SHORT COMMUNICATIONS

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Towards extinction-free experimental diffraction data on Al_2O_3

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Abstract

Using 58 keV (0.214 Å) synchrotron radiation we have obtained virtually extinction-free data on Al_2O_3. Refinement of a multipole model against these data produced deformation densities of high quality, which compare well with theoretical maps.

1. Introduction

It is presently well known and accepted that synchrotron radiation offers basic advantages in the experimental determination of electron density distributions [EDD (Graafsma *et al.*, 1997; Bolotovsky *et al.*, 1995)]. However, it was not until the development of two-dimensional detectors, such as imaging plates and CCD-based (charge-coupled device) systems, that experimental EDD determinations became feasible on a larger scale at synchrotron sources. The two-dimensional detectors have not only considerably reduced the data collection time, but also improved the data quality, since the method is intrinsically less sensitive to beam fluctuations in space and time.

In this study we have collected datasets for Al_2O_3 at multiple wavelengths in order to obtain extinction-free data by extrapolation to zero wavelength (Palmer & Jauch, 1995; Hester & Okamura, 1996). The various data sets are still being analyzed and we present here the results obtained at the highest energy of 58 keV, which proved to be of excellent quality and virtually extinction-free.

2. Data collection

The measurements were performed using the materials science beamline at the European Synchrotron Radiation Facility, which is situated at a wiggler insertion device (Kvick & Wulff, 1992). The beam was monochromated by a double-crystal Si(111) monochromator, with the first crystal cryogenically cooled by liquid nitrogen. Harmonic rejection and beam steering were performed by two X-ray mirrors, one preceding and the other following the monochromator. The beam was unfocused and defined by a slit system to be 0.25 × 0.25 mm^2 and its intensity was monitored by a Si photodiode in transmission. A feedback system on the second monochromator crystal ensured a constant incident beam intensity on the Si photodiode. The sample, a 125 μm diameter ruby sphere, was cooled to 120 K by a nitrogen cryostream cooler (Oxford Cryosystems Cryostream).

Two data sets were collected at 58 keV with a Siemens 1K × 1K Smart detector with 0.03° rotation per frame and exposure times 1.2 and 5 s, respectively. Both data sets contained two settings of φ, 90° apart and covered 90° in ω, ensuring a completeness of almost 100% and a redundancy bigger than 12. The crystal-to-detector distance was 4.5 cm. The integration was performed online with the Siemens *SAINT* program.

3. Data reduction analysis

The 5223 integrated reflections have been merged using *SORTAV* (Blessing, 1987), yielding 432 unique structure-factor amplitudes (in the $\sin\theta/\lambda$ range 0–1.25 $Å^{-1}$). Only 12 F's showed $I < 3\sigma(I)$. The internal agreement factors as well as the number of multiple measurements as a function of $\sin\theta/\lambda$ are given in Table 1. It is interesting to note that, contrary to measurements at conventional sources, the internal agreement factor is practically constant as a function of $\sin\theta/\lambda$, which is a result of the high flux of the synchrotron beamline used.

4. Refinement

In order to describe the electron density of Al_2O_3, the following strategy was used: first a conventional *xyz* U^{ij} refinement was performed on all 462 structure-factor amplitudes in order to check the quality of the data and to estimate isotropic extinction using the Becker–Coppens formalism. Whatever the model, the extinction parameter always refined to zero within estimated standard error. The agreement factors are given in Table 2. A high-order refinement ($\sin\theta/\lambda > 0.9$ $Å^{-1}$) was perfomed. Convergence was obtained after 3 cycles, yielding excellent agreement indices (Table 2). The *xyz* U^{ij}'s were fixed at high-order values for the multipolar refinement (Hansen & Coppens, 1978; program *MOLLY*). P_v, κ, then P_{lm}, κ' and in the final step all scale, positional, thermal and electron density parameters were refined together, yielding an R factor of 0.0135 (Table 2). During this refinement, no extinction correction was deemed necessary. At the end of the refinement, 7 reflections with $\sin\theta/\lambda < 1$ $Å^{-1}$ had $(||F_o| - |F_c||/\sigma)$ greater than 3.

5. Discussion

Fig. 1 gives the experimental deformation density map calculated in the O1—Al—O2 plane

$$\Delta\rho = V^{-1}\sum_{\mathbf{H}}[|F_o|e^{i\varphi_m} - |F_c|e^{i\varphi_c}]e^{-2\pi i\mathbf{H}.\mathbf{r}},$$

Table 1. *Internal agreement and statistics on multiple reflections*

	$R_1(I)$	$wR(I)$	N_{terms}	N_{means}
$s < 0.461$	0.0580	0.0661	211	25
$0.461 < s < 0.581$	0.0494	0.0710	251	20
$0.581 < s < 0.665$	0.0442	0.0599	260	26
$0.665 < s < 0.732$	0.0586	0.0735	340	24
$0.732 < s < 0.788$	0.0523	0.0690	265	21
$0.788 < s < 0.838$	0.0577	0.0693	307	22
$0.838 < s < 0.882$	0.0487	0.0716	307	24
$0.882 < s < 0.922$	0.0531	0.0745	353	25
$0.922 < s < 0.959$	0.0523	0.0672	302	21
$0.959 < s < 0.993$	0.0605	0.0921	284	22
$0.993 < s < 1.025$	0.0556	0.0856	279	23
$1.025 < s < 1.056$	0.0607	0.0822	352	26
$1.056 < s < 1.084$	0.0606	0.0781	321	23
$1.084 < s < 1.111$	0.0583	0.0794	261	23
$1.111 < s < 1.137$	0.0637	0.0873	255	23
$1.137 < s < 1.162$	0.0542	0.0723	185	17
$1.162 < s < 1.186$	0.0665	0.0756	252	27
$1.186 < s < 1.208$	0.0624	0.0763	192	27
$1.208 < s < 1.230$	0.0663	0.0736	142	23
$1.230 < s < 1.252$	0.0708	0.0725	102	18

where φ_m refers to the phase of the best multipolar model and the index c refers to the spherical atom model. Fig. 1 was calculated on all data with $\sin\theta/\lambda < 0.9$ Å^{-1} revealing very well the bonding in the system, the longest Al—O1 (1.966 Å) bond being less populated than Al—O2 (1.849 Å). Also, the nonbonding density around oxygen is clearly seen.

Fig. 2 gives the static deformation density map calculated from our actual multipolar model in the same orientation as Fig. 1. This map compares well the experimental Ag $K\alpha$ maps of Lewis *et al.* (1982) and the theoretical results obtained by Blaha & Schwarz (1996) with the *Wien*95 *DFT* program, and by Rerat and coworkers (Rerat & Lichanot, 1996) from periodic HF (Hartree–Fock) calculations. However, one has to keep in mind that a free atom model led to $R(F) = 0.0161$ with a goodness-of-fit of 1.58 compared with values of 0.0135 and 0.0137, respectively, for the best multipolar model. This is mainly due to the fact that the Al valence scattering factors are nonzero only for data with $\sin\theta/\lambda < 0.4$ Å^{-1}, *i.e.* 35 reflections only. The multipole analysis is also possibly not the best model to recover all the valence density, but, as the quality of this high-energy data set from Al_2O_3 is excellent, we now have the opportunity to test more appropriate electron density models for simple systems.

In conclusion, these high-energy data show without ambiguity that we have now reached the necessary experimental accuracy to be able to test HF or LDF theory on periodic simple systems. This is currently under investigation and will be published in the future.

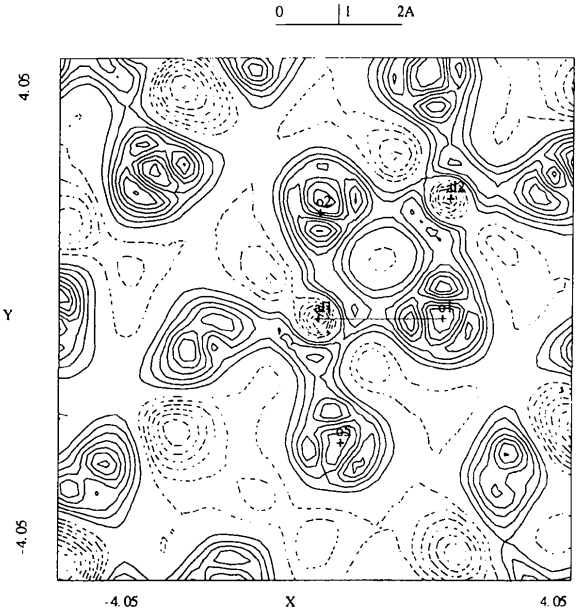

Fig. 1. Experimental dynamic deformation electron density map in the O1—Al—O2 plane; contours 0.05 e Å^{-3}, dashed lines negative, no zero contours.

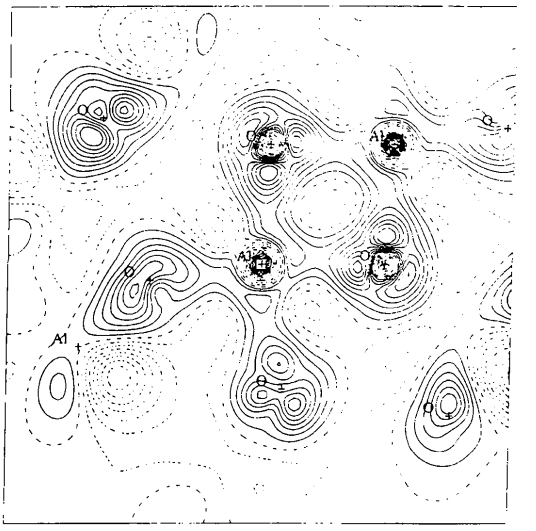

Fig. 2. Model static deformation electron density map in the O1—Al—O2 plane; contours as in Fig. 1.

Table 2. *LS refinement results*

Sinθ/λ cut off (Å^{-1})	Type of refinement	$R(F)$	$wR(F)$	GOF	N_{ref}
0.9< sinθ/λ < 1.25	Spherical atom	1.40	1.66	1.27	288
All data	Spherical atom	1.61	1.92	1.58	462
All data	Multipolar analysis	1.35	1.58	1.34	462

	x	y	z	U^{11}	U^{22}	U^{33}	U^{12}	U^{23}	U^{13}
Al	0	0	0.352105 (5)	0.00125 (2)	0.00125	0.00156 (3)	0.000625	0	0
O	0.30626 (2)	0.30626	1/4	0.00181 (3)	0.00181	0.00223 (3)	0.00083 (3)	0.00022 (1)	−0.00022

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