Reduction of Extinction Effects by Multiple Wavelengths Measurements

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Introduction

The chemical and physical properties of solids depend very sensitively on the distribution of bonding electrons between atoms. These distributions have been measured by conventional single crystal X-ray diffraction for some decades. The method has proved adequate in softer materials where crystal perfection is limited. In hard materials, the highly perfect nature of the crystals is often a difficulty. This is due to the inaccuracy of the corrections conventionally used to account for extinction (multiple re-scattering), before interpreting the data by applying kinematic theory of diffraction. These corrections are large for the low order scattered beams, the ones most sensitive to the distribution of bonding electrons. As the extinction depends on the radiation wavelength used, the extrapolation of the measured intensities to the zero wavelength can give extinction free estimates of the kinematic structure factors. Extinction-free structure factor can be recalculated from the following expression:

$$\ln(F_\lambda) = \ln(F_{\lambda=0}) - C\lambda^2 \qquad (1)$$

Here we report results of the multi-wavelength measurements for corundum α-Al_2O_3. The X-ray data has been compared with extinction free absolute scale quantitative convergent beam electron diffraction data (QCBED) from [1].

Experimental

Nine full sphere data sets up to $(\sin\theta/\lambda)=1.1$Å^{-1} were collected at room temperature from one crystal of α-Al_2O_3 in the range of 0.25-0.84 Å X-radiation wavelengths using BL14A beam line. The single crystal had natural faces and a relatively large volume of 0.0019 mm^3 to improve low counting statistics at higher photon energies. A high-speed 8-channel avalanche photodiode detector (APD) with a counting linearity up to 10^8 cps was used for low photon energies to avoid counting losses, which can introduce extinction-like effects to low Bragg angle strong reflections. Yttrium Aluminium Perovskite, $YAlO_3$:Ce, (YAP) scintillation detector was more effective at higher photon energies.

Results and discussion

Fig. 1 presents the synchrotron X-ray structure factors ln(F) corresponding to QCBED data in Table 1 as a function of λ^2. Trend lines show linear dependencies for most of reflections, except the strongest low order reflections, and expression (1) appears to give a valid zero-wavelength extrapolation for these reflections. For the strongest reflections the 'extinction-free' structure factors were obtained from a linear extrapolation of the three highest photon energy points. The zero-wavelength X-ray structure factors, which correspond to those measured by QCBED, are presented in Table 1. The two strongest (030) and (116) reflections are still significantly less than the corresponding measured by QCBED. This can be attributed to the continued presence of extinction-like effects in those reflections. The extrapolation is generally not unique, and extinction is always present to some extent despite the very high photon energy. One must not infer the absence of extinction without having additional strong evidence at hand. This evidence can be QCBED measurements.

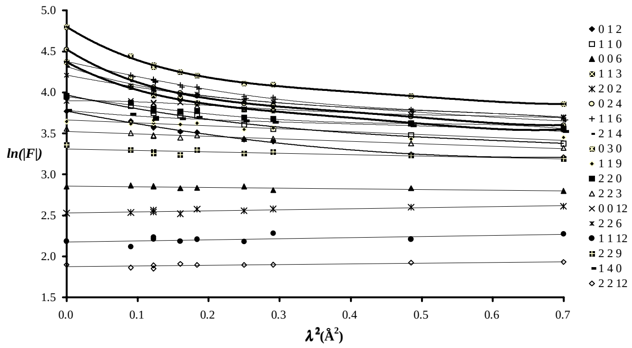

Table 1. *Comparison of structure factors for α-Al_2O_3.*

sinθ/λ	(hkl)	|F|,IAM§	|F|,QCBED	|F|,X-λ=0.7Å$	|F|,X-λ=0Å‡
0.127	1,0,1	0	0.05(6)	0	0
0.144	1,-1,2	46.4	47.20(3)	45.8(3)	44(2)
0.210	1,1,0	60.2	57.2(1)	55.8(5)	53(2)
0.231	0,0,6*	12.5	17.8(2)	18.2(2)	17.7(3)
0.240	2,-1,3	74.2	78.4(1)	73.3(4)	81(7)
0.255	2,0,2*	13.6	12.4(2)	13.7(1)	12.8(2)
0.288	2,-2,4	92.7	93.3(6)	85.4(2)	94(6)
0.313	1,1,6	102.2	102.9(1)	90.8(3)	81(5)
0.356	3,-1,4	75.9	75.7(6)	73.5(3)	76(3)
0.364	0,3,0	137.0	136.8(2)	119.5(4)	124(13)
0.406	1,1,9*	43.1	42.8(1)	43.02(1)	39(1)
0.421	2,2,0*	53.5	53.6(4)	53.4(2)	53(2)
0.436	2,2,3*	35.8	35.4(5)	35.9(1)	36(1)
0.462	0,0,12*	53.7	54.8(8)	52.3(3)	50(3)
0.480	2,2,6*	70.2	71.0(9)	69.2(1)	69(3)
0.508	1,1,12	9.6	11.1(2)	9.35(2)	9.1(1)
0.545	2,2,9*	27.3	26.5(3)	27.8(1)	29.4(9)
0.556	1,4,0*	44.3	41.4(9)	45.1(1)	45(1)
0.625	2,2,12	6.8	10(3)	6.7(1)	6.81(5)

**Reflections used for scaling. §Independent Atom Model (IAM). $X-ray data scaled to the IAM high angle (sin./.>0.55Å-1) structure factors, no extinction applied. ‡X-ray multi-wavelength structure factors extrapolated to the zero-interaction limit (λ=0Å).*

The combination of high-energy synchrotron X-ray diffraction and QCBED should allow the extinction-free absolute-scale measurements and should improve the reliability of the electron charge density maps in such hard materials as α-Al_2O_3.

References

[1] V. A. Streltsov, P. Nakashima & A. W. S. Johnson, J. Phys. Chem. Solids. In press. (2001).

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