New Opportunities for Charge Density Studies Using the FAST Area Detector *

Christian W. Lehmann, Alexander Karaulov, and Michael B. Hursthouse
School of Chemistry and Applied Chemistry, University of Wales, Cardiff, U.K.

Z. Naturforsch. **48a**, 63–67 (1993); received April 29, 1992

The requirements for charge density studies of more complex molecules have been realized by use of the FAST area-detector diffractometer in conjunction with a rotating-anode generator, which allows to collect large quantities of diffraction data within less than two days, independent of unit cell size. Oxalic acid dihydrate has been chosen for test experiments. Data collection strategies are described and preliminary results are presented. These show that data of sufficiently high quality for charge density studies can be collected.

Key words: Charge and deformation density; Area detectors; Oxalic acid dihydrate.

Introduction

The determination of the exact charge density distribution in the crystal is mostly dependent on the model describing the structure factor F. With the introduction of multipole models considerable progress towards this aim has been made.

As is widely accepted, the method therefore offers a potential to determine molecular properties beyond the level of atom connectivity and geometrical parameters. Like any crystallographic least-squares method, multipole models [1–3] depend upon the overdetermination of data against variable parameters. Experimentally it is not always easy to meet this requirement. Mainly the available time to collect the diffraction data, expressed in seconds per reflection, determines the accuracy of the data available for the refinement and also puts a limit to the size of unit cells one can investigate on a reasonable time scale. Therefore many potential molecules for charge density studies had to be discarded because of their size.

In order to overcome this restriction, ways must be sought to increase the rate of data collection. This can be achieved in a number of different ways.

Reducing the time spent measuring each reflection by increasing the intensity is one possibility, which requires either more powerful X-ray tubes (so far not readily available) or a rotating-anode generator. With approximately ten times higher photon flux per area this can reduce the measuring time considerably. In the past this has not been followed to a great extent, probably because this type of X-ray source was known to have frequent operating problems. However, the situation has much improved now.

Even faster data collection is possible by detecting more than one reflection at a time. Therefore an area-sensitive detector is required, covering as much of the Ewald-sphere as possible as reflections are passing through its surface.

This type of device has only recently become available for small-molecule work, where a number of special requirements have to be met. The classical area detector, the X-ray film, is unsuitable owing to its limited dynamic range. For the type of data measurement required for charge density studies, a system with excellent quantum efficiency for wavelengths smaller than 1.0 Å, a good dynamic range and the option to resolve the diffracted spots in three dimensions are necessary.

We decided to follow both options, combining a rotating-anode generator and a FAST area detector, which we believe to be competitive with established sequential diffractometers and scintillation counters in terms of accuracy. The experimental set-up and some first results are presented here.

It should be stressed that this experimental set-up has been in operation successfully for routine room-temperature-data collection for more than a year, yielding R-values down to 2–3% [4].

* Presented at the Sagamore X Conference on Charge, Spin, and Momentum Densities, Konstanz, Fed. Rep. of Germany, September 1–7, 1991.

Reprint requests to Dr. C. W. Lehmann, School of Chemistry and Applied Chemistry, College of Cardiff, POBOX 912, Cardiff CF1 3TB, U.K.

0932-0784 / 93 / 0100-0063 $ 01.30/0. – Please order a reprint rather than making your own copy.

Experimental Set-up

In our experiments the X-ray source is a Delft-Instruments (Enraf-Nonius) rotating-anode generator FR571 equipped with a Mo-target. Monochromatised radiation (graphite-monochromator) is generated at 2.5 kW and a focal spot size of 300 μm. This corresponds to a photon flux ten times higher compared to a sealed tube operated at the same power.

The FAST area detector (Fig. 1) consists of a phosphor of the chemical composition Gd_2O_2S:Tb converting X-rays into visible light, which is subsequently detected by a TV-camera. In order to enhance the observed light intensity an image intensifier is used, which determines the quality of the data to a great extent [5].

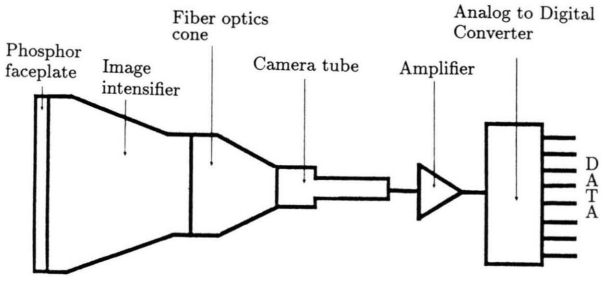

Fig. 1. Principal elements of the FAST detector (reproduced with permission from FAST Users Manual).

The analog signal from the camera after amplification is converted to an 8 bit signal, which is stored in a 512 × 512 pixel array (18 bit deep), the so-called mass store. This stores the diffraction pattern of a predefined angular range (e.g. 0.15°), the frame, which is then processed.

The detector is arranged in such a way (Fig. 2) that the input screen area at a crystal-to-detector distance of 40 mm covers an angular range in 2Θ of 56°. The detector is mounted on rails to vary that distance and hence the resolution. The rails can rotate around the centre of the diffractometer (conventional 2Θ-axis) to measure at different swing angles.

In order to collect data up to a resolution of $\sin\Theta/\lambda = 1.0\,\text{Å}^{-1}$, two settings of the detector are sufficient, normally chosen at $2\Theta = -25°$ and $2\Theta = -65°$.

The crystal is currently moved with a $\varkappa$-axis goniometer allowing orientation and rotation of the crystal around any particular axis. During data collection the crystal is positioned at a constant angle of $\varkappa = 0°$ and is rotated around ω with an ω-range of typically 200°.

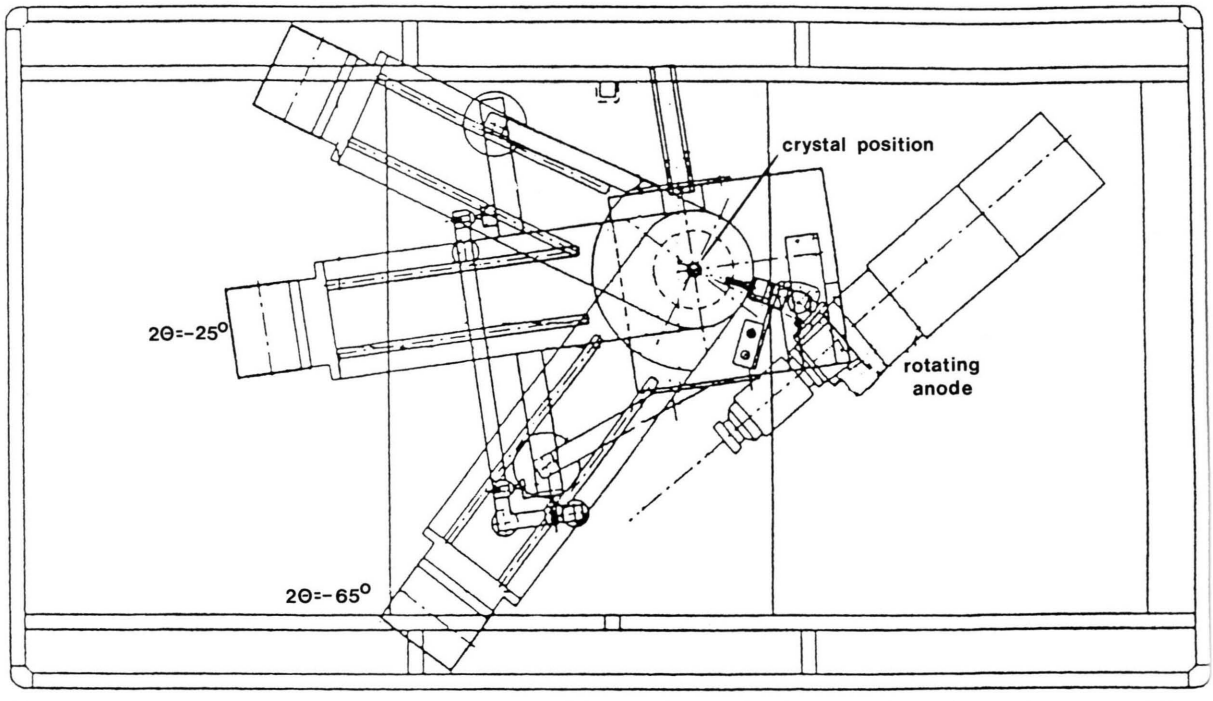

Fig. 2. Experimental set-up of the FAST-system on top of the rotating anode. The two swing angles used are shown (after [5], page 3).

In order to get the required proportion of the reflections within the limiting sphere into the diffracting position (including the cusp area of rotation around one axis), the crystal is subsequently rotated to $\varkappa = 134°$ ($\chi = 90°$) and also given different positions around the ϕ mounting axis followed by two ω-scans of 70° each [6]. Figure 3 is a precession-photo-type representation of measured diffraction spots of the test sample oxalic acid dihydrate, prior to merging.

With this method a complete hemisphere of data has been measured including many multiple observations (Table 1) with a total of 41 hours beam-time exposure. This measuring time is only dependent on the angular rotation speed, and will be the same for any data set independent of the unit cell size.

The raw data, obtained as counts per pixel, must subsequently be converted into integrated reflection intensities. Methods for this task are well described in the literature [7, 8]. They are based upon fitting an

Sample	Oxal1	Oxal2
T/K	100	291
Measured refl.	9031	7194
Unique refl.	2563	1952
Reference refl.	yes	no
Merging		
R-factor	2.5%	4.7%
Final multipole		
R-factor	3.4%	4.4%
wR-factor	3.3%	5.9%

Table 1. Experimental results for oxalic acid dihydrate ($C_2H_2O_4 \cdot 2H_2O$), oxal1 low-temperature CAD-4 measurement, oxal2 room-temperature FAST measurement.

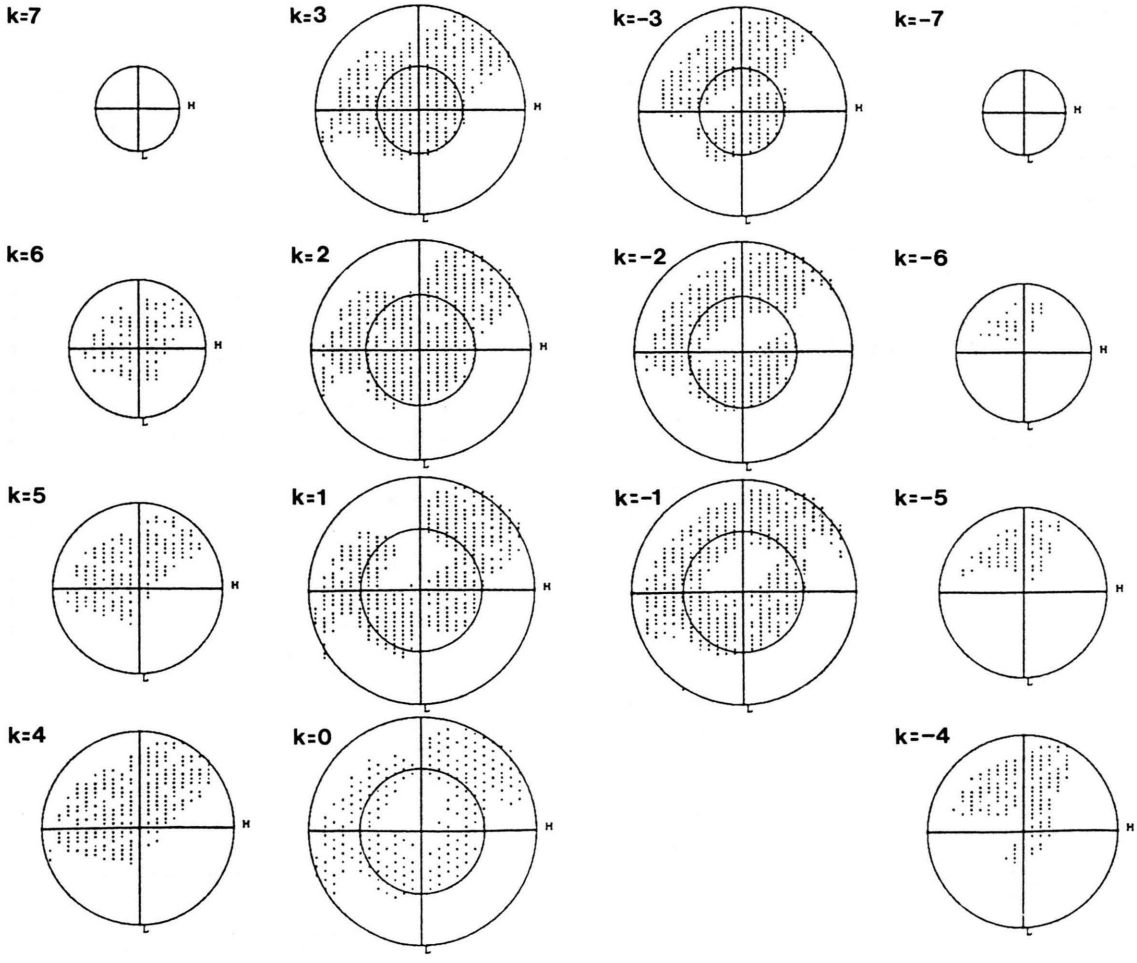

Fig. 3. Precession-type representation of the limiting sphere covered by measurement (unmerged). The inner circle of each layer (k from 7 to −7) represents 25° resolution in Θ, the outer circle 50°, respectively.

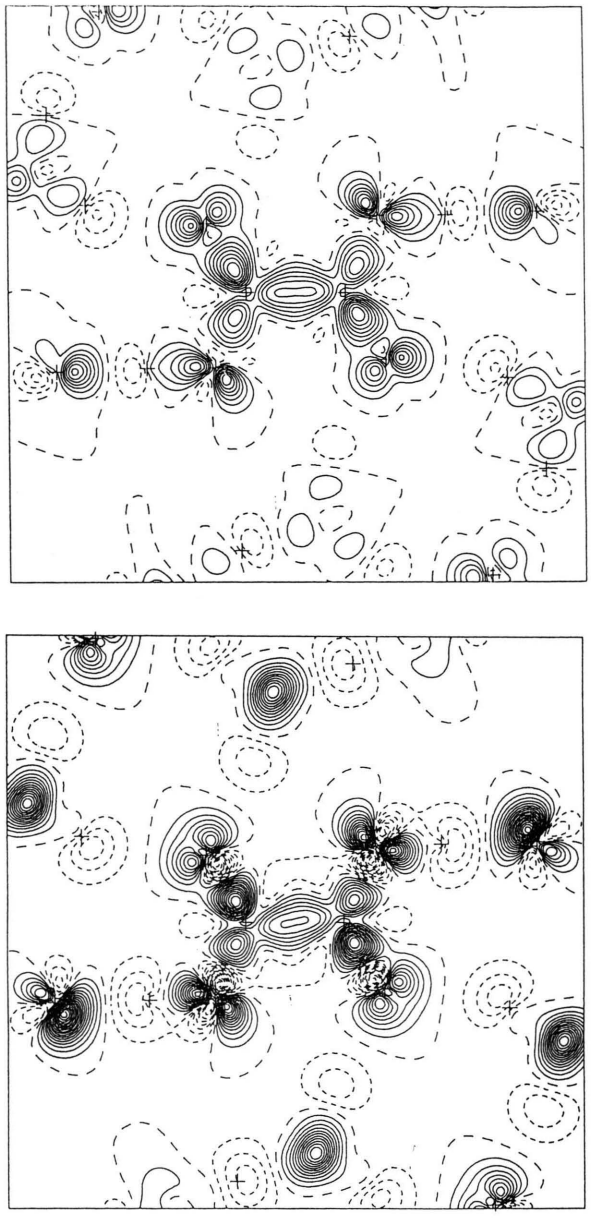

Fig. 4. Static deformation density maps of oxalic acid. Top 100 K CAD-4, bottom RT FAST. Layers at 0.1 $Å^{-3}$ intervals, solid contours positive, dashed contours zero (long) and negative (short). Atomic positions marked by +.

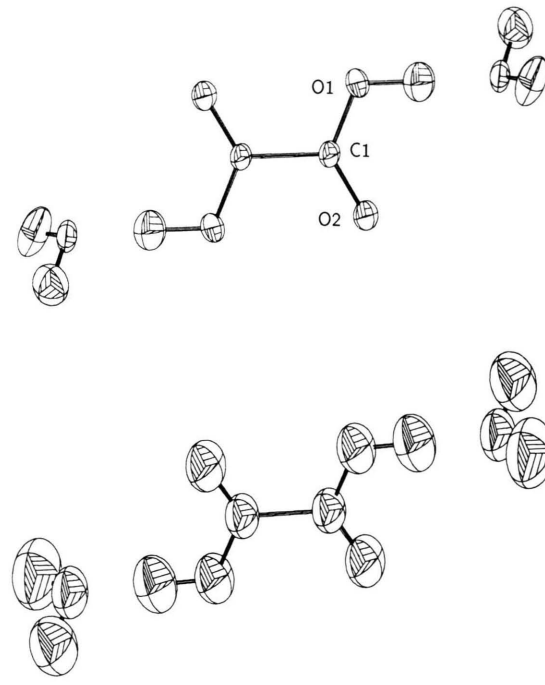

Fig. 5. ORTEP-plot [14] of oxal1 (top) and oxal2 (bottom) with displacement parameters from [12] and [13]. Ellipsoids are drawn at 80% probability.

ellipsoid of variable size and shape at a precalculated position with the measured pixel intensities.

Currently the small-molecules-version of MADNES [9] is used for this purpose. In principle there are two modes of operation possible. One is to obtain integrated intensities online, which means the images containing the pixel information are evaluated as the measurement proceeds. The other method stores all images (frames) on disk and the intensity evaluation becomes independent of the measurement. With this method, a data set accumulates to more than one gigabyte of disk space. Its usage is therefore limited.

The resulting integrated intensities together with their hkl-values can then be treated as usual. (To achieve reduction of atomic thermal motion, as required for charge density studies, an Oxford Cryostream Cooler has been fitted and is operational at the time of print.)

Test Experiments

For testing the quality of the set-up, oxalic acid dihydrate was chosen, since it has served as a standard in an IUCr-project on charge density [10]. As an in-house reference, a high-resolution data set was collected at low temperature on a conventional sealed-tube CAD-4 (oxal1). The room-temperature data set (oxal2) is the first successful high-resolution data col-

lection using the FAST system. Table 1 summarises the most important experimental parameters.

The multipole refinements for oxal1 and oxal2 are based on the POP-program [11]. Neutron coordinates for all atoms and anisotropic displacement factors for the hydrogen atoms reported in the literature were used for oxal1 [12], oxal2 [13]. During the multipole refinement all atomic coordinates were fixed to positions obtained from the neutron experiment. In order to avoid scaling problems, arising from the differences between the anisotropic displacement factors of the neutron and the X-ray experiment, the displacement factors of carbon and oxygen atoms were allowed to refine freely. The monopole and multipole functions were included subsequently in the refinement.

The obtained results are graphically presented in the form of static deformation maps (Fig. 4).

Conclusion

The most important result obtained from our work so far is, as we believe, the proven ability of the machine to collect data with sufficient accuracy for charge density studies. The main potential is to obtain large data sets almost independently of time. Since the results presented here belong to rather preliminary studies, it is not appropriate to discuss features of the electron density mapping in great details. However, main features of the low-temperature study are reproduced in the maps generated from the FAST data set. The higher temperature does obviously affect the density around the atomic positions. However, the strong hydrogen bonding features of oxalic acid dihydrate reduce the amplitude of room-temperature vibrations, which in terms of direction compare well between the two data sets (Figure 5). The differences in the density around the hydrate water molecules is due to the definition of the plane being plotted. In both cases the vectors C(1)–O(1) and C(1)–O(2) define the plane, whereas the water molecules adopt slightly different positions owing to the change in temperature.

The near future will see better data-collection strategies at low temperature with major long-term developments concerning the evaluation of integrated intensities going on.

[1] M. A. Spackman and R. F. Stewart, Methods and Applications in Crystallographic Computing (S. R. Hall, T. Ashida, eds.), Oxford 1984.
[2] N. K. Hansen and P. Coppens, Acta Cryst. **A 34,** 909 (1978).
[3] F. L. Hirshfeld, Acta Cryst. **B 27,** 789 (1971).
[4] Work carried out by the UK-SERC crystallography service, to be published.
[5] C. Kiers, in: Proceedings of the Sixth FAST User's Meeting, Grenoble, France (Bram Schierbeek, ed.), 13 (1990).
[6] N. H. Xuong, C. Nielsen, R. Hamlin, and D. Anderson, J. Appl. Cryst. **18,** 342 (1985).
[7] L. Sjölin and A. Wlodawer, Acta Cryst. A **37,** 594 (1981).
[8] R. F. D. Stansfield and G. J. McIntyre, "Online Evaluation of Position-Sensitive Detector (PSD) Diffraction Data", Proceedings of a Conference on Neutron Scattering in the Nineties, IAEA, Vienna (1985).
[9] J. Pflugrath and A. Messerschmidt, Munich Area Detector NE System, Version 11. Sept. 1989 (1989).
[10] P. Coppens, J. Dam, S. Harkema, D. Feil, R. Feld, M. S. Lehmann, R. Goddard, C. Krüger, E. Hellner, H. Johansen, F. K. Larsen, T. F. Koetzle, R. K. McMullan, E. N. Maslen, and E. D. Stevens, Acta Cryst. **A 40,** 184 (1984).
[11] B. M. Craven and H.-P. Weber, X. He, POP-Procedure TR-87-2., Dept. of Crystallography, University of Pittsburgh, USA (1987).
[12] R. H. Feld, Dissertation, Philipps-Universität, Marburg (Lahn) 1980.
[13] P. Coppens and T. M. Sabine, Acta Cryst. **B 25,** 2442 (1969).
[14] C. K. Johnson, ORTEP Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, USA (1976).