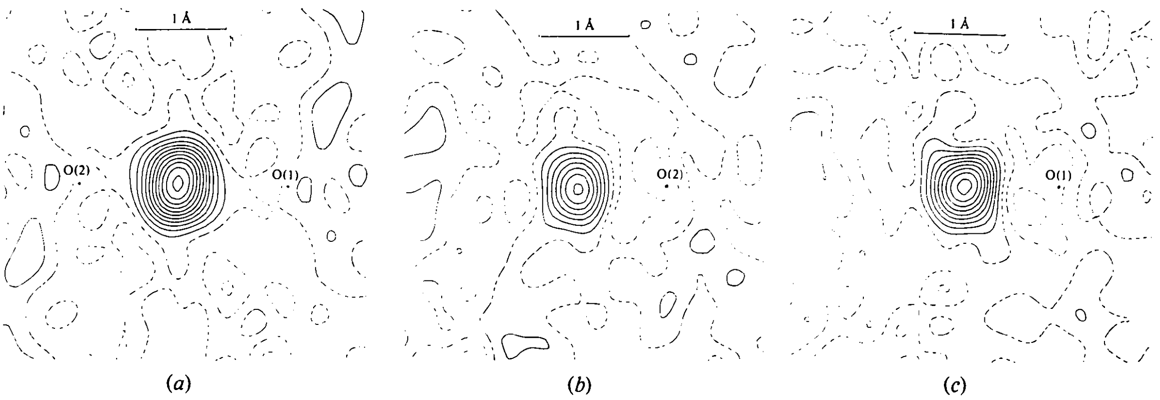

Fig. 7. Experimental difference electron density in planes perpendicular to the bond axis at the midpoint of the bonds: (*a*) C—C; (*b*) C—O(1); (*c*) C—O(2). Contours as in Fig. 4.

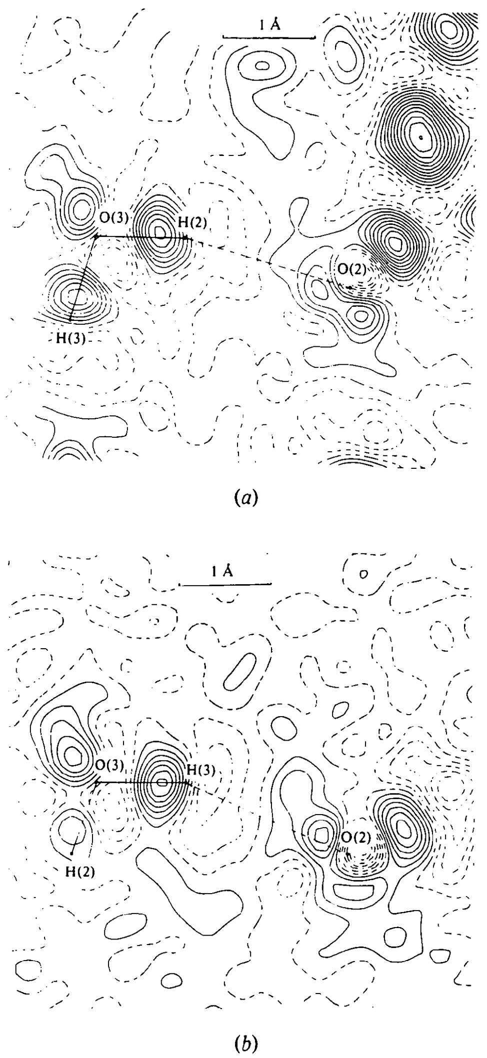

Fig. 8. Experimental difference electron density for the long hydrogen bonds (*a*) in the plane through O(3), H(2) and O(2), (*b*) in the plane through O(3), H(3) and O(2). Contours as in Fig. 4.

Coppens, 1980) there are no significant differences for the maximum bond densities. For the lone-pair densities we note a systematic difference. This is not surprising since these maxima are very close to the nuclei, a region where the deformation densities are very sensitive to the scale factor.

Nevertheless, there are slight differences on the qualitative level as well. For example, the elongation of the C—C bond perpendicular to the bond axis, Fig. 7(*a*), used as an argument for experimental evidence of appreciable π character in this bond, is here much less pronounced. The asymmetry of the O lone-pair density of the water molecule, Fig. 6, is more clearly observed in this study.

Table 4. *Equivalent isotropic thermal parameters* (Å^2 × 10^5) *of heavy atoms, defined according to Willis & Pryor* (1975)

	(*a*)	(*b*)	(*c*)	(*d*)
C(1)	870 (5)	947 (5)	956 (5)	1019 (6)
O(1)	1217 (5)	1309 (5)	1337 (5)	1393 (6)
O(2)	1219 (5)	1316 (5)	1333 (5)	1418 (6)
O(3)	1202 (5)	1307 (5)	1327 (5)	1392 (6)

(*a*) Feld (1980); neutron study.
(*b*) Koetzle & McMullan (1980); neutron study.
(*c*) This work: X-ray study, high order, no TDS correction applied.
(*d*) Stevens & Coppens (1980); X-ray study, high order.

Table 5. *Maximum bond and lone-pair densities* (e Å^{-3}) *for* (*a*) *this study and* (*b*) *Stevens* (1980)

	(*a*)	(*b*)
C—C	0·56	0·65 (3)
C—O(1)	0·37	0·38 (2)
C—O(2)	0·46	0·49 (2)
O(1)—H(1)	0·32	0·27 (4)
O(1) l.p.	0·32	0·42 (6)
O(2) l.p.1	0·27	0·50 (8)
O(2) l.p.2	0·22	0·38 (8)

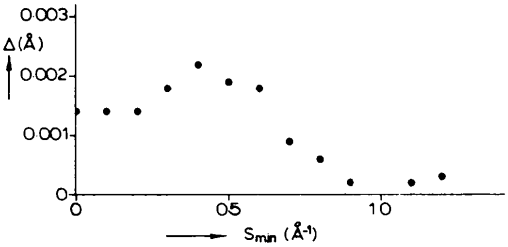

Fig. 9. The shift Δ (Å) *versus* the low-angle threshold value $S_{\rm min} = \sin\theta/\lambda$ (Å^{-1}). Δ is the distance between the positions of O(3) which result from refinements with indicated $S_{\rm min}$ value and the one using $S_{\rm min} = 1{\cdot}0$ Å^{-1}.

Similar distortions of lone-pair densities have been observed by van der Wal & Vos (1979). In a subsequent study van der Wal (1982) showed that small variations of positional parameters destroyed the observed lone-pair asymmetry. Therefore, the accuracy of that study was judged to be too low to answer the question whether or not quantum-chemical calculations on clusters of molecules, not showing any perturbation of lone-pair density, are adequate for a description of H bonding in crystals. In order to see whether small variations in positional parameters would destroy the observed asymmetry, this small effect was studied in further detail. Positional parameters may be biased by aspherical bonding features around the atoms and will depend on the refinement techniques used. The shift in the positions of O(3) which resulted from refinements with varying low-angle threshold value $S_{\rm min}$ ($S = \sin\theta/\lambda$) is shown in Fig. 9. We see that the maximum variation in the position of O(3) is about 0·002 Å occurring at an $S_{\rm min}$ value of 0·4 Å^{-1}. This shift is only moderate, probably as a consequence of the very large amount of high-order data and the rather symmetric overall bonding features around the O(3) atom. With O(3) in the shifted position the electron difference density in the O lone-pair region was calculated. The main differences with the original calculation are in the immediate neighbourhood of the nucleus of this atom. The asymmetry in the O lone-pair density remains in both maps. In the same way, no essential differences in the asymmetry were observed when the coordinates of the O(3) atom were taken from the neutron study of Koetzle & McMullan (1980).

The perturbation of the lone-pair density, which is observed clearly in the study of Stevens & Coppens (1980) and in this work, may therefore serve as a reliable experimental feature which, for example, may be used to judge the accuracy of theoretical electron density calculations of molecules in crystals.

5. Correction for thermal diffuse scattering

It is well known that, in particular for soft, molecular crystals, integrated intensities as derived from X-ray diffraction experiments may contain an appreciable contribution due to inelastic scattering by phonons (thermal diffuse scattering) which is not eliminated by the usual background subtraction. A calculation to correct for the total inelastic scattering would require a proper model for lattice vibrations and even in the case that this would be available, computing times would become excessive. Therefore, in practice, it is only feasible to calculate the first-order TDS, which is known to contribute most to the phonon scattering (Kroon & Vos, 1979). In order to estimate the effect of such a TDS correction upon structural parameters of α-oxalic acid dihydrate, calculations have been performed by means of the program *TDS*1 (Helmholdt & Vos, 1977). With this program first-order TDS contributions can be calculated in the long-wave approximation taking appropriate account of the elastic anisotropy of the crystal and assuming infinite resolution of the experiment.

For the calculation of the correction factor $\alpha_1 = I_{1,\rm TDS}/I_B$, with $I_{1,\rm TDS}$ the integrated intensity of the first-order TDS and I_B the Bragg intensity, the experimental conditions as described in § 3 were used. The orientation of the crystal with respect to the Cartesian axial system of the PW 1100 diffractometer (Philips, 1974) is given in Table 6. The elastic constants were taken from Gerlich & Haussühl (1975).

As stated in § 2 a total number of 46 994 reflexion profiles have been recorded. A proper account of the anisotropy of the TDS would require application of a correction factor to each of the reflexion intensities separately. In order to see whether excessive computing time could be avoided some preliminary calculations were performed by computing α_1 for several high-order reflexions for which a ψ rotation (rotation about the scattering vector) as performed in the experiment was simulated. For three reflexions the results are shown in Fig. 10. We see that variations in the correction factor α_1 are of the order of a few per cent. In view of the many approximations involved and the corresponding possible errors in the final α_1 values [see *e.g.* Scheringer (1973), Stevens (1974)] it was considered an acceptable procedure to apply the TDS correction to the averaged intensities.

Table 6. *The orientation matrix of the α-oxalic acid crystal*

The columns of the matrix contain the components of the reciprocal-lattice vectors **a***, **b*** and **c*** (in reciprocal-lattice units) with respect to the Cartesian axial system of the PW 1100 diffractometer.

0·02174	−0·03320	0·06060
−0·10345	0·09330	−0·00029
−0·05865	−0·17696	−0·01158

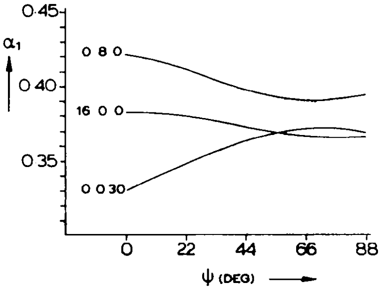

Fig. 10. Variation of the correction factor α_1 with rotation about the scattering vector ψ as performed in the experiment for the reflexions 080, 16,0,0 and 0,0,30.

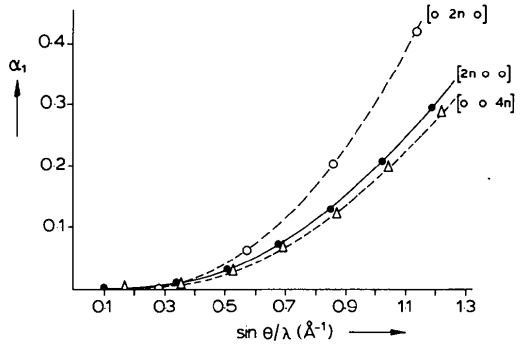

Fig. 11. Correction value α_1 for a series of reflexions $2n$,0,0. 0,$2n$,0 and 0,0,$4n$ with n starting at 1, *versus* sin θ/λ.

Large correction factors, up to 50% for intensities at high Bragg angles, were found. The anisotropic character of the α_1 factor is evident from Fig. 11.

The corrected structure factors were used in a spherical-atom refinement analogous to that in § 3. The results are shown in Table 7. Comparison with the values obtained with uncorrected data (Table 3), shows that, as expected, the positional parameters are insensitive to the correction, but large changes in temperature factors are observed, *i.e.* the increase of the U_{ii} is 12 ± 2%. The effect of an accompanying increase of the scale factor, in this case 0·7%, has been noticed before (Helmholdt & Vos, 1977).

Analogous to the procedure of § 3, the experimental deformation density was calculated by Fourier summation of the TDS-corrected data. The differences between the resulting map and the one shown in Fig. 4 (from data which were not corrected for TDS) occur only in the nuclear regions and are at most 0·05 e Å^{-3}. The values at the bonds are virtually the same. These observations are analogous to those of Helmholdt & Vos (1977) in a study of ammonium hydrogen oxalate hemihydrate whereas de With, Harkema & Feil (1976), in a study of pyrazine, observed differences of the order of 0·15 e Å^{-3} on the bonds and in the lone-pair regions.

Table 7. *Discrepancy indices, scale factors, fractional atomic coordinates* ($\times 10^5$), *thermal parameters* (Å^2 $\times$ 10^5) *resulting from high-order refinement and a subsequent full-angle refinement for the scale factor only, using TDS-corrected data*

R = 0·040; R_w = 0·026; N_o = 1479; sin θ/λ range 1·0–1·3 Å^{-1} (except for FA scale); goodness of fit 1·10; HO scale 16·57 (8); FA scale 16·69 (1).

	x	y	z
C(1)	−4496 (5)	5879 (11)	5195 (2)
O(1)	8501 (5)	−5604 (13)	15007 (2)
O(2)	−22121 (5)	24237 (12)	3629 (2)
O(3)	−45151 (5)	63088 (12)	17858 (2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
C(1)	1042 (7)	1234 (10)	859 (6)	169 (6)	−6 (6)	295 (4)
O(1)	1380 (8)	2030 (12)	840 (6)	502 (6)	72 (6)	267 (4)
O(2)	1279 (7)	1919 (11)	1032 (6)	582 (6)	68 (6)	397 (4)
O(3)	1283 (8)	1943 (11)	990 (6)	285 (6)	109 (6)	427 (4)

6. Conclusion

The positions of heavy atoms which were determined from this data set agree to within 0·002 (1) Å with the values as found from neutron diffraction, probably due to the large amount of significant high-order data. The positional parameters are hardly affected by a TDS correction.

The temperature factors which were found are not in concurrence with any of the published values which were considered here: those of the X-ray study of Stevens & Coppens (1980) and of the neutron studies of Feld (1980) and of Koetzle & McMullan (1980). A one-phonon TDS correction caused a large increase of 12% for the U_{ii}. It is therefore submitted that, in order to make a meaningful comparison between thermal parameters obtained by the several participants of the oxalic acid project possible, a TDS correction on the measured intensities is a prerequisite.

Despite differences in thermal parameters, the electron densities, as displayed by difference maps, agree very well on the qualitative level with the densities as published by Stevens & Coppens (1980). Quantitatively the densities on the bonds also agree; only the lone-pair peak heights disagree. This is not very surprising as the density in these regions close to the nuclei is very sensitive to slight variations in the scale factor. Application of TDS-corrected data for the calculation of difference electron density maps did not give significant deviations with respect to the maps which were obtained from data which were not corrected for one-phonon scattering.

The perturbation of the water O lone-pair density is clearly confirmed by this study. This experimentally determined feature may now well serve to judge the accuracy of theoretical electron density calculations of clusters in crystals.

We wish to thank Mr G. J. van Hummel for assistance during the measurements and calculations and Dr R. B. Helmholdt for supplying us with program *TDS*1.

Note added in proof: This paper is based on an analysis of one of the four X-ray and five neutron data sets measured for the IUCr Commission on Charge, Spin and Momentum Densities project on the comparison of structural parameters and electron density maps of oxalic acid dihydrate to be published in Section A of *Acta Cryst.* (Coppens *et al.*, 1984). It gives more detailed information on the conditions of data collection, the determination and treatment of experimental errors, the correction for thermal diffuse scattering and the discussion of the polarization of the water molecule than is in the Commission report.

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