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Determining the crystallographic orientation of Avogadro silicon spheres

Moreton Moore,[a]* Stephen Downes[b]* and David Bayliss[b]

[a]Department of Physics, Royal Holloway University of London, Egham, Surrey TW20 0EX, UK, and [b]National Physical Laboratory, Teddington, Middlesex TW11 0LW, UK. Correspondence e-mail: m.moore@rhul.ac.uk, stephen.downes@npl.co.uk

Highly polished spheres, manufactured from silicon single-crystal material, are used in the X-ray crystal density method (XCDM) to determine the Avogadro constant. If the measurement uncertainty associated with this method can be reduced to 0.01 p.p.m., it would be possible to redefine the SI unit of mass, the kilogram, in terms of a fixed number of atoms of a definite species. The spheres are manufactured with a nominal mass of 1 kg and nominal diameter of 90 mm and a surface roughness of 0.5 nm (peak to valley). A goniometer has been constructed to enable the crystallographic orientation of these spheres to be determined using the back-reflection Laue technique. Two spheres have been successfully orientated in this manner by identifying two orthogonal ⟨100⟩ directions.

1. Introduction

Knowledge of the crystallographic orientation of mechanically polished silicon spheres is needed to establish whether crystallographic direction influences (*a*) the thickness of the native oxide that forms after polishing and (*b*) the structure and depth of damage to the crystal lattice at the Si/SiO_2 interface induced by the polishing process. The characterization of the surface is an important step in providing a possible new definition of the kilogram.

2. A new definition of the kilogram?

The kilogram, *equal to the mass of the International Prototype of the Kilogram*, is the last of the seven base units of the Système International d'Unités (SI) to be defined by a physical artefact rather than derived from naturally occurring physical phenomena (Quinn, 1994–1995). A definition based on a physical artefact presents unique problems both in its maintenance and dissemination (Quinn, 1991), the most significant of which concerns the manner in which the International Prototype Kilogram 'K' ages. The stability of 'K', a cylinder of platinum–10% iridium alloy, and of the 90 national standard copies all made from the same type of alloy, is dependent on the accretion of surface contaminants (Davidson, 2001). Furthermore, the effect of cleaning (Girard, 1990) is to remove only those contaminants that are physisorbed to the surface (Cumpson & Seah, 1996). This has resulted in the mass of some copies increasing by as much 75 µg over the past 100 years (Girard, 1994) and compares poorly with an uncertainty of just a few µg achievable when comparing masses during the dissemination of the unit of mass to the user community. These concerns have led to several projects which aim to provide a new definition of the kilogram (Downes, 1998).

One possibility is to relate the kilogram to an atomic mass. The kilogram could be defined as $10^3 N_A u$, where N_A is the Avogadro constant and u the unified atomic mass unit. To make such a definition viable, the uncertainty with which N_A would need to be known must be reduced to 0.01 p.p.m. A direct value of N_A can be determined through the X-ray crystal density method, XCDM (Deslattes, 1994; Becker, 2001), where the lattice parameter a_0, density ρ and molar mass M of a single crystal are measured. For a perfect single crystal, composed of a single element with n atoms per unit cell, the Avogadro constant is given by the ratio of the molar volume V_{mol} to the atomic volume V_{at}:

$$N_A = \frac{V_{mol}}{V_{at}} = \frac{nM}{\rho a_0^3}. \quad (1)$$

Historically, silicon is chosen as the crystal material because it can be prepared in a form that is extremely pure with a near-perfect crystal structure (Zulehner, 1994). The following quantities are determined: (i) the volume occupied by a single Si atom; (ii) the macroscopic density of the same crystal; and (iii) the molar mass and, thus, the isotopic composition of the Si crystal (silicon has three stable isotopes, ^{28}Si, ^{29}Si, ^{30}Si).

For real crystals, the application of the XCDM and equation (1) requires the lattice parameter to be an invariant quantity of nature within the limits of the desired uncertainty, when the influence of residual defects and isotopic composition are accounted for (Becker, 2001). Combined optical and X-ray interferometers (Bonse *et al.*, 1971; Nakayama & Fujimoto, 1997) are used to determine the spacing of the (220) lattice planes. A crystal's molar mass is determined by absolute measurements of the isotopic abundances of its three stable isotopes. The abundance-ratio measurements are made by means of an isotope-ratio gas mass spectrometer, which is described in detail by De Bièvre *et al.* (1994).

The most accurate means by which the density of a crystal can be determined is by direct measurement of mass and volume (Fujii *et al.*, 1995). A sphere is an ideal shape for the measurement of its dimensions, and hence volume. It has no edges or corners that would make it vulnerable to damage and its volume can be determined by one parameter, its mean diameter. The mass of such artefacts must be comparable with the International Prototype Kilogram to facilitate their accurate weighing. Spheres are now manufactured for the

Avogadro Project with nominal diameters of 90 mm and asphericities of the order of 50 nm (Leistner & Giardini, 1994). Their deviations from roundness have a strong cubic symmetry that is correlated with crystallographic direction, resulting from different values of hardness (Collins *et al.*, 1997).

Knowledge of the composition and structure of the surface of Avogadro spheres is vital when making corrections to the measured volume and density. The mean diameter is determined by optical interferometric length measurements, whereby a sphere is placed within a quartz etalon and a light beam from a frequency-stabilized He-Ne laser is divided into two beams pointing at opposite ends of the interferometer. From the phase difference of the interfering beams, with and without the sphere in place, a diameter can be determined (Fujii *et al.*, 1995). The presence of a native oxide on a sphere's surface causes a phase retardation of the light beam on reflection from the oxide and a systematic difference between the observed and real diameters (Fujii *et al.*, 1999). Spectroscopic ellipsometry has been used to determine the oxide thickness on Avogadro spheres. A recent study (Kenny *et al.*, 1999) has suggested a dependence of oxide thickness on crystallographic orientation for such artefacts. Furthermore, measurements made with ion beam analysis of mechanically polished silicon substrates have shown damage to the crystal lattice at the Si/SiO_2 interface (Downes, 2001), which is dependent on crystallographic orientation. The optical constants of these damaged regions may be significantly different from those of the single crystal and cause an overestimation of the oxide thickness when interpreting the measured ellipsometric spectra. It is hypothesized by the authors that mechanically polished Avogadro spheres may also contain significant levels of damage at the Si/SiO_2 interface.

3. Experimental details

A three-stage goniometer has been assembled to accommodate Avogadro spheres. Accurate rotation about the vertical axis was achieved by an Apex goniometer, whilst rotation about two other axes (one of which being horizontal) was achieved by two Huber goniometers, one riding on the other (see Fig. 1). The Apex goniometer was arranged so that its rotation axis was intersected by the X-ray beam and was also aligned with the vertical diameter of the sphere. Eucentric positioning of the sphere with the uppermost goniometer was made through the sphere support, which was attached directly to a threaded collar. A mounting frame, which attached rigidly to the X-ray tube shield, enabled the collimator and film holder to be replaced with a sliding stylus to mark temporarily a sphere's surface *in situ*, once the desired orientation had been accurately established from Laue photographs. The X-ray collimator, or sliding stylus of the same diameter, could be placed in two V supports, one of which is visible on the left-hand side of the photograph (Fig. 1). In this way, X-rays were directed towards the centre of the sphere and the precise position of the point where the X rays were incident upon the sphere surface could be recorded.

Two spheres have been successfully orientated in this manner by identifying two orthogonal ⟨100⟩ directions using the back-reflection Laue technique. Agfa Strukturix D7 film (cut to 165 × 120 mm) was held in a light-tight plane-film holder, with its normal accurately set along the direction of the incident X-ray beam. The perpendicular distance between the film and the spot on the silicon sphere from which X-rays were reflected was measured as approximately 39 mm. This figure was later revised to 38.0 mm, once a perfectly symmetrical Laue pattern had been obtained, following careful angular adjustments to the sphere.

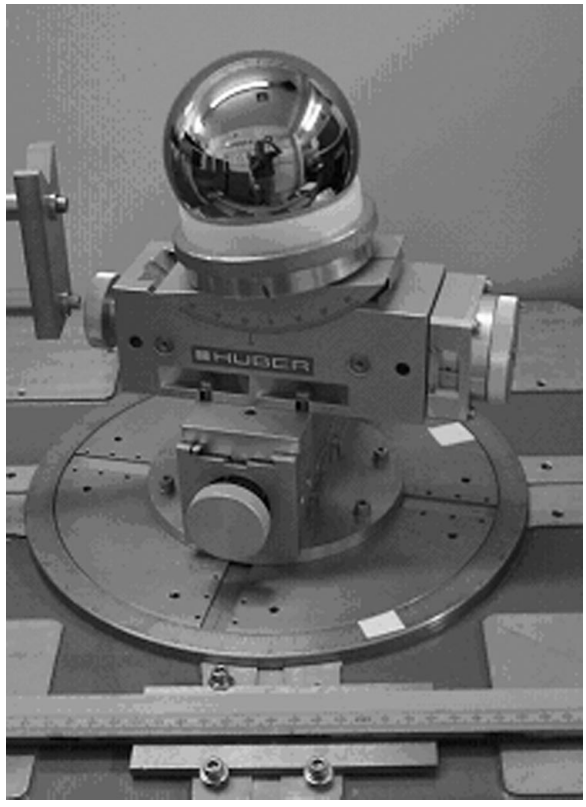

Figure 1
Avogadro sphere supported by the goniometer.

The X-ray beam consisted of collimated (1 mm) unfiltered copper radiation from a sealed tube, run at 40–45 kV and 15 mA from a 30-year-old Enraf–Nonius TN20 X-ray generator. Exposure times (2–3 h) were relatively long; but as only a few Laue photographs were required from only two silicon spheres, this was not a serious disadvantage.

Twelve major X-ray reflections were used for measurements: four 117, four 115 and four of 026 type, symmetrically disposed about the [001] tetrad axis. The radial distances of the 026 reflections measured from the centre of the Laue pattern were all 28.50 ± 0.25 mm. Taking the angle (36.87°) between the [026] and [001] directions as α, $\tan\alpha = 1/3$ and $\tan 2\alpha = 3/4$. Thus, the distance from the flat film to the nearest point on the sphere was (4/3)28.5 = 38.0 mm. The accuracy for the angular setting for the silicon sphere was estimated to be 7 min of arc (= 0.12°, being half the 2α variation measured from the film). The surface orientations were permanently marked at a later stage by laser etching.

The impact of crystallographic orientation on oxide thickness will now be investigated using spectroscopic ellipsometry. Ion beam analysis will be used to give additional information concerning the possibility of damage at the Si/SiO_2 interface arising from the mechanical polishing process.

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