

Application Note SC-XRD 523

Crystallography at the Absorption Edge

- PHOTON III and APEX3 for easy handling of high absorption and strong fluorescence

Introduction

Absorption and fluorescence can introduce severe systematic errors during an X-ray diffraction experiment. Software must exactly correct these errors during data processing to produce accurate intensities for precise structure determination.

Absorption

When X-rays interact with crystals they are transmitted, scattered, diffracted or absorbed. Absorption decreases the intensity of incident and diffracted X-rays as they travel through the absorbing medium. Absorption is governed by the equation $I/I_0 = e^{-\mu t}$ where I/I_0 is the fraction of incident intensity, t the path length, and μ the linear absorption coefficient of the material.

For Mo $K\alpha$ radiation and organic crystals, μ is of the order of 0.1 mm^{-1} , so absorption effects may safely be neglected. The use of Cu $K\alpha$ radiation and/or the introduction of heavy atoms in the sample increases μ , reaching in extreme cases more than 100 mm^{-1} . For a relatively small $50\text{-}\mu\text{m}$ crystal with a linear absorption coefficient of 100 mm^{-1} , this equates to a loss of intensity of more than 99%.

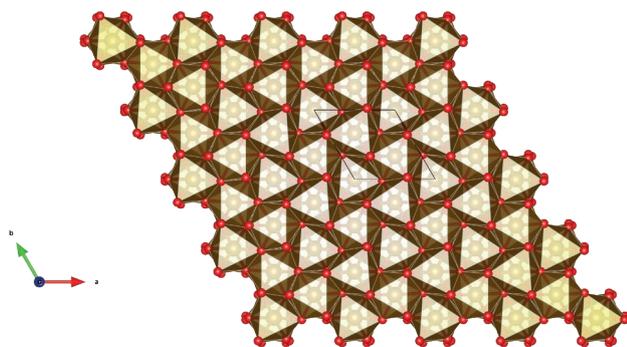
It is clear that in such cases severe systematic errors will arise and intensities will need to be corrected for absorption effects very carefully and accurately.

Fluorescence

If the energy of the incident X-rays is high enough to eject electrons in the K shells of the sample's atoms, the absorption rises drastically. The X-ray wavelength at which this occurs is called the K absorption edge. The absorbed energy is then emitted as fluorescence when the vacant energy levels are quickly filled with electrons from higher levels. X-rays resulting from this process are emitted with an energy that is characteristic for that atom. Thus, fluorescence does not have the same wavelength as the incident radiation, and it is emitted from the sample in all directions.

The examination of iron-containing materials with Cu $K\alpha$ X-rays is useful to study the deleteriousness of this effect. The absorption edge for iron atoms is close to Cu $K\alpha$ radiation, leading to considerable absorption of the incident radiation by the iron atoms, and the subsequent production of extensive Fe $K\alpha$ fluorescence. This fluorescence significantly increases the background of the diffraction pattern.

As with absorption, high background levels from fluorescing samples need accurate correction during data processing to exclude systematic errors and preserve the excellent data quality.



Picture 1: Crystal structure of hematite.

Strong Absorption and Fluorescence from a Hematite (Fe₂O₃) Sample

To demonstrate the impact of both effects in a structure determination experiment, an Fe₂O₃ sample with strong absorption and fluorescence was mounted on a dual-source D8 VENTURE diffractometer. The experiment was carried out using Cu $K\alpha$ radiation. The linear absorption coefficient for hematite with Cu $K\alpha$ is a whopping 112 mm⁻¹. The crystal chosen was a small hematite splinter with a size of 20 × 30 × 40 μm³ that attenuates Cu $K\alpha$ X-rays between 89.3% and 99.8%. A control experiment was performed using Mo $K\alpha$, where hematite's linear absorption coefficient is only 14 mm⁻¹.

A black grain of hematite from Lake Michigan sand was crushed between two microscope slides and the resulting particles were covered with Parabar 10312™ oil for better inspection. The oil also served as adhesive to affix the crystal to the sample holder. Samples were mounted using a Mitegen MicroMount™ with an aperture size of 100 micrometers.

Hematite, Fe₂O₃, is an iron oxide that has the same crystal structure as corundum. In the lattice of hematite, the oxygen atoms form a hexagonal close-packing structure in which two-thirds of the gaps between the octahedra are occupied by iron ions (Picture 1). Hematite crystallizes in the rhombohedral spacegroup R-3c with $a = 5.0357(3)$ Å and $c = 13.7632(8)$ Å at 100 K.



Picture 2: D8 VENTURE diffractometer with PHOTON III detector and two 1μS 3.0 X-ray sources.

Crystallographic data were acquired using a D8 VENTURE dual-source diffractometer equipped with a Mo 1μS 3.0 and a Cu 1μS 3.0 with the brand-new HELIOS EF optics, a KAPPA goniometer and a PHOTON III mixed-mode detector (Picture 2). The experiments were performed at 100 K (Table 1).

Data for all experiments were collected with a combination of phi and omega scans. APEX3 software was used for unit cell determination, data integration (SAINT), and scaling and absorption correction (SADABS). Structure solution and refinement were performed with the APEX3 implementation of SHELXTL. Data were processed to 0.78 Å, the practical limit for Cu $K\alpha$ radiation.

Experiment 1

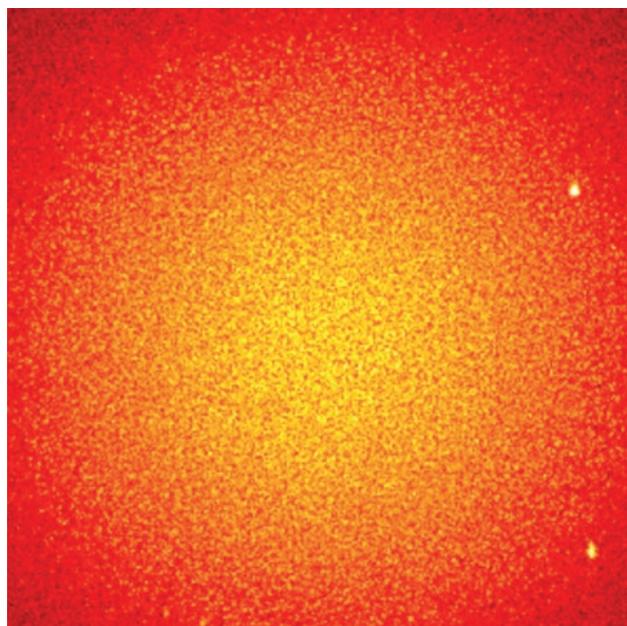
This is the control experiment that was performed with Mo $K\alpha$. This experiment provides the benchmark as no fluorescence is observed and absorption effects are mild, although not absent. The structure refined very well with a reliability criteria $R1$ of 0.085%.

Experiment 2

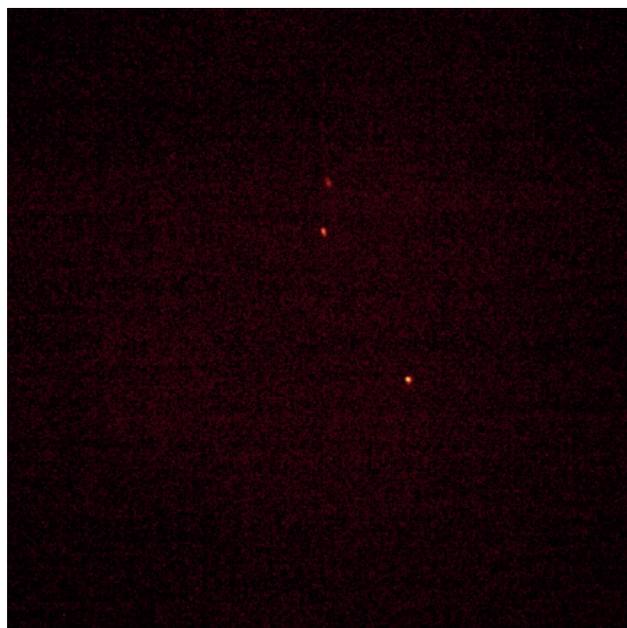
This is the experiment where the fluorescence effect is the strongest (Picture 3). As fluorescence is emitted in all directions its intensity is reduced inversely to d^2 , where d is the distance from the detector to the crystal. Although the Cu source and optics combination provides more than a magnitude more flux on the sample than in Experiment 1, exposure times were increased to maintain meaningful $I/\sigma(I)$ values compared to Experiment 1 to counteract the strong absorption in the sample.

Experiment 3

This experiment is similar to Experiment 2 with identical absorption effects. However, the detector-to-crystal distance was doubled, leading to a fluorescence background reduced by a factor of 4 (Picture 4). Fluorescence drops from about 6 X-rays for a 16 s frame at 4 cm to about 1.5 X-rays at 8 cm. Picture 3 and Picture 4 are displayed at the same contrast level and illustrate the difference in observed fluorescence. They cover the same angular detector range. It should be noted that with the large active area of the PHOTON III 14 ($14 \times 10 \text{ cm}^2$) the larger crystal to detector distance only resulted in a moderate increase in the overall data collection time.



Picture 3: Fluorescence at 4 cm.



Picture 4: Fluorescence at 8 cm.

Table 1: Selected parameters for the individual experiments.

Experiment	1	2	3
Source	Mo $I\mu\text{S}$	Cu $I\mu\text{S}$	Cu $I\mu\text{S}$
μ [mm^{-1}]	14.09	112.98	112.98
$\mu \times r$	0.25	2.02	2.02
d [cm]	5	4	8
No. frames	1707	3508	5178
Exp. time [$\text{s}/1^\circ$]	1-3	4-16	4-16
Total exp. time [h]	1.11	10.68	15.1
Redundancy	24.0	15.7	13.0
Unique data	76	76	76
R_{int} [%]	1.41	2.94	2.48
$R1$ (obs. refl.) [%]	0.85	1.23	1.18
$wR2$ (all data) [%]	1.94	3.73	3.90
residuals [\AA^{-3}]	0.217/0.189	0.477/0.247	0.255/0.474

Discussion

All experiments yield high-quality structures. The control Experiment 1, Mo K α with little absorption and no fluorescence, refines with exceptionally good reliability criteria of $R1=0.85\%$ and $wR2=1.94\%$.

APEX3 software accurately corrects for both high background caused by fluorescence and severe absorption caused by Cu K α radiation. This is clearly demonstrated by comparing Experiment 2 and Experiment 3. Although Experiment 2 was performed at shorter distance to maximize the effect from fluorescence, and Experiment 3 was carried out at longer distance to minimize effects of fluorescence, both experiments result in good structure determinations that are similar in quality to the control experiment. (Experiment 2: $R1=1.23\%$ and $wR2=3.73\%$. Experiment 3: $R1=1.18\%$ and $wR2=3.90\%$.) Even the strong fluorescence was successfully corrected as background during data integration (SAINT) and multiscan correction methods for very strong absorption were successfully applied during absorption correction (SADABS).

Table 2 lists the principal anisotropic atomic displacement parameters (\AA^2) of the Fe and O atoms. In the case of strong absorption, thermal parameters are important to consider, as the shape and size of the atoms' thermal parameters can be strongly affected by absorption. Absorption is more severe at low diffraction angles, which to some extent cancels out the general decrease of intensity with increasing 2θ . Because the general decrease is caused by thermal motion of the atoms, the apparent thermal motion is incorrectly decreased by absorption effects. This results in thermal parameters that are systematically too small and, in severe cases, even physically impossible negative thermal motion or 'non positive definite' atoms will appear.

Table 2 Selected principal anisotropic displacement parameters (\AA^2).

Experiment	Atom	U11	U22	U33
1 Mo K α	Fe	0.0042(2)	0.0042(2)	0.0050(3)
	O	0.0060(8)	0.0051(6)	0.0031(7)
2 Cu K α , 4cm	Fe	0.0039(3)	0.0039(3)	0.0054(4)
	O	0.0057(6)	0.0050(5)	0.0062(6)
3 Cu K α , 8 cm	Fe	0.0041(4)	0.0041(4)	0.0063(5)
	O	0.0062(6)	0.0061(5)	0.0059(6)

Thermal parameters of Experiment 1 serve as the standard, as absorption was much lower compared to the other experiments. With accurate absorption corrections, it is possible to maintain similarly sized thermal parameters for Experiments 2 and 3, although they suffer from severe absorption. The principal anisotropic displacement parameters of the oxygen atom are more isotropic for Experiments 2 and 3 and the shape follows that of the Fe atom ellipsoid better.

Conclusion

APEX3 and PHOTON III based instruments provide solutions that tackle difficult crystallographic challenges and give best-quality data. Severe absorption and fluorescence from atoms at the K absorption edge can be accurately corrected by software in the APEX3 suite. The sensitive PHOTON III detectors combined with high flux μS sources ensure that every diffraction experiment will yield a successful result.

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