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X-RAY K ABSORPTION IN ELEMENTS W(74) TO U(92), AND K SCREENING NUMBERS

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Abstract

Values are recorded for the K absorption edges of elements 74, 76 to 83 inclusive, 90, and 92. Absorption is noted due apparently to the material of the slit but not to the passage of rays through the wedges formed by the jaws of the slit. An attempt is made to determine Sommerfeld's screening numbers for the K shell from empirical data, on the assumption that the first term screening number is a linear function of the atomic number. Since this assumption leads to negative values for the "relativistic" screening number, it is conluded that Sommerfeld's term formula does not account for all the curvature of the lines in the Moseley diagram.

I. Absorption Edge Values

The K absorption edges of nearly all the elements studied in this investigation have already been measured by de Broglie,[1] Siegbahn and Jönsson,[2] and Duane, Shimizu, Fricke, and Stenstrom.[3] Since these values are somewhat in disagreement, it was considered useful to carry out this investigation, employing a spectrograph previously used in the measurement of emission wave-lengths.[4]

X-rays were allowed to fall on the crystal on each side of the axis in succession, giving an absorption edge toward each end of the photographic plate; so that the distance between edges, together with the distance between the slit and the plate, gave the angle of deviation without reference to any other point on the plate. In the case of a few plates reference was made to the tungsten $K\alpha$ line, whose position (208.62 x-units) was assumed known. An ordinary 200,000 volt Coolidge tube with tungsten filament and target was used. The tube was run at about 170,000 volts (or somewhat less for the lower atomic numbers) and 4 milliamperes. The exposures varied from 40 to 100 milliampere hours, depending upon the screen thickness.

The samples studied were in the form of sheets of the element, except in the cases of Hg (80), where the sample consisted of a drop pressed between two pieces of glass; Th (90), where the element was powdered; and U (92), where the powdered acetate was used. The total thickness of the sample varied from about 0.1 mm for some sheets to about 1 mm for the powders. The samples were placed between the slits, or between the second slit and the plate. In some cases two elements (not of successive atomic number)

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[1] M. de Broglie, J. de Physique p. 161 (May–June 1916).

[2] Siegbahn and Jönsson, Phys. Zeits. **20,** 251 (1919).

[3] Duane and Shimizu, Phys. Rev. **14,** 522 (1918); Duane, Fricke, and Stenstrom, Nat. Acad. Sci. Proc. **6,** 607 (1920).

[4] J. M. Cork, Phys. Rev. **25,** 197 (1925); and Stephenson and Cork, Phys. Rev. **27,** 138 (1926).

were photographed simultaneously. All the spectra were of the first order. Exposures and measurements were made at approximately a uniform temperature of 22°C.

For finite slit width an edge on a plate is not sharp; the change in blackening takes place throughout a region, if there is no overexposure. In this investigation the measurements were made to the center of this region. For the spectrograph used, this gave directly the distance between the ideal edges.

The order of magnitude of the probable error in λ is estimated to be $\pm .00010$A; giving for ν/R, from ± 3 for W (74) to ± 8 for U (92), and for $(\nu/R)^{1/2}$, from ± 0.02 for W (74) to ± 0.05 for U (92).

Table I gives the values obtained for the wave-lengths of the absorption edges, together with the frequencies ν/R and their square roots. The wave-lengths recorded by the other investigators are reprinted for convenience. All the values recorded were obtained photographically except those of Duane and his collaborators, who used the ionization method. Their wave-length values, moreover, are averages from several orders, so that they must be slightly increased in order to be comparable with all the other values, which are for first order only and are not corrected for refraction in the crystal.

TABLE I

K absorption edges. Constants used: log $2D = 0.78235$[5] for calcite at 22°; log $R = 0.040353$.

Z	λ(Angstroms) de B[1] (phot.)	S., J.[2] (phot.)	D. F. S. S.[3] (ion.)	present (phot.)	ν/R present	$(\nu/R)^{1/2}$ present
74 W			.1781	.17822	5113	71.51
76 Os			.1683	.16755	5439	73.75
77 Ir				.16209	5622	74.98
78 Pt	.152	.1578	.1581	.15770	5778	76.02
79 Au	.149	.1524	.1534	.15320	5948	77.12
80 Hg	.146	.1479	.1491	.14893	6119	78.22
81 Tl	.142	.1427	.1448	.14441	6310	79.44
82 Pb	.138	.1385	.1410	.14049	6486	80.54
83 Bi	.133	.1346	.1372	.13678	6678	81.62
90 Th		.1127	.1131	.11270	8085	89.92
92 U		.1048	.1075	.10658	8550	92.46

II. ABSORPTION DUE TO SLIT MATERIAL

On almost every plate there appeared absorption edges characteristic of the material of the slit faces in the second (i.e., the fine) slit. Thus for lead slits the K edge of lead was obtained and in fact the radiation was so much reduced on the short wave-length side of the edge that it was found difficult to obtain the K edge of the next heavier element, bismuth. In this case platinum faced slits were employed. Other materials used on the slit faces were tungsten and tantalum, each of which gave its characteristic edge. The effect was not observable for long wave-length x-rays in such cases as with the iron slits in the Siegbahn vacuum spectrograph.

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[5] Siegbahn, "The Spectroscopy of X-Rays" (1925) § 19.

An obvious hypothesis for the explanation of this phenomenon would be that the penetration of the short wave-length x-rays into the material of the wedges forming the jaws of the slit, makes the slit effectively wider for these rays. In order to eliminate the effect, then, new slits were made of thick lead plates, with faces parallel and shaped at such an angle as to reduce to a negligible amount the possible penetration of rays falling on the photographic plate in the neighborhood of the lead edge. But the effect was not materially diminished.

If the above penetration hypothesis were correct, the absorption edge due to the material of the slit would appear on the plate displaced toward long wave-lengths with respect to an edge due to a sheet of material traversed by all the x-rays passing through the slit. Moreover, for a slit .15 mm thick, the additional transmission would be such a small part of the total that only a slight decrease in blackening would be expected on the short wave-length side of the edge.

Faced by the dilemma offered by the occurrence of absorption due to the material of the jaws of the slit but apparently not to penetration of this material by the rays, we must consider a second possibility: namely, that for this short wave-length radiation the jaws of the slit possess an effective range of absorption extending somewhat beyond their boundaries. While on its face improbable, it is not inconceivable that such an effect might occur due to a possible appreciable cross-section possessed by the quanta of hard x-rays. Such a property might play a part in other phenomena, such as the reduction of intensity of x-rays at angles close to grazing angles of emergence from the target face of an x-ray tube.

III. THE *K* SCREENING NUMBERS

The investigations of Sommerfeld and Wentzel[6,7] have shown that the x-ray term values may be represented by the following infinite series in powers of α, where $\alpha = 2\pi e^2/hc$:

$$\frac{\nu}{R} = \frac{[Z-s(Z,n,k_1)]^2}{n^2} + \alpha^2 \frac{[Z-d(n,k_1)]^4}{n^4}\left(\frac{n}{k_2}-\frac{3}{4}\right) + \cdots \qquad (1)$$

$$+ \alpha^{2p}[Z-d]^{2(p+1)} f_{2p}(n,k_2) + \cdots\cdots .$$

Here Z denotes the atomic number, n the total quantum number (equal to 1 for the K shell, 2 for the L shell, etc.) and k_1, k_2 the two quantum numbers characteristic of the sublevels of a shell. An irregular or screening doublet is formed by two levels with the same n and the same k_2 but different k_1, and a regular or relativistic doublet by two levels with the same n and the same k_1 but different k_2. The first-term screening number s and the relativistic screening number d are functions which must be obtained empirically. In general, one may determine s and d for all the levels within a shell by making use of certain regularities[6] in the doublet differences. In the K shell,

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[6] Sommerfeld and Wentzel, Zeits. f. Physik **7,** 86 (1921).

[7] Wentzel, Zeits. f. Physik **16,** 46 (1923).

however, there are of course no doublets, and it may easily be seen that for the observed K terms (i.e., K absorption edges) of any number of elements, the number of unknowns, $s(Z)$ and d, is always greater by one than the number of available Eqs. (1).

In an attempt to overcome this difficulty, the following graphical method suggested by Dr. O. Laporte is used here: For several arbitrary values of d as a parameter, s is plotted as a function of Z; and *that value of d is considered most probable, for which $s(Z)$ is most nearly linear with Z, at least for the higher values of Z.* The validity of the remainder of this discussion rests upon this single assumption. Its plausibility is made clear by a glance at the curves $s(Z)$ for the other shells, as plotted in Sommerfeld's book.[8]

The s-values of successively deeper shells (· · · M, L) become more nearly linear with Z as the outer disturbing effect of the addition of electrons belonging to different sub-groups diminishes; for instance, only a slight change of slope is noticed in the two curves for the L shell in the neighborhood of the rare earths. Sommerfeld inserts the K screening number as a dotted straight line.

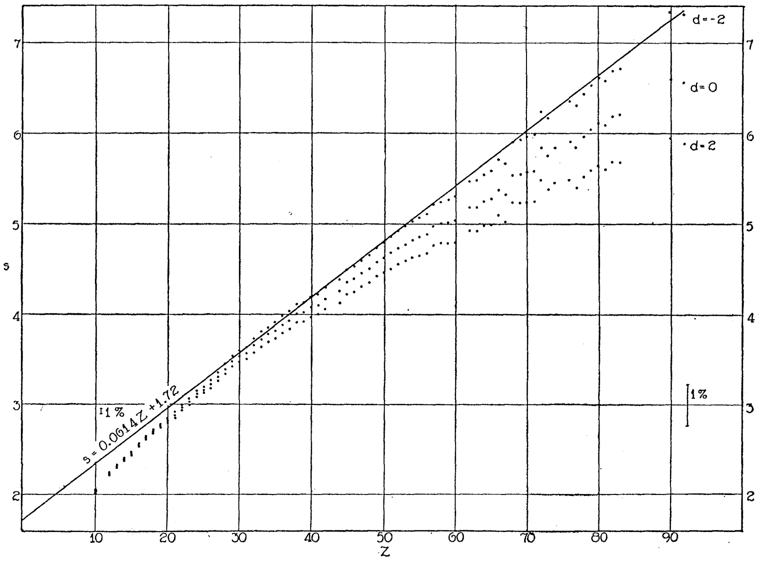

Fig. 1. The first-term K screening number s plotted against atomic number Z for the parametric values $d=-2, 0, 2$, assigned to the relativistic K screening number d.

Surface influences might be expected to cause the curve for the K shell to depart appreciably from linearity for the lowest values of Z and even for values somewhat higher than that (10 Ne) at which the L shell becomes complete.

Because of the slow convergence of Eq. (1) for the K shell ($n=k_1=k_2=1$), especially for high values of Z, it is convenient to sum the series from the

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[8] Sommerfeld, "Atombau und Spektrallinien," 4. Aufl., fig. 95.

second term on, remembering that Eq. (1) was derived from Sommerfeld's relativistic term formula for hydrogen-like orbits, which in our case becomes

$$\frac{\nu}{R}=\frac{2}{\alpha^2}[1-(1-\alpha^2 Z_{\text{eff}}^2)^{1/2}]. \tag{2}$$

Here Z_{eff} stands for $Z-s$ in the first member, and for $Z-d$ in all higher members of the series expansion (1). Therefore Eq. (1) becomes

$$\frac{\nu}{R}=\frac{2}{\alpha^2}\{1-[1-\alpha^2(Z-d)^2]^{1/2}\}-(Z-d)^2+[Z-s(Z)]^2. \tag{3}$$

Now knowing ν experimentally for any element, we may insert a value for the parameter d and solve for s. The frequency ν, corrected to eliminate Sommerfeld's relativistic correction terms, has been called the "reduced frequency": $\nu_{\text{red}}=R(Z-s)^2$.

The figure shows the family of Z, s curves for $d=-2$, 0, 2. Intervals indicating the change in ordinate due to an arbitrary change of one percent in term value, are marked at abscissas 10 and 92 to show the increased sensitivity of s to small relative errors in ν, as Z increases.

The term values for $Z<74$ in the figure are from Siegbahn[9] except for the later determinations for 10 Ne (by critical potential),[10] 14 Si,[11] 28 Ni,[12] 30 Zn,[12] 36 Kr,[13] 54 X,[13] and 68 Zr.[14]

The best value for d, as the figure shows, is approximately $d=-2$, which gives for $Z>26$, $s=0.0614Z+1.72$ within about the limits of experimental error.

If we limit ourselves to easily interpretable, i.e., positive values of d, we are forced to be content with a curve somewhat downward. Thus it is to be concluded that Sommerfeld's "relativity correction" does not account for all the curvature in the Moseley diagram for the K term wherein $(\nu/R)^{1/2}$ is plotted against Z. In order that the correction account for the curvature, it would be necessary that $(\nu_{\text{red}})^{1/2}$, and consequently s, be linear with respect to Z.

Though we have conventionally used a value with six digits[5] for the calcite grating distance D, it may be noted that the probable error of 0.03 percent in D[15] may lead to uncertainty not only in the values of the energy levels themselves, but also in the shapes of such curves as are drawn in the figure. This is true especially when the energy values plotted extend over a wide relative range. A change of 0.03 percent in D would, however, have only about the same effect on the shape of our curve as a change on the order of 0.04 in d. In the present case, then, the uncertainty in D may be neglected.

[9] Siegbahn, "The Spectroscopy of X-Rays" § 26.

[10] Holweck, Comptes rendus, **182,** 53 (1926).

[11] Lindh, Zeits. f. Physik **31,** 210 (1925).

[12] Walter, Zeits. f. Physik **30,** 350 (1924).

[13] M. de Broglie and Lepape, Comptes rendus **176,** 1611 (1923).

[14] Martin, Roy. Soc. Victoria Proc. **35,** 2 p. 164 (1923).

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

Although recent theoretical investigations have developed expressions somewhat different from Eq. (1) for term values, the newer viewpoint has been embodied, up to the present, in no formula as satisfactory as (1), so far as agreement with observation is concerned. For this reason (1) has been used in the present discussion, as an empirical formula. Its accuracy, indeed, has been confirmed by the deduction by Heisenberg and Jordan[16] on the basis of the matrix mechanics, of an expression for the energy contributed by the spin and the relativistic variation of the mass of the electron. This deduction, which neglects higher order terms, yields in the case of x-ray terms a quantity which agrees exactly with the second term on the right hand side of Eq. (1), provided the factor Z^4 in the Heisenberg-Jordan expression be replaced by $Z_{\rm eff}{}^4$; that is, provided the same screening be assumed to affect both the contribution due to the mass variation and that due to the spin.

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[16] Heisenberg and Jordan, Zeits. f. Physik **37**, 263 (1926).