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Precision Redetermination of Standard Reference Wavelengths for X-Ray Spectroscopy*

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This investigation is designed to determine with high accuracy the wavelength ratios of 5 standard x-ray reference lines: Cr $K\alpha_2$, Cu $K\alpha_1$, Mo $K\alpha_1$, Ag $K\alpha_1$, and W $K\alpha_1$. Most measurements were obtained with a double-crystal spectrometer in reflection. However, a few were taken with the instrument converted to a high-precision single-crystal spectrometer, and some tungsten determinations were made in transmission. Since estimated errors (±1 ppm) are the lowest ever claimed for this type of work, the apparatus, including adjustment, calibration, and corrections, are described in considerable detail. Novel features include: use of a high-intensity, narrow-focus rotating-target tube for most measurements, calibration of the spectrometer circle to 0.1 sec with an angular interferometer, and a careful selection of 5 crystals (1 calcite, 2 quartz, and 2 silicon) from more than 100 samples tested. Bragg angles were determined for 20 different combinations of crystals and wavelengths. With an assumed wavelength value for one selected line, this gave an overdetermined set of 20 equations for 9 unknowns (4 wavelengths and 5 grating constants), which was solved by a least-squares adjustment. If the value for Mo $K\alpha_1$ is provisionally taken as 707.831 xu, the resulting values for the other wavelengths are: Cr $K\alpha_2$, 2288.854±0.003 xu; Cu $K\alpha_1$, 1537.370±0.002 xu; Ag $K\alpha_1$, 558.2486 ±0.0006 xu; W $K\alpha_1$, 208.5770±0.0003 xu. However, the primary quantities determined are the wavelength ratios, which are invariant with respect to a choice of the primary defining reference line. The question of adopting a definitive standard is left open for the present.

I. INTRODUCTION

A. Purpose of Investigation

IN an extensive program of re-evaluating x-ray wavelengths on a consistent scale, preliminary measurements[1] with a double-crystal spectrometer and calcite crystal indicated that the ratio of wavelength of the Cu $K\alpha_1$ and Mo $K\alpha_1$ lines now current in the literature[2] is in error by about 20 ppm. These lines have been used directly or indirectly as reference lines for many other measured wavelengths. In order to establish the relative wavelengths of a selected group of lines which could be used to put older measurements on a more consistent basis and to form a foundation for new determinations, a systematic program of new high-precision measurements has been carried out. This program yielded ratios of wavelengths of five selected reference lines: Cr $K\alpha_2$, Cu $K\alpha_1$, Mo $K\alpha_1$, Ag $K\alpha_1$, and W $K\alpha_1$, with accuracies of the order of 1 ppm.

While it is desirable to express all of these wavelengths in absolute terms, relative wavelength measurements are still substantially more precise than absolute ones. Any relative scale of x-ray wavelengths should be based on some selected reference line rather than the grating constant of a crystal as is the case of the x unit.[3] Any of the above-mentioned wavelengths may be chosen as a standard with a defined value and the wavelength of the other four readily computed from the present results. The choice of the most suitable standard will be left open at this point.

B. Procedure

An extensive series of determinations has been carried out over a period of almost two years, with most measurements obtained on a double-crystal spectrometer using a reflected beam. However, in certain cases it was converted into a high-precision single-crystal instrument by substituting a slit system for the first crystal. In some measurements with tungsten the second crystal was used in transmission. Five different crystals were employed: one calcite, two quartz, and two silicon. These were selected from over a hundred samples tested and are believed to be as nearly perfect as any available for this type of work.

The resulting data were assigned appropriate weights and then used in a least-squares analysis to give the "best" value of each wavelength and the "best" lattice constant for each individual crystal used. This technique treated each item of input data symmetrically. It yields not only the adjusted "best" values, but also probable errors of these values and the correlations between such errors. While the evaluation was made on the basis of the currently accepted figure of 707.831 xu as the wavelength of the Mo $K\alpha_1$ line, this choice is only a provisional one for computational purposes. The wavelength ratios obtained, as well as the errors, are invariant with respect to this arbitrary choice.

Hence any one of the five lines measured may now be designated as *the primary* standard of all x-ray wavelengths, and the remaining four lines immediately obtained as secondary standards. The entire experiment

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

[2] A. E. Sandström, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 30, p. 78.

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

described here can be repeated in any laboratory and with any crystals; the agreement between such experiments will depend primarily on the quality of the set of crystals used and the precision of the angular measurements.

C. Selection of Wavelengths

In x-ray spectroscopy, measurements are made with single-crystal, curved-crystal, and double-crystal spectrometers, in which the x-ray intensity is recorded by ionization, counter, or photographic techniques. In order for all of the various methods to yield the same value of the wavelength, the primary considerations in selecting a standard reference line are symmetry, narrow width, and intensity. In ionization and counter techniques, the peak of the line (by extrapolation of center of chords[4]) has been used as a measure of the wavelength; and in the photographic method, the setting of the cross hair on the "center" of the line has been the standard procedure, although microphotometer traces have been employed in some cases. It is surprising that in the relatively few cases[5] where both the photographic and counter or ionization techniques have been used to measure the same wavelengths, the resulting values are in such excellent agreement, even for lines of appreciable asymmetry. However, to attain the highest precision in the measurement of standard reference lines, those possessing asymmetry should not be used.

The molybdenum $K\alpha_1$ has been the predominant standard reference line for wavelength measurements[6,7] of less than 1 Å, and indirectly for many L and M[8] lines of longer wavelength. The copper $K\alpha_1$ line has been the primary standard for crystallographic[9] measurements, and also for wavelength measurements greater than 1 Å. The latter possesses an asymmetry[5] of 1.12 and is included as a standard reference line only because of its accepted prior use and convenience. Three additional lines have been included in the present measurements. The tungsten $K\alpha_1$ is a symmetrical line which has been extensively used as a reference line for high-energy x-ray and γ-ray spectroscopy. The physical characteristics of tungsten, its high melting point and thermal conductivity, make it the best of all materials for constructing a high-intensity x-ray tube. The silver $K\alpha_1$ line is also symmetrical, and its wavelength is intermediate between that of tungsten and molybdenum. In the longer wavelength region (not vacuum) the chromium $K\alpha_2$ is the only strong symmetrical line available. Both silver and chromium are easily electroplated onto copper to form excellent x-ray targets.

Because of their narrow width and symmetry, sharp γ-ray lines of the order of 0.5 Å would in principle be ideal primary standards for x-ray spectroscopy. Wavelength measurements have recently been made by one of the authors[10] (JAB) with a double crystal spectrometer, using a 100-mCi Fe^{57} γ-ray source. Calcite crystals were used in the (1 ± 1) positions, and gave a full width at half-maximum intensity of 7.3 sec. The counting rate at the peak was 0.5/sec, with a background of 0.02/sec. In the $(1-2)$ position the intensity was 0.16 counts/sec at the peak, and the width was about 4 sec. The widths in both cases are wider than expected from theory, portraying the imperfections of crystals which has been evident in almost all crystals recently tested in this laboratory. In order for a γ-ray source to be comparable to a selected x-ray line as a primary standard, the following requirements are essential: (1) The source strength should be least 1 Ci and preferably 10 Ci, with a half-life of many months. (2) The source dimensions should be less than 1×5mm, since larger sources will require crystals of much higher perfection than have been tested in this laboratory to date.

Thus the size and strength of a feasible γ-ray source, as well as the limitations of available crystals, make its practical use as a primary standard inferior to comparable x-ray lines, e.g., W $K\alpha_1$.

II. APPARATUS

The high accuracy of the present x-ray diffraction measurements, which is of the order of 1 ppm, is greater than any recorded in the literature. Details of apparatus, alignment procedures and corrections applied have been described to justify the probable error. Furthermore, the alignment procedure for the double-crystal spectrometer as used in our laboratory has never been described in detail.

A. X-Ray Tube

Most of the measurements were taken with a rotating target x-ray tube. The target was 4 in. in diameter and 2 in. in length, rotating on two ball bearings, one inside the vacuum and one outside. Between the bearings is a rotating shaft precision finished for roundness and polished by diamond tool techniques. On this shaft two Neoprene rubber seals are placed back to back with a small space between them for Apiezon C oil, which formed the rotating vacuum seal. The target was rotated at 4000 rpm, and a vacuum of better than 10^{-6} mm was produced by a 60 liter/sec oil diffusion pump after a few days operation. The life of the seals and bearings was from one to three thousand hours; they could be replaced in two to three hours.

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[6] E. Ingelstam, Nova Acta Reg. Soc. IV (Uppsala) **10**, No. 5 (1937).

[7] B. B. Watson, W. J. West, D. A. Lind, and J. W. M. DuMond, Phys. Rev. **75**, 505 (1949).

[8] E. Lindberg, Nova Acta Reg. Soc. IV (Uppsala) **7**, No. 7 (1931).

[9] *International Tables for X-Ray Crystallography, Vol. 3, Physical and Chemical Tables*, edited by K. Lonsdale (Kynoch Press, Birmingham, England, 1952–62).

[10] J. A. Bearden, Bull. Am. Phys. Soc. **9**, 387 (1964).

The principal advantage of this type of x-ray tube for wavelength measurements lies in its high intrinsic intensity, which in turn requires a highly focused electron beam of uniform density. This has been obtained by use of a straight tungsten wire filament located approximately 0.25 mm from the bottom of a rectangular slot and insulated from it so that 500- to 600-V bias could be applied. The focusing voltage was supplied by Zener diodes in series with the tube current. The actual size of the focal spot was adjustable from 0.3×10 mm, to 1.5×10 mm. The filament current ranged from 20 to 30 A, providing target currents up to 200 mA at 50 to 60 kV dc. However, most of the measurements were made at lower voltages and currents.

The difficulties involved in brazing Mo to machinable metals have thus far prevented the building of a Mo rotating target. Hence the molybdenum wavelength measurements were made with a Machlette AEG 50 fine focus x-ray tube. The focal spot was 2.5 mm wide and the projected height as viewed was the same. A similar tube with a Cu target was used for one series of measurements in order to get a direct Mo $K\alpha_1$ to Cu $K\alpha_1$ wavelength ratio under identical experimental conditions. The Cu $K\alpha_1$ wavelength was the same as that measured with the rotating target tube, within the experimental error.

The W $K\alpha_1$ measurements required an independent arrangement of tube and double-crystal spectrometer. A 250-kV 10-mA Westinghouse industrial dc unit, equipped with a tungsten target Machlette tube having a projected focal spot of approximately 3×3 mm, was used for this purpose. The x-ray tube and its lead housing were mounted on one end of a stone table 65×240×20 cm. The spectrometer and first crystal were mounted on a machinist's cast iron surface plate 60×150 cm, which rested on the stone table. The distance from the focal spot to the first crystal was 90 cm, and to the second 180 cm. The small diffraction angles (4° for second-order calcite) required the large separation of x-ray source and crystals so that lead stops could be inserted to prevent x rays scattered at small angles from entering the detector.

B. High-Voltage Equipment

Except in the case of the tungsten tube described above, the high voltage was obtained from a three-phase 80-kV, 56-kW transformer with built-in silicon rectifiers, connected so that the output dc (14% ripple) could be made either positive or negative with respect to ground. Two 0.5-mF 80-kV condensers were used to further reduce the ripple. The input voltage was adjusted by ganged Variacs, and the output voltage was controlled by a series tube, amplifier, and a zero-phase-shift voltage divider.[11] Likewise the tube current was regulated by amplifier and impedance changer in series with the filament transformer. The stability of the x-ray intensity with the rotating target x-ray tube was equal to that of the regular sealed-off commercial tubes.

C. Temperature Control

In the measurement of diffraction angles to within ±0.1 sec, it was necessary to maintain the spectrometer and crystal at a constant temperature within ±0.1°C not only during the measurement, but for several hours before, in order that all parts of the spectrometer attain equilibrium. The room was controlled by a system which cooled the incoming air (approximately 800 ft^3/min) to less than 40°F to remove moisture, and then was heated by fast response steam heater coils. The temperature of the room at the position of the spectrometer was sensed by a resistance thermometer which was part of the bridge circuit of an automatic temperature controller. This controller adjusted the amount of steam flowing through the heater coils in proportion to the temperature deviation from the control value 25.0°C. The temperature usually varied by less than ±0.2°C over a 24-h period.

The spectrometer temperature was further stabilized by enclosing it in an insulating box of 1-in.-thick Styrofoam. A small section of the Styrofoam was removable for quickly changing the spectrometer from the $(1+n)$ to the $(1-n)$ positions, and reading the microscopes. The temperature near the second crystal was monitored by a 0.01°C reading thermometer. This temperature varied less than 0.05°C during the recording of a measurement.

Some of the latter measurements have been made with a new room-temperature regulator. Incoming air at 45 to 50°F is now supplied from a new air conditioning system for the entire building. The resistance thermometer is used as above, but the bridge unbalance is fed into a dc amplifier system which controls the phase of pulses actuating six silicon controlled rectifiers in a three-phase circuit. The output (maximum power 9 kW) is connected to electric heaters in the incoming air duct. With the new arrangement the temperature in the spectrometer housing enclosure has been held within ±0.02°C.

D. Selection of Crystals

Since 1930 this Laboratory has been engaged in a search for highly perfect samples of crystals suitable for x-ray spectroscopy. More than a hundred crystals of calcite, silicon, quartz, and beryl have been cut and ground parallel to an atomic plane (in many cases polished), etched, and studied by the double crystal $(1-1)$ technique of measuring the resolving power, percent reflection, and intensity in the "tails." Approximately ten of these approach theoretical perfection, measured with a copper target x-ray tube with projected focal spot width of the order of 1 mm or less. The crystal

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[11] C. L. Conner, Electronics **35**, 52 (1962).

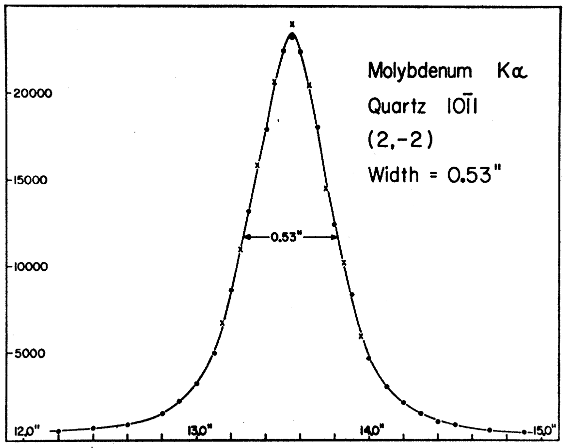

FIG. 1. Repeated runs on the (2−2) rocking curve for the Mo $K\alpha$ with quartz (10$\bar{1}$1) crystals. The width at half-maximum intensity is 0.53 sec. The dots and crosses represent two independent runs.

surfaces vary in size from 30×77 mm to 30×30 mm. From these, the best specimens of calcite, quartz, and silicon were selected for the present measurements. They appear to be the equal or better than any crystals reported in the literature; yet when these crystals were examined[12] by a recently developed technique, they showed inhomogeneities that could easily produce errors of as much as a second of arc in spectroscopic measurement of wavelength.

These errors have been minimized in the present work by careful alignment of the crystals on the double-crystal spectrometer, so that the same small area of the crystal was used for the measurement of the diffracted peaks in both the + and − orders. The same technique was used when the crystal and slit were aligned for the single-crystal modification of the spectrometer, which is essentially an inverted Siegbahn "tube spectrograph." The final errors in the present work were to a large extent due to the crystal imperfections; future improvements in x-ray spectroscopy will depend primarily on the procurement of better crystals.

E. The X-Ray Spectrometer

The general plans, specifications, and requirements for the double-crystal spectrometer were developed by Compton[13] in 1926, and the Société Genevoise of Switzerland designed a high-precision spectrometer with these requirements, and built two for the University of Chicago. Experience of one of the present authors (JAB) with one of these instruments suggested some modifications and improvements, and a spectrometer was designed incorporating these revisions. In addition to the spectrometer built for The Johns Hopkins University in 1930, the Société Genevoise built three others; one was shipped to Japan and destroyed by the armed forces just after the war; one was sent to Italy; and a second one went to the United States; the last two are both lost. The precision circle of the famed Siegbahn tube spectrograph is now usable only over an interval of some 30°. Thus, in addition to the requirements of better crystals for x-ray spectroscopy, additional precision spectrometers are also needed.

The spectrometer is a massive (approximately 500 lb) instrument, with two independent precision circles approximately 25 cm in diameter. Four special microscopes with precision cross-hair slides are provided for measuring the angle of rotation of the second crystal, and one for the detector or ionization chamber angle. The four microscopes are placed in pairs 180° apart, and 26°40′ between each pair. The first crystal is usually mounted on a rigid slide 21 cm from the main second crystal axis. The circles are driven by worm gears and a reduction gear; a vernier dial permits advancing the crystal angle in steps as small as 0.01 sec. The precision of the cone bearing and worm gear drive is indicated in Fig. 1, where a repeated run on the (2−2) rocking curve for the Mo $K\alpha$ with quartz (10$\bar{1}$1) crystals is shown. A recent addition to the spectrometer of an angular interferometer[14] facilitates the changing of angles by 0.01 sec increments.

F. Calibration of the Spectrometer

In calibrating the precision circle, the four microscopes were mounted 90° apart and the multiple microscope procedure described by Marzolf[14] was used to determine the true angles from 0° to 90° to 180° to 270° and to 0°. Likewise, the 90° separations of all 5° lines were established. Three microscopes were placed 45° apart, and the error in the position of the 45°, 135°, 225°, and 315° lines measured. The three microscopes were then placed 30° apart, and the errors in the 30° and 60°, etc., lines established.

The development of the angle-measuring interferometer[14] made it possible to step off repeated angles of approximately 5° to within a few hundredths of a second, and also to subdivide the 5° interval into any fraction. The interferometer was used to subdivide the 30° intervals and establish the error in each 10-min line of the entire circle. The entire calibration measurement was repeated four times with four observers, and a fifth observer was used over a 40° interval of the calibration. This was done to include in the calibration a judgment micrometer setting error of different observers. An IBM 1620 was used to calculate the average error as indicated by the four microscopes in their usual position for each of the 2160 lines on the circle; the reading of one particular microscope designated A was used as a reference value in tabulating the correction. The probable error in the correction for each line was calculated from the

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[12] A. Henins and J. A. Bearden, Bull. Am. Phys. Soc. **8**, 313 (1963).

[13] A. H. Compton, Rev. Sci. Instr. **2**, 365 (1931).

[14] J. G. Marzolf, Rev. Sci. Instr. (to be published).

readings of the four or five observers, and in only a few of the 2160 lines did it exceed 0.1 sec, and on most was of the order of 0.05 sec. A new interferometer, which is capable of measuring angles greater than 30°, has been built for this spectrometer within the past year. With it, a further improvement in the accuracy of the calibration could be made; but, as indicated above, crystal imperfections are at present the limitation in x-ray spectroscopy.

G. Recording Equipment

In precision recording of x-ray data, where the maximum capability of spectrometer and associated equipment is required, the operator should be able to continuously observe the output data, plotted as final experimental curves. Unexpected changes in recorded x-ray intensity can be observed and all the electronic and x-ray meters checked immediately to determine whether or not the change was real or instrumental.

The x-ray quanta were detected by a sodium iodide crystal coupled to an EMI 6097B photomultiplier. A noninverting transistor preamplifier with a gain of 15 was mounted at the base of the photomultiplier. An amplifier and channel analyzer were used to reduce background and furnish uniform output pulses which were fed into the plotting system.

A small computer, using Packard-Bell 200 kc/sec germanium circuit modules as logical elements, serves to transmit this information to a Calcomp digital plotter. The digital plotter is limited to a maximum input pulse rate of 200 cps, which is much slower than the count rate at the x-ray detector. Since as many as 20 000 counts might be recorded in a single counting interval, it is not sufficient for the computer merely to reduce the pulse rate to the plotter. Therefore, the plotting computer fulfills two functions. First, in order to reduce plotting time, the computer determines the incremental change in the number of counts between successive counting intervals. Secondly, it advances the x position of the plotter as the spectrometer angle setting is changed.

The heart of the intensity (or $y-$) plotting section of the computer is a pair of 15-stage reversible binary scalars. These scalars are constructed so that when a scalar is counting downward and reaches zero, the counting direction is reversed so that successive pulse inputs are recorded as upward counts. Labeling the two counters as A and B, one can explain the logical operation as follows: (1) initially, the A scalar contains the total number of pulses recorded during the previous counting interval and the B scalar is at zero; (2) pulses from the next counting interval are fed to both A and B, such that A counts downward and B counts upward; (3) at the end of (2), B contains the total number of counts accepted during the interval and A contains the incremental change (the sign of the increment is determined by whether or not A reached zero during the count interval); (4) the contents of A are then fed to the plotter at a 200 cps rate by counting A downward to zero with a pulse generator that also feeds the appropriate $+$ or $-$ y-plotter channel. At the next pulse counting interval, the above sequence of operations is repeated with the operations of A and B interchanged. The capacities of A and B and the logical circuitry are such that a maximum of 32 000 counts can be fed to the computer during any count interval, and the maximum increment is $\pm 16\,000$.

The x-plotting section of the computer operates in two modes. In the manual mode, the computer advances the plotter in the x direction by an externally preset amount. In the automatic mode the angular position of the spectrometer is transmitted in digital form to the computer; this information then determines how far the plotter must advance in the x direction.

The computer operates cyclically. During the count cycle, pulses from the x-ray detector enter scalars A and B. The y-plot cycle is then initiated, followed by the x-plot cycle. Finally the computer is reset to accept a new count input.

The recording point of the plotter moves in increments of 0.010 in. along both x and y axes. The plotting width x is 10 in., and the y axis can extend to any length up to 120 ft. The above controls permit the plotting of any portion of an x-ray diffraction to almost any desired scale.

The accuracy is greater than normally obtained when plotted by hand and, more importantly, this method eliminates human errors. More than 3000 diffraction curves have been plotted during the past year, and the wavelength of the peak intensity determined. When the curves are expanded to the 10-in. plotter width, the accuracy of locating the peak of a symmetrical line is statistically 0.1% of the half-width. Repeated measurements, using the interferometer to monitor crystal angles, on curves of 20 sec width (at half-maximum intensity) with 20 000 to 30 000 counts for points near the peak gave an average deviation of the line center of ±0.02 sec. Similarly, lines of 200 sec in width have been measured to 0.2 sec.

H. Adjustment of Double-Crystal Spectrometer

The crystal on the main axis of the spectrometer was supported by springs holding the diffracting plane of the crystal lightly against three adjustable screw supports. The plane formed by the three rounded ends of the screws was adjusted parallel to and on the axis of rotation as follows. The crystal was replaced by a plane parallel mirror 25×35 mm, aluminum-coated on one side, which was placed in contact with the three screws. A visual auto-collimating telescope was used to adjust the screws until the reflected image of the cross hair in the 180° rotation positions coincided. The telescope is equipped with a level by which its optical axis can be adjusted horizontally within one sec of arc. With the telescope leveled thus, the base screws of the spectrometer were adjusted until the axis of rotation was vertical, as indicated by the coincidence of the direct and reflected cross-hair images. A low-power microscope of approximately 100 magnification equipped with a divided scale was set up above the mirror and approximately on the axis of rotation of the spectrometer, and focused on the edge of the mirror in contact with the three screws. By 180° rotations, the three screws were adjusted to make the mirror edge coincide with the axis of the spectrometer, while it was maintained parallel to the axis by telescopic observations. The surface of the mirror was located within 0.01 mm of the axis of rotation and parallel to it within 1 sec.

The first crystal was mounted on a slide midway between the second crystal and the focal spot of the x-ray tube, with the slide axis perpendicular to the line joining the focal spot and the axis of the spectrometer. A good machinist's square gives ample precision in determining this perpendicular. This condition permits different wavelengths to be selected by moving the crystal with the slide and without requiring any readjustment of the spectrometer or x-ray tube position. The autocollimating telescope was then moved into a position such that its axis coincided with the center of the slide. This was accomplished by moving the slide as close to the telescope as possible, focusing on a suitable mark on the slide, and then moving the slide as far away from the telescope as possible. If the cross hair and the mark remained in coincidence, this adjustment was completed. A plane parallel mirror was then placed in the first crystal holder, and with the telescope level, the three-point support of the first crystal holder was adjusted normal to the telescope axis. By this method the planes formed by the two sets of three-point crystal supports were made parallel to the spectrometer axis within ±1 sec.

The crystals, whose surfaces had been ground parallel to the desired atomic planes (to within ±5 sec, although such accuracy is not required for most measurements), were then put in position and the first crystal slide adjusted so as to diffract the x ray (usually copper $K\alpha$) across the spectrometer axis. A detector without slits was placed in approximate position and the second crystal adjusted to its $(1-1)$ diffracting position. The slide position was readjusted until the diffracted beam was incident on each crystal at its center, as indicated by observing the x-ray intensity as a thin lead wedge was moved along the crystal surface.

Appropriate slits and lead stops were inserted to prevent scattered x rays from entering the detector. Finally, horizontal slits near the x-ray tube and at the detector were adjusted in a plane normal to the axis of rotation, with the telescope and level, within 0.1 mm.

I. Adjustment of Single-Crystal Spectrometer

The development of a high-power rotating target x-ray tube with a focal spot area of 0.3×10 mm provides an x-ray source of extremely high intrinsic intensity, and has made possible the construction of a single-crystal spectrometer superior to the double-crystal instrument for wavelengths greater than that of the Cu $K\alpha_1$ line. The x-ray take-off angle from the rotating target was approximately 3°, giving a projected beam width of 0.015 mm, which formed the first slit of the spectrometer. The second slit was 0.015 mm wide and was placed immediately before the single crystal, which was on the main axis of the spectrometer. The separation of the slits was 500 mm, giving an angular collimation of 6 sec of arc, which is less than the calcite single-crystal diffraction pattern width at 1.5 Å. The intensity was ample to make measurements at Bragg angles greater than ±50°. Stability of the focal spot maintained θ within ±0.1 sec over several hours operation; a complete measurement of 2θ required approximately 15 min. Other advantages of the single-crystal spectrometer are: (1) different wavelengths can be measured with no readjustment of the spectrometer or x-ray tube; (2) the line diffraction profile is identical for both $180°\pm2\theta$ diffraction peaks.

The three-point crystal support was aligned as in the double-crystal technique. The rotating target x-ray tube was leveled, making the focal spot length vertical and hence parallel to the spectrometer axis. A flat mirror was put in place of the crystal and set parallel to the x-ray beam by visual observation of total reflection. The second slit was adjusted horizontally until equal intensity passed the mirror when it was rotated from one 180° position to the other. With the mirror set parallel to the x-ray beam and intercepting approximately one-half of the total intensity, a horizontal slit of 0.5 mm in width was used to measure the intensity at the bottom and top of the part of the beam passing the mirror. Equal intensity at top and bottom indicated parallelism of the slits and axis to better than 30 sec.

J. Vertical Divergence, Misalignment, Tilt, and Temperature Corrections

It has long been recognized that measured wavelengths in x-ray spectroscopy require a correction due to vertical divergence of the beam. An equation for this correction was given by Williams[15]; afterwards Parratt[16] disagreed and published a different expression. A more basic approach was taken by Schwarzchild[17] and extended by Merrill and DuMond[18] and by Schnopper.[19] The last three sources include the effects of crystal tilt and of misalignment (i.e., centers of the two slits lying in different horizontal planes). These various results are

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[15] J. H. Williams, Phys. Rev. 40, 636 (1932).

[16] L. G. Parratt, Phys. Rev. 47, 882 (1935).

[17] M. M. Schwarzschild, Phys. Rev. 32, 162 (1928).

[18] J. J. Merrill and J. W. M. DuMond, Ann. Phys. (N. Y.) 14, 166 (1961).

[19] H. W. Schnopper, Cornell University Research Report No. 13, Contract AF 49(638)-402, 15 April 1962 (unpublished).

presented in quite different forms, so that it is not always straightforward to compare them.

A careful reanalysis of the whole problem has resulted in the following expression for correction of double-crystal spectrometer wavelengths based on measurements in the $(m\pm n)$ positions (for the single-crystal case, $\delta_1=0$):

$$\Delta\theta_n=+(2\sin\theta_m\tan\theta_n)\delta_1\Psi+(\delta_2\Psi/\cos\theta_n)-\tan\theta_n\left[\frac{\Psi^2}{2}+\frac{a^2+b^2}{24L^2}\right],$$

where δ_1 and δ_2 are the angular tilts of the two crystals, θ_m and θ_n their respective Bragg angles, a and b the two slit heights, L the distance between slits, and Ψ the angular misalignment (departure from horizontal), and $\Delta\theta_n$ the correction to the apparent (measured) Bragg angle θ_n, all angles being expressed in radians. This is an approximate expression based on assumptions which are easily fulfilled in the present measurements. A more rigorous expression would, for example, contain terms in δ_1^2 and δ_2^2; but, in the present instance, these are far smaller than the cross terms in $\delta_1\Psi$ and $\delta_2\Psi$. Consequently, the tilt errors are completely negligible unless coupled with misalignment. In the present experiment all terms in Ψ are relatively small compared with the vertical divergence correction.

The latter correction checks the expression given by Williams[15] rather than that of Parratt.[16] Schnopper's[19] result is in a form which makes direct comparison difficult. However, a comparison of one of his numerical cases with the Williams formula shows good agreement.

In the present measurements the primary concern is the establishment of wavelength ratios with use of several different crystals. Hence all measurements have been made as close as possible to a selected standard temperature; for convenience this has been chosen as 25°C. During a given run the temperature was maintained constant within ±0.1°C and, in general, from one series of measurements to another the temperature was within ±0.3°C. In a few cases where the temperature during a run differed from 25.0C° by 0.1°C or more, a correction for expansion of the crystal has been made to reduce all values to the same temperature. The thermal expansion coefficient of silicon[20] is $2.32\times10^{-6}(°\mathrm{C})^{-1}$, and in sec

$$\Delta\theta=0.47(t-25.0)\tan\theta.$$

Calcite has two expansion coefficients[21]: $25.14\times10^{-6}(°\mathrm{C})^{-1}$ parallel to the optic axis and $-5.58\times10^{-6}(°\mathrm{C})^{-1}$ perpendicular to this axis. Hence for the 211 cleavage plane

$$\Delta\theta=2.10(t-25.0)\tan\theta.$$

Quartz also has two expansion coefficients,[21] $\alpha_\perp=13.37\times10^{-6}(°\mathrm{C})^{-1}$ and $\alpha_\parallel=7.97\times10^{-6}(°\mathrm{C})^{-1}$; thus for the $10\bar{1}1$ and $10\bar{1}\bar{1}$ planes

$$\Delta\theta=2.36(t-25.0)\tan\theta.$$

III. RESULTS

A. Method of Adjustment

In order to make the present measurements directly comparable to the two most widely used wavelength tables, those of Sandstrom[22] and of Cauchois and Hulubei,[23] we have provisionally adopted the Mo $K\alpha_1$ as a standard and taken its wavelength as exactly 707.8310 xu. This is only a provisional choice and does not affect the relative wavelength values to be computed here.

One method of procedure would be as follows: (1) Compute the grating constant of each crystal from its Bragg angles as measured with the Mo $K\alpha_1$ line; (2) for each of the other lines, use these grating constants to obtain a set of wavelength values; (3) take an appropriate weighted average of these results to obtain a recommended wavelength for each of the other x-ray lines. However, this procedure would not employ all of the data to the best advantage in a symmetrical way. For example, the Bragg angle for a particular crystal with Mo $K\alpha_1$ might be rather inaccurate, but the values for the same crystal with Cu $K\alpha_1$ and Cr $K\alpha_2$ might be of higher precision. The high-precision determination of the ratio of the last two wavelengths would then be obscured by the inaccuracy of the first measurement.

Actually each angular measurement yields a value of $\lambda/2d$ for the appropriate combination of wavelength and crystal grating constant. Using the Bragg equation as corrected for index of refraction, this relation may be expressed as follows:

$$\frac{\lambda}{2d}=\left(\frac{\sin\theta_n}{n}\right)\left[1-\frac{4d^2}{n^2}\left(\frac{\delta}{\lambda^2}\right)\right], \qquad (1)$$

where λ is the wavelength, d the grating constant for infinite order (i.e., d_∞), n the order of diffraction, θ_n the Bragg angle for this order, and $\delta\equiv1-\mu$, μ being the index of refraction.

Thus there results an overdetermined system of M equations (total number of combinations of wavelengths and crystals employed) for m unknowns (number of grating constants plus wavelengths, excluding Mo $K\alpha_1$ which is provisionally fixed by definition). Each equation will, in general, carry a different weight as determined by its estimated error. The obvious way of treating such a system of equations symmetrically is to perform a least-squares adjustment (for

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[20] D. F. Gibbons, Phys. Rev. **112**, 137 (1958).

[21] *Handbook of Chemistry and Physics* (The Chemical Rubber Publishing Company, Cleveland, Ohio, 1962), 44th ed. pp. 2326–29. Note sign error in $\alpha_\perp$ for calcite.

[22] Reference 2, pp. 182–5.

[23] Y. Cauchois and H. Hulubei, *Longueurs d'Onde des Emissions X et des Discontinuités d'Absorption X* (Hermann et Cie., Paris, 1947).

TABLE I. Experimental data and weighted averages of $\lambda/2d$. The cleavage (100) plane was used for the calcite crystal C; for quartz, the (10$\bar{1}$1) and the (10$\bar{1}\bar{1}$) were used with crystals Q1 and Q2, respectively; for silicon, S1 and S2, the (111) plane was used except where otherwise indicated in the *notes* column; when other planes were used for S1 or S2, the results in the $\lambda/2d$ column have been converted into terms of d (111). Single-crystal measurements are indicated by SC in *notes* column; all others were double-crystal determinations. Some measurements on W, indicated by T in *notes* column, were taken using transmission; all others employed reflection. The values used for δ/λ^2, where δ is the decrement of the index of refraction ($\delta \equiv 1-\mu$), were as follows: calcite 3.69×10^{-6} Å^{-2}; quartz, 3.60×10^{-6} Å^{-2}; silicon, 3.22×10^{-6} Å^{-2}. The first two values are taken from Sandström[2] and the last was obtained from I. Henins and J. A. Bearden, Phys. Rev., **135**, A890 (1964). The Cu $K\alpha_1$ diffraction data for silicon crystal S1 were taken from the above Henins and Bearden paper.

Line	Crystal	Order	Notes	Runs	Series	θ_{av}	$\lambda/2d$	Wt.
Cr $K\alpha_2$	C	1		1	1	22°11′48.57″	0.37773829	1
		1	SC	1	1	22°11′49.44″	0.37774219	1
		2		6	1	49°04′12.79″	0.37774376	4
		2	SC	3	1	49°04′11.73″	0.37774207	3
							0.37774241	
	Q1	2		2	1	43°18′58.67″	0.34299895	1
		2	SC	2	1	43°18′57.30″	0.34299653	1
							0.34299774	
	S1	1		1	1	21°27′22.66″	0.36574519	1
		1	SC	2	1	21°27′21.26″	0.36573888	1
							0.36574204	
	S2	1	(400)	1	1	57°38′06.55″	0.36573831	
Cu $K\alpha_1$	C	1		2	1	14°41′59.25″	0.25372004	1
		2		1	1	30°29′41.1″	0.25372113	1
		3		3	2	49°34′03.93″	0.25372066	3
		2	SC	1	1	30°29′41.52″	0.25372200	1
							0.25372086	
	Q1	3		4	1	43°43′20.64″	0.23038423	
	Q2	3		4	1	43°43′21.28″	0.23038498	
	S1	1		5	2	14°13′21.80″	0.24566080	1
		3		5	2	47°28′31.57″	0.24565907	3
							0.24565950	
	S2	1	(400)SC	2	1	34°33′53.73″	0.24565949	
Mo $K\alpha_1$	C	4		9	2	27°51′27.11″	0.11681766	
	Q1	3		5	3	18°33′19.60″	0.10607218	
	Q2	4		4	2	25°06′22.36″	0.10607334	
	S1	4		7	3	26°53′58.17″	0.11310580	
Ag $K\alpha_1$	C	5		7	2	27°25′46.18″	0.09213085	
	Q1	5		4	1	24°43′35.18″	0.08365671	
	S1	5		7	2	26°29′19.37″	0.08920385	
W $K\alpha_1$	C	5		22	4	9°54′38.68″	0.03442258	3
		5	T	17	1	9°54′38.39″	0.03442249	1
							0.03442256	
	Q1	5		2	1	8°59′28.35″	0.03125638	
	S1	7		7	2	13°29′30.28″	0.03332924	3
		4	(211)-T	1	1	10°52′02.22″	0.03332854	1
							0.03332907	
	S2	3	(400)	3	1	13°21′02.50″	0.03332900	

details on this procedure see, for example, Bearden and Thomsen[24] or Cohen, Crowe, and DuMond[25]). While the right-hand sides of these equations are actually correlated through the δ's in the correction terms, these terms are so small that the effect may be ignored.

B. Data

The experimental data obtained are given in Table I. In this table a *run* denotes a sequence of curves taken

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[24] J. A. Bearden and J. S. Thomsen, Nuovo Cimento Suppl. **5**, 267 (1957), Appendix B and Sec. C.

[25] E. R. Cohen, K. M. Crowe, and J. W. M. DuMond, *The Fundamental Constants of Physics* (Interscience Publishers, Inc., New York, 1957), Chap. 7.

TABLE II. Input data for least-squares analysis.

Item	Wavelength	Crystal	$\lambda/2d$	Error (ppm)	Wt.
1	Cr $K\alpha_2$	C	0.3777 4241	2.0	4
2	Cu $K\alpha_1$	C	0.2537 2086	2.0	4
3	Mo $K\alpha_1$	C	0.1168 1766	2.0	4
4	Ag $K\alpha_1$	C	0.0921 3085	2.0	4
5	W $K\alpha_1$	C	0.0344 2256	2.309	3
6	Cr $K\alpha_2$	Q1	0.3429 9774	2.0	4
7	Cu $K\alpha_1$	Q1	0.2303 8423	2.828	2
8	Mo $K\alpha_1$	Q1	0.1060 7218	2.0	4
9	Ag $K\alpha_1$	Q1	0.0836 5671	2.828	2
10	W $K\alpha_1$	Q1	0.0312 5638	4.0	1
11	Cu $K\alpha_1$	Q2	0.2303 8498	2.828	2
12	Mo $K\alpha_1$	Q2	0.1060 7334	2.0	4
13	Cr $K\alpha_2$	S1	0.3657 4204	2.828	2
14	Cu $K\alpha_1$	S1	0.2456 5950	2.0	4
15	Mo $K\alpha_1$	S1	0.1131 0580	2.0	4
16	Ag $K\alpha_1$	S1	0.0892 0385	2.0	4
17	W $K\alpha_1$	S1	0.0333 2907	2.828	2
18	Cr $K\alpha_2$	S2	0.3657 3831	4.0	1
19	Cu $K\alpha_1$	S2	0.2456 5949	2.828	2
20	W $K\alpha_1$	S2	0.0333 2900	4.0	1

TABLE III. Origin values for least-squares analysis.

i	v_i	v_{io}(xu)
1	$\lambda_{\mathrm{Cr}\ K\alpha_2}$	2288.8500
2	$\lambda_{\mathrm{Cu}\ K\alpha_1}$	1537.3669
3	$\lambda_{\mathrm{Ag}\ K\alpha_1}$	558.2466
4	$\lambda_{\mathrm{W}\ K\alpha_1}$	208.5758
5	$2d_{\mathrm{C}}$	6059.2849
6	$2d_{\mathrm{Q1}}$	6673.1056
7	$2d_{\mathrm{Q2}}$	6673.0352
8	$2d_{\mathrm{S1}}$	6258.1295
9	$2d_{\mathrm{S2}}$	6258.1295

alternately in the $(m, +n)$ and $(m, -n)$ positions (or in the case of single crystal measurements, in the $+n$ and $-n$ positions) in a continuous series of observations; the value of n is listed in the *order* column. In most cases a *run* consists of six or eight curves, but in occasional instances there are as few as four or as many as twelve. A *series* consists of one or more runs taken within a few days time without any readjustment in the spectrometer. Where two or more *series* are recorded, they are usually separated by an interval of several months with many other measurements intervening.

Comparison of two series of measurements taken at different times showed differences of 1 to 8 ppm for various cases, with an average discrepancy of about 3.6 ppm. This difference was significantly greater than that estimated from the internal errors within a particular series, so that the latter were of minor importance in weighting the data. To obtain the values of θ_{av} listed in Table I, weights of 1, 2, or 3 were assigned to each individual run, with two considerations in mind: (1) Data taken during the latter portion of the experiment was, in general, given greater weight, due to a more precise alignment procedure; (2) weights were, in general, assigned to give comparable weight to each series of runs. The latter criterion recognizes the fact that accumulation of a large number of runs within one series did not give as much information as a few additional runs in a second series at a later time.

For each angle θ_{av} shown in Table I, $\lambda/2d$ is calculated by Eq. (1). In many instances two or more values are obtained for the same combination of crystal and wavelength by use of different orders or different techniques, as indicated. In such cases the weighted average of $\lambda/2d$ was obtained as shown in Table I. These weights were assigned on the basis of the order involved (higher orders were given greater weight due to the larger angles involved) and the number of runs and series going into each θ_{av}.

The resulting set of values is summarized in Table II, including the errors (*standard deviations*) to be associated with each value of $\lambda/2d$. In assigning these errors, the chief emphasis was put on *relative* weights. The absolute values of the errors were roughly estimated from the results of a preliminary adjustment on part of the data and from the discordance between different series, as explained above. In most cases values representing two or more series were assigned an error of 2 ppm and those representing a single series an error of 2.828 ppm, i.e., half the weight. For measurements with tungsten both figures were multiplied by $\sqrt{2}$ (i.e., weights were halved), due to the significantly small angles involved. A few exceptions to this scheme were made where the number of runs involved was excessively large or excessively small.

C. Least-Squares Adjustment

The 20 equations resulting from Table II, involving 4 unknown wavelengths and 5 grating constants, are actually all linear. However, it is convenient to reduce them to a simpler "linearized" form as follows: For each variable a so-called origin value v_{io} is chosen which lies close to the true value of v_i, as shown in Table III. The origin values are taken from prior determinations or from a preliminary adjustment. The "linearized" variables x_i are now defined through the relation

$$x_i = [(v_i - v_{io})/v_{io}] \times 10^6. \tag{2}$$

Consider a typical equation such as that given by item 1 of Table II. This may be written

$$v_1 = C_1 v_5.$$

Taking the logarithmic derivatives and expressing the result in terms of small differences from the origin values yields

$$(\Delta v_1/v_1) - (\Delta v_5/v_5) = (\Delta C_1/C_1) \equiv (C_1 - C_{1o})/C_{1o}, \tag{3}$$

where $C_{1o} = v_{1o}/v_{5o}$, i.e., the origin value for v_1. By Eq.

TABLE IV. "Linearized" equations for least-squares analysis.

Item	Equation	Wt.
1	$x_1-x_5=-0.50$	4
2	$x_2-x_5=0.04$	4
3	$-x_5=0.69$	4
4	$x_3-x_5=0.87$	4
5	$x_4-x_5=1.45$	3
6	$x_1-x_6=4.46$	4
7	$x_2-x_6=7.42$	2
8	$-x_6=-0.19$	4
9	$x_3-x_6=6.22$	2
10	$x_4-x_6=6.41$	1
11	$x_2-x_7=0.13$	2
12	$-x_7=0.19$	4
13	$x_1-x_8=4.79$	2
14	$x_2-x_8=1.30$	4
15	$-x_8=-0.35$	4
16	$x_3-x_8=4.70$	4
17	$x_4-x_8=8.71$	2
18	$x_1-x_9=-5.41$	1
19	$x_2-x_9=1.26$	2
20	$x_4-x_9=6.61$	1

(2) this becomes

$$x_1-x_5=[(C_1-C_{1o})]/C_{1o}\times10^6. \tag{4}$$

The right-hand side is now readily calculable in terms of the experimental C_1 (the value listed for $\lambda/2d$ in Table II) and the origin values given in Table III, which fix C_{1o}. The resulting set of equations are listed in Table IV.

This overdetermined set of 20 equations for 9 unknowns is now solved by the standard least squares procedure.[24,25] The results, together with the errors are shown in Table V.

The errors obtained from the inverse matrix of the normal equations are standard deviations based on internal consistency, i.e., those implied by the standard deviations assigned somewhat arbitrarily to the input data in Table II. These have been converted to probable errors through multiplication by the factor 0.6745 (strictly valid only for a Gaussian distribution) and to the basis of external consistency by multiplication by the factor $(\chi^2/\langle\chi^2\rangle)^{1/2}=(10.727/11.0)^{1/2}$, based on the standard χ^2 test. This last factor is virtually unity, indicating that the rather crude assignment of errors in Table II represents a fortuitously good choice.

TABLE V. Least-squares solution and χ^2 test.

Variable	Adjusted value	Error (ppm)[a]
x_1	1.828	1.098
x_2	2.043	1.007
x_3	3.543	1.122
x_4	5.581	1.265
x_5	1.981	0.900
x_6	−2.055	0.945
x_7	0.511	1.137
x_8	−0.778	0.915
x_9	1.943	1.589
	$\chi^2=10.727$	
	Expected $\langle\chi^2\rangle=M-m=20-9=11$	

[a] Errors quoted are probable errors based on external consistency.

TABLE VI. Probable errors and correlation coefficients.

Probable errors (ppm)

λ_{Cr}	λ_{Cu}	λ_{Ag}	λ_{W}	d_{C}	d_{Q1}	d_{Q2}	d_{S1}	d_{S2}
1.10	1.01	1.12	1.27	0.90	0.95	1.14	0.92	1.59

Correlation coefficients

	λ_{Cr}	λ_{Cu}	λ_{Ag}	λ_{Mo}	d_{C}	d_{Q1}	d_{Q2}	d_{S1}	d_{S2}
λ_{Cr}	1.00	0.45	0.43	0.40	0.56	0.55	0.13	0.47	0.40
λ_{Cu}		1.00	0.43	0.42	0.56	0.45	0.29	0.55	0.48
λ_{Ag}			1.00	0.38	0.56	0.45	0.13	0.56	0.29
λ_{W}				1.00	0.52	0.38	0.12	0.47	0.40
d_{C}					1.00	0.45	0.16	0.50	0.38
d_{Q1}						1.00	0.13	0.41	0.31
d_{Q2}							1.00	0.16	0.14
d_{S1}								1.00	0.35
d_{S2}									1.00

Since the adjusted values all arise from a common least-squares adjustment, their errors are not statistically independent of one another. Hence, in order to compute the correct error for any product or quotient of these quantities, correlation coefficients are required. Such cases occur in calculations of wavelength ratios, grating constants ratios, and values of $\lambda/2d$ (which give predicted values for the Bragg angles). These coefficients are shown in Table VI, with the probable errors repeated there for convenience. (Since the matrix is symmetric the lower half of the off-diagonal elements are omitted.)

The probable error e_y in a derived quantity

$$y=x_i^a x_j^b \tag{5}$$

is now given by

$$e_y^2=(ae_i)^2+2abr_{ij}e_ie_j+(be_j)^2, \tag{6}$$

where e_i and e_j are the probable errors of x_i and x_j, respectively, and r_{ij} is the correlation coefficient. Thus, to obtain the probable error of the ratio $d_{\mathrm{Q1}}/d_{\mathrm{Q2}}$, one takes $i=6$, $j=7$, $a=1$, and $b=-1$ and obtains

$$e^2=0.95^2-2\times0.13\times0.95\times1.14+1.14^2=1.39^2 \tag{7}$$

giving a probable error of approximately 1.4 ppm.

The adjusted values for the original variables are readily obtained through Eq. (2) and are presented in Table VII. These represent a set of consistent values relative to the Mo $K\alpha_1$ line.

TABLE VII. Adjusted values of wavelengths and grating constants (based on assumed value $\lambda_{\mathrm{Mo}\,K\alpha_1}=707.831$ xu).[a]

	Adjusted values	
$\lambda_{\mathrm{Cr}\,K\alpha_2}$	$=(2288.854\pm0.003)$ xu	(1.1 ppm)
$\lambda_{\mathrm{Cu}\,K\alpha_1}$	$=(1537.370\pm0.002)$ xu	(1.0 ppm)
$\lambda_{\mathrm{Mo}\,K\alpha_1}$	$=707.8310$ (assumed value; see Sec. IIIA.)	
$\lambda_{\mathrm{Ag}\,K\alpha_1}$	$=(558.2486\pm0.0006)$ xu	(1.1 ppm)
$\lambda_{\mathrm{W}\,K\alpha_1}$	$=(208.5770\pm0.0003)$ xu	(1.3 ppm)
$2d_{\mathrm{C}}$	$=(6059.297\pm0.006)$ xu	(0.9 ppm)
$2d_{\mathrm{Q1}}$	$=(6673.092\pm0.006)$ xu	(0.9 ppm)
$2d_{\mathrm{Q2}}$	$=(6673.039\pm0.008)$ xu	(1.1 ppm)
$2d_{\mathrm{S1}}$	$=(6258.125\pm0.006)$ xu	(0.9 ppm)
$2d_{\mathrm{S2}}$	$=(6258.142\pm0.010)$ xu	(1.6 ppm)

[a] All grating constnts are given for 25°C. Errors are *probable errors* based on *external consistency*.

TABLE VIII. Adjusted wavelength ratios.

Adjusted wavelength ratios		
$(\lambda_{\mathrm{Cr}\ K\alpha_2}/\lambda_{\mathrm{Cu}\ K\alpha_1})$	$=1.488\,811\pm0.000002$	(1.1 ppm)
$(\lambda_{\mathrm{Cr}\ K\alpha_2}/\lambda_{\mathrm{Mo}\ K\alpha_1})$	$=3.233\,617\pm0.000004$	(1.1 ppm)
$(\lambda_{\mathrm{Cr}\ K\alpha_2}/\lambda_{\mathrm{Ag}\ K\alpha_1})$	$=4.100\,063\pm0.000005$	(1.2 ppm)
$(\lambda_{\mathrm{Cr}\ K\alpha_2}/\lambda_{\mathrm{W}\ K\alpha_1})$	$=10.973\,667\pm0.000014$	(1.3 ppm)
$(\lambda_{\mathrm{Cu}\ K\alpha_1}/\lambda_{\mathrm{Mo}\ K\alpha_1})$	$=2.171\,945\pm0.000002$	(1.0 ppm)
$(\lambda_{\mathrm{Cu}\ K\alpha_1}/\lambda_{\mathrm{Ag}\ K\alpha_1})$	$=2.753\,917\pm0.000003$	(1.1 ppm)
$(\lambda_{\mathrm{Cu}\ K\alpha_1}/\lambda_{\mathrm{W}\ K\alpha_1})$	$=7.370\,757\pm0.000009$	(1.2 ppm)
$(\lambda_{\mathrm{Mo}\ K\alpha_1}/\lambda_{\mathrm{Ag}\ K\alpha_1})$	$=1.267\,9495\pm0.0000013$	(1.1 ppm)
$(\lambda_{\mathrm{Mo}\ K\alpha_1}/\lambda_{\mathrm{W}\ K\alpha_1})$	$=3.393\,620\pm0.000004$	(1.3 ppm)
$(\lambda_{\mathrm{Ag}\ K\alpha_1}/\lambda_{\mathrm{W}\ K\alpha_1})$	$=2.676\,463\pm0.000004$	(1.3 ppm)
$(d_{\mathrm{Q1}}/d_{\mathrm{Q2}})$	$=1.000\,0080\pm0.0000014$	(1.4 ppm)
$(d_{\mathrm{S2}}/d_{\mathrm{S1}})$	$=1.000\,0027\pm0.0000015$	(1.5 ppm)

However, the choice of Mo $K\alpha_1$ as a reference line was purely a provisional one; the primary result of this study is the relative values of the various wavelengths. These are presented in Table VIII with appropriate errors calculated with the aid of Table VI. Table VIII also shows the ratios of grating constants for the two quartz crystals and the two silicon crystals, with the appropriate errors. In all cases the resulting errors are less than would be obtained by treating the quantities as statistically independent.

IV. CONCLUSIONS

(1) The wavelength ratios presented in Table VIII are recommended for general adoption in setting up a primary system of x-ray reference standards. Any one of the five lines might be used to define a wavelength standard and combined with these ratios to obtain the wavelength of the others. The errors in Table VIII show that the accuracy of the reference system will be almost equally good for any such choice.

(2) The grating constants given here are presented primarily as a matter of information and are applicable only to the particular crystals used in this laboratory. It seems clear from the ratios in Table VIII that there is a statistically significant difference between the constants of the two quartz crystals and possibly even between those of the two silicon crystals. Hence the high-precision values quoted here can not be used to obtain an effective constant applicable to all crystals of a given kind; this constant must be determined for the particular sample in question.

(3) The errors quoted in Tables VII and VIII are probable errors. These are all of the order of 1 ppm. They are *not* to be interpreted as limits of error; it is to be expected that there may well be errors of several ppm in some of the output data. With this understanding, the authors believe these estimates to be reasonably realistic, without additional allowance for systematic error (except possibly for Cr $K\alpha_2$).

The data involve three different kinds of crystals, different samples of the same crystal, determinations by both single-crystal and double-crystal techniques, and some transmission measurements along with the reflection ones. The results are expressed in terms of ratios and are not significantly affected by external calibration of any of the apparatus. It is true that the circle calibration is involved, which may produce an error of the order of 1 ppm for each determination. However, since the circle was read in many different places, the resulting error even here should be largely statistical.

There should be, in principle, small corrections for crystal asymmetry and other spectrometer window effects, which have been studied in detail by Merrill and DuMond,[18] Sauder,[26] and Marzolf.[27] This could affect first-order calcite measurements of Cr $K\alpha_2$ by the order of 5 ppm. For the corresponding case with Cu $K\alpha_1$, Sauder's calculations indicate an anomalously small correction due to fortuitous cancellation of terms. In general, the corrections fall off with higher order and decreasing wavelength, and are substantially smaller for quartz and silicon than for calcite. Hence, the effect on the adjusted values is estimated to be less than 1 ppm and has been ignored; possibly the probable error for Cr $K\alpha_2$ should be slightly increased.

(4) Table IX gives a comparison of the wavelength values of Table VII with those given in the tables of Sandström[22] and of Cauchois and Hulubei.[23] It is clear that the present results imply substantial changes in presently accepted ratios among some of these standards. This is particularly true of the wavelength ratio between Cu $K\alpha_1$ and Mo $K\alpha_1$, which is altered by 17 to 20 ppm. The reason for this discrepancy in the literature is not clear; but it seems possible that in the past an unduly low error has been assigned to Larsson's[28] excellent tube spectrometer measurement of Mo $K\alpha_1$.

(5) As indicated by the above discussion, x-ray spectroscopy has long been troubled by the fact that reproducibility of various measurements was better than their absolute accuracy. To avoid this, it is suggested that future precision determinations of reference lines should be made using two or more crystals, preferably of different kinds, under as many different conditions as possible, with repetitions after some interval of time

TABLE IX. Comparison of wavelength values (xu) for five reference lines.

Line	Present authors	Sandström[a]	Cauchois[b]
Cr $K\alpha_2$	2288.854	2288.89	2288.89
Cu $K\alpha_1$	1537.370	1537.396	1537.40
Mo $K\alpha_1$	707.831	707.831	707.831
Ag $K\alpha_1$	558.2486	558.253	558.235
W $K\alpha_1$	208.5770	208.573	208.571

[a] See Ref. 2, pp. 182–185.

[b] Y. Cauchois and H. Hulubei, *Longueurs d'Onde des Emissions X et des Discontinuités d'Absorption X* (Hermann et Cie., Paris, 1947).

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has elapsed. Wherever there is an appreciable amount of overdetermination, the use of the least-squares technique as employed here is also recommended.

(6) In the longer wavelength region ($\lambda > 1.5$ Å) the single-crystal spectrometer described here is capable of an accuracy substantially equal to that of a double-crystal instrument and has some advantages from the standpoint of convenience.

Note added in proof. The authors have just completed a report giving tables of recommended values for all x-ray emission lines and absorption edges, which is now in the course of publication. In this report, for reasons stated there, the W $K\alpha_1$ line has been adopted as the *primary standard for x-ray wavelengths*, with the value $\lambda_{\mathrm{W}\,K\alpha_1} = 0.2090100$. (This is believed to represent the value in *angstroms* within a probable error of 5 ppm.) The ratios given in Table VIII are, of course, equally as valid for this definitive choice as for the provisional one used in the present paper.

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Thermal Boundary Resistance between Solids and Helium below 1°K†

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Results are reported from measurements of the thermal boundary resistance between liquid He^3 and copper or epoxy resin, and between solid He^3 or liquid He^4 and copper. Measurements were made in the range 0.05 to 0.9°K and at pressures up to 395 psi. No quantitative agreement has been found with theory. Above 0.11°K, the thermal boundary resistance of liquid He^3 and liquid He^4 both have a temperature dependence stronger than T^{-3}. Below 0.11°K the thermal boundary resistance of He^3 varies as T^{-3} over the full pressure range in the liquid. In the case of He^4 at low pressure, however, the stronger temperature dependence continues to the lowest temperature measured (0.075°K). It is not clear whether the qualitative difference in the behavior of liquid He^3 and liquid He^4 is associated with zero sound in liquid He^3.

I. INTRODUCTION

The transfer of heat between liquid helium and a solid body in contact with the liquid produces a temperature discontinuity at the interface of the two media. This phenomenon, which may be considered as a thermal boundary resistance, was first discovered for liquid He^4 by Kapitza in 1941.[1] In 1957, Lee and Fairbank[2] observed similar behavior for liquid He^3, which served to prove that the boundary resistance was not a characteristic of superfluid He^4. Indeed, thermal boundary resistances have been reported for the interface between dissimilar solids at low temperatures,[3,4] including solid He^3.[5]

Khalatnikov[6] has developed a theory for the thermal boundary resistance of liquid He^4 from considerations essentially of the radiation and absorption of thermal phonons at the liquid-solid interface. The boundary resistivity R, defined as the temperature drop at the boundary divided by the energy flux, may be calculated from the equation

$$R = \frac{15h^3}{16\pi^5 k^4} \frac{\rho_s c_t^3}{\rho_{\mathrm{He}} c_{\mathrm{He}}} \frac{10^{-7}}{F} \frac{1}{T^3}, \qquad (1)$$

where h is Planck's constant, k Boltzmann's constant, ρ_s the density of the solid, ρ_{He} the density of the helium, c_t the velocity of transverse acoustic waves in the solid, and c_{He} the velocity of acoustic waves in helium. F is a function of the ratio of velocities of longitudinal and transverse acoustic waves in the solid. Thus the theory predicts a boundary resistance proportional to the inverse third power of the temperature, a dependence on the nature of the solid through $\rho_s c_t^3/F$, and a dependence

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