Measurement of the \{220\} lattice-plane spacing of a $^{28}$Si x-ray interferometer

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Abstract

The spacing of the \{220\} lattice planes of a $^{28}$Si crystal, used to determine the Avogadro constant by counting silicon atoms, was measured by combined x-ray and optical interferometry to a relative accuracy of $3.5 \times 10^{-9}$. The result is $d_{220} = (192 014 712.67 \pm 0.67)$ nm, at 20.0°C and 0 Pa. This value is greater by $(1.9464 \pm 0.0067) \times 10^{-6} d_{220}$ than the spacing in natural Si, a difference which confirms quantum-mechanics calculations. This result is a key step towards a realization of the mass unit based on a conventional value of the Planck or the Avogadro constant.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

We participated in a project ending with an accurate measurement of the Avogadro constant \cite{1}, $N_A$, by counting the atoms in a silicon crystal. This could make it possible to realize the mass unit on the base of the mass of an atom \cite{2}. Since the molar Planck constant, $N_A h$, is known via the measurement of the Rydberg constant \cite{3}, this measurement will also lead to a value of the Planck constant, $h$, and, in turn, to a kilogram realization based on a conventional value of $h$.

The measurement equation is $N_A = n M / (\rho a^3)$, where $M$ is the molar mass, $\rho$ the density, $a^3$ the cubic unit cell volume and $n$ the number of atoms per unit cell. The lattice parameter $a$—that is, the unit-cell edge—is one of the quantities required to determine $N_A$. The most accurate way to measure it is by means of combined x-ray and optical interferometry, which was first demonstrated by Bonse and Hart \cite{4} in 1965 and soon applied by Deslattes \cite{5} to measure the lattice parameter of a Si crystal. Subsequently, scanning x-ray interferometry was improved step-by-step \cite{6–9} and the uncertainty of the lattice parameter of a number of Si crystals with a natural isotopic composition was reduced to $3 \times 10^{-8}$.

To bypass difficulties in measuring the molar mass of natural Si crystals \cite{3}, the $N_A$ measurement in \cite{1} relied on a crystal highly enriched with the $^{28}$Si isotope, whose lattice parameter had to be measured for the first time. In addition, since—in order to ensure continuity to mass metrology—the relative uncertainty of any kilogram realization and, in turn, of the $N_A$ determination must not exceed $2 \times 10^{-8}$, the uncertainty of the lattice parameter measurement had to be tenfold reduced to $3 \times 10^{-9} a$. To achieve this improvement in accuracy, we extended the measurement capabilities of x-ray interferometry to many centimetres \cite{10} and manufactured a $^{28}$Si interferometer with an unusually long analyser.

In this paper, the measurement of the lattice parameter of the $^{28}$Si crystal and the relevant error budget are described. Parallel surveys of lattice strain, carried out by means of phase-contrast x-ray topography at the INRIM, two-crystal Laue diffractometry at the National Institute of Standards and Technology (NIST, USA) \cite{11}, and a novel self-referenced lattice comparator at the National Metrology Institute of Japan \cite{12} found no evidence for crystal imperfections, thus confirming the significance of the measured value. The measured value was also connected to the lattice parameter of the natural Si reference-crystals of the PTB \cite{13} and the INRIM \cite{10, 14}. Eventually, the measurement result is compared with the value expected from quantum-mechanics calculations \cite{15, 16}.

2. Measurement method

2.1. Experimental apparatus

The combined x-ray and optical interferometer is shown in figure 1. It consists of three crystal blades, 1.20 mm thick,
so cut that the {220} planes are orthogonal to the crystal surfaces. The {220} diffracting planes were chosen on the basis of their greatest reflectivity. X-rays from a Mo K$_\alpha$ source are split by the first crystal and recombined, via two transmission crystals, by the third, called the analyser. As shown in figure 1, the interference pattern was imaged onto a multianode photomultiplier tube through a pile of eight NaI(Tl) scintillator crystals. The equivalent pixel size projected on the interferometer is $(1 \times 1.8)$ mm$^2$.

When the analyser is moved along a direction orthogonal to the {220} diffracting planes, a periodic variation in the transmitted and diffracted x-ray intensities is observed, the period being the diffracting-plane spacing. To cope with the highly demanding request of accuracy, the INRIM extended the crystal-displacement capabilities to 5 cm. This magnification made more numerous effects visible and reproducible. In addition, it allowed wider crystal parts to be surveyed, thus increasing confidence in the crystal perfection and in the mean lattice parameter value. The analyser movement is an extremely difficult task; it requires nanoradian attitude-control and picometre vibration and position controls. The analyser displacement and rotation are measured by optical interferometry; the necessary picometre and nanoradian resolutions are achieved by polarization encoding and phase modulation.

2.1. X-ray interferometer

The production of the $^{28}$Si crystal started with the isotope enriched Si$_3$ gas; subsequently, after conversion of the enriched gas into SiH$_4$, a polycrystal was grown by chemical vapour deposition. Eventually, a 5 kg $^{28}$Si boule was grown and purified by application of the float-zone technique. The pulling speed was so chosen as to reduce the self-interstitial concentration; no doping by nitrogen was applied. The growth axis was [100].

In order to exploit the large displacement capability, the PTB manufactured an interferometer with an unusually long analyser, which is shown in figure 2. To avoid lattice stresses, the surface damage produced by grinding must be removed by chemical etching; our choice was a cupric-ion etching because the amount of stock removal can be precisely controlled and it affords superior geometrical control than the usual HNO$_3$–HF one. However, because of etching anisotropy, the final crystal surfaces are quite rough; the influence of surface roughness on the lattice parameter measurement will be discussed in the next section.

The concentrations of carbon and oxygen in the interferometer crystals are extremely low [19], 1.07(10) \times 10^{15} \text{cm}^{-3} and 0.369(33) \times 10^{15} \text{cm}^{-3}, respectively. The concentration of vacancy-related defects is 0.33(11) \times 10^{15} \text{cm}^{-3}.

As shown in figures 1 and 2, the analyser embeds front and rear mirrors. To nullify the error due to the different ways the displacement is measured by the x-ray and optical interferometers, by projecting on the normals to the mirror and diffracting planes, these mirrors were accurately polished parallel to the {220} planes, to within 10 µrad in the worst uniformity and stability, the experiment is carried out in a thermo-vacuum chamber.

In practice, $d_{220}$ is determined by comparing the unknown period of the x-ray fringes against the known period of the optical ones. This is done by measuring the x-ray fringe fraction at the ends of increasing displacements $m\lambda/2$, where $m = 1, 10, 100, 1000, 3000$ and 30,000. The time required for counting each x-ray fringe is unacceptable. Therefore, we started from the approximation $\lambda/(2d_{220}) = n/m = 1648.28$ and measured the fringe fraction only at the displacement ends with accuracy sufficient for predicting the integer number of fringes in the next displacement over the increasing sequence. Consequently, the $\lambda/(2d_{220})$ ratio is updated and its accuracy increases at each step.

The least-squares method is applied to reconstruct x-ray fringes and to determine their phases at the displacement ends [18]. The input data are about 300 subsequent photon-counts made over 100 ms windows and at about 4 pm displacement intervals; a typical sample contains six x-ray fringes, covers a distance of 1.2 nm and lasts 30 s. Each $d_{220}$ measurement is the average of about nine values collected in measurement cycles during which the analyser is repeatedly moved back and forth along the selected displacement. The visibility of the x-ray fringes approached 50% with a mean brilliance of 500 counts s$^{-1}$ mm$^{-2}$. 

2.2. Measurement procedure

The measurement equation is $a = \sqrt{8}d_{220} = \sqrt{8}m\lambda/(2n)$, where $d_{220}$ is the spacing of the {220} planes, the $\sqrt{8}$ factor accounts for the different spacings and orientations of the {100} and {220} planes, and $n$ is the number of x-ray fringes observed in a displacement of $m$ optical fringes having period $\lambda/2$. The laser source operates in single mode and its frequency is stabilized against that of a transition of the $^{127}$I$_2$ molecule. This ensures the calibration of the optical interferometer with a negligible uncertainty. To eliminate the adverse influence of the refractive index of air and to ensure millikelvin temperature...
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Figure 2. Photograph of the \(^{28}\text{Si} \) analyser crystal on its silicon support. The crystal size is \((60 \times 14 \times 31) \) mm\(^3\), with a \((49 \times 1.2 \times 19) \) mm\(^3\) blade. The crystal temperature is measured inside the copper block.

The residual misalignment was measured with 2 \( \mu \)rad resolution. The analyser trajectory was sensed and controlled on-line to bisect the angle between these normals to within 5 \( \mu \)rad. Eventually, the measured \( d_{220} \) value was corrected for the remaining trajectory imperfections.

The symmetric analyser shape allows it to be reversed; measurements were carried out with the x-rays crossing the crystal in both directions so that surface effects, as well as others systematic effects, could be investigated.

3. Results

3.1. Phase-contrast topography

The analyser has been tested for the lattice perfection. To this end, \( d_{220} \) measurements were made over 1 mm displacements at 50 different subsequent analyser positions. X-ray intensities were recorded by means of a vertical pile of eight NaI(Tl) scintillator crystals. Hence, the data were processed to obtain a \( d_{220} \) value in \( 50 \times 8 \) pixels, \((1 \times 1.8) \) mm\(^2\) each. The relative \( d_{220} \) variations are shown in figure 3; figure 4 shows the relevant histogram. The obverse and reverse orientations correspond to the interferometer crystals mounted as they were in the boule and in a reversed arrangement.

3.2. Lattice-spacing measurement

Figure 5 shows the diffracting-plane spacing values measured along the line displayed in figure 3, which indicates the laser-beam propagation. These values are insensitive to Abbe’s error, an error due to parasitic rotations combined with an offset between the trajectories of the points sensed by the x-rays (located on the line in figure 3) and the laser beam (the impinging point on the front mirror). In addition to interpolating the measurement results to obtain the \( d_{220} \) values in the points having a zero Abbe’s offset, parasitic rotations were sensed and nullified on-line. The values in figures 3 and 5 are the averages of different surveys carried out between November 2009 and July 2010; the error bars indicate the standard deviations of the data sets.

The upper (obverse) plot of figure 5 shows an outlier, which survived to the averaging; it is also visible in the
corresponding panel of figure 3. As shown in the bottom (reverse) plot, it disappears when the analyser is reversed. Therefore, we inferred that it does not indicate an actual $d_{220}$ variation, but an apparent one. An explanation is a surface effect; the phase difference between the interfering x-rays, which is the basic measured quantity, records the crystal surface, as well as any extraneous material on it. Although this phase-contrast image is weaker by orders of magnitude than the lattice image, at the sensitivity level we are operating it could affect the measurement result. Because of the cupric-ion etching used to remove the grinding damage, the analyser surfaces display a texture with 100 µm periodicity and 10 µm peak-to-valley amplitude [14]. Since we surmised that the observed outlier originates from this texture or from a residual contamination, we removed this datum from any subsequent analysis.

Apart from this outlier, none of the measured $d_{220}$ values was exactly re-observed in different surveys. However, as shown in figure 6, a 61% correlation can be observed between the results of measurements made with the analyser mounted with the same orientation. This quantifies the measurement sensitivity and repeatability. In contrast, figure 7 shows that no overlapping is possible between the results of measurements made with the observe and reverse mounting of the analyser. Figures 6 and 7 evidence again the presence of surface effects: the measurements made with the same analyser orientation are correlated, but correlation is lost when the analyser is reversed. Among the many crystals we examined [10, 13, 14], this is the first one displaying a $d_{220}$ profile having flatness and smoothness only limited by the residual scattering of the data and by surface effects.

To acquire the mean lattice parameter of the analyser, the $d_{220}$ values measured along the lines displayed in figure 3 were averaged and the corrections listed in table 1 were taken into account. Measurements started in November 2009 and were repeated in May and July 2010; the results are compared in figure 8.

### 3.3. Measurement uncertainty

An exemplar error budget is given in table 1. A detailed analysis of corrections and of error contributions can be found in [10, 13, 14], which give also the results of test measurements aimed at establishing a firm link with the $d_{220}$ values of natural Si crystals used as input data for the calculation of a self-consistent set of values of physical constants [3]. In addition to the trajectory and Abbe’s errors already discussed in sections 2.3 and 3.2, we draw attention to a couple of points which deserve particular attention.

In the first place, it must be noted that the largest correction is due to the diffraction of the laser beam. At this level...
of accuracy, the relation \( \lambda = c/\nu \) between the wavelength and frequency of a plane wave (the symbols having the usual meanings) is not valid; energy disperses outside the region in which it would be expected to remain, wavefronts bend, and their spacing varies from one point to another and it is different from the wavelength of a plane wave. Fortunately, the relevant correction depends only on laser-beam divergence, not on specific characteristics of the beam, such as the intensity profile [17]. In July 2010, a preliminary checking of this result was made by replacing the fibre collimator with a new one. The beam divergence is the width of its angular power-spectrum and was measured with the aid of a converging lens. It changed from 0.170(8) mrad—the value relevant to all the previous measurements—to 0.189(9) mrad; consequently, the correction changed from the 7.26(65) \( \times 10^{-9} \) \( d_{220} \) value given in table 1 to 8.92(72) \( \times 10^{-9} \) \( d_{220} \). More important, a change of the laser beam-profile was detected. As expected and as figure 8 shows, the result of the 7 July measurement is consistent with the previous values, to within their measurement uncertainties.

In the second place, a new systematic effect became apparent. To avoid power dissipation inside the vacuum chamber and temperature gradients, the pointing system of the laser beam, including the electro-optical crystal for phase modulation, is outside the chamber, rigidly clamped to it. However, to cut off the vibrations of the vacuum chamber, the experiment platform inside the chamber rests on three O-rings. Owing to their limited stiffness, the hysteresis, and to the mass of the analyser carriage (about 2 kg), the analyser displacement causes random misalignment and a systematic tilt of about 200 mrad mm\(^{-1}\) between the laser beam and the optical interferometer. In this way, in addition to increasing noise and scattering of the measured values, the variation of the lengths of the optical paths of the laser beam through the interferometer causes a systematic error. A separate experiment quantified it as \((1.37 \pm 1.20) \times 10^{-9} \) \( d_{220} \). At present, we either corrected the measured values (from 2009/11/04 to 2010/05/05) or applied a feedforward compensation of the tilt by counter-rotating the platform (from 2010/05/10 onwards).

4. Discussion

The final value at 0 Pa and 20.0 °C,

\[
d_{220}^{(28Si)} = 192,014,712.67(67) \text{ am}, \tag{1}
\]

is the mean of the measurement results shown in figure 8. The relative uncertainty is 3.5 \( \times 10^{-9} \). To act with caution, the uncertainty of (1) is the mean uncertainty of each single measurement in figure 8, not the value reduced by the mean.

4.1. Accuracy assessment

To assess the accuracy of (1), in preliminary experiments, we remeasured \( d_{220} \) in the natural Si interferometers WASO4.2A [13] of the PTB and MO*4 [10] and WASO4 [14] of the INRIM. The \( d_{220} \) differences of the same WASO4.2A and MO*4 interferometers and a sample of the WASO4 boule were also measured by Laue diffractometry [20]. Hence, data analysis allowed the \( d_{220} \) differences of the MO*4 and WASO4.2A crystals with respect to the WASO4 one to be independently determined. Figure 9 compares the differences between the \( d_{220} \) values measured by combined x-ray and optical interferometry with those observed in the crystal comparisons. The \( d_{220} \) differences expected from the different impurity concentrations are also given. To within the relevant uncertainties, all the differences are identical. The discrepant \( d_{220} \) difference between the MO*4 and WASO4 interferometers predicted from the different impurity concentrations is due to the high and, presumably, inhomogeneous contamination of this crystal by carbon.

Point defects, mainly carbon, oxygen and vacancies, strain the crystal. The \( N_A \) determination required that the defect-concentration differences between the samples used for the lattice parameter and density measurements are accounted...
for [19]. Therefore, to extrapolate the measured value of the interferometer lattice parameter to the lattice parameters of the two $^{28}\text{Si}$ spheres used to determine $N_0$ [11], we registered the distance from the seed crystal, 306 mm, of the 50 mm line along which the measured $d_{220}$ values were averaged (in a direction transverse to the growth axis). Figure 10 compares the $d_{220}$ value given in (1) with the value at the same 306 mm axial position obtained by interpolating—according to a smooth polynomial model of the impurity concentrations—the values measured at the NIST [11] in samples cut at 176.5 mm, 302.0 mm and 420.5 mm distances from the seed crystal, and with different orientations of the $\{220\}$ planes. By observing that before the $d_{220}$ values could be compared the different point-defect concentrations in both the $^{28}\text{Si}$ and WASO04 boules—a sample of the WASO04 boule was the NIST’s transfer standard—had to be considered, figures 10 and 9 confirm the measurement consistency as well as the absence of undetected lattice strains.

### 4.2. Comparison with quantum-mechanics calculations

After extrapolation to an impurity-free crystal, the $^{28}\text{Si}$ lattice parameter is larger by 1.9464(67) $\times 10^{-6}a$ than the parameter of the natural Si crystal WASO04, similarly extrapolated to an impurity-free crystal [14].

The dependence on isotopic composition is a combined effect of thermodynamics and quantum mechanics [15, 16]. The interatomic distance minimizes the Gibbs free energy with respect to the cell volume. In addition to the elastic energy, the free energy depends on the phonon energy as well as on the entropy associated with temperature. While the elastic energy sets an equilibrium distance independent of nuclear mass, the phonon energy does not. Anharmonic effects imply a greater equilibrium distance and they cause thermal expansion. Since heavier isotopes have smaller phonon energy, they set a smaller distance. Entropy increases with temperature and has an opposite effect. At zero temperature, only the zero-point phonon energy survives so that $^{28}\text{Si}$ has the greater lattice parameter; this is a pure quantum-mechanical effect. When temperature increases, the lattice parameter difference decreases, as a consequence of the increasing entropy. At room temperature, the entropy contribution is roughly the same as that of the phonon energy and it halves the zero-temperature difference.

The result of quantum-mechanics calculations of the lattice parameter difference, $2.03 \times 10^{-6}a$, between $^{28}\text{Si}$ and natural Si [21] is in excellent agreement with the value we found.

### 5. Conclusions

In this paper the spacing of the $\{220\}$ lattice planes of a $^{28}\text{Si}$ crystal has been given with a relative uncertainty of $3.5 \times 10^{-9}$. The plane spacing was measured in a direction transverse to the crystal growth axis and we assumed that it is the same for the whole set of $\{220\}$ planes related by symmetry transformations, as it should be.

Strain and stress have been observed to lead to unequal values in different directions [22, 23], but, as discussed in the previous section and in [19], no hint of residual strain has been detected in the $^{28}\text{Si}$ boule [11]. In addition, the x-ray interferometer has been designed so as to minimize the self-weight deformation and the residual strain due to gravity has been calculated by the finite element method to correct the measurement result [24]. A novel two-crystal Laue diffractometer is being developed to compare the spacings of a set of $\{220\}$ planes and to check the unit-cell perfection.

Figures 6 and 7 show that the observation of minute residual strain, at the 1 nm m$^{-1}$ scale and below, is prevented by measurement noise and surface effects. Investigations are under way to increase the measurement resolution by an order of magnitude and to eliminate surface effects. These improvements aim at the observation of residual strain and the reduction of the measurement uncertainty to $10^{-9}d_{220}$.

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