

Reconciliation of *ab initio* theory and experimental elastic properties of Al_2O_3

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Ab initio calculations of the basic properties of solids have advanced significantly, and it is now possible to simply access a crystal structure database, and from the given constituent atoms and their positions, calculate reasonably accurate values for elastic constants and thermomechanical properties that may be derived from them. However, progress has been impeded by a unique discrepancy involving the sign of one of the elastic constants of an important material: Al_2O_3 . In this letter, this longstanding discrepancy is resolved with experimental measurements. © 2004 American Institute of Physics. [DOI: 10.1063/1.1773924]

One of the fundamental challenges in physics has been to calculate *ab initio*, beginning with just the constituent atoms, the basic properties of solids, such as the equilibrium positions of the atoms, the free energy, etc. A particular challenge for a basic calculation would be to determine, given the positions of the atoms, the derivatives of the free energy with respect to the atomic positions, i.e., the elastic constants and their higher-order derivatives. With advances in *ab initio* methods^{1–3} and the speed of computational hardware, it is now feasible to access a database of crystal structure and use computer software to obtain usable (i.e., reasonably accurate) values for all elastic constants and derivable thermomechanical properties that have not yet been experimentally measured. This possibility has been tested² on many materials for which experimental data are available, and the results indicate that such software has arrived. However, there has been one outstanding discrepancy: The theory and a longstanding experimental measurement⁴ yield opposite signs for an elastic constant of a basic and technologically important material, Al_2O_3 . In this letter, we review the theoretical calculation and report the results of a recent experimental measurement which at last resolves this discrepancy.

A contributor to the discrepancy is the crystal structure of Al_2O_3 , which is trigonal, with three-fold rotational symmetry about one axis and two-fold rotational symmetry about another, perpendicular axis. Somewhat contrary to this symmetry, elastic constants are defined in terms of a Cartesian coordinate system with axes x_1 , x_2 , and x_3 , and the values of the elastic constants may depend on how the Cartesian axes are aligned with the crystal axes. Prior to 1952, two alignments (referred to as obverse and reverse) were in use for trigonal crystals, and these gave different signs for one of the elastic constants. With standards set in 1949 (Ref. 5) and 1952 (Ref. 6), there is now no ambiguity as to how Cartesian coordinate axes are to be fixed to a trigonal structure: x_3 along the three-fold axis and one of the crystal's primitive lattice vectors must have a positive x_3 component, a negative x_2 component, and no x_1 component. Consequently, there should be no ambiguity in the values (and signs) of elastic constants. The current discrepancy between theory and ex-

periment is not simply a lack of vigilance in adhering to the standard, because in both the theoretical work and the experimental measurement, great pains were taken to follow the standard and document the steps. Furthermore, the magnitude of the elastic constant in question is sufficiently small so that the sign error could be attributed to an actual bias in the theoretical calculation. Thus, a verification of the theory required a resolution of the discrepancy.

For Al_2O_3 , there are six independent elastic constants, c_{11} , c_{33} [longitudinal distortions in the x_1 (or x_2) and x_3 directions], c_{44} (shear distortion in the x_1 or x_2 directions), c_{12} , c_{13} , and c_{14} (more complicated distortions). The discrepancy for Al_2O_3 involves c_{14} , which represents a “parallelogram” distortion in the x_2 – x_3 plane associated with a force in the x_1 direction acting on a surface element with a normal in the x_1 direction. The sign of c_{14} gives the sense of the distortion.

The original experiment which established the elastic constants of Al_2O_3 and the sign of c_{14} , was that of Wachtman *et al.*⁴ at what was then the United States National Bureau of Standards (NBS)⁷ in Gaithersburg, MD. The published paper indicated that the researchers selected the correct standard for the trigonal elastic constants and were well aware of the care required to insure that the crystal orientation, etc., adhered to the standard. Of course, since the NBS measurement, there have been other measurements of the elastic constants of Al_2O_3 , but while the magnitudes of the elastic constants agreed well, there was no independent determination of the sign of c_{14} ; either the later measurements were insensitive to the sign of c_{14} (as will be discussed later), and/or it was simply assumed that the NBS sign was correct. The NBS experiment will be discussed further after the present experimental measurement is described.

The experimental method used for the present measurements was resonant ultrasound spectroscopy (RUS).^{8–14} This method is based on the fact that a crystalline sample with a particular shape, size, and set of elastic constants, will oscillate at small amplitude in normal modes at particular natural frequencies. By measuring a sufficient number of the natural frequencies (with the number greater than the number of independent elastic constants), and knowing the shape, size, density, and crystallographic orientation of the sample, one may determine all of the independent elastic constants of the

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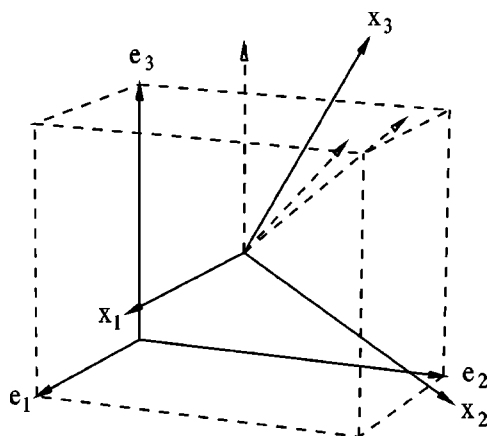


FIG. 1. The orientation of the crystallographic (x_1 , etc.) and sample (e_1 , etc.) unit vectors. The trigonal primitive lattice vectors are indicated as dashed vectors.

material. One uses a computer program to calculate natural frequencies from some assumed elastic constants, and then adjusts the elastic constants to acquire a “least-squares” fit to the experimentally measured natural frequencies. The high precision and accuracy of the RUS method has been demonstrated in many applications.¹⁴

For measuring the sign of c_{14} , the shape and crystalline orientation of the sample is important. The sample shape used in the present measurement of Al_2O_3 was a rectangular parallelepiped; for later discussion, the edges will be represented by orthogonal vectors e_1 , e_2 , and e_3 . If the crystallographic orientation of the sample is such that the vectors \hat{x}_1 , \hat{x}_2 , and \hat{x}_3 (which are fixed to the crystal structure as previously discussed) are parallel to the edges, then it is impossible to determine the sign of c_{14} ; that is, either sign of c_{14} would give the same set of natural frequencies. In order to determine the sign of c_{14} , neither \hat{x}_2 nor \hat{x}_3 may be parallel to any edge. Using the forward calculation, it was found that aligning \hat{x}_1 along e_1 and rotating \hat{x}_3 away from e_3 by an angle of 30° about \hat{x}_1 would yield the greatest difference in the natural frequencies for the two different signs of c_{14} . This requirement for nonparallel orientation also applies to a pulse-echo measurement (as for the NBS measurement); in this case, the sign of c_{14} is most readily determined if the \hat{x}_2 and \hat{x}_3 axes are at 45° from the direction of propagation of the pulse. In either case, the sign which one would obtain for c_{14} depends on exactly how the crystallographic axes are oriented; thus great care must be taken in orienting and preparing a sample. An illustration of the 30° orientation discussed above is shown in Fig. 1.

The sample used in the present experiment was 99.9% pure synthetic sapphire, obtained commercially.¹⁵ The as-obtained sample had opposite faces which were normal to the crystal \hat{x}_3 axis to within $\pm 1^\circ$. The sample was scratched in one corner for reference in subsequent orientation and handling. At each step in the sample preparation, sketches of the sample and relevant environment were made so that there could be no question as to the final orientation of the crystal axes (\hat{x}_1 , etc.) relative to the sample edges (e_1 , etc.). Steps with sketches included: (a) The mounting of the sample for Laue backreflection (for determining the direction of the \hat{x}_1 and \hat{x}_2 axes) together with the orientation of the recording film; (b) the use of a computer-graphic program for calculating the Laue backreflection pattern and visualizing simulta-

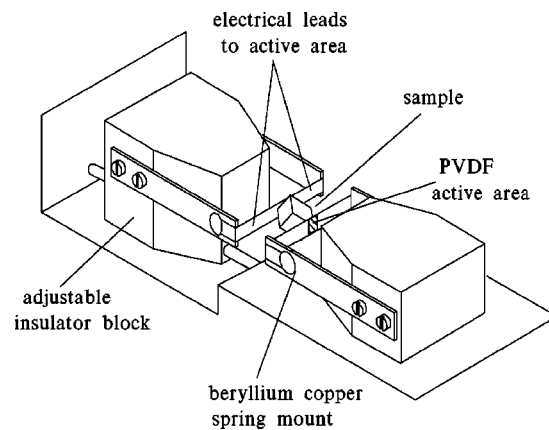


FIG. 2. The apparatus for making RUS measurements on the crystalline samples of Al_2O_3 , polished to rectangular parallelepipeds.

neously the positions of the Al and O atoms in a primitive unit cell, the unique orientation of the \hat{x}_i axes with the atoms, and the resulting Laue pattern as it would appear on the recording film; (c) cutting the sample so as to align the final e_1 with \hat{x}_1 ; (d) mounting the sample on a 30° wedge to produce the rotation about the \hat{x}_1 axis; and (e) polishing the sample faces so that the angle between \hat{x}_3 and e_3 was 30° while e_1 remained along \hat{x}_1 . The final dimensions of this sample were $0.729 \times 1.067 \times 0.836$ mm (± 0.001 mm). A second sample, with dimensions of $0.765 \times 1.032 \times 0.810$ mm (± 0.001 mm), was prepared in a similar fashion, but with an initial rotation of 86° about the \hat{x}_3 axis; this gave a diminished dependence on the sign of c_{14} , but provided a clear test of the data analysis and a means of corroborating the results from the first sample. In all relevant steps, the signs of the rotation angles were carefully noted.

The apparatus for making RUS measurements on the samples is illustrated in Fig. 2.¹² In the illustration, a rectangular parallelepiped sample is supported by transducers at diametrically opposite corners. One transducer excites the vibration of the sample, and the other monitors the sample response and detects resonance frequencies, which correspond to the natural frequencies of the sample.

The measured natural frequencies were analyzed in the standard manner for RUS, with the elastic constants adjusted so that the calculated frequencies provide a least-squares fit to the measured frequencies. For each sample, the fit included the frequencies of the lowest modes, up to a point where the signal-to-noise reduced the precision in determining the natural frequency; for the first sample, the lowest 15 modes were used, and for the second sample, 16 modes were used. By adjusting the elastic constants for each sample, all of the included frequencies could be fit to within a few tenths of a percent. The resulting elastic constants which provided the least-squares fit to the measured frequencies are shown in Table I.

The first two lines in Table I are for the first and second samples, respectively, and the third line gives the difference in percent. The fourth line gives the averages for the two samples, and may be taken as the final results of the experimental measurement; the percents in the third line may be taken as a good representation of the accuracy of the results, which is limited primarily by the measurements of the sample dimensions and the angles relating the crystal axes to the sample edges. (The stability of the method for determin-

TABLE I. Experimental and theoretical values of the elastic constants of Al_2O_3 , and percent differences. The literature value of c_{14} has a sign correction.

Elastic constant	c_{11}	c_{33}	c_{44}	c_{12}	c_{13}	c_{14}
Sample 1 (10^{11} Pa)	4.970	5.023	1.474	1.622	1.149	0.224
Sample 2 (10^{11} Pa)	4.980	5.043	1.473	1.632	1.160	0.226
Difference (%)	0.2	0.4	0.1	0.6	0.9	0.8
Average (10^{11} Pa)	4.975	5.033	1.474	1.627	1.155	0.225
Literature ^a (10^{11} Pa)	4.973	5.009	1.468	1.628	1.160	0.219
Difference (%)	0.0	0.5	0.4	-0.1	-0.5	2.8
Theory (10^{11} Pa)	4.950	4.860	1.480	1.710	1.300	0.200
Difference (%)	0.5	3.4	-0.4	-5.1	-12.6	11.2

^aSee Ref. 16.

ing the elastic constants was tested by repeating the process with different experimental frequencies removed from the fit; at worst, c_{12} and c_{13} varied by less than 4%.) The sign of the elastic constant c_{14} was clearly positive for both samples. The fifth line in Table I presents representative values of the elastic constants of Al_2O_3 taken from the existing literature,¹⁶ and the sixth line presents the percent difference with the experimental results of this letter. For this comparison, the sign of the literature value of c_{14} has been changed. Except for this sign, the experimental results are in excellent agreement. The last two lines of Table I show the values of the elastic constants of Al_2O_3 determined with the *ab initio* theory and the percent difference with the experimental results of this letter.

At this point, one can only speculate about an error in the determination of the sign of c_{14} in the NBS experiment.

The acoustic measurements and the x-ray measurements were made in two separate laboratories, and this may have led to some handling or communication error. In any case, the results of the theory, which has given good agreement with other trigonal materials, and the two samples measured here, have now removed the discrepancy.

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