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LATTICE SPACINGS IN CLEAR CRYSTALLINE QUARTZ AND THEIR VARIABILITY

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Although quartz has been widely used as a standard substance for the calibration of x-ray diffraction cameras and, to a lesser extent, for admixture with specimen materials in routine x-ray analysis, it appears that no fully indexed list of its lattice spacings has yet been published. The purpose of this note is (*a*) to present such a list of spacings, and (*b*) to discuss its reliabillty for calibration purposes in the light of a recently observed variability in the properties of quartz.

Attention was first drawn to variations in the lattice-parameters of clear crystalline quartz by the author (Keith, 1950) who, on the basis of a limited number of accurate measurements, suggested that they are more likely to be caused by impurities than by some form of lattice defect. More extensive researches have since been carried out on the variable behavior of large numbers of quartz samples in the neighborhood of the $\alpha \rightleftharpoons \beta$ inversion temperature (Keith and Tuttle, 1952; McDowell and Vose, 1952; Fieldes, 1952; and Sabatier, 1953) and also on variations in lattice spacings (Keith and Tuttle, *loc. cit.*); these have yielded results which agree well with earlier work, and which support the view that impurities are primarily responsible for the observed variations. In view of this agreement and of the considerable interest now shown in the properties of quartz, a brief discussion of the variability of its lattice-parameters—with particular reference to the quartz calibration standard—will now be given.

Bradley and Jay (1933) were the first workers to realize the practical advantage of establishing the lattice-parameters of clear quartz as a standard with which other lattice spacings may be compared experimentally, and they therefore tabulated values of the Bragg angles observed for some fifteen high angle reflections with CuK_α radiation. Lipson and Wilson (1941) later determined the lattice-parameters of one particular quartz specimen with greater accuracy (1 part in 10^5 relative to Siegbahn's values of the characteristic x-ray wave-lengths), and then revised

the existing table of Bragg angles accordingly. The possible occurrence of appreciable variations in the lattice spacings of different samples of mineral quartz was not, apparently, considered seriously by these authors: it seems likely that they relied upon the results of the measurements made by Bradley and Jay, on two clear and two slightly contaminated colored quartzes, as having established an adequate degree of constancy in the lattice-parameters.

However, it was later pointed out by the author (*loc. cit.*) that the method adopted by Bradley and Jay, which depended upon the assumption of a constant and slightly incorrect value for the axial ratio (c/a), would have tended to obscure rather than bring to light, any slight varia-

TABLE 1

Sample (all at 18° C.)	"a" Angstroms	"c" Angstroms	Axial Ratio c/a
Brazilian quartz	4.91248_8	5.40422_7	1.10010
Synthetic quartz (Grown at 292° C.)	4.91312_3	5.40471_3	1.10006
Synthetic quartz (Grown at 369° C.)	4.91274_2	5.40442_5	1.10008
Synthetic quartz (Grown at 388° C.)	4.91263_6	5.40439_6	1.10010

tions which may have existed. Being led by indirect evidence to suspect the reliability of the quartz calibration standard for very accurate work, he used a 19 cm. powder camera, which had been calibrated by two independent direct methods, in order to determine the lattice-parameters of a very large single crystal of Brazilian quartz, and also of three synthetic samples grown at different temperatures. These measurements, in which an accuracy of 1 part in 10^5 was attained, revealed variations in the lattice-parameters of at least 1 part in 10^4; and gave results for the Brazilian quartz which were considerably smaller than those published by Lipson and Wilson but which agreed moderately well with Bradley and Jay's values. Analysis of these results, which are tabulated in Table 1, indicates a progressive decrease in the axial ratio as the lattice parameters increase. The significance of this variation becomes at once apparent if the differences in the lattice-parameters of the various samples, taken in pairs, are used to derive values for the ratio

$$\left(\frac{\Delta a}{a} \Big/ \frac{\Delta c}{c}\right),$$

of which the mean is found to be 1.39 (neglecting pairs of parameters not

different by more than the experimental error). Inclusion in this scheme of Bradley and Jay's and of Lipson and Wilson's figures for the lattice-parameters increases the mean ratio to 1.70, which differs by only 30% from the known ratio $(S_{11}/S_{33}) = 1.307$ of the isothermal strain components, or moduli of compliance, of quartz (Cady, 1946). The interpretation of the results which immediately suggests itself is one in terms of the distortion of the lattice by impurities. It is known (Bragg and Gibbs, 1925) that fairly wide channels, which are parallel to the optic axis, exist in the quartz lattice; these may account for the large observed ratio of the relative increments in lattice-parameters, since it is probable that their influence would be such as to cause any stresses, set up by impurity atoms or ions imprisoned within the lattice, to have a larger effect in the plane normal to the optic axis than in the direction parallel to it. It is implied in this interpretation that the impurities normally found in quartz tend to increase its lattice-spacings, a result which would be expected regardless of whether the impurities are accommodated interstitially or substitutionally (as a solid solution), the radius of Si^{4+} ion being smaller than that of any other ion likely to replace it. On this basis, the Brazilian quartz which was studied would seem to be of fairly high purity, having lattice-parameters smaller than those given by Lipson and Wilson, and smaller than almost all other quoted values.

In their recent paper, Keith and Tuttle have listed the spacings of the (234) planes of some twenty quartz specimens of diverse origins, and these show considerable variations approaching, in a few cases, 1 part in 10^3. Concerning their results it is significant that:

(*a*) the lowest spacing which they record (for an unspecified temperature) is only 1 part in 2×10^4 larger than that obtained by the author for Brazilian quartz at 18° C.,

(*b*) the spacing recorded for a synthetic sample, not believed to contain any marked impurity, agrees extremely well with the author's values for similar synthetic samples, and

(*c*) all the samples known to be impure (notably germanium-bearing synthetic crystals) have spacings considerably larger than the majority of other samples, and they also exhibit anomalous inversion temperatures.

From this evidence it seems reasonable to conclude (i) that it is correct to attribute the variability of the lattice-parameters of quartz to the presence of impurities as has previously been done by Keith and Tuttle and by the author, and (ii) that the lattice spacings determined for the large single crystal of Brazilian quartz are probably very close to the correct values for pure uncontaminated material. The well-known reluctance of crystals to maintain relative perfection and grow to large

sizes in the presence of impurities, and also their tendency to reject impurities during growth, would support the latter conclusion.

For the calibration of x-ray diffraction cameras, the use of fragments of large single crystals of clear quartz is advisable and, even then, the reliability of the method is limited to an accuracy of about 0.01%. Where

TABLE 2. LATTICE SPACINGS OF QUARTZ AT 18° C.

Index $hk \cdot l$	Spacing Å	Relative Intensity	2θ	Index $hk \cdot l$	Spacing Å	Relative Intensity	2θ
100	4.2544	80	20.862	402	.98967	20	102.209
101	3.3428	100	26.526	115	.98930		102.262
110	2.4563	60	36.550	313	.98705	20	102.587
102	2.2809	60	39.474	304	.97819	15	103.890
111	2.2361	50	40.298	230	.97602	15	104.217
200	2.1272	60	42.458	231	.96047	30	106.634
201	1.9794	50	45.802	232	.91796	10	114.088
112	1.8176	80	50.146	403	.91587	20	114.492
202	1.6714	40	54.882	411	.91497	10	114.668
103	1.6588	20	55.336	224	.90877	10	115.858
211	1.5412	70	59.970	215	.89703	20	118.334
113	1.4526	20	64.046	314	.88873	15	120.152
300	1.4182	10	65.792	106	.88118	5	121.880
212	1.3818	40	67.756	412	.87800	15	122.632
203	1.3747	40	68.154	305	.85962	5	127.284
301	1.3717	30	68.324	116	.84564	5	131.246
104	1.2893	30	73.370	501	.84051	3	132.813
302	1.2557	40	75.672	404	.83570	3	134.346
220	1.2281	30	77.686	206	.82941	20	136.458
213	1.1996	30	79.898	413	.82523	20	137.935
221	1.1976	10	80.056	330	.81875	10	140.360
114	1.1838	30	81.182	502	.81159	40	143.268
310	1.1800	40	81.500	225	.81138		143.358
311	1.1528	30	83.850	331	.80951	20	144.166
312	1.0814	40	90.840	240	.80399	30	146.681
400	1.0635	10	92.814	315	.79701	20	150.222
105	1.0476	20	94.656	241	.79524	10	151.196
401	1.0436	20	95.136	234	.79117	40	153.588
214	1.0344	25	96.256	216	.78582	20	157.151
223	1.0147	25	98.768				

greater accuracy than this is not required, as is generally the case, quartz calibrations are very convenient, and the inclusion of further relevant data may well be of assistance to other workers.

The spacings given in the Table 2 were determined for the sample of Brazilian quartz mentioned above. They refer to 18° C., are expressed in Angstrom units (relative to the following wavelengths CuK_{α_1}

$= 1.540501$ Å, $CuK_{\alpha_2} = 1.544345$ Å, $CuK_{\alpha} = 1.541782$ Å), and have been corrected for eccentricity and absorption errors; they are given to five significant figures which corresponds to the limit of their probable accuracy when applied to quartz samples chosen at random. The relative intensities of the x-ray reflections are approximate, having been estimated visually from a powder photograph. A table of values of 2θ is also included, where θ is the Bragg angle for the reflection of CuK_{α_1} radiation by a given lattice plane.

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Note by G. W. Brindley

Dr. H. D. Keith's statement that "no fully indexed list of its lattice spacings has yet been published" requires modification in view of the recently issued *A.S.T.M.* x-ray index card No. 5-0490 which contains accurate indexed data for quartz obtained by Swanson and Fuyat (*NBS circular* **539**, Vol. III, 1953) who give the lattice spacings a 4.913, c 5.405 Å at 25° C. relative to λ 1.5405 Å (CuK_{α_1}). This, of course, does not detract from Dr. Keith's discussion of the accuracy of quartz spacing determinations and of their suitability for calibrating x-ray diffraction cameras.

Note by M. L. Keith

The small sample of quartz received from Dr. H. D. Keith has a simple, sharp inversion (H 573.4°, C 573.3°). The thermal record shows no evidence of multiple or complex inversion.

Tuttle and I found growth zoning and resultant complex inversion to be common in samples from Brazilian crystals; of course, recognition of growth zoning by thermal methods requires a sample representative of all zones, ideally a granular sample prepared by crushing a slice cut normal to the c axis.