Selection of W $K\alpha_1$ as the X-Ray Wavelength Standard

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Precision measurements have shown that the x-unit scale of x-ray wavelengths based on Mo $K\alpha_1 = 707.831$ xu is about 20 ppm smaller than that in general use for Cu $K\alpha_1$ and longer wavelengths, and for substantially all crystal parameters. Furthermore, the conversion from the Cu $K\alpha_1 = 1.537400$ kxu to Å has been increased from 1.00202 to 1.002056±5 ppm. New techniques permit wavelength measurements to be made with relative probable errors of ±1 ppm. New wavelength and crystal-parameter tables are now necessary, and this plus the newly developed precision technique provides the opportunity for introducing an x-ray wavelength standard. In an investigation to select the best wavelength to be designated as the standard, the following studies have been carried out: relative measurements of five wavelengths with five crystals, employing a least-squares adjustment; γ-ray study of single-crystal diffraction patterns and the use of a γ-ray wavelength as a standard; crystal imperfections and their effect on wavelength measurements; effect of chemical impurities on grating constants; and redetermination of the absolute wavelength scale. The requirements of a standard are analyzed and the advantages of the W $K\alpha_1$ line listed. Its wavelength is 0.209010 0 Å±5 ppm on the absolute scale, and without error as the designated standard. With this standard, new wavelength tables (separate publication) have been prepared, which include a large number of new measurements of secondary wavelength standards used as reference lines in many original measurements. Probable errors on both the relative and the absolute scale have been included.

INTRODUCTION

THE relative and absolute scales of x-ray wavelengths and lattice parameter values have recently[1-3] been revised by several times the previously estimated probable errors. In a precision measurement[1] of five x-ray wavelengths with five crystals, it was shown that the Mo $K\alpha_1$ and shorter wavelengths were on a scale approximately 20 ppm less than that of the Cu $K\alpha_1$ and Cr $K\alpha_2$ wavelengths. New measurements[2-4] of the absolute wavelengths of x rays showed that the previously adopted $\lambda_g/\lambda_s = \Lambda$ of 1.00 202±10 ppm should be increased to 1.002056±5 ppm (both probable errors), when measured with respect to the Cu $K\alpha_1$ = 1.537400 kxu. This new value of Λ and the above wavelength ratio experiments[1] indicate that most previously published[5] x-ray wavelengths of less than 1000 xu, which in general were measured relative to the Mo $K\alpha_1$, require the conversion factor $\Lambda = 1.00076$, whereas the longer wavelengths and most crystal dimensions require the factor $\Lambda = 1.002\ 056$.

The major part of the above discrepancies does not lie in the lack of rigor in the definition[6] of the xu (by the calcite d_∞ at 18°C = 3029.45 xu), but rather in errors in the measurement of the Bragg angle for the Mo $K\alpha_1$ line,[1] new wavelength conversion factor measurements,[2,3] and corrections to older measurements of the conversion factor for Lamb shift.[4] In a recent study[3] of selected calcite crystals, the Bragg angle θ for Cu $K\alpha_1$ was measured in the third order for seven samples. An eighth sample was excluded for the present comparison, since it was known to contain an abnormally high percentage of impurities and gave a low value of d_∞. The average third-order θ reduced to 18°C was 49°34′23.9″. If we combine this with the xu definition $d_\infty = 3029.45$ xu, we obtain

$$\lambda_{\text{Cu } K\alpha_1} = 1537.395 \text{ xu},$$

compared with Siegbahn's[7] recommended value of 1537.396 xu. Thus these seven crystals average very close to those used in the Siegbahn laboratory. However, measurements[8] in the Uppsala laboratory on the Mo $K\alpha_1$ line with some of the same crystals which gave Cu $K\alpha_1 = 1537.396$ xu resulted in a wavelength of the Mo $K\alpha_1 = 707.831$ xu, whereas our use of the above seven calcites for measuring the Ag $K\alpha_1$ and the measurements[1] of five wavelengths with five crystals are all consistent with a value of Mo $K\alpha_1 = 707.843$ xu if the Cu $K\alpha_1$ is taken as 1537.396 xu. Previous measurements in other laboratories[9-13] have also indicated that the Mo $K\alpha_1 = 707.831$ xu was in error on the basis of average calcite $d_\infty = 3029.45$ xu.

Wavelength corrections due to the above re-evaluation of both relative[1] and absolute x-ray wavelengths[2-4] require a completely new listing of all x-ray wavelengths, absorption edges and crystal dimensions, and hence provide an excellent opportunity for the introduction of a wavelength standard analogous to the krypton

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[3] J. A. Bearden, Phys. Rev. 137, B181 (1965).

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[5] See tables, A. E. Sandström, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 30, pp. 78–245; Y. Cauchois and H. Hulubei, *Longueurs d'onde des Émissions X et des Discontinuités d'Absorption X* (Hermann et Cie., Paris, 1947).

[6] M. Siegbahn, *Spektroskopie der Röntgenstrahlen* (Springer-Verlag, Berlin, 1931), pp. 42–44.

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[13] J. J. Merrill and J. W. M. DuMond, Phys. Rev. 110, 79 (1958).

standard for optical light (a krypton line is now used to define the standard meter). A previous adoption of a standard x-ray line would not have removed the need for a major revision, since the wavelength errors are large compared with the variations in d_∞ of calcite crystals. However, improved techniques for selecting crystals[14] and the measurement of Bragg angles[1,15] now make it practical to measure wavelengths to the order of 1 ppm, if several crystals are carefully selected and calibrated with a number of reference lines. The adoption of a wavelength standard now appears necessary; this should be selected for maximum convenience and precision.

Possible variations in the calcite grating constant were pointed out by Siegbahn[16] as early as 1919. Later measurements[11] indicated such variations, but these were of the same order of magnitude as errors in measurements. In fact, experimental errors have often been much larger than suspected; for example, in a paper on atomic constants, Cohen and DuMond[17] conclude from a statistical analysis that the product Nd_∞^3 (Avogadro's number N times the measured d_∞^3 in xu) for a number of crystals measured in several laboratories differed by approximately 75 ppm, depending on whether the measurement was made with the Mo $K\alpha_1$ or Cu $K\alpha_1$ x rays. This implies a 25 ppm discrepancy in the wavelength ratio in the opposite direction to the 20 ppm revision noted above. It now appears[2,3] that the precision of the older data was considerably overestimated.

In 1958 Merrill and DuMond[13] discussed the advisability of designating a particular x-ray wavelength as a standard and suggested the choice of Mo $K\alpha_1 = 707.849$ xu, which resulted from the Bragg angle of $\theta_1 = 6°42'36.0''$ obtained with their crystal, together with $d_1 = 3029.04$ xu. Later DuMond[18] suggested the use of a weighted average of five wavelength standards. The present report describes measurements which have been made primarily in the author's laboratory over the past four years to determine the best reference wavelengths for x rays, γ rays, and crystal parameter measurements.

Previously published wavelength tables do not have any probable errors assigned to the various wavelengths. With the adoption of a wavelength standard in angstroms, new tables should provide a probable error for each wavelength relative to the standard, and also a second probable error based on its absolute wavelength in angstroms. Such tables[19] have recently been prepared (separate publication). These also include a large number of remeasured reference wavelengths.

CONSIDERATIONS IN THE SELECTION OF A WAVELENGTH STANDARD

In principle any x-ray line could be chosen and assigned an arbitrary value, for example, Cu $K\alpha_1$ = 1.000 000 Cu unit. Then in every calculation involving comparison with theory, the use of a conversion factor would be required. Since the vast majority of such calculations do not attain a precision better than 10 ppm, this appears to be an unnecessary source of confusion and errors, provided an absolute wavelength standard can be defined whose wavelength in centimeters or angstroms is known within a few ppm. Of course, for the most precise calculations, e.g., atomic constants, a conversion factor differing from unity by a few ppm will be required, and this factor will change slightly as the precision of the absolute x-ray wavelength measurements is increased.

Selection of a Wavelength Region

In selecting the wavelength to be used as a standard, primary consideration should be given to the researches which require the highest precision and are most affected by errors arising in making the relative measurements. In this regard the energy scale of the highly important γ-ray spectrum is very dependent on the use of a short wavelength standard. The most precise γ-ray measurements have been those of Knowles,[20] who has measured the ratio of the third order annihilation radiation to the first order of a γ ray of Ta^{182}, and then compared the third order of this radiation relative to the W $K\alpha_1$ line. In this work the angles were measured to the order of 0.01 sec, which is indicative of the precision that can be attained in the measurement of narrow, symmetrical lines where the diffraction angle is of the order of a few degrees.[15] Another recent problem[21] which required high accuracy in the short-wavelength region was the location of the lead absorption edge for use in the μ-meson mass determination.

The greatest use of x-ray wavelengths has of course been in the measurement of crystal parameters. These measurements require wavelengths of 1.5 to 2.7 Å, and unfortunately involve the use of x-ray lines of considerable asymmetry. The latter, together with crystal imperfections and the technique of measuring lattice constants, in general limit the accuracy of determining crystal dimensions to no better than 20 or 30 ppm.[22] Furthermore, crystallographers have reported their measurements in angstroms, which introduces an additional probable error of ± 5 ppm, due to the error in the conversion ratio. Thus a secondary standard, e.g., Cu $K\alpha_1$ and Cr $K\alpha_2$, with a probable error of ± 1 ppm relative to a standard, is entirely adequate for crystallographic measurements. In the field of x-ray spectroscopy, shorter wavelengths have frequently been used

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as reference wavelengths for the measurement of weak spectral lines.

It should be emphasized that the designation of a particular wavelength as *the x-ray standard* does not imply that all crystals and/or spectrometers must be calibrated by direct comparison to this wavelength. Convenient *secondary standards* with probable errors of the order of ±1 ppm are already available[1] which are adequate for general use. The designated standard wavelength will be of primary value in the highly precise researches whose objective is the establishment of new or better secondary standards. This paper is mainly concerned with the selection of a *primary standard* whose characteristics are such that future measurements of secondary standards can be made with the highest precision.

Symmetry and Width Effects

X-ray spectra are recorded by photographic, counter, and ionization techniques. It would appear that the asymmetry of a line would influence the measurement of its wavelengths by the different techniques. However, this was not observed in the measurements[23] made on the K series elements from germanium to titanium. Increased precision in the measuring techniques should make such an effect observable, and hence only highly symmetrical lines should be considered for a wavelength standard.

The width of a line is of prime importance in the precision with which its wavelength can be measured. γ-ray sources, which emit narrow symmetrical lines, would make ideal standards if they could be made with an intrinsic intensity comparable to that available from x-ray tubes. In x-ray sources the linewidth is roughly proportional to its wavelength. In two recent γ-ray[20] and x-ray[1] measurements, the center of the observed symmetrical line profile has been located within a few thousandths of its observed width (not, of course, the natural width of the γ-ray line). Thus in principle the peak of a narrow [e.g., $WK\alpha_1$ in (2,+5) is 30 sec] short wavelength line can be located with a higher precision than its angular position can be read on the divided circle. The error in the reading of the divided circle is constant and hence its error in parts per million decreases with increased Bragg angle (the precision of the interferometer method is 1 ppm for angles from 3° to 30°). Disregarding other considerations, this would suggest that the long-wavelength symmetrical lines (e.g., Cr $K\alpha_2$) could be measured more accurately with a divided circle than the short wavelengths. However, this advantage is offset by the errors in the large index of refraction and anomalous dispersion corrections, the effect of surface treatment[24] on the index of refraction correction, single crystal diffraction pattern asymmetry,

and the very important shift in wavelength due to chemical effects.

For a symmetrical line, it is immaterial whether the wavelength is defined by the peak (obtained by division of chords[25]) or the mean, i.e., centroid.[26] In general the peak position has been accepted as the wavelength criterion for both symmetrical and asymmetrical lines, and has been so employed in all measurements in this laboratory. In the designation of a wavelength standard the peak is recommended as the most precise indicator of wavelength.

Source Requirements

Failure to use high-order diffraction angles has undoubtedly limited the precision of single-crystal spectrometers, and in particular those with photographic recording. This has been due at least partially to the broad focal properties of conventional x-ray tubes producing a low intrinsic intensity, whereas high intensity is required for recording high orders of diffraction. The effect of crystal imperfections[14] has limited the attainable precision in double-crystal spectroscopy. The error is greatly minimized by the use of a small, high intrinsic source, e.g., the small focal spot (0.01×5 mm projected size) of a high-power rotating target x-ray tube[27] with a controllable cathode focusing. The best target materials for both conventional and rotating target x-ray tubes are those of highest melting point and thermal conductivity, which results in tungsten possessing the highest power rating per square millimeter of any target material.

A further requirement is that the wavelength of the x-ray source be independent of chemical and isotopic effects. The $K\alpha_1$ lines of the elements of high atomic number are less affected by chemical combination than those of low Z. Merrill and DuMond[13] stated that the Mo $K\alpha_1$ is almost surely reproducible to ±10 ppm. Rogosa and Schwarz[28] were unable to observe any shift in the wavelength peak of the Mo $K\alpha_1$ for separated isotopes of Mo^{92}, Mo^{95}, and Mo^{100}. Shortly afterwards Wertheim and Igo[29] studied the problem theoretically and showed that the expected shift for Mo $K\alpha_1$ was of the order of 5 ppm, about half the minimum value detectable by Rogosa and Schwarz. The theoretical shift for W $K\alpha_1$ should be substantially greater. However, as long as "natural abundances" of the W isotopes remain constant within 1% the W $K\alpha_1$ line should furnish a satisfactory standard, at least for the present.

A highly concentrated γ-ray source of dimensions comparable to x-ray focal spots yields intensities of the order of 10^4 smaller than that emitted by an x-ray tube. A 1-Ci γ-ray source (e.g., Fe^{57}) concentrated on an

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[24] J. A. Bearden, Bull. Am. Phys. Soc. 7, 339 (1962).

[25] J. A. Bearden, Phys. Rev. 43, 94 (1933).
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[27] J. A. Bearden and J. S. Thomsen (to be published).
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area of 5 mm×5 mm used with a two-calcite crystal spectrometer would give a peak counting rate of the order of 3 per second in the $(1,\pm 1)$ and approximately 0.8 in the $(2,\pm 2)$ positions. The Bragg angle is $8°8'46''$ for the $(1,\pm 1)$ and $16°24'40''$ for the $(2,\pm 2)$ measurement. The effective length of "perfect" crystal required is 36 and 18 mm, respectively, and the procurement of such crystals is extremely difficult.[14] The small intensity would still restrict measurements to the first and second orders, where the index of refraction (known only to the order of 1%) corrections are roughly 160 ppm for the first order and 40 ppm for the second.

Crystal Considerations

As mentioned above, the index of refraction correction for all crystals in the first order, which was most used in previous wavelength measurements, is of the order of 160 ppm. Very few refraction measurements have been made which are of sufficient accuracy to be used for the precise correction of wavelengths in low orders. In the case of germanium crystals, which some experimenters[30] have recently labelled as the most perfect crystals, no experimental measurements are available. Theories[31] are available for calculating the index of refraction, each leading to a different value, and selection of one of these is required for correcting wavelengths. In the germanium crystal, anomalous dispersion has its maximum and minimum values near 1.1 Å (± 20 to 30 ppm) and has an appreciable negative value at the wavelength of the Mo $K\alpha_1$ line. In order to minimize refraction effects with this crystal, very short wavelengths are essential. Anomalous dispersion effects in calcite, quartz, and silicon occur at longer wavelengths, and the errors introduced in wavelength measurements from this effect are of the order of ± 1 ppm for wavelengths less than 1 Å. In all cases the calculated value of the index of refraction is most precise at the shortest wavelengths.

The single-crystal pattern of germanium is shown in Fig. 1, for the 14.413-keV Fe57 γ ray ($\lambda = 0.860\,231$ Å on W $K\alpha_1 = 0.209\,010\,0$ Å*), which is near the Mo $K\alpha_1$ wavelength. The error introduced into the wavelength measurement by the asymmetry of this crystal is several ppm, but the exact correction has not been calculated as yet. The use of crystals of lower atomic weight or much shorter wavelengths reduces the error in the wavelength measurement due to the asymmetry of the crystal pattern.

Large single crystals of geometrical perfection are exceedingly rare[14] and, even in the best crystals, sharply bounded elements generally occur whose planes differ
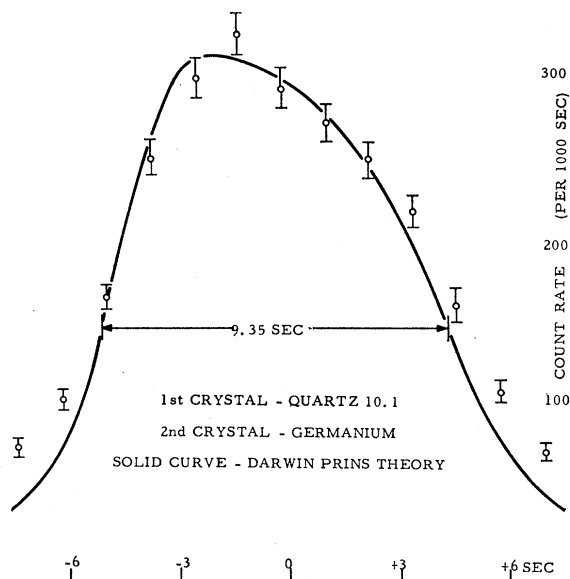

FIG. 1. The solid curve is the theoretical Darwin-Prins single-crystal rocking curve and the experimental points are shown with standard deviations.

from the average by as much as a second of arc. Since all wavelength measurements, except those made in transmission, require a rotation of the crystal by $180°\pm 2\theta$, the failure of the x-ray beam to be diffracted from exactly the same crystal element in both positions introduces an appreciable error in the wavelength measurement. Grinding and etching crystal surfaces parallel to the atomic plane, precise alignment of the crystal parallel to and on the axis of the spectrometer, and the use of a narrow x-ray beam minimize this error.[1] Further perfection in the growing of synthetic crystals[32] could alleviate some of these problems.

EXPERIMENTS

Crystal Imperfections

In a paper[14] describing a double-crystal spectrometer technique for critically testing crystals with the W $K\alpha_1$ radiation, x-ray photographs of the type shown in Fig. 2 were obtained where exposures (a), (b), and (c) were made with our best quartz crystal, and (d), (e), and (f) with a Steeg and Reuter selected quartz. In each set of exposures the center one was made with the crystal adjusted to the peak of the $(2,-2)$ rocking curve, and the other two exposures with the crystal set at the half-intensity points of the same curve. If the crystal had been perfect, each exposure would have been an exact image of the focal spot of the tungsten x-ray tube. Structure in the exposure indicates crystal im-

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[31] H. Kallmann and H. Mark, Ann. Physik **82**, 585 (1927); J. A. Prins, Z. Physik **47**, 479 (1928); H. Honl, Z. Physik **84**, 1 (1933); J. A. Wheeler and J. A. Bearden, Phys. Rev. **46**, 755 (1934).

[32] R. D. Deslattes, J. L. Torgesen, B. Paretzkin, and A. T. Horton, *Advances in X-Ray Analysis* (Plenium Press, Inc., New York, to be published) Vol. 8; Richard D. Deslattes, Bur. Std. Techn. Note 236, 1964, p. 33.
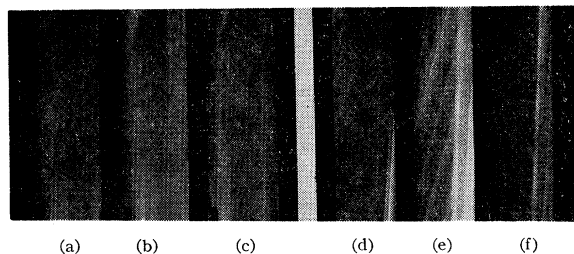
(a)   (b)   (c)   (d)   (e)   (f)

FIG. 2. The three exposures on the left were taken of a "best" quartz crystal at the peak and half-intensity points of the rocking curve. The three exposures on the right were made with average quartz. Structure indicates crystal imperfections.

perfections, and the variation in the structure exhibited in the three exposures is a measure of the angular orientations of the individual crystal elements. In the examination of more than 100 crystals (selected for high quality), only three calcite, two small silicon, and two quartz crystals were found suitable for precision x-ray spectroscopic work.

In a study of nine selected calcite crystals[3] for the purpose of determining their grating constant d_∞ in angstroms, their densities were determined, the chemical impurities were measured spectroscopically, and the lattice constants were measured with both Ag $K\alpha_1$ and Cu $K\alpha_1$ x rays. A definite correlation was established such that the parameters of an ideally pure $CaCO_3$ calcite were established. Each of these crystals exhibited imperfections, as noted above, but the measured value of d_∞ was constant for each crystal if, in the two $180°\pm2\theta$ x-ray measurements, the same small diffracting area of the crystal element was used.

The above effect was also clearly exhibited in the density and x-ray measurements made on 18 high-purity silicon crystals.[2] The crystal imperfection test showed these silicon crystals to be very poor. The crystals were ground (in most cases polished) parallel to the atomic planes. The x-ray beam used was 0.03 mm wide and 2 mm high, and the spectrometer accurately aligned to restrict the diffraction measurements to the same small crystal element for each of the $180°\pm2\theta$ measurements. In this experiment, both the relative density measurements and the x-ray diffraction measurements implied probable errors of about 1 ppm in the mean values.

From the above experiments, chemical impurities appear to alter the d_∞ of a crystal and correspondingly its density, but crystallizing conditions apparently govern the degree of lattice imperfections that occur. Crystallographers have concluded that powder diffraction methods of measuring d_∞ are superior to Bragg single-crystal measurement. The crystal perfection of most substances is inferior to the highly selected ones studied here, and for such crystals the above measurements certainly support their conclusion. However, if the x-ray beam is restricted such that a very small element (area preferably tested for perfection) of the single crystal is used for the $180°\pm2\theta$ positions, the d_∞ thus measured

is valid, and the six or seven corrections necessary in the powder crystal method are practically eliminated.

Thus crystal imperfections are a primary limitation in the precision measurement of x-ray wavelengths. These are best avoided by examining and testing the crystal with penetrating short-wavelength radiation. The effects are minimized by using the crystal in transmission where only a small surface area is employed. Hence a short-wavelength x-ray line possesses advantages as a standard.

γ-Ray Measurements

A 200-mCi Fe^{57} Mössbauer source has been used to study single-crystal diffraction patterns of several crystals.[33] The possible use of the source as a wavelength standard has been further evaluated by measurement of wavelength of the 14.4 keV Fe^{57} γ ray with calcite and quartz crystals in the $(1,\pm1)$ and $(2,\pm2)$ orders. The area of the source was approximately 10×10 mm, positioned such that its projected area was approximately 2×10 mm. The double-crystal spectrometer was aligned as previously described,[1] and an interferometer[15] adjusted to monitor the second crystal position over the 24-h period required to obtain, for example, a $(1,+1)$ curve. The crystal and interferometer were then set to the $(1,-1)$ position and a similar curve obtained. For the sharp γ ray the $(1,\pm1)$ diffraction curves should be the same, and likewise the $(2,\pm2)$ curves. The adjustment of the spectrometer on the low-intensity γ-ray line was an order of magnitude more difficult than in the case of an intense x-ray line. The recorded intensities at peaks ranged from approximately 0.1 counts/sec to approximately 0.6 counts/sec, requiring the utmost precautions to reduce the background to less than 0.01 counts/sec in order to give an acceptable signal-to-background ratio.

Reference to the original paper[33] shows that pronounced effects were observed which were due to crystal imperfections and a possible distortion in two of the diffraction curves probably due to a small temperature change in the $(2,-2)$ position. The 24-h period between the first and second reading of the divided circle microscopes permitted oil film variation and small temperature effects (0.1°C) to develop which produced errors of the order of at least ±5 ppm (0.25 sec in 2θ). The wavelengths measured are listed in Table I.

TABLE I. The Mössbauer 14.4-keV Fe^{57} γ-ray wavelengths in Å* based on $\lambda_{W\ K\alpha_1}=0.209\ 010\ 0$ Å*.

Crystal	Order	Wavelength Å*
Calcite	1	0.860 236
Calcite	2	0.860 237
Quartz	1	0.860 224
Quartz	2	0.860 227
	Average	0.860 231

[33] J. G. Marzolf and J. A. Bearden (to be published).

The wavelengths from the first and second order in each crystal are in agreement, but the values for the two crystals disagree. The crystals are our best, and the only explanation of the difference is the use of an extended source and experimental difficulties due to the low counting rates.

From these measurements it is concluded that the source strength would have to be increased by at least a factor of 10 or preferably 100 to make the γ-ray standard experimentally feasible. Crystal imperfections require that the source dimensions be even less than those used in the present work. Thus experimental considerations eliminate, at least for the present, the use of a γ-ray wavelength standard.

Wavelength Standard—Least-Squares Analysis

In the precision evaluation[1] of the wavelength ratio of the five x-ray lines W $K\alpha_1$, Ag $K\alpha_1$, Mo $K\alpha_1$, Cu $K\alpha_1$, and Cr $K\alpha_2$, with five selected crystals, a least-squares analysis of the measurements showed that each of the wavelengths had been measured with a probable error of approximately ± 1 ppm. This result is in contradiction to the initial conclusion reached in the section on symmetry and width effects, where it was pointed out that in principle the longer symmetrical lines should have the smallest probable errors. However, further consideration of this argument in the light of all the measurements covered in the present study indicates that it omitted at least one important factor. The major uncertainty is that introduced by crystal imperfections. The use of the smallest possible crystal area, for example, in the transmission method of measuring wavelengths, is superior to any Bragg reflection measurement. The high intensity of the W $K\alpha_1$ line allowed measurements to be made in transmission up to the seventh order. The development of an interferometric method[15] of measuring angles up to 30° with a probable error of 0.01 sec further increases the precision with which the W $K\alpha_1$ diffraction angle can be measured in transmission. Such measurements determine the grating constant of a small crystal element to a very high precision, and as indicated in the concluding paragraph of the section on crystals, this yields the real d_∞ of the particular crystal as modified by its impurity content.

THE W $K\alpha_1$ WAVELENGTH STANDARD

Considering all the factors involved in the selection of a wavelength standard, the W $K\alpha_1$ line is superior to any other x-ray or γ-ray wavelength. Its advantages as the x-ray wavelength standard are:

1. The short wavelength of the W $K\alpha_1$ can be used directly to measure the important γ-ray lines if the latter are taken in various orders. Hence the entire nuclear energy level system can be calibrated.

2. By secondary standards (already determined[1]) x-ray wavelengths and parameters of individual crystal samples can be placed on a precise scale relative to the

W $K\alpha_1$ with probable errors of approximately ± 1 ppm.

3. In diffraction measurements with the W $K\alpha_1$ in transmission, the correction for index of refraction μ is negligible (0 for equal incident and emergent angles). The anomalous dispersion correction is negligible at this wavelength for either reflection or transmission.

4. The W $K\alpha_1$ line is highly symmetrical, and any wavelength dependence on chemical effects or variations in the natural isotopic abundance of tungsten is probably well below present experimental errors.

5. The measurement of the diffraction angle θ for the W $K\alpha_1$ line in transmission is affected by crystal imperfections and asymmetries in the single-crystal diffraction patterns considerably less than that for longer wavelengths.

6. The interferometer method[15] of measuring angles is ideally suited to the transmission method, and the requirement of high precision divided circle spectrometers is unnecessary.

The average value of the measured Cu $K\alpha_1$ wavelength in absolute units is 1.540 562 Å. (This figure has actually been obtained by using the recommended value of $\Lambda = 1.002\ 076 \pm 5$ ppm previously given by the author[3] and multiplying it by the wavelength in x units of the Cu $K\alpha_1$ line, 1.537.370 xu, on which it was based. This would be completely equivalent to averaging directly the measured absolute values[2,3] for Cu $K\alpha_1$ except for the fact that the recommended average Λ is based to a small extent on other wavelengths.) The precision measurement[1] of the ratio of the Cu $K\alpha_1$ line to the W $K\alpha_1$ gave 7.370 757 ± 1.2 ppm, yielding the result

$$\lambda_{W\ K\alpha_1} = 0.209\ 010\ 0\ \text{Å} \pm 5\ \text{ppm}.$$

This numerical value of the wavelength is now proposed for use with the W $K\alpha_1$ line to define *the x-ray wavelength standard* by the relation

$$\lambda_{W\ K\alpha_1} = 0.2090\ 10\ 0\ \text{Å}^*.$$

This is a new unit of length which may differ from the angstrom by ± 5 ppm (probable error), but as a wavelength standard it has no error. In order to clearly indicate that this unit is not exactly an angstrom, it is suggested that it be designated Å*. When higher precision is attained in the absolute measurement of the W $K\alpha_1$ line, a conversion factor slightly different from unity will then be required for the extremely precise calculations, for example in atomic constants.

The definition of the Å* unit proposed here eliminates the need for a conversion factor in most cases, but does open the possibility of some confusion between the Å* unit and the angstrom. The author believes the first point outweighs the second, although this involves a factor of judgement and personal preference. Logically it would have been just as valid to define a new unit which was very close to the present x unit or even one which was completely different from both the x unit and the angstrom. However, the Å* unit, as defined

above, has been adopted by the author as a basis for a new wavelength table[19] now in publication. In any event, the most important points in the present proposal are the adoption of an emission line as a wavelength standard (rather than a calcite crystal) and the choice of W $K\alpha_1$ as the most suitable line. The numerical value assigned above, while of great importance in practical application, is secondary to these two considerations.

SECONDARY STANDARDS

Secondary standards of wavelength are desirable to provide suitable reference lines for various portions of the x-ray spectrum. The recent study by Bearden[1] *et al.* was designed to establish a group of such standards to the highest precision presently attainable.

This investigation consisted of a long series of high precision measurements using a spectrometer with a graduated circle calibrated by means of an angular interferometer. The lines studied were as follows: Cr $K\alpha_2$, Cu $K\alpha_1$, Mo $K\alpha_1$, Ag $K\alpha_1$, and W $K\alpha_1$. Five different crystals (1 calcite, 2 quartz, 2 silicon) were used, some in all wavelength measurements, giving a total of 20 different combinations, each one yielding a value of λ/d_∞. In this study the wavelength of Mo $K\alpha_1$ was provisionally taken as 707.831 xu. There then resulted 20 equations for nine unknown quantities (4 wavelengths and 5 grating constants). This system of overdetermined linear equations was solved by a least-squares adjustment with the aid of an IBM 7094 computer.

The resulting wavelength values are given in Table II. For completeness and convenience, Table II includes wavelength values on the xu scale W $K\alpha_1 = 208.577$ xu and on the absolute scale Å* (angstrom) W $K\alpha_1 = 0.2090100$ Å*. Two probable errors in parts per million
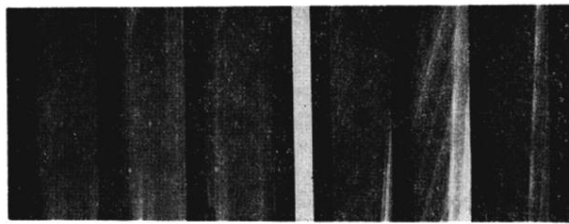
TABLE II. Secondary standards.

Reference standard $\lambda_{W\ K\alpha_1} = 208.5770$ xu	Reference standard $\lambda_{W\ K\alpha_1} = 0.209\ 010\ 0$ Å*
$\lambda_{Ag\ K\alpha_1} = 558.2486$	$\lambda_{Ag\ K\alpha_1} = 0.559\ 407\ 5 \pm 1.1$ or 5.2 ppm
$\lambda_{Mo\ K\alpha_1} = 707.831$	$\lambda_{Mo\ K\alpha_1} = 0.709\ 300 \pm 1.3$ or 5.2 ppm
$\lambda_{Cu\ K\alpha_1} = 1537.370$	$\lambda_{Cu\ K\alpha_1} = 1.540\ 562 \pm 1.3$ or 5.2 ppm
$\lambda_{Cr\ K\alpha_2} = 2288.854$	$\lambda_{Cr\ K\alpha_2} = 2.293\ 606 \pm 1.3$ or 5.2 ppm

are given; the first is relative to the W $K\alpha_1$ as *the primary standard*, and the second takes into account the probable error of ± 5 ppm in the conversion factor Λ and hence is the probable error in absolute angstroms. These probable errors are borne out by the internal consistency of the data in a χ^2 test.

(a)   (b)   (c)   (d)   (e)   (f)

FIG. 2. The three exposures on the left were taken of a "best" quartz crystal at the peak and half-intensity points of the rocking curve. The three exposures on the right were made with average quartz. Structure indicates crystal imperfections.