Measuring wavelengths and lattice constants with the Mössbauer wavelength standard

Yu. V. Shvyd'ko,[a]* M. Lucht,[a] E. Gerdau,[a] M. Lerche,[a] E. E. Alp,[b] W. Sturhahn,[b] J. Sutter[b] and T. S. Toellner[b]

[a]II. Institut für Experimentalphysik, Universität Hamburg, D-22761 Hamburg, Germany, and [b]Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA. E-mail: yuri.shvydko@desy.de

The newly proposed atomic-scale length standard, the wavelength of the ^{57}Fe Mössbauer radiation [Shvyd'ko *et al.* (2000). *Phys. Rev. Lett.* **45**, 495–498], is used to measure the wavelengths of the Mössbauer radiation of ^{151}Eu, 57.556185 (27) pm, ^{119}Sn, 51.920811 (39) pm, and ^{161}Dy, 48.334336 (19) pm, with a relative accuracy of ∼0.5 p.p.m. Also, the lattice constants of Al_2O_3 are measured in a temperature range from 286 K to 374 K. At room temperature, T = 295.65 K, their values are a = 4.759213 (8) Å, c = 12.991586 (4) Å.

Keywords: lattice constants; X-ray wavelength; wavelength standards; Mössbauer radiation; Al_2O_3.

1. Introduction

The wavelength λ_M = 86.025474 (16) pm of the ^{57}Fe Mössbauer radiation is used in the present studies as a length standard to determine the lattice constants of Al_2O_3 crystals, as well as the wavelengths of the ^{151}Eu, ^{119}Sn and ^{161}Dy Mössbauer radiation.

The advantage of the Mössbauer wavelength standard λ_M over the atomic-scale length standard most often used nowadays, *i.e.* the lattice constant of silicon, a = 543.102088 (16) pm (CODATA, 2000), is the spectral sharpness of the Mössbauer radiation, 3.5×10^{-13} in relative units, which makes its wavelength λ_M extremely well defined. It can be easily reproduced with a unique accuracy of at least $10^{-11}\lambda_M$ without any special precautions regarding temperature, pressure and chemical composition of the environment in which the nuclei are placed. By controlling these parameters, an accuracy of $3.5 \times 10^{-13}\lambda_M$, determined by the natural width of the ^{57}Fe nuclear resonance, can easily be achieved.

The first attempt to introduce the wavelength of the Mössbauer radiation as a length standard was made by Bearden (1965). However, it has only now become possible to implement it. Two developments have changed the situation. Firstly, brilliant sources of the Mössbauer radiation have become available at modern synchrotron radiation facilities worldwide. Techniques which are used to filter Mössbauer photons from the white spectrum of synchrotron radiation have been reviewed by Gerdau & de Waard (1999/2000). Secondly, recently the absolute value of the wavelength of the ^{57}Fe Mössbauer radiation has been measured to sub-p.p.m. accuracy in two independent experiments by Shvyd'ko *et al.* (2000) and Xiaowei *et al.* (2000).

Xiaowei *et al.* (2000) measured λ_M with a relative uncertainty of 0.6 p.p.m. using the method of Siddons *et al.* (1988) by comparing λ_M with the lattice constants of several silicon crystal samples. The averaged value reported by the authors is 86.02557 (5) pm.

Shvyd'ko *et al.* (2000) measured λ_M with a relative uncertainty of 0.19 p.p.m. using almost exact Bragg backscattering of X-rays from a calibrated reference silicon crystal kept in an environment with precisely controlled temperature and pressure. Its value is determined as λ_M = 86.025474 (16) pm. The corresponding Mössbauer photon energy is E_M = 14412.497 (3) eV.

The values reported in the two publications differ by 1.1 p.p.m. This is a reliable basis for precise absolute measurements with the γ-ray wavelength standard.

In the present paper it is demonstrated how the γ-ray wavelength standard can be used to measure lattice constants and radiation wavelengths. The experimental technique is described in §2. All measured values are expressed both in units of λ_M and in metres. In the latter case the value of λ_M reported by Shvyd'ko *et al.* (2000) is used.

Lattice constants of sapphire (Al_2O_3) single crystals are measured. Sapphire is a potential new material for X-ray crystal optics, especially attractive in applications to Bragg backscattering mirrors for interferometers, high-energy-resolution monochromators and analyzers, as it allows (unlike silicon) Bragg backscattering with high reflectivity for X-rays in the 10–50 keV spectral range (Shvyd'ko *et al.*, 1998; Shvyd'ko & Gerdau, 1999). Precise values of the sapphire lattice constants and their temperature dependences are required to predict Miller indices (hkl) of back reflections and relevant crystal temperatures for desired X-ray energies. However, lattice constants and thermal expansion data for Al_2O_3 reported in the literature (Kirfel & Eichhorn, 1990; Brown *et al.*, 1992; Aldebert & Traverse, 1982; Lewis *et al.*, 1982; Yim & Paff, 1973) differ by up to 100 p.p.m. This imposes large uncertainties in the prediction of back reflections and relevant crystal temperatures. To ensure more precise predictions, the lattice constants of sapphire are measured here with a relative uncertainty of less than 1 p.p.m. in the temperature range from 286 to 376 K. The experimental set-up is described in §3 and the results are presented in §4.1.

Precise knowledge of the lattice constants in sapphire as well as the ability of sapphire crystals to reflect backwards X-rays of any energy in the 10–50 keV spectral range is used further in the paper to determine the wavelength of the ^{151}Eu, ^{119}Sn and ^{161}Dy Mössbauer radiation. Mössbauer radiation of different nuclei could provide a set of reference wavelengths in the hard X-ray range with uniquely small uncertainty and easy reproducibility. In use in crystallography, X-ray and nuclear spectroscopy today is the set of wavelengths of the K_α characteristic X-rays of atoms. A set of Mössbauer wavelengths can take over this role, as brilliant Mössbauer radiation sources are available at synchrotron radiation facilities worldwide. Mössbauer radiation has at least 10^6 times smaller spectral width and is much less sensitive to the environment. However, the uncertainty in the knowledge of the absolute values of the wavelengths other than ^{57}Fe Mössbauer radiation is at best no less than ∼10 p.p.m. (Kikuta, 1994; Leupold *et al.*, 1996; Koyama *et al.*, 1996). In §4.2 we report on the measurements of the wavelength of the Mössbauer transition in ^{151}Eu, ^{119}Sn and ^{161}Dy with an accuracy of 0.8–0.4 p.p.m.

2. Method

The experimental technique exploits the fact that the wavelength λ of the radiation back-reflected from the atomic planes with Miller indices (hkl) of a crystal is related to the interplanar distance d_{hkl} by Bragg's law, $\lambda = 2d_{hkl}\sin\theta$. For backscattering it simplifies to $\lambda = 2d_{hkl}(1 - \Delta\theta^2/2)$, where $\Delta\theta = \pi/2 - \theta$ is the angular deviation from exact backscattering. If $\Delta\theta \leq (2\varepsilon)^{1/2}$, where ε is the required relative accuracy of measurements, the simple relation $\lambda = 2d_{hkl}$ is valid even for a relatively coarse angular adjustment, *e.g.* for $\Delta\theta \leq 100$ μrad the relative accuracy is better than $\varepsilon \simeq 10^{-8}$. For a precise comparison of the X-ray wavelength and the lattice constant, a small refractive

correction has to be additionally taken into account. This is introduced below.

2.1. Determination of lattice constants

In the following, the theoretical background and sources of possible uncertainties of the measurements of lattice constants in terms of λ_M are discussed.

If the crystal structure and thus the relations between the interplanar distances $d_{hkl}(a, b, c)$ and the lattice constants a, b, c are known, the lattice constants can be determined by measuring the wavelength λ of X-rays reflected backwards from different sets of atomic planes (*hkl*).

The λ-meter in our experiment is a silicon channel-cut crystal calibrated in units of λ_M. Its reflectivity is described by the dynamical theory of Bragg diffraction in perfect crystals (see, for example, Pinsker, 1978) which takes into account effects of refraction and multiple scattering. It predicts that X-rays are reflected within a spectral range centred at λ_c. The dependence of λ_c on θ and on material parameters is given by

$$(\lambda_c/2d)\big[(\lambda_c/2d) - \sin\theta\big] = -\delta(\lambda_c). \quad (1)$$

Here, d is the interplanar distance for the reflecting atomic planes of the λ-meter crystal. This expression, used by Shvyd'ko & Gerdau (1999), is valid at any angle θ including normal incidence. Obviously it reduces to the normal Bragg condition for $\delta = 0$. Here,

$$\delta(\lambda) = \frac{r_e\lambda^2}{2\pi V}\sum_a N_a\big[Z_a + f'_a(\lambda)\big] \quad (2)$$

is the real part of the correction to the complex refractive index $n(\lambda) = 1 - \delta(\lambda) - i\beta(\lambda)$ of X-rays in the reflecting crystal; r_e is the classical electron radius, V is the unit-cell volume, and N_a, Z_a and f'_a are the number of a-type atoms in the unit cell, their atomic number, and their real anomalous correction to the forward-scattering amplitude, respectively. The complex part of the correction is ignored, which is valid for weakly absorbing crystals like Si and Al_2O_3.

Combining (1) and (2) we obtain the required relation

$$\sin\theta = (\lambda_c/2d)(1 + w), \quad (3)$$

which differs from Bragg's law by a small but important correction,

$$w = \frac{2r_e d^2}{\pi V}\sum_a N_a\big[Z_a + f'_a(\lambda_c)\big]. \quad (4)$$

There is only a weak dependence of w on λ_c. It is assumed to be constant in the spectral range $\lambda_M - 0.01$ Å $\leq \lambda_c \leq \lambda_M + 0.01$ Å investigated in our experiment. This is justified as $f'_{Si}(\lambda_c)$ varies in this range at most by ± 0.003 about its average value of 0.119 (Deutsch & Hart, 1984, 1988), and thus w varies by less than 10^{-8} compared with the leading term 1.

λ_c is changed by rotating the λ-meter. The variation of the rotation angle ψ is measured in the experiment. If the rotation axis $\boldsymbol{\psi}$ of the λ-meter is by the angle ξ not exactly perpendicular to the incident beam $\mathbf{k}_0$, and the Si(777) reflecting planes build a non-zero angle η with the rotation axis $\boldsymbol{\psi}$, then the glancing angle θ of $\mathbf{k}_0$ to the Si(777) reflecting planes is not equal to ψ, and the relation between θ and ψ reads: $\sin\theta = \sin\psi\cos\eta\cos\xi + \sin\eta\sin\xi$. Combining this expression with (3), one obtains the relation between the rotation angle ψ and the wavelength λ_c selected by the λ-meter,

$$\sin\psi = (\lambda_c/2d^*) - \zeta. \quad (5)$$

Here, $\zeta = \tan\eta\tan\xi$ is the parameter which allows for a non-perfect alignment of the λ-meter. d^* is another instrumental parameter of the λ-meter given by $d^* = d\cos\eta\cos\xi/(1 + w)$. d^* is determined in the experiment.

Equation (1) can also be used to describe backscattering in the sample under study, a sapphire crystal. For this, d_{hkil}, the interplanar distance of the atomic planes in sapphire reflecting X-rays backwards, should be substituted for d.† The spectral region of back reflection is centred at

$$\lambda_c = 2d_{hkil}\Big[1 - \Delta\theta^2/2 - \delta_{Al_2O_3}(\lambda_c)\Big]. \quad (6)$$

Equation (6) is a general condition for Bragg backscattering which includes not only the deviation from normal incidence $\Delta\theta = \pi/2 - \theta \ll 1$ but also the effect of refraction. As already mentioned, owing to the $\Delta\theta^2$-dependence in (6) a deviation from normal incidence even by an angle of, for example, $\Delta\theta \simeq 0.1$ mrad changes the wavelength of the reflected radiation by only $5 \times 10^{-9}\lambda_c$. In the following, this small correction is neglected. Therefore, $2d_{hkil}$ will be used instead of λ_c in the argument of $\delta(\,)$. Also, the index Al_2O_3 is omitted for simplicity. The real part of the refraction index corrections for Al_2O_3 is calculated by (2) with $f'_a(\lambda)$ obtained from the library of anomalous scattering factors computed using relativistic Hartree–Fock–Slater wavefunctions (Kissel & Pratt, 1990; Kissel *et al.*, 1995).

In the experiment, the rotation angle ψ_{hkil} of the λ-meter at which it selects X-rays matching the backscattering reflection (*hkil*) is determined. By using (5) and (6) one obtains

$$\sin\psi_{hkil} = 2x\tilde{d}_{hkil}(\tilde{a}, \tilde{b}, \tilde{c})\big[1 - \delta(2d_{hkil})\big] - \zeta. \quad (7)$$

Here, $\tilde{d}_{hkil} = d_{hkil}/\lambda_M$, $\tilde{a} = a/\lambda_M$, $\tilde{b} = b/\lambda_M$, $\tilde{c} = c/\lambda_M$ and $x = \lambda_M/2d^*$.

Furthermore, (5) allows one to determine the reference rotation angle ψ_M at which the λ-meter selects the Mössbauer radiation,

$$\sin\psi_M = x - \zeta. \quad (8)$$

In the difference $\psi_{hkil} - \psi_M = \Delta\psi_{hkil}$, the uncertainty of the zero setting of the λ-meter drops out. One obtains

$$\Delta\psi_{hkil} = \arcsin\big\{2x\tilde{d}_{hkil}(\tilde{a}, \tilde{b}, \tilde{c})\big[1 - \delta(2d_{hkil})\big] - \zeta\big\} - \arcsin(x - \zeta). \quad (9)$$

Here, $\tilde{a}$, $\tilde{b}$, $\tilde{c}$, x and ζ are unknowns which should be determined. In principle, five independent measurements of $\Delta\psi_{hkil}$ are necessary for this.

The number of unknowns and thus the number of measurements can be reduced to four provided the λ-meter is well aligned. As is ascertained by the numerical analysis of (9), the parameter ζ can be omitted without changing the result of $\tilde{a}$, $\tilde{b}$ and $\tilde{c}$ by more than 10^{-10} in relative units if the alignment parameter $\zeta \leq 10^{-5}$. The λ-meter in our experiment is aligned better than this.

The technique described below relies on the strict fulfillment of the relation $d_{hkil}(a, b, c)$ between the interplanar distances and lattice constants. This should be the case in perfect crystals. Defects violate the periodicity of the crystal structure and thus the relation $d_{hkil}(a, b, c)$. The validity of the relation and the errors in determining the lattice constant can be checked by measuring $\Delta\psi_{hkil}$ for more back reflections (*hkil*) than required by the number of unknowns in the set of equations (9).

† In the following, four Miller indices are used to denote atomic planes of sapphire in the hexagonal basis. As usual, the relation $h + k + i = 0$ is valid.

Table 1
Miller indices (*hkil*) of selected reflections in Al_2O_3 with Bragg wavelengths $\lambda_B = 2d_{hkil}(1-\delta)$ close to λ_M.

The λ_B values are calculated by using the lattice constants at $T = 287.3$ K as obtained in the present studies. The angular deviation of the diffraction vector from the main crystallographic directions as well as the expected theoretical energy widths are also given.

(*hkil*)	λ_B (pm)	$[0001]\widehat{[hkil]}$ (°)	$[10\bar{1}0]\widehat{[hkil]}$ (°)	ΔE (meV)
(0 0 0 30)	86.60572	0.0	0.0	13.2
(1 6 $\bar{7}$ 22)	86.07066	43.2162	52.4109	1.8
(1 3 $\bar{4}$ 28)	85.97935	22.0934	46.1021	6.1
(2 6 $\bar{8}$ 20)	85.81588	48.6577	46.1021	4.5

2.2. Determination of wavelengths

The backscattering condition (6) is also used in the present studies for measuring the wavelength of the ^{151}Eu, ^{119}Sn and ^{161}Dy Mössbauer radiation. Following the procedure described in the previous section, one determines for which reflection (*hkil*) and at what crystal temperature exact back-reflection occurs for the given Mössbauer radiation and then measures the crystal lattice parameters at this temperature in terms of λ_M. From the measured interplanar distance d_{hkil} the wavelength is readily determined according to (6).

3. Experimental

The experiments were performed at the undulator beamline 3-ID at the Advanced Photon Source (Argonne).

3.1. Determination of lattice constants

Fig. 1 shows the scheme of the experimental set-up for measuring lattice constants. A crystal under study is placed on a four-circle goniometer. It can be oriented to allow back reflections of X-rays coming from the λ-meter (λ).

Sapphire crystals grown by the heat-exchange method (Schmid *et al.*, 1994) are used in the present studies. The dislocation density in the sample is 4×10^3 cm^{-2} as measured with white-beam backscattering X-ray topography (Tuomi *et al.*, 1974) by Chen *et al.* (2001). The lattice constants are measured at different crystal temperatures in the range from 286 to 376 K. The crystal is kept in a furnace and maintained at a fixed temperature with a stability of ≤ 1 mK (Lucht, 1998).

A PT100 thermoresistor is used for the measurement of the crystal temperature. It was calibrated in the Physikalisch-Technische Bundesanstalt (Braunschweig, Germany) over the temperature range 291.3–299.2 K with an accuracy of 8 mK, and at 373 K with an accuracy of 10 mK. Using this calibration a linear correction is applied to the $T(R)$ characteristic curve of the PT100 thermoresistor as given by the IEC751 standard.

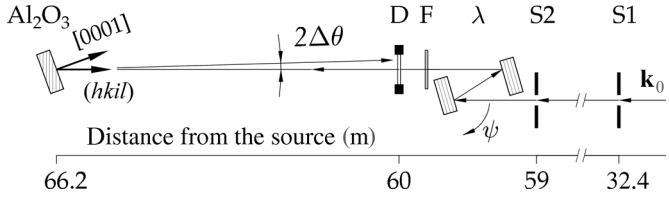

Figure 1
Experimental set-up for measuring lattice constants. X-rays after a high-heat-load monochromator (not shown) pass through the vertical slits S1 and S2 at a distance of 26.6 m. λ: λ-meter; F: ^{57}Fe foil used as a source of Mössbauer radiation of high brightness; D: semi-transparent avalanche photodiode with 0.7 ns time resolution; Al_2O_3: sapphire single crystal in a furnace on a four-circle goniometer.

The back reflections in Al_2O_3 used in the experiment are listed in Table 1.

The λ-meter is a silicon channel-cut crystal. The symmetric Bragg reflection (777) is used. The crystal is kept at a constant temperature (303.8 K) with a stability of 2 mK. The channel-cut crystal is mounted on a high-angular-resolution rotation stage KOHZU KTG-15. It has a step width of 25 nrad. The rotation angle ψ is measured with a Heidenhain ROD800C angle encoder and an IK320 interpolation electronics, rendering an angular resolution of 43 nrad.

The intrinsic relative width of the Si(777) reflection on the wavelength scale for X-rays with $\lambda \simeq 0.86$ Å is $\Delta\lambda/\lambda \simeq 3.5 \times 10^{-7}$, thus allowing wavelengths to be measured with a relative accuracy of better than 10^{-7}. To achieve this precision, two conditions have to be fulfilled: (i) the vertical divergence of the incident beam should be less than the angular width of the (777) reflection, 1.2 μrad; and (ii) the direction of the incident beam should be kept constant independent of the X-ray wavelength. To ensure this, a system of two vertical slits, S1 = 60 μm and S2 = 60 μm, at a distance of 26.6 m is used. Owing to geometrical reasons, this is expected to provide a beam divergence of 2.3 μrad. The actual divergence is measured to be 9 μrad as determined from the width of the angular reflection curve measured with Mössbauer radiation. This large divergence deteriorates the accuracy of the measurement.

If the wavelength of the radiation picked out by the λ-meter coincides with λ_M, it coherently excites the ^{57}Fe nuclei in an α-Fe foil (F) installed downstream. The foil is 6 μm thick, enriched to 95% in ^{57}Fe. The excited nuclei emit Mössbauer photons with coherent enhancement in the forward direction (Hastings *et al.*, 1991; Shvyd'ko *et al.*, 1991), with an average delay of $\tau = 141$ ns. This delay allows the discrimination of Mössbauer quanta from the incident radiation pulse of duration ∼70 ps.

The detector, a silicon avalanche photodiode (Baron, 2000), is placed immediately after the α-Fe foil at a distance $L = 6.2$ m upstream from the backscattering crystal. Its time resolution is ∼0.7 ns. The silicon wafer of thickness 100 μm absorbs ∼35% of the incident radiation pulse. The transmitted radiation is reflected from the Al_2O_3 crystals and arrives after $2L/c = 40$ ns in the detector. The resulting time delay makes the reflected pulse easily distinguishable from the incident pulse. The detector's aperture is $D^2 = 10 \times 10$ mm. Thus, only those X-rays which deviate from exact backscattering by a maximum of $\Delta\theta = D/4L = 0.4$ mrad are detected. Their relative energy dispersion is negligibly small at $0.5(\Delta\theta)^2 \leq 8 \times 10^{-8}$ [*cf.* equation (6)].

For each crystal temperature, the angles ψ_{hkil} as well as the reference angle ψ_M of the λ-meter at which it selects the Mössbauer radiation are measured. For a perfectly stable set-up the latter should be constant. Fig. 2 shows relative variations of ψ_M from run to run. The typical duration of one run (measurement at one temperature) is 4–5 h. Since the wavelength of Mössbauer radiation has no measurable variation, the graph demonstrates the stability of the experimental set-up.

3.2. Backscattering of Mössbauer radiation.

Fig. 3 shows the scheme of the experimental set-up for the observation of Bragg backscattering of Mössbauer radiation. Synchrotron radiation pulses from the undulator are monochromated at Mössbauer energies to a bandwidth of ∼1 eV with a diamond high-heat-load monochromator (not shown in Fig. 3). The radiation is further aimed at the target (T) containing Mössbauer nuclei. Mössbauer

Table 2
Excitation energy E, lifetime τ, natural energy width Γ, and target composition of selected Mössbauer nuclei (Firestone *et al.*, 1996).

Isotope	E (keV)	τ (ns)	Γ (neV)	Target
^{57}Fe	14.4	141.2	4.7	α-^{57}Fe
^{151}Eu	21.5	13.8	47.5	EuO
^{119}Sn	23.8	26.0	25.3	$^{119}Sn_2O$
^{161}Dy	25.6	41.0	15.7	Dy (at 20 K)

energy E, lifetime τ, natural spectral width $\Gamma = \hbar/\tau$ of the excited nuclear states in question, and targets used to generate Mössbauer photons are given in Table 2.

The nuclei excited with the prompt incident radiation pulses emit photons in a narrow energy band of $\sim\Gamma$ (5–50 neV) with a delay $\sim\tau$ (10–150 ns). The detector is installed slightly off the incident beam axis so that it is not overloaded with the high photon flux of the 1 eV broad beam. The prompt and the delayed radiation components hit the sapphire crystal.

In accordance with the selected isotope, the atomic planes (*hkil*) of the Al_2O_3 sample as given in Table 3 are adjusted to a position almost normal to the incident beam by observing the corresponding Bragg back reflections.† The energy widths of the back reflections are in the meV range (Table 3). The temperature variation of the backscattering energies in Al_2O_3 is typically 0.1 eV K^{-1}. Thus to observe backscattering of the prompt radiation component having an energy bandwidth of 1 eV, the crystal temperature should be correct to within $\sim$10 K. This is easy and performed at first to orient the crystal. However, to observe backscattering of the Mössbauer radiation, the crystal temperature must be tuned to the correct temperature with mK accuracy.

The crystal temperatures T at which backscattering of the Mössbauer photons is observed and their widths ΔT are given in Table 3. The corresponding energy widths ΔE are computed from ΔT by using the relation $\Delta E = E/d_{hkil}\,\mathrm{d}d_{hkil}/\mathrm{d}T\,\Delta T$ (*cf.* Shvyd'ko & Gerdau, 1999) with $d_{hkil}(T)$ values obtained from our present measurements. The experimental energy widths of the back reflections are an order of magnitude larger than the expected theoretical values. All values are given in Table 3. This is attributed to a relatively high dislocation density in the crystal. The crystal quality is another factor that deteriorates the accuracy of the present measurements.

† The angular deviation from exact backscattering is $\Delta\theta = 0.4$ mrad. The correction factor $\Delta\theta^2/2 = 8 \times 10^{-8}$ in equation (6) is ignored in the following evaluations.

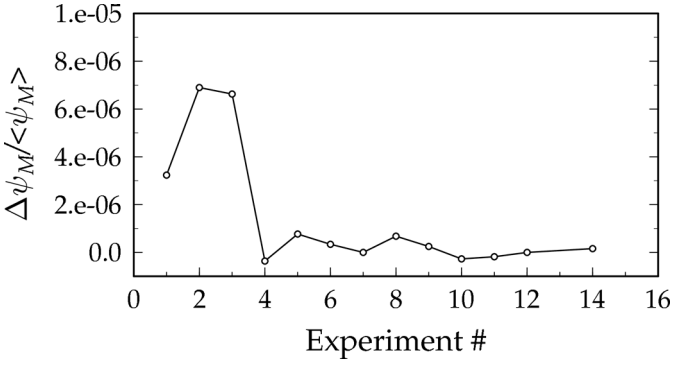

Figure 2
Relative variation (from run to run) of the reference angle ψ_M, the angle of the λ-meter at which it selects the Mössbauer radiation.

Table 3
Miller indices (*hkil*), crystal temperature T, temperature width ΔT and energy width ΔE (as measured in the experiment and as calculated with the dynamical theory) of backscattering reflections in Al_2O_3 for the ^{57}Fe, ^{151}Eu, ^{119}Sn and ^{161}Dy Mössbauer radiation.

Isotope	(*hkil*)	T (K)	ΔT (mK) (exp.)	ΔE (meV) (exp.)	ΔE (meV) (theory)
^{57}Fe	$(1\,3\,\bar{4}\,28)$	371.582 (8)	66	6.5	5.8
^{151}Eu	$(3\,2\,\bar{5}\,43)$	287.125 (8)	67	8.3	0.6
^{119}Sn	$(6\,5\,\bar{11}\,40)$	286.968 (10)	109	14.5	1.1
^{161}Dy	$(3\,2\,\bar{5}\,52)$	374.624 (40)	46	7.6	0.7

The nuclear resonance in ^{161}Dy was observed in another experiment at the undulator beamline PETRA-1 (DESY, Hamburg) with a similar backscattering set-up and with the same sapphire crystal (Shvyd'ko *et al.*, 2001). Backscattering of the ^{161}Dy Mössbauer radiation was observed from the atomic planes $(3\,2\,\bar{5}\,52)$ in sapphire at a temperature which was $\delta T = 3.04$ (1) K above the temperature of backscattering of the ^{57}Fe Mössbauer radiation from the $(1\,3\,\bar{4}\,28)$ atomic planes.

4. Data evaluation

4.1. Lattice constants of sapphire

Sapphire can be assigned to the hexagonal crystal system with two independent lattice constants $a = b$ and c. The interplanar distance in a hexagonal lattice is given by

$$d_{hkil} = \frac{1}{[(4/3a^2)(h^2 + k^2 + hk) + (1/c^2)l^2]^{1/2}}. \qquad (10)$$

For each crystal temperature, the angular differences $\Delta\psi_{hkil}$ therefore have to be measured for four different back reflections as listed in Table 1. This allows us to compose four different sets, each with three equations of type (9), yielding its own solution for the three free parameters a, c and d^* of the problem. An iteration method is used to solve these non-linear systems of equations.

From the four independent solutions, the averaged values of a and c and their standard errors are computed. The solution resulting from the combination of (0 0 0 30), $(2\,6\,\bar{8}\,20)$ and $(1\,6\,\bar{7}\,22)$ reflections is ignored, since it yields systematically significantly different values. This is attributed to the fact that the $(2\,6\,\bar{8}\,20)$ and $(1\,6\,\bar{7}\,22)$ atomic planes are almost parallel (only $\sim$7° apart; *cf.* Table 1) which, in combination with insufficient crystal quality, may cause a large error. Mean values and standard errors of a and c are given in Table 4 for different temperatures in units of λ_M and Å. The errors of a and c are primarily due to the averaging process, as described above. Other

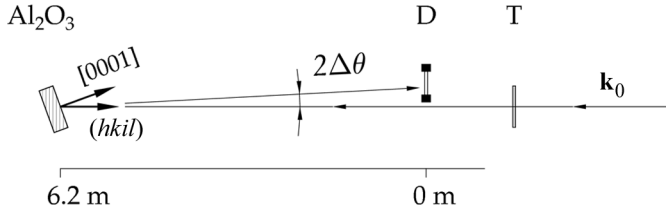

Figure 3
The scheme of the set-up for observation of backscattering of the Mössbauer radiation. An X-ray pulse after the high-heat-load monochromator (not shown) excites Mössbauer nuclei in the target T, which scatter delayed Mössbauer photons in the forward direction. D: avalanche photodiode; Al_2O_3: sapphire single crystal in a furnace on a four-circle goniometer.

Table 4
Lattice constants of Al_2O_3 in the temperature range 285.9–374.3 K.

T (K)	$\tilde{a}$ (λ_M)	$\tilde{c}$ (λ_M)	a (Å)	c (Å)	$\delta a/a$ (10^{-7})	$\delta c/c$ (10^{-7})
286.143 (8)	5.532056 (5)	15.101192 (2)	4.758977 (4)	12.990872 (2)	8.4	1.5
286.968 (8)	5.532080 (10)	15.101262 (5)	4.758998 (9)	12.990932 (4)	18.9	3.1
287.125 (8)	5.532083 (12)	15.101278 (6)	4.759001 (10)	12.990946 (5)	21.0	3.9
288.108 (8)	5.532106 (9)	15.101369 (5)	4.759020 (8)	12.991024 (4)	16.8	3.1
312.533 (9)	5.532822 (6)	15.103584 (2)	4.759636 (5)	12.992930 (2)	10.5	1.5
322.359 (9)	5.533110 (3)	15.104526 (1)	4.759884 (3)	12.993740 (1)	6.3	0.77
332.184 (9)	5.533428 (5)	15.105504 (2)	4.760158 (4)	12.994581 (2)	8.4	1.5
342.010 (9)	5.533741 (6)	15.106472 (2)	4.760427 (5)	12.995414 (2)	10.5	1.5
351.836 (9)	5.534064 (9)	15.107456 (3)	4.760705 (8)	12.996261 (3)	16.8	2.3
361.661 (9)	5.534379 (3)	15.108467 (1)	4.760976 (3)	12.997130 (1)	6.3	0.77
371.339 (10)	5.534699 (3)	15.109478 (2)	4.761251 (3)	12.998000 (2)	6.3	1.5
375.000 (10)	5.534768 (1)	15.109658 (1)	4.761310 (1)	12.998155 (1)	2.1	0.77
374.287 (10)	5.534804 (1)	15.109758 (1)	4.761341 (3)	12.998241 (1)	6.3	0.77

Table 5
Interpolation formulae for lattice constants of Al_2O_3 in the temperature range 285.857–374.287 K.

a (Å) $= \sum_{i=0}^{6} p_i (T[K])^i$	c (Å) $= \sum_{i=0}^{6} q_i (T[K])^i$
$p_0 = 16.59120$	$q_0 = 13.05720$
$p_1 = -0.2219875$	$q_1 = -8.895871 \times 10^{-4}$
$p_2 = 1.7306085 \times 10^{-3}$	$q_2 = 3.922787 \times 10^{-6}$
$p_3 = -7.1775855 \times 10^{-6}$	$q_3 = -7.039581 \times 10^{-9}$
$p_4 = 1.6704009 \times 10^{-8}$	$q_4 = 4.768008 \times 10^{-12}$
$p_5 = -2.0681896 \times 10^{-11}$	$q_5 = -5.355554 \times 10^{-19}$
$p_6 = 1.0643281 \times 10^{-14}$	$q_6 = 6.789434 \times 10^{-22}$

error sources, namely the uncertainties in T and λ_M, are about two orders of magnitude smaller.

A sixth-order polynomial is used to fit the experimental data. The polynomial coefficients are given in Table 5. One should note that these formulae are not suitable for extrapolation of the lattice constants outside the 285.9–374.3 K temperature range, and do not correspond to any theoretical model of thermal expansion. Mean values of the lattice constants and the polynomial fit are shown in Fig. 4.

With the formula given in Table 5 we can calculate at room temperature T = 295.65 K the following lattice parameters,

$$a = 4.759213\,(8)\ \text{Å}, \tag{11}$$

$$c = 12.991586\,(4)\ \text{Å}, \tag{12}$$

and linear thermal expansion coefficients

$$\alpha_a = 5.22 \times 10^{-6}\ \text{K}^{-1}, \tag{13}$$

$$\alpha_c = 5.92 \times 10^{-6}\ \text{K}^{-1}. \tag{14}$$

The relative deviations of the measured data from the values calculated with the interpolation formula are shown in Fig. 5. Large deviations of the data calculated by using the ignored combination of (0 0 0 30), (1 6 $\bar{7}$ 22) and (2 6 $\bar{8}$ 20) reflections are clearly seen here. Table 4 and Fig. 5 also reveal larger errors for a and c at lower temperatures. This is attributed to the stronger variation of the reference angle of the λ-meter, ψ_M, at the beginning of the experiments, where the measurements at lower temperature were performed (see Fig. 3 and §3.1).

The smaller relative error in the determination of c compared with that of the a lattice parameter is evidently due to the fact that all reciprocal lattice vectors of the back reflections used in the measurements are much closer to the c-axis of the crystal.

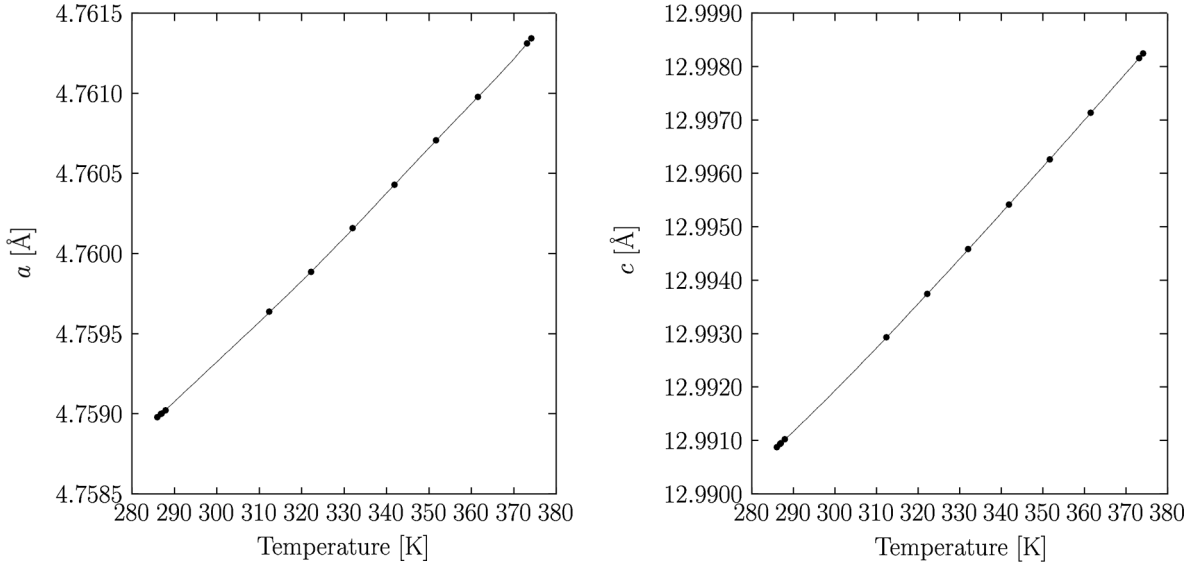

Figure 4
Lattice constants a and c of Al_2O_3. The solid line is a sixth-order polynomial fit with the parameters given in Table 5.

Table 6
Wavelengths λ and energies E of the ^{151}Eu, ^{119}Sn and ^{161}Dy Mössbauer radiation as determined by exact backscattering from an Al_2O_3 crystal.

The λ and E data for ^{57}Fe are from Shvyd'ko *et al.* (2000).

Isotope	$\tilde{\lambda}$ (λ_M)	$\delta\tilde{\lambda}/\tilde{\lambda}$ (10^{-7})	λ (Å)	$\delta\lambda/\lambda$ (10^{-7})	E (eV)
^{57}Fe	1.0	0	0.86025474 (16)	1.9	14412.497 (3)
^{151}Eu	0.66905978 (28)	4.1	0.57556185 (27)	4.7	21541.418 (10)
^{119}Sn	0.60355158 (43)	7.1	0.51920811 (39)	7.4	23879.478 (18)
^{161}Dy	0.56186073 (18)	3.3	0.48334336 (19)	4.0	25651.368 (10)

4.2. Wavelengths of the ^{151}Eu, ^{119}Sn and ^{161}Dy Mössbauer radiation

With the measured temperature dependence of the lattice parameters of sapphire (Tables 4 and 5), the crystal temperatures for backscattering of Mössbauer radiation (Table 3) and equations (10) and (6), it is now possible to determine wavelengths of the ^{151}Eu, ^{119}Sn and ^{161}Dy Mössbauer radiation. The results are presented in Table 6.

The major source of the errors for the $\tilde{\lambda}$ values are the uncertainties in the lattice parameters of sapphire. The uncertainty of λ and E includes additionally the uncertainty of λ_M.

Our results agree well with the Mössbauer energy values previously reported by Koyama *et al.* (1996) and Leupold *et al.* (1996) for ^{151}Eu, E = 21541.49 (16) eV and E = 21541.7 (5) eV, respectively, by Kikuta (1994) for ^{119}Sn, E = 23879.5 (5) eV, and by Koyama *et al.* (1996) for ^{161}Dy, E = 25651.29 (16) eV. The relative uncertainty of our data is smaller by more than one order of magnitude.

5. Discussion and conclusions

The newly proposed atomic-scale length standard, *i.e.* the wavelength of the ^{57}Fe Mössbauer radiation, was used to measure the lattice constants of Al_2O_3, as well as the wavelength of the Mössbauer radiation of ^{151}Eu, 57.556185 (27) pm, ^{119}Sn, 51.920811 (39) pm, and ^{161}Dy, 48.334336 (19) pm.

The advantages of the Mössbauer wavelength standard λ_M are its unique sharpness and easy reproducibility with a relative accuracy of at least 10^{-11}. With the advent of the third-generation synchrotron radiation facilities, brilliant sources of Mössbauer radiation have become available.

The relative experimental accuracy in the determination of the lattice constant c of Al_2O_3 is in the range 0.4–0.1 p.p.m. The relative accuracy in the determination of the lattice constant a is in the range 2–0.6 p.p.m. The relative accuracy in the determination of the wavelength of Mössbauer radiation is in the range 0.4–0.7 p.p.m.

The main factors which have deteriorated the accuracy were (i) the divergence of the beam (9 μrad instead of the expected 2 μrad), and (ii) crystal lattice defects in the Al_2O_3 sample. A perfect crystal would have allowed ten times more precise measurements.

All the measured values are given both in λ_M units and in metres. Therefore, a refinement of the λ_M value would allow one to recalculate all other values.

The measured wavelength of Mössbauer radiation could be used as a set of reference wavelengths in the hard X-ray range of the electromagnetic radiation spectrum, providing a uniquely small uncertainty and easy reproducibility.

The measured temperature dependences of the lattice constants of Al_2O_3 could be used in the design of high-energy resolution monochromators and analyzers, as the data obtained now allow one to predict more precisely Miller indices of back reflections and relevant crystal temperatures for desired X-ray energies.

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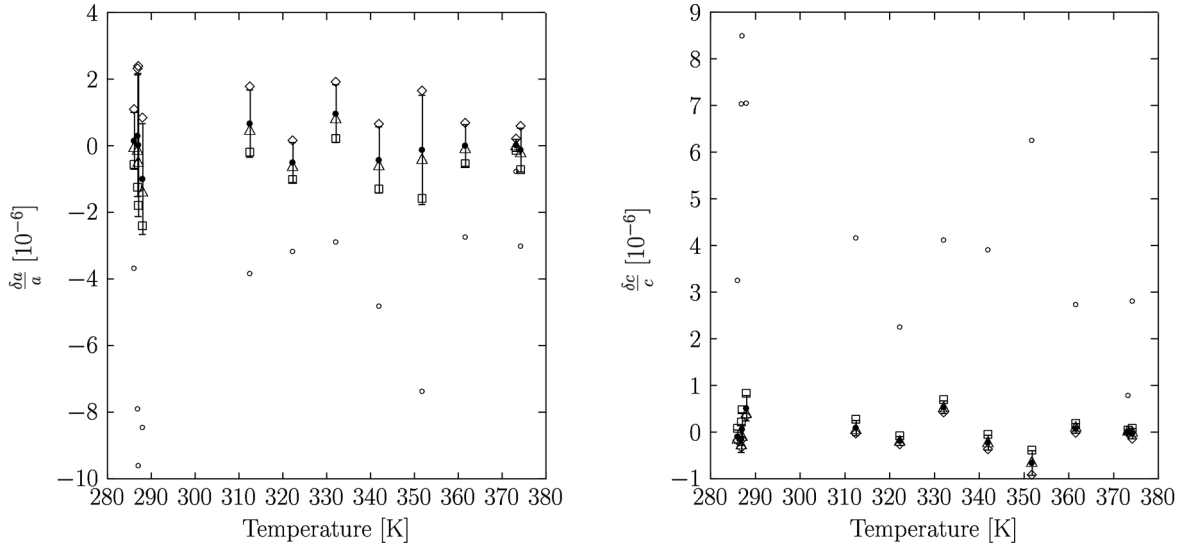

Figure 5
Relative deviation of the sixth-order polynomial fit (Table 5) from the a and c values evaluated from □: (1 3 $\bar{4}$ 28), (0 0 0 30), (1 6 $\bar{7}$ 22) back reflections; ◇: (1 3 $\bar{4}$ 28), (0 0 0 30), (2 6 $\bar{8}$ 20) back reflections; △: (1 3 $\bar{4}$ 28), (2 6 $\bar{8}$ 20), (1 6 $\bar{7}$ 22) back reflections; ○: (0 0 0 30), (1 6 $\bar{7}$ 22), (2 6 $\bar{8}$ 20) back reflections (ignored in the calculation of the average values). The average of the □, ◇ and △ values is shown by ●.

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References

Aldebert, P. & Traverse, J. P. (1982). *J. Am. Ceram. Soc.* **65**, 460–464.
Baron, A. Q. R. (2000). *Hyperfine Interact.* **125**, 29–42
Bearden, J. A. (1965). *Phys. Rev.* **137**, B455–461.
Brown, A. S., Spackman, M. A. & Hill, R. J. (1992). *Acta Cryst.* A**49**, 513–527.
Chen, W. M., McNally, P., Shvyd'ko, Yu. V., Tuomi, T., Lerche, M., Danilewsky, A. N., Kanatharana, J., Lowney, D., O'Hare, M., Knuuttila, L., Riikonen, J. & Rantamäki, R. (2001). *Phys. Status Solidi A*, **186**, 365–371.
CODATA (2000). *Rev. Mod. Phys.* **72**, 351–495.
Deutsch, M. & Hart, M. (1984). *Phys. Rev. B*, **30**, 640–642.
Deutsch, M. & Hart, M. (1988). *Phys. Rev. B*, **37**, 2701–2703.
Firestone, R. B., Shirley, V. S., Chu, S. Y. F., Baglin, C. M. & Zipkin, J. (1996). *Table of Isotopes.* New York: John Wiley.
Gerdau, E. & de Waard, H. (1999/2000). Editors. *Nuclear Resonant Scattering of Synchrotron Radiation*, Vol. 123–125. Oxford: Baltzer Science.
Hastings, J. B., Siddons, D. P., van Bürck, U., Hollatz, R. & Bergmann, U. (1991). *Phys. Rev. Lett.* **66**, 770–773.
Kikuta, S. (1994). *Hyperfine Interact.* **90**, 335–349.
Kirfel, A. & Eichhorn, K. (1990). *Acta Cryst.* **46**, 271–283.
Kissel, L. & Pratt, R. H. (1990). *Acta Cryst.* A**46**, 170–175. (Also available from http://www-Phys.llnl.gov/Research/scattering.)
Kissel, L., Zhou, B., Roy, S. C., Gupta, S. K. S. & Pratt, R. H. (1995). *Acta Cryst.* A**51**, 271–288.
Koyama, I., Yoda, Y., Zhang, X. W., Ando, M. & Kikuta, S. (1996). *Jpn. J. Appl. Phys.* **35**, 6297–6300.
Leupold, O., Pollmann, J., Gerdau, E., Rüter, H. D., Faigel, G., Tegze, M., Bortel, G., Rüffer, R., Chumakov, A. I. & Baron, A. Q. R. (1996). *Europhys. Lett.* **35**, 671–675.
Lewis, J., Schwarzenbach, D. & Flack, H. D. (1982). *Acta Cryst.* **38**, 733–739.
Lucht, M. (1998). MSc. thesis, Universität Hamburg, Germany. (Available from http://www.rrz.uni-hamburg.de/hfww/publications/diploma.html.)
Pinsker, Z. G. (1978). *Dynamical Scattering of X-rays in Crystals.* Berlin: Springer.
Schmid, F., Khattak, C. P. & Felt, D. M. (1994). *Am. Ceram. Soc. Bull.* **73**, 39–49.
Shvyd'ko, Yu. V. & Gerdau, E. (1999). *Hyperfine Interact.* **123**/**124**, 741–776.
Shvyd'ko, Yu. V., Gerdau, E., Jäschke, J., Leupold, O., Lucht, M. & Rüter, H. D. (1998). *Phys. Rev. B*, **57**, 4968–4971.
Shvyd'ko, Yu. V., Gerken, M., Franz, H., Lucht, M. & Gerdau, E. (2001). *Europhys. Lett.* **56**, 309–315.
Shvyd'ko, Y., Lerche, M., Jäschke, J., Lucht, M., Gerdau, E., Gerken, M., Rüter, H. D., Wille, H. C., Becker, P., Alp, E. E., Sturhahn, W., Sutter, J. & Toellner, T. S. (2000). *Phys. Rev. Lett.* **85**, 495–498.
Shvyd'ko, Yu. V., Smirnov, G. V., Popov, S. L. & Hertrich, T. (1991). *Pis'ma. Zh. Eksp. Teor. Fiz.* **53**, 69–73. [*JETP Lett.* (1991). **53**, 69–73].
Siddons, D. P., Hastings, J. B. & Faigel, G. (1988). *Nucl. Instrum. Methods*, A**266**, 329–335.
Tuomi, T., Naukkarinen, K. & Rabe, P. (1974). *Phys. Status Solidi A*, **25**, 93–106.
Xiaowei, Z., Yoda, Y. & Imai, Y. (2000). *J. Synchrotron Rad.* **7**, 189–195.
Yim, W. & Paff, R. (1973). *J. Appl. Phys.* **45**, 1456–1457.