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MOLYBDENUM *L*-SERIES WAVE-LENGTHS BY RULED GRATINGS

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Abstract

With plane ruled gratings having 30,000 lines per inch and 14,400 lines per inch and grating to photographic plate distances up to a meter in length in vacuo, about 160 plates were taken of the Mo *L*-series lines. The wave-lengths for $L\alpha_1$, and $L\beta_1$, as given by Siegbahn using a gypsum crystal are 5.3943A and 5.1658A. If a calcite crystal were employed and approximate correction made for refraction, wave-lengths 5.3960A and 5.1674A should be expected, whereas the average of the ruled grating measurements gave 5.4116A and 5.1832A. A comparison of the two values leads to an apparent value of the electronic charge 4.8162×10^{-10} e.s.u., being slightly higher than Bearden's value using Cu *K* lines. The possibility of the variation being due to anomalous variation in the refractive index of the crystal is discussed.

THE possibility of the absolute determination of x-ray wave-lengths by means of ruled diffraction gratings, has now been demonstrated.[1] The most precise results so far obtained[2] indicate that x-ray wave-lengths determined by the ruled grating method are somewhat longer than when determined by the crystal reflection method. Unfortunately, however, agreement regarding the magnitude of this discrepancy is still lacking. Since this wave-length difference may be given the interpretation that the Avogadro number, used in calculating the dimensions of the unit cell in the fundamental crystal lattice, was in error and hence also the value of the electronic charge, its importance is evident. In comparing wave-length values obtained by the two methods, the results from the crystal method should first be corrected for the index of refraction of the crystal. For long wave-lengths, that is, crystals of large lattice constant, this correction is appreciable and it may be further complicated at certain wave-lengths by anomalous effects.

It was the original intention in this investigation to report on the *L* series wave-lengths for the metallic elements from Mo 42 to Ba 56 and several plates were taken for each of these elements, but in view of the significance of the results it was considered more important at this time to carry out an exhaustive study with one of the elements. For various reasons molybdenum was chosen for the target material.

Granting a certain error in setting upon a spectral line in the measurement of the photographic plates, the overall accuracy is increased by having the final result depend upon large distances upon the photographic plate. For a

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[1] Compton and Doan, Proc. Nat. Acad. Sci. **11**, 598. 1925; Thibaud, Comptes rendus, **182**, 55, (1926).

[2] Wadlund, Phys. Rev. **32**, 841, (1928); Bäcklin, Dissertation, Upsala, 1928, Bearden, Proc. Nat. Acad. Sci. **15**, 528, (1928).

given wave-length, two main factors contribute to the distance between lines on the photographic plate, namely, the grating constant (i.e. distance between adjacent ruled lines) and the distance between grating and photographic plate. For large displacements the grating constant should be small and the distance between grating and photographic plate large. The dispersion also depends to a slight extent upon the value of the incident grazing angle employed, being greatest when this angle is least. The use of inside spectral orders, that is, those lying between the regularly reflected beam and the diffracted beam parallel to the grating, has been proposed,[3] since it leads to very large dispersion when the diffracted beam becomes parallel to the grating. Although this method is eminently satisfactory to show fine structure in this narrow region, its value in the absolute determination of wave-length must not be overestimated. The use of sufficiently large incident angles to give linear displacements on the plate comparable with those of high outside orders is prohibited due to the critical grazing angle for the grating material.

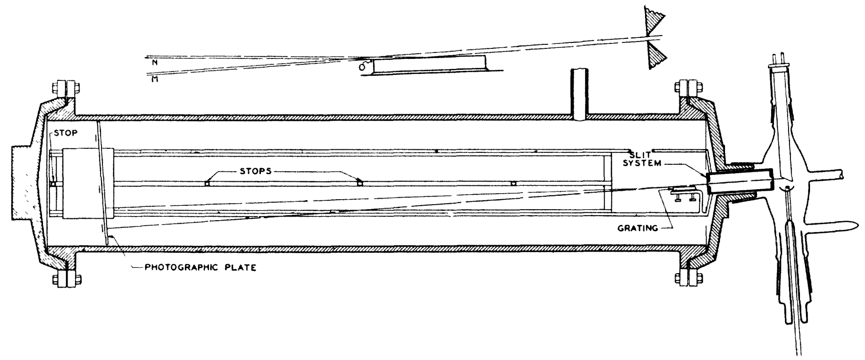

Fig. 1. Diagram of spectrometer and x-ray tube as viewed from above.

APPARATUS

For this wave-length region the complete spectrometer must be in a vacuum with no absorbing layer between the x-ray tube and diffraction chamber. Fig. 1 is a schematic drawing of spectrometer and x-ray tube as viewed from above. The x-ray tube was made of glass and provided with a water-cooled target. The cathode was an activated platinum spiral. Both cathode and anode were removable by ground glass joints. The tube as a whole was mounted on the end of the brass spectrometer tube by a ground glass to metal joint.

Radiation from the target was collimated by parallel slits so as to be incident upon the grating at grazing angles from ten to forty minutes of arc. The slits were approximately 0.05 mm in width and were adjustable in distance from 12 cm to 24 cm. In the adjustment of the grating, part of the collimated beam was allowed to miss the grating surface, giving a

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[3] Howe, Phys. Rev. **35**, 717 (1929).

beam direct to the photographic plate one edge of which was sharply defined by the shadow of the grating edge.

The photographic plate is carried by a plate holder in such a position that the direct beam is incident upon it normally. The plate holder travels upon a heavy grooved track carefully adjusted for parallelism. Four definite positions for stopping are provided by allowing the carriage to make contact with stops, the distances between which were accurately measured upon the same comparator used for the photographic plates. Two positions would have sufficed to determine the distance between plate and grating by triangulation. The photographic plates were changed by removing a metal cap from the end of the spectrometer tube, fitted by ground metal joint.

The slit system, grating and plate holder bed were all a single rigidly connected unit which could be removed completely from the tube without disturbing the adjustment. The containing brass tube had a diameter of 21 cm and a length of 110 cm. The x-ray tube and spectrometer chamber were evacuated by separate mercury vapor pumps with liquid air traps, although gas could pass freely between them through the slit system. The spectrometer tube and the end brass castings were tinned inside and out by immersion for a short time in a bath of molten tin.

The mounting for the grating was provided with adjusting screws so that the grating could be tilted in any direction. In the present investigation four different glass gratings were employed. Three of these were nominally ruled 30,000 lines per inch by Professor R. W. Wood at Johns Hopkins University, while the fourth was a 14,400 line per inch grating ruled at this University by Professor E. F. Barker and Mr. Weyrich.

CALCULATION

The fundamental grating relationship for constructive interference is

$$n\lambda = \pm d[\cos\theta - \cos\phi]$$

where θ is the small grazing incident angle and ϕ is the angle between the diffracted beam and the grating surface. The distance in Angstroms between adjacent ruled lines on the grating is represented by d, and n represents the spectral order. For the regularly reflected beam θ and ϕ are equal, while for outside orders, ϕ exceeds θ and the plus sign is used, whereas for inside orders ϕ is less than θ and the sign is negative.

The dispersion for a given setting of θ then (for outside orders) becomes:

$$\frac{\partial\phi}{\partial\lambda} = \frac{n}{d\sin\phi}\,.$$

This is not independent of θ since for smaller values of θ the value of ϕ and hence $\sin\phi$ for any particular wave-length becomes smaller.

In the upper part of Fig. 1 is shown an enlarged sketch of the grating with the direct and reflected beam. It is evident that the ray m in the direct beam and the ray n in the reflected beam have a common origin in the edge of the grating at 0. Thus by measuring on the photographic plate the distance between outside edges of direct and reflected lines and dividing by the distance between the grating edge and photographic plate the tan 2θ and hence θ is at once determined.

The origin of the spectral lines is not the edge of the grating but an effective diffracting center which may be as much as a millimeter farther from the plate if a 2 mm width of the ruled surface is employed. To determine the distance between the photographic plate and the effective grating centre, the following procedure is carried out. With some particular x-ray source, spectrograms are obtained for the photographic plate in each of the four positions. By measuring the distance between any pair of these lines sufficiently far apart on any two of the plates and solving by similar triangles the origin or effective center may be located. While two positions would be sufficient, in most cases all four positions were used for confirmation of results. Such spectra for three positions for a molybdenum target are shown in Fig. 2.

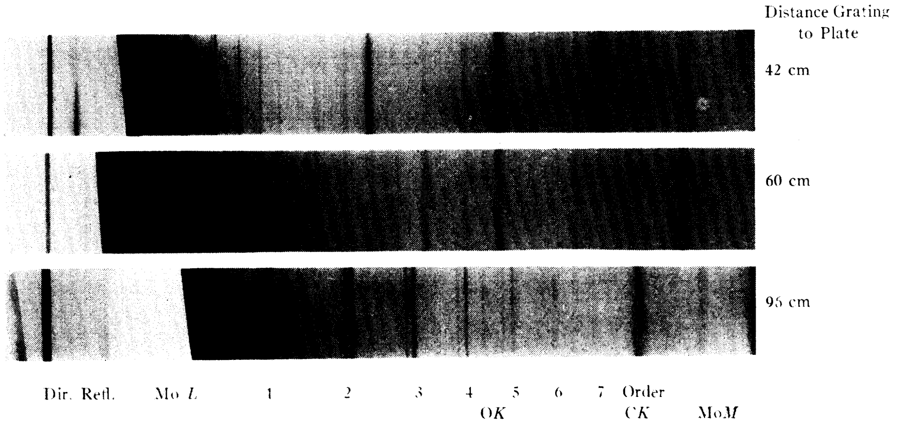

Fig. 2.

Now to calculate wave-lengths, the distance between the outside edge of the direct beam and each spectral line is measured on the comparator. This distance in each case divided by the respective normal plate to grating distance gives tan $(\theta+\phi)$ and hence the ϕ for any spectral line. Since θ is already calculated for all of the lines the approximate value of λ is at once determined. The term approximate is used, since the edge of a line may be somewhat altered in position by growth of blackening due to over exposure. This does not, however, lead to any error in the final result because the spectral line is observed in many orders, thus on the molybdenum plates shown in Fig. 2 seven orders are available for calculation. Now if the wave-lengths as calculated from the various orders show a systematic variation, the results may be made concordant by the addition or subtraction of a small amount from all observed distances of the spectral lines from the edge of the direct beam. Experience shows that errors in the value of θ by as much as 15″ of arc, would automatically be corrected by this same operation, leading always to the same final values of λ when agreement between the various orders is obtained. Thus a real error in the exact location of the edge of the direct beam or of the incident angle θ need, if not too large, produce no appreciable error in final results, if several orders of some spectral line are available on the plate. In making the wave-length calculations, particularly in obtaining the cosines of the small angles, the fifteen place 'Andoyer—Tables Trigonometriques' is invaluable.

RESULTS

The grating constant for the 30,000 line gratings was determined by an optical spectrometer using the strong lines in the mercury arc spectrum as known wave-lengths. The result of this experiment gave the number of lines per inch as 30,011 or d equal to 8, 463.3 Angstrom units. This is somewhat at variance with the result obtained by Thibaud[4] for gratings from the same source, namely 29,972 lines per inch or d equal to 8, 477 Angstrom units. This latter value would lead to even longer wave-lengths than those recorded in this paper.

Since the ruling machine was available on which the 14,400 line grating was ruled, it became possible to determine the constant for this grating in another way. This machine employed a wheel having 720 teeth mounted on the head of a screw whose pitch was nominally 1/20 of an inch. If the pitch of the screw therefore were accurately determined this would give the width of 720 lines. A special steel bar was prepared and ruled with light lines, one for every ten revolutions of the screw. This scale was then calibrated in terms of the International meter. The result showed the pitch of the ruling machine screw in the part used to be very uniform and to be 0.050008 inch, such that there were 14,397.6 lines per inch or a value of d equal to 17,641.8 Angstrom units. In all, about 160 plates were taken on molybdenum using the different gratings with different adjustments on each, as well as various plate to grating distances. The average of all calculations are given in Column 1 in the following Table I in Angstrom units.

TABLE I.

	Grating Measurement	Gypsum crystal	Calcite crystal (Calc.)	Corrected for crystal refraction
$\lambda MoL\alpha_1$	5.4116	5.3943	5.3967	5.3960
$\lambda MoL\beta_1$	5.1832	5.1658	5.1681	5.1674

The values obtained by the crystal method using a gypsum crystal are given in column 2.* Siegbahn and Hjalmar[5] have shown that if the ratio

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[4] Thibaud, J.O.S.A. and R.S.I. *17* 145 (1928).

* The values of λ published in the abstract of a paper presented at the Chicago meeting of the American Physical Society, Nov., 1930, were, by error, these values from Siegbahn with which the experimental values were compared to obtain the value of e therein given.

[5] Siegbahn and Hjalmar, Nature **115,** 85, (1925).

$d_{\text{calcite}}/d_{\text{gypsum}}$ be obtained with different wave-lengths, a variation in this quantity from 0.39976 at 1A to 0.39959 at 5.5A is observed, with anomalous peaks at 3.06A and 5.01A corresponding to the K absorption edges of calcium and sulphur respectively. This relationship may then be employed to calculate what the wave-lengths of the Mo L lines would be if measured by a calcite crystal since for gypsum, $d=7.578$A, was used at all wave-lengths. Such results are given in column 3. These values may now be corrected for the deviation to the Bragg law due to ordinary refraction in the crystal, by the approximate formula, as follows:

$$\lambda = \lambda'\left[1 - 5.4\frac{\rho d^2}{n^2}\cdot 10^{-6}\right]$$

where λ' denotes the apparent wave-length, n the spectral order, ρ and d the densityand lattice constant of the crystal respectively. For calcite this gives a correction factor of 0.014 percent for the first order spectra. Such results are recorded in column 4, and are the values to be compared with those of column 1.

It should be noted that the ratio $d_{\text{calcite}}/d_{\text{gypsum}}$ changes by as much as one half of a tenth of a percent for wave-lengths from 1A to 5A. This variation is of the nature of a difference effect and it may well be possible that the variation in calcite alone may be much greater than this.

The dispersion formula showing the effect of wave-length change upon the index of refraction as developed from polarization theory is as follows:

$$\delta = \mu - 1 = \frac{e^2}{2\pi m}\sum^{N}\frac{N_e}{\nu_e^2 - \nu_x^2}$$

where μ represents the index of refraction, N the total number of mobile electrons per cm^3, N_e the number of electrons per cm^3 having the natural frequency ν_e and ν_x represents the x-ray frequency. For x-rays in which ν_x is large compared with ν_e, the quantity δ is negative leading to a correction to the Bragg law as shown above, i.e. true wave-length less than apparent. Now as the x-ray wave-length increases or as the frequency decreases, the value of δ becomes more negative but upon passing through the K absorption limit of calcium the contribution of the calcium K electrons changes from negative to positive and at longer wave-lengths δ may actually become positive, in which case the true wave-length will be greater than the apparent.

If possibilities of error due to this variable refractive index be over looked, the values of column 1 may be compared with column 4 to determine what would be implied regarding the value of the electronic charge. The value of the electronic charge as determined by the oil drop method as corrected by Birge[6] for best values of the viscosity of air, velocity of light and transformation factors to change from International to absolute electrostatic units is $4.768 \pm 0.005 \times 10^{-10}$ abs. e.s.u. Tempering this value by the consideration of Wadlund's result from x-rays, the most probable value was

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[6] Birge, Phys. Rev. Sup. **1**, 40, (1929).

given as $(4.770 \pm 0.008) \times 10^{-10}$ e.s.u. However, in the most accurate determination by calculation, of a fundamental crystal lattice, namely that of calcite by Compton, Beets and DeFoe,[7] the Avogadro number was assumed to be $(6.0594) \times 10^{23}$ which combined with Birge's most probable value of the Faraday, $(2.89270 \pm 0.00021) \times 10^{14}$ e.s.u. means that e was assumed to be 4.7739×10^{-10} e.s.u. The calcite lattice constant as so computed agreed exactly with the value as used by Siegbahn in his wave-length determinations, namely 3.02904A at 18°C.

For the α_1 line the wave-length by ruled grating is 0.288 percent greater than the corrected crystal measurement, while for the β_1 line a difference of 0.304 percent is observed. The average of these values gives for the electronic charge the apparent value of 4.8162×10^{-10} e.s.u. and for the Avogadro number $(6.0062) \times 10.^{23}$ This value of the electronic charge is thus even larger than Bearden's value of 4.804×10^{-10} e.s.u. obtained by Cu*K* wave-lengths.

The explanation of this effect as due to a surface contraction as discussed by Zwicky[8] is unlikely. Such contractions are supposed to be only a few atomic layers deep and certainly many hundred atomic planes must cooperate in the x-ray reflection even up to 5 Angstroms. Also there is good agreement between crystal measurements by the transmission and reflection methods. Furthermore, a surface contraction would have to be interpreted as increasing the discrepancy rather than decreasing it, since instead of multiplying the observed sin θ by an average d one should use the smaller surface d.

Attempts to explain the effect by altering the general grating formula for the case of grazing incidence, narrow grating width and ruling defects seem to prove inadequate for differences as large as observed.

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[7] Compton, Beets and DeFoe, Phys. Rev. **25**, 625 (1925)

[8] Zwicky, Proc. Nat. Acad. Sci. **15**, 253 (1929).

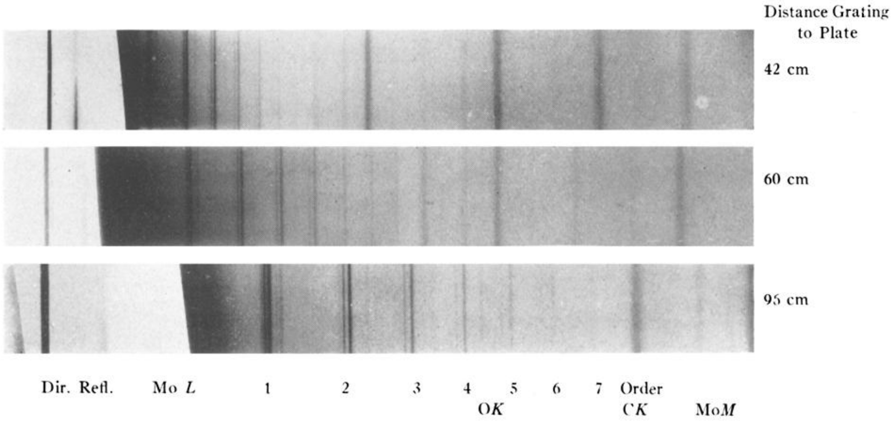
Distance Grating to Plate
42 cm
60 cm
95 cm
Dir. Refl.
Mo L
1
2
3
4
5
6
7
Order
OK
CK
MoM

Fig. 2.