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# X-Ray Wave-Lengths from Crystals and Ruled Gratings

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Energies of photoelectrons ejected by x-rays from thin foils have been measured by Kretschmar and by Robinson and his colleagues, using the magnetic spectrograph. Their values are compared with those computed from wave-lengths of the incident rays and x-ray terms of the atoms in the foils, using (a) wave-lengths measured with crystals, based on the actual calcite spacing rather than the conventional one; (b) ruled grating wave-lengths, which are higher by 0.25 percent. Using Birge's value of $e$, 4.7668 $\times 10^{-10}$ e.s.u., Bearden's value for the calcite spacing becomes $(3027.91 \pm 1.0)10^{-11}$ cm. To get photoelectron energies from crystal wave-lengths, accurate x-ray terms are worked out by a new plan, which avoids uncertainties involved in using absorption-edge wave-lengths. Term differences are obtained from x-ray line spectra, and are added to the value of some low term obtained from optical spectra. Birge's values of universal constants are employed in getting photoelectron energies. These energy values average 0.36 percent higher than those computed from crystal wave-lengths, or 0.61 percent higher than those from ruled-grating wave-lengths. This fact supports, but does not conclusively prove, the correctness of crystal wave-lengths based on the actual calcite grating space.

## 1. Magnitude of the Discrepancy Between Crystal and Ruled-Grating Wave-Lengths

The work of Bearden, Cork and his colleagues[1] and other investigators shows that x-ray wave-lengths measured with ruled gratings are consistently higher than those obtained with crystals. Bearden found that the discrepancy $P$ is 0.22 percent in the region 1.4 to 2.3A; Cork found 0.29 percent for two $L$ series lines at about 5A. Data of Howe,[2] Purdom and Cork, and Witmer and Cork cover the range from 3.7 to 25A. Their values indicate that $P$ lies between 0.3 and 0.5 percent over this whole region. Siegbahn and Magnusson[3] found $P=0.17$ percent for oxygen $K\alpha$ (23.6A).

It has been customary to express ruled-grating wave-lengths in terms of the unit $10^{-11}$ cm, while crystal wave-lengths are based on the conventional grating space of calcite, 3029.45 X.U., which is employed in Siegbahn's treatise and by nearly all x-ray spectroscopists. Here we need crystal wave-lengths based on the actual calcite grating space, so I have recomputed Bearden's[4] value, using Birge's latest values of the universal constants involved, as quoted below. The result is $(3027.91 \pm 1.0)10^{-11}$ cm at 20°C. In view of the above-mentioned spread of the data of Cork and his colleagues, it is not worth while to recompute them; but employment of this grating space raises Bearden's $P$-values to 0.25 percent. For the purposes of this paper we may take the value of $P$ to be 0.25 percent up to 3A, and at least 0.25 percent for greater wave-lengths. [It must be emphasized that the calcite spacing is so accurately known and so nearly constant from one good crystal to another that we cannot remove the difficulty by changing its value. Further, Bearden[5] estimates the experimental error of his ruled-grating measurements as 0.01 percent.]

It is probable that the question of which scale is correct can be decided by grating work in the region of very soft x-rays, where higher orders of the $K$ and $L$ series lines of light elements can be compared with optical standards. However, x-ray line widths are great in that region, and so far we have no conclusive evidence from such studies. Meanwhile, two arguments favoring the correctness of the crystal wave-lengths have been presented. (1) Bearden[6] showed that wave-lengths from measurements of the dispersion of x-rays in crystal quartz are in close agreement

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[1] For bibliography, see Bearden, Phys. Rev. **39**, 1 (1932) and Purdom and Cork, Phys. Rev. **44**, 974 (1933).

[2] C. E. Howe, Phys. Rev. **35**, 717 (1930).

[3] Siegbahn and Magnusson, Zeits. f. Physik **87**, 291 (1934).

[4] Bearden, Phys. Rev. **38**, 2089 (1931).

[5] Bearden, Phys. Rev. **37**, 1224 (1931).

[6] Bearden, Phys. Rev. **39**, 1 (1932).

with crystal values; (2) Birge[7] pointed out that certain universal constants calculated from ruled-grating wave-lengths do not agree with mean values obtained from experiments which do not involve x-ray measurements, while there is much better agreement if crystal wave-lengths are employed.

The purpose of this paper is to present a third line of evidence which supports the crystal values. It consists in comparing the energies of photoelectrons ejected from thin films by monochromatic x-rays with the values to be expected from the wave-lengths of the incident rays and the energy levels of atoms in the films. The data employed are those of Kretschmar and of Robinson, Andrews and Irons.[8] The discussion in both papers requires reconsideration for two reasons. Improved values of the universal constants are available; and, more important in its effect on the interpretation of the data, we shall use a method for getting x-ray energy levels which yields more accurate values than that employed by Siegbahn in calculating the tables in his treatise. The improvement of these energy levels is the chief point of novelty. Robinson[9] used his older data to compute x-ray terms, and considered whether they should be compared with those obtained from crystals or from ruled-gratings. Here the viewpoint is converse. We obtain accurate term values from x-ray and optical spectra, using the crystal scale, and show that they agree better with the photoelectric results than those computed from the ruled-grating scale.

## 2. A Method for Obtaining X-Ray Terms

As Siegbahn[10] says, the determination of x-ray absorption edges is usually afflicted with greater errors than the measurement of lines. This is shown by double crystal spectrometer measurements. Ross[11] finds that in passing from Zr (40) to I (53) the width of the main $K$-absorption edge increases from 13 to 38 volts while Allison[12] shows that in passing from Zr (40) to Ag (47) the width of $K\alpha_2$ runs from 6.9 to 11.3 volts, $K\alpha_1$ being slightly narrower. This difference in widths, and the presence of fine structure on the short wave-length side of the main absorption edge are not, however, the only considerations. So far, there is no theory to indicate what point in the absorption edge should be taken as corresponding to ejection of an electron to a position of rest at infinity. Indeed, Sandström[13] showed that in some cases, and presumably in all, the middle of an absorption edge corresponds to the energy required to raise an electron to the first unfilled shell at the periphery of the atom. For example, in the elements preceding gold the $O_{\text{IV, V}}$ level is incomplete. For these elements the line $L_{\text{III}}$–$O_{\text{IV, V}}$ ($L\beta_5$) agrees well with the middle of the $L_{\text{III}}$ absorption edge, but for elements from gold to uranium the $O_{\text{IV, V}}$ shell is complete and the $L_{\text{III}}$ edge lies at shorter wave-lengths than the $L\beta_5$ line. Furthermore, we cannot expect that the value of the term difference $L_{\text{I}}L_{\text{II}}$ (for example), obtained from line combinations, will agree with the measured difference of the $L_{\text{I}}$ and $L_{\text{II}}$ absorption limits. This is due to the fact[14] that the azimuthal selection principle holds true for edges as well as for lines, so that electrons ejected from the $L_{\text{I}}$ and $L_{\text{II}}$ shells by frequencies corresponding to the $L_{\text{I}}$ and $L_{\text{II}}$ edges, respectively, should land on different peripheral levels of the atom.

For these reasons it is often desirable not to use tables of term-values, but rather to work with tables of *term differences obtained from lines*, like those prepared by Idei[15] for heavy elements. To obtain more accurate term values, we add such term differences to values of small x-ray terms obtained from optical spectra. The method will be made clear by applying it to gold. In the isolated gold atom, the configuration of the outer electrons is $5d^{10}6s$. The $O$ terms with azimuthal number $l=2$ are the energies required to remove a $5d$ electron, leaving the ion in the condition $5d^96s$. These energies can be obtained, theoretically, in two ways:

(1) From observation of the sequences $5d^96s\,ms$,

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[7] Birge, Phys. Rev. **40**, 228 (1932).

[8] Kretschmar, Phys. Rev. **43**, 417 (1933); Robinson, Andrews and Irons, Proc. Roy. Soc. **A143**, 48 (1933).

[9] Robinson, Phil. Mag. **14**, 605 (1932).

[10] Siegbahn, *Spektroskopie der Röntgenstrahlen*, 2nd Ed., p. 336.

[11] Ross, Phys. Rev. **44**, 977 (1933).

[12] Allison, Phys. Rev. **44**, 63 (1933).

[13] Sandström, Zeits. f. Physik **66**, 784 (1930).

[14] Siegbahn, Zeits. f. Physik **67**, 567 (1931).

[15] Idei, Sci. Rep. Tohoku Imp. Univ. **19**, 559 (1930); also Siegbahn's treatise, p. 352.

or $5d^9 6s\,mp$, etc. (where $m=6$, 7, etc.), and computations of their limits.[16] The lowest term of the $5d^9 6s\,ms$ sequence is known, but unfortunately higher terms are not identified with certainty so we must attack the problem in another way.

(2) The energy required to remove a $5d$ electron is the same as that required for the process: removal of the $6s$ electron followed by excitation of the ion from $5d^{10}$ to $5d^9 6s$. From the work of McLennan and McLay and of Sawyer and Thompson[17] we find that the $\nu/R$ value corresponding to removal of the $6s$ electron is 0.68, and that the ion has the following low terms, its normal state being taken as the origin:

| | | $\nu/R$ |
|---|---|---|
| $5d^{10}$: | $^1S_0$ | 0 |
| $5d^9 6s$: | $^3D_3$ | 0.137 |
| " | $^3D_2$ | 0.161 |
| " | $^3D_1$ | 0.253 |
| " | $^1D_2$ | 0.270 |

Thus there are four terms which take the place of the two terms $O_{\text{IV, V}}$ of the customary x-ray energy diagram. If the $6s$ electron were removed from the ion, the triplet $D$ terms with $j=3$ and 2 would approach the $O_{\text{IV}}$ term of the *ion* as a limit and the other two would approach $O_{\text{V}}$. However, we do not need to consider this matter in detail because in the $L$ and $M$ spectra of gold the terms $O_{\text{IV, V}}$ are not resolved. We may use the mean of the four $D$ terms, weighted according to their statistical weights. This is 0.19, so $O_{\text{IV, V}}=0.68+0.19$ or 0.87 $\nu/R$ units. The uncertainty is negligible compared with that involved in getting $O_{\text{IV, V}}$ from lines and absorption edges. Having $O_{\text{IV, V}}$, we obtain the x-ray terms of the isolated gold atom from Idei's table of level differences, using 3029.45 X.U. for the grating space of calcite. Table I gives results, with those for other elements discussed in this paper, obtained by similar methods.

TABLE I. *$\nu/R$ values for x-ray terms of Cu, Ag, Pt and Au.* (Based on the conventional calcite grating space 3029.45 X.U.)

| | Cu 29 | Ag 47 | Pt 78 | Au 79 |
|---|---|---|---|---|
| $L_{\text{I}}$ | — | 279.29 | 1022.69 | 1057.98 |
| $L_{\text{II}}$ | 70.73 | 260.21 | 978.12 | 1012.25 |
| $L_{\text{III}}$ | 69.26 | 247.51 | 852.32 | 878.56 |
| $M_{\text{I}}$ | 9.26 | 53.58 | 243.39 | 253.08 |
| $M_{\text{II}}$ | — | 43.28 | 223.46 | 232.68 |
| $M_{\text{III}}$ | — | 41.02 | 195.33 | 202.79 |
| $M_{\text{IV}}$ | 0.78 | 28.24 | 162.74 | 169.45 |
| $M_{\text{V}}$ | | 27.62 | 156.85 | 163.13 |
| $N_{\text{I}}$ | — | 7.59 | 53.70 | 56.68 |
| $N_{\text{II}}$ | — | 3.13 | 45.40 | 48.14 |
| $N_{\text{III}}$ | — | | 38.69 | 40.77 |
| $N_{\text{IV}}$ | — | 0.94 | 24.86 | 26.68 |
| $N_{\text{V}}$ | — | | 23.66 | 25.30 |
| $N_{\text{VI}}$ | — | — | 6.04 | 7.09 |
| $N_{\text{VII}}$ | — | — | 5.75 | 6.72 |
| $O_{\text{I}}$ | — | — | 8.06 | 8.53 |
| $O_{\text{II, III}}$ | — | — | 4.62 | 4.95 |
| $O_{\text{IV, V}}$ | — | — | 0.72 | 0.87 |

It is necessary to estimate the accuracy of the data in Table I. We must consider how much the terms Cu $M_{\text{IV, V}}$, Ag $N_{\text{IV, V}}$, and Au and Pt $O_{\text{IV, V}}$ are changed when atoms of these elements enter the solid phase. Data which would provide a direct answer are not in existence, so we must estimate the change from other evidence. It is reasonable to assume that (1) the deeper a term lies in the atom, the less it will be affected by change of phase, so that the energy change of an absorption edge will be mainly due to shift of the upper level; (2) the alteration of a small x-ray term of a metal atom, due to solidification, should be less than that due to chemical combination. This judgment is based on the fact that, in general, heats of vaporization of metals are low compared with heats of formation of salts.

Hanawalt[18] measured absorption edges for elements in the vapor phase and in other states of aggregation. Two of these, zinc and mercury, have monatomic vapors. The following list shows $\Delta\nu/R$, the shift of an absorption edge of the solid or liquid relative to that of the vapor:

| | |
|---|---|
| Zn, solid, $K$, | $-0.11$, |
| Hg, liquid, $L_{\text{III}}$, | $+0.18$. |

Shifts observed in passing from one compound of an element to another are usually larger; according to the extensive work of Lindh,

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[16] These sequences form a part of the $I^b$ spectrum of neutral gold. The existence of such spectra was first pointed out by Mohler and Ruark, J. O. S. A. **7**, 819 (1923) in the case of thallium. Beutler (Zeits. f. Physik **86**, 495 (1933) and later papers) has made extensive studies of absorption lines in $I^b$ spectra, which are very useful in calculating x-ray terms by the methods here set forth.

[17] McLennan and McLay, Trans. Roy. Soc. (Canada) **22**, 103 (1928); Sawyer and Thompson, Phys. Rev. **38**, 2294 (1931).

[18] Hanawalt, Phys. Rev. **37**, 715 (1931).

Stelling and others,[19] they can be as high as 1.5 $\nu/R$ units, but broadly speaking, values larger than 0.5 $\nu/R$ units are associated with large change of valence. Further information may be obtained from Valasek's[20] work on the wave-length of $K\beta_1$ from sulfur and its compounds. The maximum shift of this line in passing from one compound to another was 0.11 $\nu/R$ units.

It seems fair to take 0.4 $\nu/R$ units as the maximum possible error in the data of Table I, due to our use of small terms of the isolated atoms. The error in level differences may sometimes be 0.4, though evidence from internal consistency of the wave-length data indicates it is usually smaller, and the maximum overall error is therefore 0.8 of a unit. This value is small compared with the widths of absorption edges (that of tungsten $L_{\mathrm{III}}$ is 2.5 $\nu/R$ units) and considering the uncertainties in the interpretation of edges, we may justly claim that the values in Table I are more accurate than those based on absorption measurements. The values for the silver $L$-limits agree well with those of van Dyke and Lindsay,[21] but not with those given in Siegbahn's book.

## 3. Analysis of the Data of Kretschmar and of Robinson, Andrews and Irons

Kretschmar, using the magnetic spectrograph, measured the energy of photoelectrons ejected from thin films by Mo $K\alpha$-rays, in order to obtain $e/m$. If $e$ is expressed in electromagnetic units, the equation used becomes

$$\frac{e}{m}=\frac{2Rc(h/e)[\nu/R-(\nu/R)_A]}{(Hr)^2-R^2(h/e)^2[\nu/R-(\nu/R)_A]^2}. \tag{1}$$

$R$ is the Rydberg constant for infinite mass; $\nu$ is the wave number of the incident x-rays; $(\nu/R)_A$ refers to an absorption limit of the atoms in the film; and $H$ and $r$ are the magnetic field employed, and the radius of curvature for a photoelectron moving in that field. Kretschmar made the ingenious suggestion that if the value of $h/e$ obtained from the limit of the continuous x-ray spectrum is used, the resulting value of $e/m$ is independent of the grating space assumed, because the effect of the grating space on $h/e$ is balanced by its effect on the wave-lengths. A value of $e/m$ computed in this way throws no light on the question as to which wave-length scale is correct. However, the $\nu/R$ value for a photoelectron may be written as

$$\frac{\nu^*}{R}=\frac{e}{h}\frac{c}{R(e/m)}\left[\left\{1+\left(\frac{eHr}{mc}\right)^2\right\}^{\frac{1}{2}}-1\right]. \tag{2}$$

If one employs in this equation the best values of $e/m$ and $e/h$ obtainable from experiments which do not involve x-rays, then Kretschmar's determinations of $Hr$ yield values of $\nu^*/R$ which can be compared with $(\nu/R)-(\nu/R)_A$, as obtained from crystal spectra and from ruled-grating spectra.

Birge[7] has given values of $e/m$ and $h/e$ obtained from data which do not make use of x-rays. These are based on a least squares solution in section $h$ of his paper. However, the values of $e/m$ employed in this solution are higher than those indicated by recent data, which he would no doubt include if the computation were repeated now. Therefore, it seems best to use the most recent values of universal constants which he has published,[22] using data from all sources. These are:

$e=(4.7668\pm0.0038)10^{-10}$ e.s.u.,
$e/m=(1.7592\pm0.0011)10^{7}$ e.m.u./gram,
$e/h=(2.4303\pm0.0029)10^{6}$ e.m.u./erg sec.,
$c=(2.99796\pm0.00004)10^{10}$ cm/sec.,
$R=109{,}737.42\pm0.06$ cm$^{-1}$.

The $\nu/R$ values for the x-ray lines employed, on the basis $d_{\mathrm{calcite}}=3027.91$ X.U., are as follows:

| | | | |
|---|---|---|---|
| Mo $K\alpha_1$ | 1288.06 | Cu $K\alpha_1$ | 593.04 |
| Cu $K\alpha_2$ | 591.56 | Cu $K\beta$ | 656.24 |

Detailed comparisons of photoelectric energies with those computed from crystal spectra are too voluminous to record here. Table II gives typical data and Table III presents a summary of the results.

Altogether, thirty-seven values were studied, and the measured energy of the photoelectrons is higher than the computed value in all cases

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[19] Siegbahn, 2nd ed., p. 278 ff. See also Barnes, Phys. Rev. **44**, 141 (1933).

[20] Valasek, Phys. Rev. **43**, 612 (1933).

[21] van Dyke and Lindsay, Phys. Rev. **30**, 562 (1927).

[22] Birge, Phys. Rev. **42**, 736 (1932).

TABLE II. *Typical data on photoelectrons from gold.* (Robinson, Andrews and Irons.) Incident radiation, Cu $K\alpha_1$.

| Absorption level | $(\nu/R)_A$ ($d=3027.91$ X.U.) | $(\nu/R)-(\nu/R)_A$ (Crystal values) | Observed $\nu^*/R$ for ejected electrons | Percent discrepancy |
|---|---|---|---|---|
| $M_{\mathrm{I}}$ | 253.21 | 339.83 | 341.9 | 0.62 |
| $M_{\mathrm{V}}$ | 163.21 | 429.83 | 432.5 | 0.62 |
| $N_{\mathrm{I}}$ | 56.71 | 536.33 | 539.7 | 0.63 |
| $N_{\mathrm{IV,\,V}}$ | 25.77 | 567.27 | 570.6 | 0.58 |

TABLE III. *Discrepancy between photoelectric and crystal values of* $(\nu/R)-(\nu/R)_A$.

| | Kretschmar, using Mo $K\alpha_1$ | Robinson, using Cu $K\alpha_2$, $K\alpha_1$ and $K\beta$ |
|---|---|---|
| Gold | 0.23% | 0.61% |
| Silver | 0.24 | 0.45 |
| Copper | 0.18 | −0.04 |
| Platinum | 0.24 | |
| Weighted mean: | 0.23 | 0.50 |

except two. These are Robinson's electron lines Cu $K\alpha_2-$Ag $L_{\mathrm{I}}$ and Cu $K\alpha_1-$Cu $L_{\mathrm{III}}$, for which the percentage discrepancy is $-0.04$. Thus the photoelectric values of $(\nu/R)-(\nu/R)_A$ are about 0.36 percent higher than the crystal values (average of the two mean values in Table III). The discrepancy would be 0.61 percent if we employed the higher wave-lengths from ruled grating.

## CONCLUSIONS

The photoelectric measurements support the crystal scale rather than the ruled grating scale. They do not quite suffice to *prove* that the former is correct because of the possibility of errors in measurements of the energies of photoelectrons, and because some of the universal constants may be wrong by amounts greater than the probable errors now assigned to them. As to the first point, retardation of electrons in the film from which they are ejected would lower their energy, while the values recorded here are higher than the ones from crystal wave-lengths. As to the second point, use of a lower value of $e/m$, such as the value $1.757\ 10^7$ e.m.u./gram obtained in the recent spectroscopic work of Kinsler and Houston and of Gibbs and Williams[23] would reduce the photoelectron energies by 0.12 percent, so agreement with crystal values would be improved. The possibility of reconciling the photoelectric energies with the ruled-grating scale appears, however, quite remote.

I am indebted to Professor R. T. Birge for information concerning universal constants, and to Dr. Victor Hicks for helpful discussions. March 8, 1934.

*Note added in proof:* A letter from Dr. Robinson informs me that as a result of recalibration of his apparatus it appears that his *Hr* values may be 1 part in 1200 to 1 part in 1500 too high. This correction is such as to reduce the discrepancy between observed photoelectric energies and those computed from crystal spectra.

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[23] Kinsler and Houston, Phys. Rev. **45**, 104 (1934); Gibbs and Williams, Phys. Rev. **44**, 1029 (1933).