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Author(s): Massa, E.; Mana, G.; Ferroglio, L.; Kessler, E. G.; Schiel, D.; Zakel, S.
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The lattice parameter of the $^{28}$Si spheres in the determination of the Avogadro constant

E. Massa†§, G. Mana†, L. Ferroglio†, E.G. Kessler‡, D. Schiel‡ and S. Zakel‡

† INRIM – Istituto Nazionale di Ricerca Metrologica, Str. delle Cacce 91, 10135 Torino, Italy
‡ NIST – National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899-1070 USA
§ PTB – Physikalisch-Technische Bundesanstalt, Bundesallee 100, D-38116 Braunschweig, Germany

Abstract. The Avogadro constant has been determined by atom counting in two enriched $^{28}$Si spheres. Atoms were counted by exploiting their ordered arrangement in the spheres and calculating the ratio between sphere and the unit cell volumes. This paper describes how the values of the sphere lattice-parameters and, consequently, their unit-cell volumes, were obtained.

PACS numbers: 06.20.-f, 06.20.Jr, 07.05.Kf

1. Introduction

We participated in an international project aimed at determining the Avogadro constant, $N_A$, by means of a highly enriched $^{28}$Si crystal. Isotope enrichment and crystal production were completed in 2007 and a 5 kg boule with an enrichment higher than 99.99% was made available for measurements [1]. As shown in Fig. 1, two slices were taken from the $^{28}$Si boule – whose centers are at 229 mm and 367.5 mm distance from the seed crystal – and shaped as quasi-perfect spheres. The atoms in two 1 kg quasi-perfect single-crystal Si spheres were counted by exploiting their ordered arrangement [2, 3]; consequently, the counting required the calculation of the ratio between the sphere and unit-cell volumes. To determine their lattice parameters and, consequently, their unit-cell volumes, an x-ray interferometer was manufactured from the material between the spheres, the spacing of its $\{220\}$ lattice planes was measured by combined X-ray and optical interferometry, the homogeneity of the boule lattice-parameter was checked by two-crystal Laue diffractometry, and the gradients of impurity concentrations were determined by infrared spectroscopy.

After briefly outlining the diffractometer and interferometer operations, this paper describes in detail the measurement results and gives the values of the boule lattice-parameter at the locations of the interferometer and the spheres.

§ To whom correspondence should be addressed (e.massa@inrim.it)
2. Two-crystal Laue diffractometry

Figure 2 shows the two-sources, two-crystals X-ray diffractometer made at the NIST for accurate comparison of the lattice parameter of highly perfect Si crystals [4]. An optical heterodyne interferometer is used to measure and control - by a combination of a stepping motor and a piezoelectric driver - the angular position of the transfer crystal with an uncertainty of 2 nrad. The crystal samples to be compared reside on a highly precise translation sled which makes a remote exchange possible. The crystals are mounted on mechanical flexures allowing approximate alignment of the crystal tilt around the diffraction vector. Piezoelectric tippers directly underneath the crystals ensure fine adjustment. Two {440} rocking curves are simultaneously recorded by rotating the transfer crystal while alternately blocking the sources. If the transfer and sample crystals have equal lattice parameters, then the two rocking curves peak at the same angular setting. However, if there is a difference, they will peak at different angles, the relevant difference being

$$\Delta \theta = 2(\Delta d/d) \tan(\Theta_B),$$

where $\Theta_B$ is the Bragg angle and the $\Delta d/d$ strain is the relative difference between the diffracting-plane spacing of the transfer and sample crystals. The transfer crystal serves as a reference only on short times. Actually, each sample is compared to this...
3. X-ray interferometry

The combined X-ray and optical interferometer of the INRIM is shown in Fig. 3. It consists of three crystals so cut that the \{220\} planes are orthogonal to the crystal surfaces. X rays are split by the first crystal and recombined, via two transmission crystals, by the third, called the analyzer. When the analyzer is moved along a direction orthogonal to the \(f_{220}\) planes, a periodic variation in the transmitted and diffracted X-ray intensities is observed, the period being the diffracting-plane spacing.

The analyzer embeds front and rear mirrors, so that its displacement is measured by optical interferometry; the necessary picometer resolution is achieved by polarization encoding and phase modulation. The laser source realizes the meter according to its definition; it operates in single-mode configuration and its frequency is stabilized against that of a recommended transition of the \(^{127}\text{I}_2\) molecule. To eliminate the adverse influence of the refractive index of air, the experiment is carried out in vacuum.

The relevant measurement equation is

\[
d_{220} = \frac{a}{\sqrt{8}} = \frac{m\lambda}{2n},
\]

where \(d_{220}\) is the spacing of the \{220\} lattice planes, \(a\) is the lattice parameter, and \(n\) is the number of X-ray fringes observed in an analyzer displacement of \(m\) optical fringes having period \(\lambda/2\).

The interferometer operation was extended to displacements of 5 cm. In order to exploit this ample displacement capability, the PTB manufactured an interferometer having an unusually long analyzer crystal (Fig. 3). This interferometer made more numerous systematic 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 value of the lattice parameter.
Table 1. Measured values of the $^{28}$Si $\{220\}$ lattice-plane spacing.

<table>
<thead>
<tr>
<th>position</th>
<th>$d_{220}$</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>INRIM</td>
<td>306</td>
<td>192014712.67(67)</td>
</tr>
<tr>
<td>NIST</td>
<td>306</td>
<td>192014712.75(1.19)</td>
</tr>
</tbody>
</table>

@ 20.0 °C and 0 Pa

4. Results

4.1. Lattice parameter of the $^{28}$Si crystal - X-ray interferometry

The $^{28}$Si X-ray interferometer was taken between the spheres and the lattice parameter was measured at the 306 mm distance from the seed crystal (Fig. 1). In order to ensure a reliable link between the measured value and the lattice parameter of natural Si, the $d_{220}$ spacing of the MO*4, WASO4.2A, and WASO04 natural crystals of INRIM and PTB were re-measured with the new apparatus [5, 6, 7, 8, 9]. Next, the $^{28}$Si interferometer was integrated in the experiment and the diffracting-plane spacing value given in table 1 was measured. The error budget of this measurement is given in [10]; additional details can be found in [5, 6, 7, 8, 9].

4.2. Lattice parameter of the WASO04 crystal

A sample of the natural Si WASO04 crystal, cut at a 143 cm distance from the seed crystal, has been used as a reference for the NIST measurement of the $^{28}$Si lattice-parameter by two-crystal Laue diffractometry. The WASO04 crystal was grown and purified by application of the float-zone technique by Wacker Siltronic in January 1995. It was doped with nitrogen to prevent precipitation of vacancies and self-interstitials; detailed information about the crystal characterization can be found in [8, 11]. The homogeneity of its lattice parameter was investigated by the PTB and NIST [12, 13]. Three X-ray interferometers were cut at 91 cm and 87 cm distances from the crystal seed. The measured values of the $\{220\}$ lattice plane spacing of these interferometers at the 22.5 °C temperature have been extrapolated to 20.0 °C by use of the thermal expansion coefficients given in [14]. The value of the $\{220\}$ lattice plane spacing of the NIST sample has been extrapolated from the value measured at the 87 cm position, by taking account of the different carbon, oxygen, and nitrogen concentrations in the WASO04 crystal. The results are to be found in table 2.

Table 2. Measured values of the WASO04 $\{220\}$ lattice-plane spacing.

<table>
<thead>
<tr>
<th>sample</th>
<th>position</th>
<th>$d_{220}$</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSSA</td>
<td>91</td>
<td>192.0143388(32)</td>
<td>[5]</td>
</tr>
<tr>
<td>WS04:INRIM</td>
<td>87</td>
<td>192.0143380(10)</td>
<td>[8]</td>
</tr>
<tr>
<td>GAMS6-I</td>
<td>87</td>
<td>192.0143380(10)</td>
<td>[9]</td>
</tr>
<tr>
<td>WS04:NIST</td>
<td>143</td>
<td>192.0143374(10)</td>
<td>this paper</td>
</tr>
</tbody>
</table>

@ 20.0 °C and 0 Pa
Table 3. Carbon, oxygen, and boron concentrations in the $^{28}$Si boule. The measurements carried out at the same axial coordinate have been averaged. The uncertainties do not include calibration; the relevant contributions are 6.4% (carbon), 8.4% (oxygen), and 8.2% (boron).

<table>
<thead>
<tr>
<th>position mm</th>
<th>$N_C$ $10^{15}$ cm$^{-3}$</th>
<th>$N_O$ $10^{15}$ cm$^{-3}$</th>
<th>$N_B$ $10^{15}$ cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>175.4</td>
<td>0.182(86)</td>
<td>0.196(13)</td>
<td>0.020(2)</td>
</tr>
<tr>
<td>180.8</td>
<td>0.179(86)</td>
<td>0.213(13)</td>
<td>0.020(2)</td>
</tr>
<tr>
<td>277.2</td>
<td>0.902(86)</td>
<td>0.318(13)</td>
<td>0.005(2)</td>
</tr>
<tr>
<td>303.9</td>
<td>1.000(86)</td>
<td>0.366(13)</td>
<td>0.003(2)</td>
</tr>
<tr>
<td>318.7</td>
<td>1.124(86)</td>
<td>0.391(13)</td>
<td>0.004(2)</td>
</tr>
<tr>
<td>416.2</td>
<td>2.645(86)</td>
<td>0.435(13)</td>
<td>0.129(40)</td>
</tr>
<tr>
<td>419.8</td>
<td>2.990(86)</td>
<td>0.440(13)</td>
<td>0.344(40)</td>
</tr>
</tbody>
</table>

4.3. Impurity concentration in the $^{28}$Si crystal

Atom counting presupposes a perfect and pure crystal. Our $^{28}$Si boule is dislocation free; it was purified by the float-zone technique, no doping by nitrogen was used, and the pulling speed was so chosen as to reduce the self-interstitial concentration. Point defects by carbon, oxygen, and boron atoms, as well as vacancy-related defects, strain the crystal; to apply the necessary corrections, the PTB measured their concentrations by infrared spectroscopy. Results are given in [3, 15] and are summarized in table 3 and Fig. 4. It must be noted that, to extrapolate the mean lattice parameter of the $^{28}$Si spheres, only the concentration differences between the different parts of the $^{28}$Si boule matter. The concentration of the vacancy-related defects was measured by positron life time spectroscopy. Since the measured concentration, $3.3(1.1) \times 10^{14}$ cm$^{-3}$, is similar to that found in the natural Si crystal WAS004 [16], the same uniformity of the defect concentration was assumed. Therefore, vacancy-related defects were not considered. The contamination by hydrogen was investigated by deep level transient spectroscopy, no contamination greater than the $2 \times 10^{13}$ cm$^{-3}$ detection limit was found.

We built a smooth model of the mean impurity-concentrations along the crystal axis by approximating them with low order polynomials, $c_C$ (carbon), $c_O$ (oxygen), and $c_B$ (boron). The measurement results, as well as the fit residuals, indicate the presence of short range concentration fluctuations, both in the transverse and axial directions.

Figure 4. Concentrations of carbon (blue), oxygen (red), and boron (green).
Therefore, only one measurement result for each axial position was considered and, as indicated in table 3, the results of measurements carried out in samples having the same axial coordinate have been averaged. For the same reason, the ordinary (non weighted) least-squares criteria was used to find the approximating polynomials. Since only the differences of the defect concentrations between the X-ray interferometer and the spheres are of interest, the uncertainties given in table 3, as well as the error bars in Fig. 4, do not include calibration. They show only the typical measurement repeatability and short-range fluctuations, determined from both measurements at the same axial coordinate and the fit residuals. Calibration and model uncertainties have been taken again into consideration when calculating the concentration differences of interest. This analysis confirms the concentration differences given in [3], which were independently obtained without averaging the measurement results and by taking into account the actual measurement uncertainties and Birge’s ratio.

The interpolating functions were added to build the relative lattice parameter differences with respect to an arbitrary reference

\[ \epsilon(z) = \epsilon_0 + \beta_C c_C(z) + \beta_O c_O(z) + \beta_B c_B(z), \] (3)

where \( z \) is a coordinate along the boule axis (Fig. 5). The additive parameter \( \epsilon_0 \) was introduced to fit this model to the experimental data. The relevant strain coefficients, \( \beta_C = -6.9(5) \times 10^{-24} \text{ cm}^{-3} \) (carbon), \( \beta_O = 4.4(2) \times 10^{-24} \text{ cm}^{-3} \) (oxygen), and \( \beta_B = -5.6(2) \times 10^{-24} \text{ cm}^{-3} \) (boron), were measured in purposely doped crystals and are given in [17].

4.4. Lattice parameter of the \( ^{28}\text{Si} \) crystal - Two-crystal Laue diffractometry

As it is shown in Fig. 1, three pairs of samples, of about \( (20 \times 12 \times 0.5) \text{ mm}^3 \), were cut from the \( ^{28}\text{Si} \) boule; they were taken at a distance from the seed crystal of 176.5 mm, 302 mm, and 420.5 mm (two samples from each position, at different distances from the boule center). Of each sample, the NIST measured the diffracting-plane strain in three different sample locations, with the samples mounted in both the obverse and reverse configurations. Therefore, twelve different measurements were
carried out and averaged at each axial location. Results are summarized in table 4, where the statistical contribution determined from the measurements at the same axial coordinate has been included in the uncertainty.

The measured strains and those calculated according to (3) are compared in Fig. 5. It is to be noted that no curve fitting has been made, but a constant has been removed from the NIST data to minimize their squared residuals with respect to the model (3). By taking the lattice parameter value at a distance of 306 mm from the seed crystal as a reference, the sphere strains were calculated both by (3) and by interpolating linearly the NIST data. Results are given in table 5, where the spectrometer-calibration and model contributions to the total uncertainty of the sphere-strain predicted by (3) have been included.

All strains were measured with reference to the spacing of the \{220\} lattice planes of the WS04:NIST sample, the absolute value of which is given in table 2. The model (3), with the \(\epsilon_0\) additive constant as a free parameter, was fitted to the data. Hence, the strain at the 306 mm location and 21.132 °C is

\[
\epsilon(z = 306 \text{ mm}) = 1.9518(33) \times 10^{-6}.
\]

The relevant \(^{28}\text{Si} \{220\}\) plane spacing, \(d_{220}(\text{WS04:NIST})\[1 + \epsilon(z = 306 \text{ mm})]\), is given in table 1. The thermal expansion coefficients of natural Si and \(^{28}\text{Si}\) used to trace back this value to 20.0 °C are given in [14] and [18].

<table>
<thead>
<tr>
<th>position (mm)</th>
<th>temperature (°C)</th>
<th>(\epsilon(z)) ((10^{-6}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>176.5</td>
<td>21.135(7)</td>
<td>1.9573(11)</td>
</tr>
<tr>
<td>302.0</td>
<td>21.133(6)</td>
<td>1.9577(22)</td>
</tr>
<tr>
<td>420.5</td>
<td>21.129(7)</td>
<td>1.9328(41)</td>
</tr>
</tbody>
</table>

\[\epsilon \leq 21.132 \, ^{\circ}\text{C}\]

**Table 4.** Lattice-parameter differences between the \(^{28}\text{Si}\) samples and the WS04:NIST crystal.

**Figure 6.** Comparison between the values of the \{220\} plane spacing at the 306 mm position of the \(^{28}\text{Si}\) boule measured by X-ray interferometry (INRIM) and two-crystal Laue diffractometry (NIST).
Table 5. Strain of the AVO28-S5 and AVO28-S8 spheres with respect to the lattice parameter of the X-ray interferometer.

<table>
<thead>
<tr>
<th></th>
<th>AVO28-S5</th>
<th>AVO28-S8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$10^{-9}$</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>INRIM</td>
<td>4.21(70)</td>
<td>−5.88(1.31)</td>
</tr>
<tr>
<td>NIST</td>
<td>5.68(1.10)</td>
<td>−7.85(2.46)</td>
</tr>
</tbody>
</table>

Table 6. Lattice parameter of the AVO28-S5 and AVO28-S8 spheres.

<table>
<thead>
<tr>
<th></th>
<th>AVO28-S5</th>
<th>AVO28-S8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>am</td>
<td>am</td>
</tr>
<tr>
<td>INRIM</td>
<td>543099624.0(1.9)</td>
<td>543099618.5(2.0)</td>
</tr>
<tr>
<td>NIST</td>
<td>543099625.0(3.4)</td>
<td>543099617.6(3.6)</td>
</tr>
</tbody>
</table>

$\theta$ 20.0 °C and 0 Pa

5. Conclusions

The lattice parameter values of the AVO28-S5 and AVO28-S8 spheres used in [2] to determine $N_A$ were obtained by extrapolating, according to the contamination concentrations, the value measured by the INRIM at the 306 mm location [10]. In table 6, they can be compared with the values obtained by interpolating the values measured by the NIST at the 176.5 mm, 302 mm, and 420.5 mm locations (table 4).

Figure 6 compares the $d_{220}$ values measured by the NIST and INRIM at the 306 mm distance from the seed crystal (table 1). Though the NIST value and its uncertainty depend on the INRIM measurement of the WAS004 lattice-parameter, the NIST and INRIM data have only a 21% correlation. In fact, though the measurement method is the same, most of the uncertainty contributions to the $\{220\}$ plane spacing of the crystals AVO28-XINT and WS04:NIST (from which the NIST value in Fig. 6 is derived) are independent. The 21% correlation arises from the corrections for diffraction of the laser beam (100% correlated) and the measurements of the crystal temperatures (50% correlated). By observing that – before the NIST and INRIM measurement results could be compared – the different point-defect concentrations along the axes of both the WAS004 and $^{28}$Si boules had to be considered, Fig. 6 confirms the consistency of all measurements as well as absence of undetected crystal imperfections.

Acknowledgments

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