Charge Density Studies Using CCD Detectors: Oxalic Acid at 100 K Revisited

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Abstract

The charge density of oxalic acid dihydrate has been redetermined from 100 K X-ray diffraction data using a SMART CCD diffractometer. The quality of the data has been carefully analyzed and shown to be at least as good as that obtained using a point detector. The positional and thermal parameters obtained from least-squares refinement and the main features of difference density maps are comparable with those obtained by a number of laboratories as part of the IUCr electron density project. In particular, the comparison study has been completed by two multipole refinements carried out in parallel using both the current data set and that of a previous study [Stevens & Coppens (1980). *Acta Cryst.* B**36**, 1864–1876].

1. Introduction

The advent of CCD detectors for X-ray diffraction experiments has produced a remarkable increase in the speed with which routine structures may be determined. Although the data are perfectly adequate for routine structure determination, it has not been demonstrated that the data quality is sufficient for charge density studies. In an attempt to answer this question, it was decided to remeasure oxalic acid dihydrate and compare the results with those obtained in the 'Project on Comparison of Structural Parameters and Electron Density Maps of Oxalic Acid Dihydrate' commissioned by the IUCr (Coppens, 1984), as well as with later studies on the same structure.

2. Experimental

A well faceted crystal of oxalic acid dihydrate of the dimensions $0.25 \times 0.23 \times 0.18$ mm was glued to the tip of a diamond-cleaved 0.1 mm thin-walled capillary and mounted on a Siemens SMART Platform diffractometer. The sample was cooled to 100.0 (1) K with an Oxford Cryosystems Cryostream cooling device. Preliminary examination and final data collection were carried out with graphite-monochromated Mo $K\alpha$ radiation. In order to avoid any contamination of the data with the $\lambda/2$ harmonic (Kirschbaum *et al.*, 1997), the generator was run at 35 kV and 50 mA. Intensity data were collected using $0.3°$ ω scans with a detector

distance of 3 cm. The maximum redundancy in the data was obtained using four φ settings – 0, 90, 180, 270° – for each detector position. Five detector positions were used, ensuring overlap of the data: $-35, -65, -95, -109$ and $-50°$ in 2θ. 60 s frames were measured for the three lowest-resolution detector positions and 120 s frames for the two high-resolution positions. For the first four detector positions, 600 frames were measured for each φ setting. For the final detector setting only 500 frames were measured.†

3. Data reduction

The unit cell [$a = 6.1024$ (1), $b = 3.4973$ (1), $c = 11.9586$ (2) Å, $\beta = 105.771$ (1)°] and orientation matrix were determined from the XYZ centroids of 8192 reflections with $I > 20\sigma(I)$ obtained from the frames of the first two detector positions (-35 and $-65°$). These two runs were integrated together (*SAINT*; Siemens, 1996). Subsequent runs were integrated separately, but with no further refinement of the orientation matrix. The intensities were first corrected for beam inhomogeneity and decay, and the e.s.d.'s adjusted using the program *SADABS* (Sheldrick, 1998). An absorption correction was then applied ($T_{\min} = 0.949$, $T_{\max} = 0.983$) and symmetry and multiply measured reflections averaged with the program *SORTAV* (Blessing, 1987). The absorption correction was applied with *SORTAV* (Blessing, 1987) rather than *SADABS* (Sheldrick, 1998) in order to obtain reasonable values for T_{bar} in the absence of known face indices and corresponding dimensions. A further revision of the e.s.d.'s was carried out *via* a bivariate analysis of the data with respect to $\sin\theta/\lambda$ and intensity.

A total of 46 067 reflections was measured [of which 29 753 had $I > 2\sigma(I)$] with only 154 reflections missing to $\sin\theta/\lambda = 1.34$ Å^{-1} ($-16 < h < 16, -8 < k < 8, -31 < l < 31$). 5166 reflections were unique, of which 2589 had been measured more than nine times (symmetry equivalents plus multiple measurements) and only 650 had been measured less than three times. After rejection

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† Lists of atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: FR0004). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Summary of least-squares refinements*

Hydrogen coordinates for (II), (III) and (IV) fixed at neutron positions with isotropic thermal parameters from (I).

Refinement	(I)	(II)	(III)	(IV)
Sin θ/λ range (Å^{-1})	0.00–1.20	1.00–1.34	0.00–1.34	0.00–1.20
N_{obs}	3860	2895	5166	3860
N_v	50	37	50	108
Scale factor	1.812 (2)	1.87 (2)	1.813 (4)	1.812 (4)
$R(F^2)$†	0.0540	0.1170	0.0457	0.0532
$wR(F^2)$†	0.0769	0.1630	0.0777	0.0299
$R(F)$ [$I > 2\sigma(I)$]	0.0281	0.0423	0.0282	0.0190
S	1.01	0.84	0.86	0.73

† All reflections.

of 2294 abnormal outliers (*e.g.* clipped reflections from the frame edges) and 5 statistical outliers, the merging R values were $R_1 = 0.032$ and $R_2 = 0.024$ for 4878 means.

4. Refinements

Starting coordinates were taken from Stevens & Coppens (1980), hereafter SC, and all refinements were carried out on F^2 using the *XD* (Koritsanszky *et al.*, 1995) suite of programs. Four different refinements were carried out using statistical weights throughout and the results are summarized in Table 1. Refinement (I) is a traditional independent atom refinement. Refinement (II) is a high-angle refinement ($1.00 < \sin \theta/\lambda < 1.34$ Å^{-1}) with the H atoms fixed at the neutron positions (values from Feld *et al.*, 1978) and isotropic thermal parameters fixed at the values obtained from refinement (I). Refinement (III) is a kappa refinement to assign atomic charges (Coppens *et al.*, 1979). The hydrogen positional and thermal parameters were fixed as in refinement (II). A complete atom-centered multipole refinement was carried out in (IV), where the nonspherical atomic electron density (Coppens, 1997) is given by

$$\rho_{at}(\mathbf{r}) = P_c \rho_{core}(r) + P_v \kappa^3 \rho_{valence}(\kappa r)$$
$$+ \sum_{l=1}^{l_{max}} \kappa'^3 R_l(\kappa' r) \sum_{m=0}^{l} P_{lm\pm} d_{lm\pm}(\theta, \varphi).$$

The H atoms were treated as in (II) with one atom-directed dipole and quadrupole population varied. All other atoms were refined as previously described (Stevens & Coppens, 1980) up to the hexadecapole level
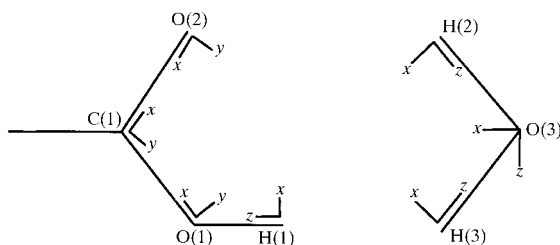
Fig. 1. Local coordinate system used to define multipoles.

with mirror symmetry imposed in the plane of the oxalic acid molecule and in the bisecting plane perpendicular to the plane of the water molecule. The local coordinate systems used to define the multipoles is shown in Fig. 1. Isotropic extinction was included in all four refinements, however, the value obtained from refinement (I) was held constant for the high-angle refinement. For purposes of comparison, particularly of the multipole refinements, an identical set of refinements was carried out using the SC data and the results compared. As the SC data only extend to $\sin \theta/\lambda = 1.2$ Å^{-1}, the current data were also limited to this resolution for refinement (IV).
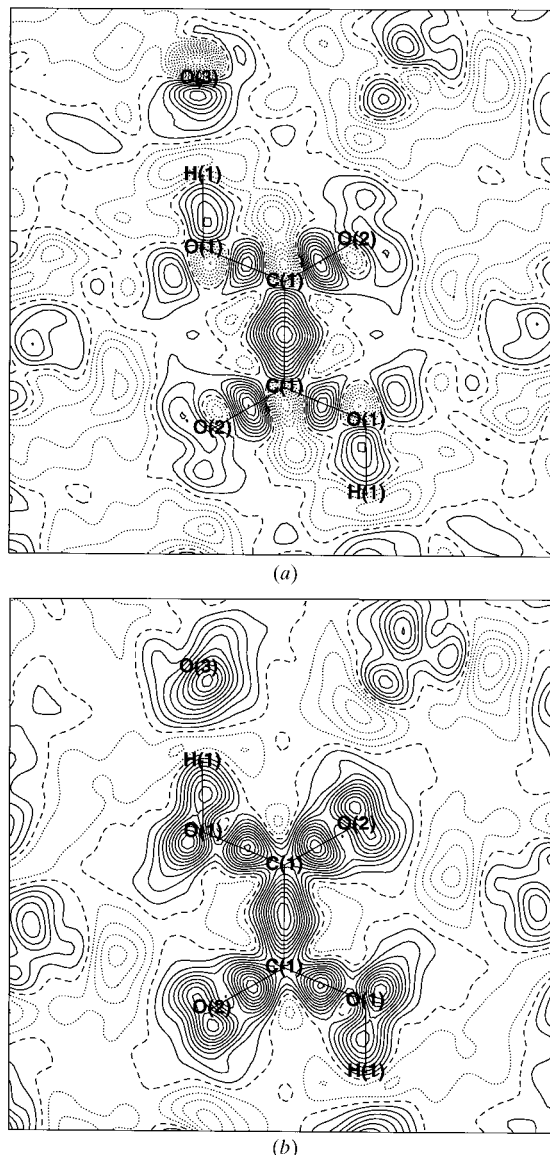
Fig. 2. Difference map after high-order refinement – data cut-off at $\sin \theta/\lambda = 0.9$ Å^{-1} for reflections with $F^2 > 2\sigma(F^2)$; (*a*) this work; (*b*) SC. Contour level: 0.05 e Å^{-3}.

Table 2. *Comparison of unit-cell parameters*

This work	IUCr study
$a = 6.1024\,(1)$ Å	$\bar{a} = 6.102\,(6)$ Å
$b = 3.4973\,(1)$ Å	$\bar{b} = 3.501\,(7)$ Å
$c = 11.9586\,(2)$ Å	$\bar{c} = 11.964\,(17)$ Å
$\beta = 105.771\,(1)\,^{\circ}$	$\bar{\beta} = 105.80\,(5)\,^{\circ}$

5. Charge density maps

Difference density maps in the molecular plane were computed (*XD*; Koritsanszky *et al.*, 1995) after the high-angle refinements. To make the comparison as meaningful as possible, a cut-off of $\sin\theta/\lambda = 1.2$ Å^{-1} was also imposed for the present data during this refinement. For the case of the SC data the scale factor was rerefined on all the data after the high-order refinement owing to the incompleteness of the high-order data, as previously discussed (Stevens & Coppens, 1980). Comparison maps with a $\sin\theta/\lambda$ cut-off of 0.9 Å^{-1} are presented in Fig. 2. In both cases only reflections with $F_o^2 > 2\sigma(F_o^2)$ were included in the summations.

Model deformation density maps after the multipole refinement were also computed for the same plane with the same cut-offs and are compared in Fig. 3. The coefficients for the summations are $(F_{\mathrm{mul}} - F_{\mathrm{iam}})$. In addition, in order to judge the completeness of the refinement and the quality of the data, the corresponding residual maps were computed after the multipole refinement (Fig. 4).

6. Discussion

Why choose to collect data at 100 K? In order to compare point-detector data with those obtained with a CCD it was important to choose a temperature for which there was already extensive data available. The most common temperature of the IUCr study (Coppens, 1984) was 100 K and this was also the temperature of the SC data which we have chosen for the most detailed comparison.

A comparison of unit-cell parameters is given in Table 2. All metric parameters fall well within the range previously quoted (Coppens, 1984).

Examination of the reflection statistics (Table 3) with respect to $F_o^2/\sigma(F_o^2)$ (Q) and $\sin\theta/\lambda$ (S), as obtained from *SORTAV* (Blessing, 1987), indicates the expected trends with respect to the merging R values *versus* Q or S, and suggests that the data should be adequate for a charge density study.

Positional parameters of the non-H atoms obtained from refinements (I) and (II) have been compared with those obtained from similar refinements by SC or Dam *et al.* (1984), hereafter DHF, from X-ray data as well as those obtained from neutron data (Koetzle & McMullan, unpublished). Refinement (I) agrees well with SC [average positional discrepancy 0.0010 (5) Å], less well with DHF [average positional discrepancy

0.0017 (3) Å] and, not surprisingly, poorly with the neutron data [average positional discrepancy 0.0018 (8) Å]. Better agreement was obtained from the high-order refinement (II), the corresponding average discrepancies being 0.0012 (9), 0.0012 (3) and 0.0007 (6) Å. The largest discrepancy in all cases is for O(3), which, in the worst case, is close to 0.002 Å.

Although the Hirschfeld (1976) rigid-bond test is obeyed in the current study (differences of mean-square displacement amplitudes along the bonds being ≤ 0.001 Å^2), there are some striking differences in the thermal displacement parameters compared with other

(*a*)
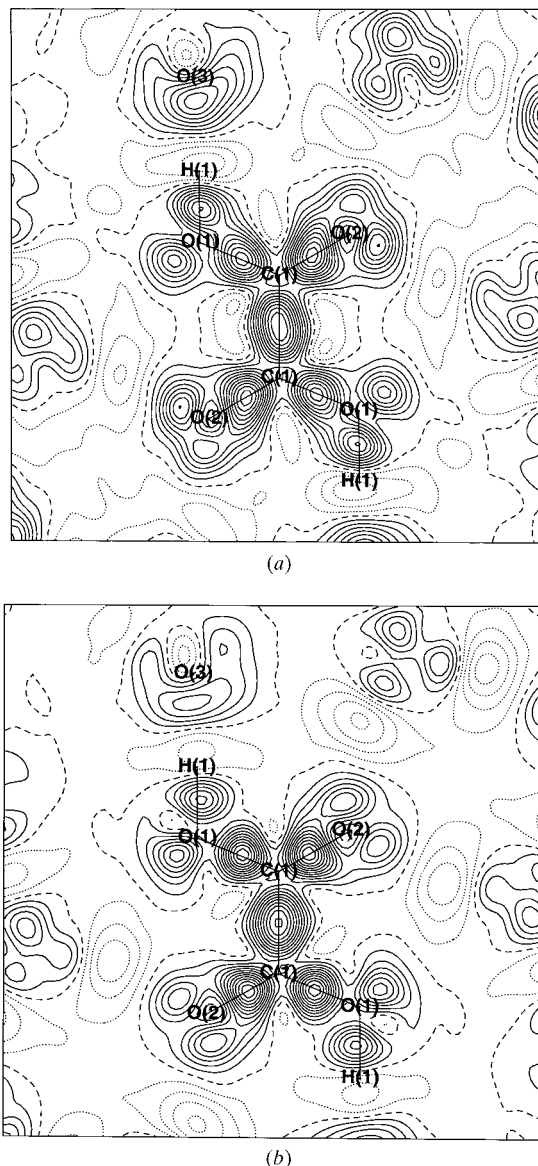

(*b*)

Fig. 3. Model map after multipole refinement: data cut-off at $\sin\theta/\lambda = 0.9$ Å^{-1} for reflections with $F^2 > 2\sigma(F^2)$; (*a*) this work; (*b*) SC. Contour level: 0.05 e Å^{-3}.

Table 3. *Reflection statistics with respect to (a) intensity and (b) resolution*

	R_1	R_2	wR	N_{terms}	N_{means}
(a)					
$Q < -2.0$	0.0527	0.0610	0.0758	8	4
$-2.0 < Q < -1.0$	0.4186	0.4591	0.4343	156	41
$-1.0 < Q < 0.0$	0.9073	0.9195	0.8695	3157	443
$0.0 < Q < 1.0$	0.8215	0.8215	0.8745	8342	1033
$1.0 < Q < 2.0$	0.3585	0.3668	0.4385	4621	566
$2.0 < Q < 3.0$	0.2105	0.2358	0.2622	3449	404
$3.0 < Q < 4.0$	0.1380	0.1622	0.1732	2522	292
$4.0 < Q < 6.0$	0.0963	0.1137	0.1194	4499	468
$6.0 < Q < 8.0$	0.0710	0.0856	0.0866	3551	333
$8.0 < Q < 10.0$	0.0543	0.0666	0.0656	2553	230
$10.0 < Q < 20.0$	0.0346	0.0417	0.0418	7804	634
$20.0 < Q < 50.0$	0.0219	0.0288	0.0252	5232	382
$50.0 < Q$	0.0144	0.0173	0.0161	547	48
(b)					
$S < 0.500$	0.0192	0.0235	0.0227	3891	313
$0.500 < S < 0.600$	0.0241	0.0245	0.0304	3262	214
$0.600 < S < 0.650$	0.0286	0.0265	0.0370	1900	129
$0.650 < S < 0.700$	0.0327	0.0295	0.0431	2126	155
$0.700 < S < 0.750$	0.0385	0.0345	0.0483	2790	181
$0.750 < S < 0.800$	0.0467	0.0391	0.0571	3343	207
$0.800 < S < 0.850$	0.0479	0.0378	0.0575	2998	213
$0.850 < S < 0.900$	0.0533	0.0423	0.0608	3682	270
$0.900 < S < 0.950$	0.0657	0.0502	0.0730	3872	289
$0.950 < S < 1.000$	0.0772	0.0577	0.0854	3343	298
$1.000 < S < 1.050$	0.1026	0.0750	0.1140	3418	352
$1.050 < S < 1.100$	0.1119	0.0778	0.1197	3169	386
$1.100 < S < 1.150$	0.1081	0.0823	0.1253	2296	388
$1.150 < S < 1.200$	0.1449	0.1041	0.1642	2393	451
$1.200 < S < 1.250$	0.1334	0.1054	0.1520	2347	480
$1.250 < S < 1.300$	0.1525	0.1165	0.1821	1253	396
$1.300 < S < 1.350$	0.1433	0.1139	0.1776	358	156

$Q = F_o^2/\sigma(F_o^2)$, $S = \sin\theta/\lambda$, $R_1 = \Sigma|Y - \bar{Y}|/\Sigma|Y|$, $R_2 = [\Sigma(Y - \bar{Y})^2/\Sigma Y^2]^{1/2}$, $wR = \{\Sigma w[(Y - \bar{Y})/\sigma(Y)]^2/\Sigma w[Y/\sigma(Y)]^2\}^{1/2}$, where $Y = F_o^2$.

components [1.037 (12)]. The values obtained from a second neutron study (Feld, 1980) reported for the same temperature differed by 15%, again suggesting a problem with temperature calibration across these experiments.

If, as has been suggested, the integrated intensities of the weak reflections are overestimated by the current integration algorithm (*SAINT*; Siemens, 1996) the displacement parameters would indeed be reduced. To examine this possibility, the ratio between F_o^2 for the current data and that of SC, appropriately scaled using
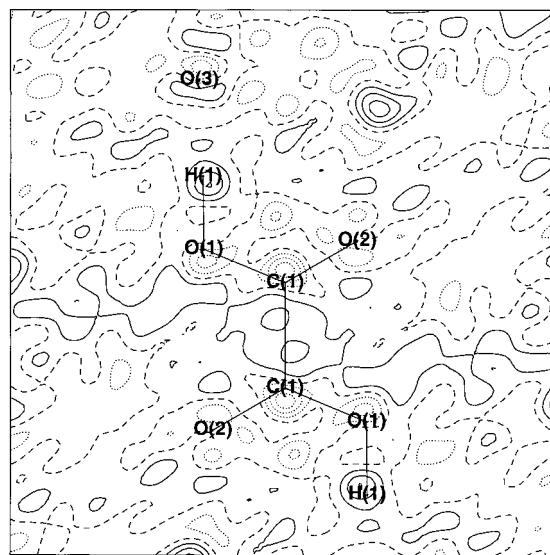
(a)

(b)

Fig. 4. Residual map after multipole refinement; data cut-off at $\sin\theta/\lambda = 0.9$ Å^{-1} for reflections with $F^2 > 2\sigma(F^2)$; (a) this work; (b) SC. Contour level: 0.05 e Å^{-3}.
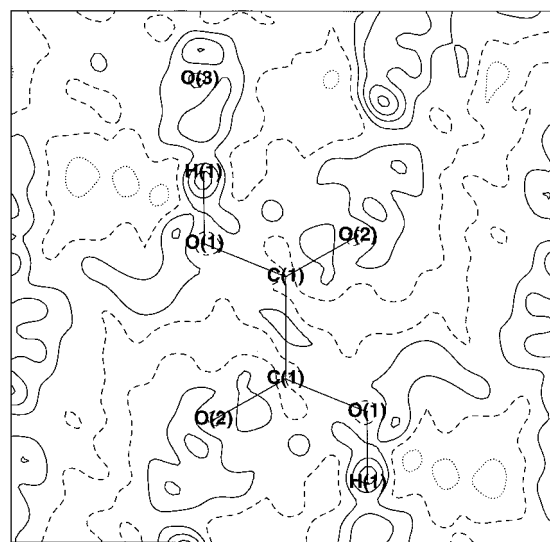
studies. The values fall in the same range as reported in the IUCr study (Coppens, 1984), however, all three refinements gave values that were systematically smaller than those obtained by SC. The mean of the ratios of the U^{ii} parameters for the two studies is 0.95 (3). In contrast, the values are quite similar to the values reported by DHF, the average ratio for the two comparable refinements (I) and (II) being 1.02 (2). It is tempting to suggest that the thermal parameters are too small owing to the presence of TDS contamination in the intensity data, as argued by DHF. However, no TDS correction was applied to the data in the SC study either. It is, of course, possible that the experimental temperatures were not identical, although all three experiments were calibrated in the same way (potassium dihydrogen phosphate, KDP, 122 K), or that there was a difference in crystal quality. At first sight, the agreement of thermal parameters from refinement (II) with those obtained from neutron data (Koetzle & McMullan, unpublished results) appears more satisfying, the average ratio being 1.01 (4). However, the ratio for U^{11} [0.965 (6)] is systematically smaller than for the two other principal

Table 4. *Comparison of the results of the kappa refinements*

	This work		SC	
	q	κ	q	κ
O(1)	−0.42 (3)	0.976 (3)	−0.18 (3)	0.986 (3)
O(2)	−0.51 (2)	0.972 (3)	−0.32 (3)	0.973 (3)
O(3)	−0.63 (3)	0.960 (3)	−0.44 (4)	0.968 (4)
C(1)	0.27 (3)	1.032 (5)	−0.06 (5)	0.990 (7)
H(1)	0.49 (2)	1.49 (6)	0.29 (3)	1.20 (3)
H(2)	0.41 (2)	1.34 (3)	0.35 (2)	1.22 (3)
H(3)	0.41 (2)	1.34 (3)	0.35 (2)	1.22 (3)

the scale factors from the final multipole refinements, has been calculated for all reflections common to the two data sets and the results are reported in Fig. 5. It can be seen that the agreement for the strong reflections is good, however, either the CCD detector has indeed overestimated the weak intensities or else they are underestimated by the scintillation counter.

The main purpose of this study was to examine the charge density and compare with previous studies. First the atomic charges were estimated from a kappa refinement. The results are given in Table 4 and compared with those obtained from the SC data. The most striking difference is the positive charge obtained for the C atom from the CCD data compared with a small negative charge obtained using the point-detector data. Indeed, in agreement with chemical intuition, a charge of +0.69 on C is predicted by *ab initio* calculations for the gas phase oxalic acid molecule (6-31G* basis set, *SPARTAN*; Wavefunction, Inc., 1995), hence, this observed difference is satisfying.

Difference density maps from the current data and the SC data are presented in Fig. 2. The maps were prepared after high-order refinements, as described above. It is clear that the main features of the maps are the same with respect to the bonding and lone-pair regions, however, there are much deeper negative regions close to the nuclear positions for the current data, particularly for the C atom. In contrast, a similar map reported by DHF also has negative regions of similar magnitude.

Comparison of the model maps (Fig. 3) again shows qualitative agreement. All regions agree to within one contour level (0.05 e Å^{-3}), except for the lone-pair regions for O(2) and O(3), which are significantly sharpened in the current study compared with those obtained with the SC data. We note that the differences in the data are real as parallel refinements were carried out using the original SC data and the current data, and identical maps prepared. Indeed, although the current data set extends to sin θ/λ = 1.34 Å^{-1}, it was truncated at 1.20 Å^{-1} in the refinement to make the comparison as meaningful as possible. However, in the present study all the data were available, whereas in the previous study, only data calculated to be observable was measured for sin θ/λ > 0.90 Å^{-1}.

Examination of the multipole populations gives no indication of this discrepancy observed in the model maps, most populations from the parallel refinements agreeing to within 2 e.s.d.'s (Table 5). The striking exception is the difference in the monopole populations (P_v). This must be a simple difference in the partitioning of the charge density between atom centers in the model as there is no discernible difference in the model maps
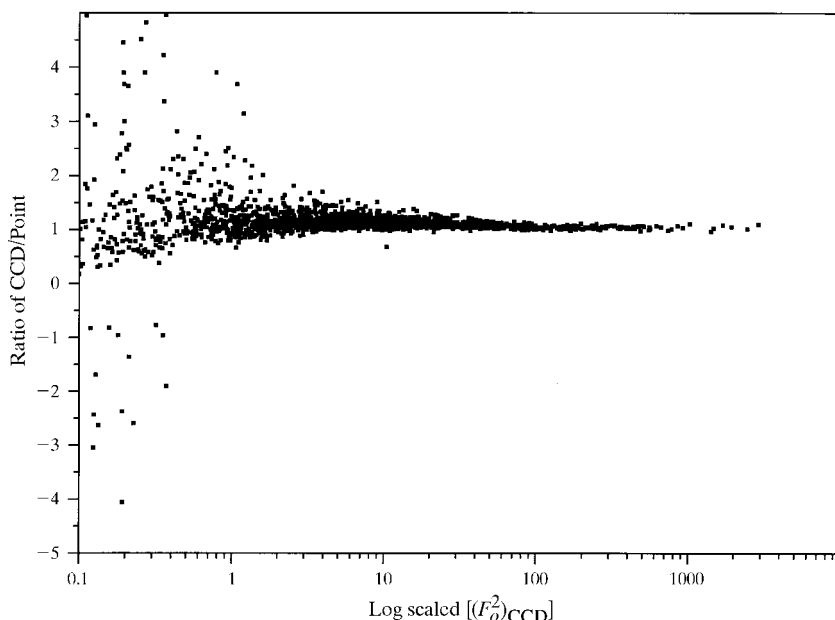

Fig. 5. Ratio between scaled F^2 for CCD and point-detector data with respect to log F^2.

Table 5. *Comparison of refined multipole parameters*

	C(1)		O(1)		O(2)		O(3)	
	This work	SC	This work	SC	This work	SC	This work	SC
κ'	0.981 (3)	0.974 (4)	0.974 (3)	0.987 (2)	1.000 (5)	0.978 (2)	1.014 (6)	0.999 (3)
P_v	3.87 (4)	4.31 (3)	6.22 (3)	6.06 (2)	6.47 (3)	6.27 (2)	5.83 (5)	5.77 (3)
P_{+11}	0.026 (14)	0.063 (8)	−0.015 (9)	−0.028 (4)	−0.051 (10)	−0.045 (6)	−0.100 (9)	−0.082 (5)
P_{-11}	−0.015 (11)	0.018 (6)	0.001 (7)	−0.055 (5)	0.010 (8)	0.010 (4)	−0.021 (8)	0.011 (5)
P_{20}	−0.264 (12)	−0.255 (7)	−0.032 (10)	−0.008 (6)	−0.078 (10)	−0.062 (7)	−0.015 (8)	−0.037 (5)
P_{+22}	0.072 (12)	0.069 (7)	−0.045 (9)	−0.040 (4)	−0.003 (9)	−0.039 (6)	−0.022 (8)	−0.016 (5)
P_{-22}	−0.044 (11)	−0.031 (6)	0.027 (9)	0.022 (5)	0.040 (8)	0.003 (5)	−0.013 (8)	−0.006 (5)
P_{+31}	0.031 (13)	0.017 (7)	0.012 (10)	0.019 (4)	−0.014 (10)	0.005 (5)	0.124 (8)	0.090 (4)
P_{-31}	0.009 (11)	−0.013 (6)	−0.028 (9)	−0.039 (4)	−0.015 (9)	−0.012 (4)	0.020 (8)	0.024 (4)
P_{+33}	0.287 (14)	0.301 (7)	0.079 (9)	0.076 (4)	0.057 (9)	0.034 (4)	0.013 (8)	−0.001 (4)
P_{-33}	0.030 (16)	0.067 (7)	0.012 (10)	−0.011 (4)	0.016 (8)	−0.007 (4)	0.006 (8)	−0.006 (4)
P_{40}	0.038 (16)	0.026 (8)	0.010 (13)	0.017 (6)	−0.001 (13)	0.006 (6)	−0.019 (11)	−0.002 (5)
P_{+42}	0.009 (17)	0.016 (8)	0.021 (12)	0.014 (5)	−0.003 (11)	−0.013 (5)	0.062 (10)	0.071 (5)
P_{-42}	−0.018 (17)	−0.010 (8)	0.007 (11)	−0.005 (6)	−0.010 (11)	−0.000 (5)	−0.001 (10)	0.018 (5)
P_{+44}	−0.061 (20)	−0.031 (9)	−0.001 (10)	0.028 (5)	−0.008 (10)	−0.007 (5)	−0.010 (10)	0.012 (5)
P_{-44}	−0.051 (15)	−0.007 (8)	0.032 (10)	0.029 (4)	0.010 (10)	−0.002 (4)	−0.003 (10)	−0.009 (5)

	H(1)		H(2)		H(3)	
	This work	SC	This work	SC	This work	SC
κ	1.00	1.00	1.00	1.00	1.00	1.00
P_v	0.75 (2)	0.87 (1)	0.93 (2)	0.86 (1)	0.93 (2)	0.86 (1)
P_{10}	0.197 (21)	0.253 (12)	0.392 (20)	0.384 (11)	0.392 (20)	0.384 (11)
P_{20}	0.330 (31)	0.330 (20)	0.275 (22)	0.243 (13)	0.275 (22)	0.243 (13)

H(3) populations are constrained equal to H(2).

around the carbon position, however, it is also in accordance with the result obtained from the kappa refinement. We note that the e.s.d.'s of the multipole parameters (Table 5) for the CCD study are approximately twice those from the SC data. This implies that the SC data are of superior quality, however, the e.s.d.'s from the CCD data are still as good as those typically reported for similar studies.

The residual maps (Fig. 4) both show similar inadequacies in the model for the H atoms. The most striking difference between the CCD and SC data is the deeper negative regions close to the nuclear positions obtained with the CCD data. Elsewhere, the noise levels are of similar magnitude, but more randomly distributed from the CCD study.

7. Conclusions

Clearly the data obtained are adequate for a charge density analysis. It is also possible that the weak data, contrary to popular wisdom, are actually better than those from point detectors (Fig. 5). Following informal discussions at the 1997 ACA meeting† it seems possible that even better data will be obtained using narrower frames (*e.g.* 0.1°). From our own observations (Kirschbaum *et al.*, 1997) it is not necessary to eliminate the λ/2

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† Contributors to the discussion were the authors, Drs W. Clegg, P. Coppens, C. S. Frampton, T. Koritsanszky, F. K. Larsen, P. M. Mallinson, M. R. Pressprich and E. D. Stevens.

contamination by reducing the generator voltage as was performed in the present study. However, although the effect on routine structure refinement has been shown to be negligible, the effect of applying the small correction to the intensity data has yet to be determined for charge density studies.

References

Blessing, R. H. (1987). *Cryst. Rev.* **1**, 3–57.
Coppens, P. (1984). *Acta Cryst.* A**40**, 184–195.
Coppens, P. (1997). *X-ray Charge Densities and Chemical Bonding.* Oxford University Press.
Coppens, P., Guru Row, T. N., Leung, P., Stevens, E. D., Becker, P. J. & Yang, Y. W. (1979). *Acta Cryst.* A**35**, 63–72.
Dam, J., Harkema, S. & Feil, D. (1984). *Acta Cryst.* B**39**, 760–768.
Feld, R. H. (1980). Ph.D. thesis. Philipps Universität Marburg/Lahn.
Feld, R. H., Brown, P. J. & Lehmann, M. S. (1978). *Acta Cryst.* A**34**, S28.

Hirschfeld, F. L. (1976). *Acta Cryst.* A**32**, 239–244.

Kirschbaum, K., Martin, A. & Pinkerton, A. A. (1997). *J. Appl. Cryst.* **30**, 514–516.

Koetzle, T. F. & McMullan, R. Unpublished results.

Koritsanszky, T., Howard, S., Mallison, P. R., Su, Z., Richter, T. & Hansen, N. K. (1995). *XD. A Computer Program Package for Multipole Refinement and Analysis of Electron Densities from Diffraction Data. User's Manual*. University of Berlin, Germany

Sheldrick, G. M. (1998). *SADABS*. University of Göttingen, Germany. To be published.

Siemens (1996). *SAINT. Program to Integrate and Reduce Raw Crystallographic Area Detector Data*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Stevens, E. D. & Coppens, P. (1980). *Acta Cryst.* B**36**, 1864–1876.

Wavefunction, Inc. (1995). *SPARTAN*4.0. Wavefunction, Inc., Irvine, California, USA.