Precise Measurement of the Lattice Parameters of Sapphire in the Temperature Range 4.5 K - 250 K Using the Mössbauer Wavelength Standard

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1 Introduction

Lattice parameters of sapphire (\(\alpha\)-\(\text{Al}_2\text{O}_3\)) single crystals are measured in the temperature range from 4.5 K to 250 K. Sapphire is a potential new material for x ray crystal optics, especially attractive in applications as Bragg back-scattering mirrors for interferometers, high-energy resolution monochromators, and analyzers, since it allows (unlike silicon) exact Bragg back-scattering with high reflectivity for x rays in the 10-50 keV spectral range [2, 11, 12]. Precise values of the sapphire lattice parameters and their temperature dependences are required to select suitable back-reflections and relevant crystal temperatures for desired x ray energies. However, lattice parameters and thermal expansion data for \(\alpha\)-\(\text{Al}_2\text{O}_3\) reported in the literature [16, 17, 20, 18, 19, 14] differ by up to \(10^{-4}\). This imposes large uncertainties in the prediction of the back-reflections and the relevant crystal temperatures. To ensure more precise predictions, the lattice parameters of \(\alpha\)-\(\text{Al}_2\text{O}_3\) are measured in this work with a relative uncertainty of less than \(6 \times 10^{-6}\), extending our previous results for temperatures between 286 K and 374 K [6]. The temperature region below 250 K is of special interest for x ray back-scattering because—compared to room temperature and above—the thermal expansion of \(\alpha\)-\(\text{Al}_2\text{O}_3\) is lower, leading to less strict requirements in stability of the temperature control for the crystals which are used as x ray optical elements. This is especially important for x ray energies above \(\approx 30\) keV. Also the thermal conductivity of \(\alpha\)-\(\text{Al}_2\text{O}_3\) rises at low temperature, making \(\alpha\)-\(\text{Al}_2\text{O}_3\) a potential material for high-heat-load monochromators for synchrotron radiation. The thermal conductivity measured in \(\alpha\)-\(\text{Al}_2\text{O}_3\) is up to \(200\) W cm\(^{-1}\) K\(^{-1}\) around 30 K [3], which is higher than the thermal conductivity of any other mono-crystalline material suitable for x ray optics. This may become important at the synchrotron radiation facilities of the fourth generation (TESLA, LCLS), since such sources will provide a beam intensity and heat load that is several orders of magnitude higher compared with today’s facilities.

2 Method

The experimental technique exploits the fact that the wavelength \(\lambda\) of the radiation back-reflected from the atomic planes with Miller indices \((hkl)\) of a crystal is related to the inter-planar distance \(d_{hkl}\) by Bragg’s law \(\lambda = 2d_{hkl} \sin \theta\). For back-scattering it simplifies to \(\lambda = 2d_{hkl}(1 - \Delta \theta^2/2)\) with \(\Delta \theta = \pi/2 - \theta\) as angular deviation from exact back-scattering. If \(\Delta \theta \leq \sqrt{2\epsilon}\), where \(\epsilon\) is the required relative accuracy of measurements, the simple relation \(\lambda = 2d_{hkl}\) is valid even for a relatively coarse angular adjustment. The lattice parameters are derived from measurements of the wavelength of the x rays reflected under the exact back-scattering condition. For this purpose a silicon channel-cut crystal, the so-called \(\lambda\)-meter, is used in the experiment. The symmetric Bragg reflection \((777)\) is applied. By rotating the \(\lambda\)-meter the wavelength of the transmitted radiation is changed. This instrument is calibrated in units of the wavelength \(\lambda_M\) of the Mössbauer radiation of \(^{57}\text{Fe}\) [10] during the experiment.

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The experimental setup is shown in Fig. 1. The method is discussed in detail in [6]. The rotation angle $\psi_{hkil}$ where the $\lambda$-meter selects the x rays matching the backscattering reflection $hkil$ is

$$\psi_{hkil} = 2 \delta d_{hkil}(\tilde{a}, \tilde{b}, \tilde{c}) [1 - \delta (2d_{hkil})],$$

(1)

where $d_{hkil}$ is the inter-planar distance$^1$ and $\tilde{a}, \tilde{b}, \tilde{c}$ are the lattice parameters in $\alpha$-$\text{Al}_2\text{O}_3$; and $x = \lambda_M/2d^*$, with $d^*$ the inter-planar distance of the reflecting atomic planes in the $\lambda$-meter, corrected by refraction and non-perfect angular alignment. Variables notated with a tilde are in units of $\lambda_M$ while others are in SI units.

The reference rotation angle where the $\lambda$-meter selects the Mössbauer radiation from the $^{57}\text{Fe}$ foil is

$$\sin \psi_{M} = x.$$  

(2)

The combination of Eqs. 1 and 2 leads to the following expression which is used to evaluate the inter-planar distances:

$$\Delta \psi_{hkil} = \arcsin \left\{2x \delta d_{hkil}(\tilde{a}, \tilde{b}, \tilde{c}) [1 - \delta (2d_{hkil})] \right\} - \arcsin \{x\}. $$

(3)

Herein, $\Delta \psi_{hkil} = \psi_{hkil} - \psi_{M}$.

With $a = b$ in the hexagonal $\alpha$-$\text{Al}_2\text{O}_3$ lattice, there are three unknowns $\tilde{a}, \tilde{c}, d^*$ to be determined in the experiment. Thus at least three measurements of $\Delta \psi_{hkil}$ for different back-reflections $(hkil)$ are required. The measurements are repeated at temperatures of the $\alpha$-$\text{Al}_2\text{O}_3$ of 250 K, 200 K, 150 K, 100 K, and 4.5 K.

This method allows direct measurement of the lattice parameters $a$ and $c$ in units of $\lambda_M$. In the range from 100 K to 4.5 K a technique of relative measurements was used additionally.

3 Experimental

The experiment was performed at the low energy branch of the undulator beamline at the PETRA $e^-/e^+$ storage ring at DESY/HASYLAB (Hamburg, Germany) [5, 4].

Figure 1 shows the experimental setup. The crystal under study is placed on a 4-circle goniometer. It can be oriented to allow for back-reflections of x rays transmitted by the $\lambda$-meter ($\lambda$). The back-reflections $(0 0 0 30), (1 6 7 22), (1 3 4 28), (2 6 8 20)$ are used in the experiment. They are selected by their Bragg wavelength $\lambda_B = 2d_{hkil}(1 - \delta)$ being in the proximity of $\lambda_M$.

$^1$In the following, four Miller indices are used to denote the atomic planes of $\alpha$-$\text{Al}_2\text{O}_3$ in the hexagonal basis, where $h + k + i = 0$. 

Figure 1: Experimental setup for measuring lattice parameters: x rays after a high-heat-load monochromator (not shown) are collimated by passing through the vertical slits S1 and S2; $\lambda$: $\lambda$-meter; F: $^{57}\text{Fe}$ foil used as a source of Mössbauer radiation; D: semi-transparent avalanche photodiode with 0.7 ns time resolution; $\alpha$-$\text{Al}_2\text{O}_3$: sapphire single crystal in a LHe flow cryostat on a 4-circle goniometer.
The crystal is kept in a liquid helium flow cryostat. By temperature controlled electric heating, it is possible to maintain the crystal at a fixed temperature with a stability of some mK [9]. The λ-meter crystal is kept at a constant temperature (303.8 K) with a stability of ≈ 10 mK. It is mounted on a high-resolution angular rotation stage.

If the wavelength of the radiation picked out by the λ-meter coincides with λ_M, it excites coherently the ⁵⁷Fe nuclei in an α-Fe foil (F) installed in the beam. The excited nuclei emit Mössbauer photons with coherent enhancement in the forward direction [7, 8], with an average delay of τ = 141 ns. This delay allows for discrimination of the Mössbauer quanta from the synchrotron radiation pulse. The detector, a semi-transparent silicon avalanche photo-diode [15], with a time resolution of ≃ 0.7 ns, is placed immediately after the λ-meter at a distance L ≈ 6 m upstream from the back-scattering crystal. The transmitted radiation is reflected from the α-Al₂O₃ crystal and arrives after 2L/c = 40 ns in the detector, which makes the reflected pulse easily distinguishable from the incident pulse.

4 Data evaluation and results

Sapphire can be assigned to the hexagonal crystal system with two independent lattice parameters a = b and c. The inter-planar distance in a hexagonal lattice is given by:

\[ d_{hkil} = \frac{1}{\sqrt{\frac{4}{3}a^2 (h^2 + k^2 + hk) + \frac{1}{c^2}l^2}}. \]  

(4)

For each crystal temperature, the angular differences Δψ_{hkil} have been measured for the four different back-reflections. This allows us to compose four different sets, each with three equations of type Eq. 3, yielding its own solution for the three free parameters a, c, and d*. An iteration procedure is used to solve these nonlinear systems of equations.

From the four independent solutions, the averaged values of a and c and their standard errors can be computed.

The lattice parameters of α-Al₂O₃ in the temperature range from 4.5 K to 374 K, including our recently published results for temperatures above 286 K [6], are shown in Fig. 2. For the computation of the lattice parameters in SI units the value λ_M = 86.025474(16) pm from [10] was used. The errors of \( \hat{a} \) and \( \hat{c} \), which are relatively below 6 \times 10^{-6}, are primarily due to the averaging process, as described above.

![Figure 2: Lattice parameters a (blue) and c (red) in α-Al₂O₃. Left panel: Results from the present work and [6]. Right panel: Detailed view on the results for temperatures below 100 K. The solid lines are fits with functions Eq. 5 and the parameters from Eq. 7. The variations of a at 25 K and 65 K are caused by temperature instability.](image-url)
5 Discussion

In the Debye model of thermal expansion, the linear expansion coefficient $\alpha$ has a $T^3$ dependence for $T \to 0$, and is constant for $T > \Theta_D$ (where $\Theta_D$ is the Debye temperature), see e.g. [13]. We have fitted the following function that resembles this behavior to the data of the present work and of [6]:

$$x(T) = (x_{44}T^4 + x_{04}) w(T) + (x_{11}T + x_{01}) [1 - w(T)]$$

$$w(T) = \frac{1}{1 + \exp \left( \frac{\sqrt{T} - \sqrt{\Theta_x}}{\sqrt{\Delta \Theta_x}} \right)}. \quad (5)$$

Herein, $x$ takes the values $a$ or $c$, respectively. The polynomial terms in parentheses represent the limiting temperature dependence of $\alpha$ as described above, and $w(T)$ and $1 - w(T)$ are weighting factors that provide a smooth transition between the $T \to 0$ and $T \to \infty$ regions. Since the weighting factor of the low temperature term extends far into the range above $\Theta_x$, the Debye temperature is expected to be $\Theta_D \gg \Theta_x$. The Debye temperature can be estimated to be 995 K for the sub-lattice of O atoms, and 890 K for the Al sub-lattice, cf. [2], p.63.

From Eq.5 one can now calculate the linear thermal expansion coefficients for the limiting cases of low and high temperature$^2$:

$$\alpha_x(T) = 4 \frac{x_{44}/x(0\text{~K})}{T^3}; \quad T \to 0$$

$$\alpha_x(T) = \frac{x_{11}/x(374\text{~K})}{T}; \quad T \gg \Theta_x. \quad (6)$$

The fit curves are shown in Fig. 2 together with the measured results for $a$ and $c$. The relative accuracy of the fit is about $4 \times 10^{-6}$ which is close to the measurement uncertainty at low temperature. Therefore, it seems evident that possible relative deviations from the Debye model are below $4 \times 10^{-6}$.

From Eqs. 6 we obtain the following approximate expressions for the thermal expansion coefficients in the limiting cases:

$$\alpha_a = 1.3(1.0) \times 10^{-12} \text{~K}^{-1} \cdot (T/\text{K})^3; \quad T \to 0$$

$$\alpha_c = 1.79(35) \times 10^{-12} \text{~K}^{-1} \cdot (T/\text{K})^3; \quad T \to 0$$

$$\alpha_a = 6.2(2) \times 10^{-6} \text{~K}^{-1}; \quad T \gg 200\text{~K}$$

$$\alpha_c = 7.07(8) \times 10^{-6} \text{~K}^{-1}; \quad T \gg 200\text{~K} \quad (7)$$

6 Conclusions

In the present work and [6], the lattice parameters of $\alpha$-Al$_2$O$_3$ have been measured in a temperature range from 4.5 K to 374 K with relative errors below $6 \times 10^{-6}$. A data fit shows that our results are, within a relative accuracy of about $4 \times 10^{-6}$, compatible with the Debye model of thermal expansion, where the thermal expansion coefficient shows $T^3$ dependence for $T \to 0$ and is constant for higher temperatures $T > \Theta_D$.

The accuracy of the present study is more than one order of magnitude below the expected $10^{-7}$ which is a theoretical limit of the experimental technique. The main error sources are the large divergence of the incoming beam and crystal defects in $\alpha$-Al$_2$O$_3$, but also temperature shifts inside the experimental station during the measurements.

The present results will be useful for predicting Bragg back-reflections and relevant crystal temperatures which are needed for a high-resolution $\alpha$-Al$_2$O$_3$ back-scattering monochromator. Two cases can be distinguished:

i) For temperatures above $\approx 50$ K it is possible to tune the back-scattering monochromator to any given x ray energy between 10 and 50 keV. This is done by selection of a back-reflection $(hkl)$ with $2d_{hkl}$ close to the desired x ray wavelength $\lambda$, and adjustment of the temperature.

ii) For temperatures below $\approx 40$ K the relative change of the lattice parameters of $\alpha$-Al$_2$O$_3$ is not more than $6 \times 10^{-6}$. This leads to a set of fixed wavelengths $\lambda_{hkl}$ of back-reflected x rays which are stable even for a rather coarse temperature accuracy and high heat load.

$^2$The value 374 K in the second line in Eq. 6 is the maximum temperature used in the determination of the fit.
References