THE ABSORPTION OF X-RAYS BY IRON, COBALT, NICKEL AND COPPER[1]

By F. K. Richtmyer and F. W. Warburton

Abstract

X-ray absorption coefficients of Fe, Co, Ni and Cu, for wave-lengths below the K absorption limit, have been measured by the use of a large spectrometer with a selected calcite crystal giving a beam of exceptional purity. The chief difficulty was to secure uniform films of the pure metals. It is found that the sequence of values of the atomic coefficients is that of the atomic numbers, not that of atomic weights, and that the *variation with atomic numbers* is as the fourth power, as previously suggested, the relation $\mu_a = 22.4 \times 10^{-27} N^4 \lambda^3 + \sigma_a$, holding within experimental error for all the ten elements for which the results have been obtained, from $N=6$(C) to $N=82$(Pb), except possibly iron for which the experimental value is 3 per cent too low. The values for *carbon, lead and tungsten* are preliminary and are taken from data not yet published.

Method of producing a thin uniform sheet of cobalt suggested by Kayko. Chemically pure oxide was compressed to a thin placque, then reduced in a furnace by an atmosphere of hydrogen.

SINCE the work of Moseley the significance of atomic number, as distinguished from atomic weight, in connection with a number of the properties of the elements, has come to be very fundamental. But most of these properties have to do with frequency phenomena rather than with energy relations. Thus in the case of cobalt and nickel, in which the orders of atomic numbers and of atomic weights are inverted, Duane and Hu have shown[2] that the frequencies of the K absorption limits of the two elements are in the same order as the atomic numbers.

It is to be expected that where energy relations, as distinct from frequencies, are involved, the atomic number, rather than atomic weight, of the element would also be fundamental. And Duane has shown[3] that the intensity of the general radiation from the elements Fe, Co, Ni and Cu follows the sequence of atomic numbers, not that of atomic weights. Further Owen,[4] Richtmyer,[5] and others have shown that the

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[1] Grateful acknowledgment is made for a grant from the Heckscher Research Council of Cornell University to F. K. Richtmyer. Without this grant this work would have been quite impossible.

[2] Duane and Hu, Phys. Rev. **14,** 516 (1919)

[3] Duane, Phys. Rev. **11,** 491 (1918)

[4] Owen, Proc. Roy. Soc. **94,** 510 (1919)

[5] Richtmyer, Phys. Rev. **18,** 13 (1921)

atomic absorption coefficient of x-rays is a simple function of the fourth power of the atomic number.

The atomic absorption coefficient is defined in the following way. Numerous researches have shown that for any given substance for wavelengths less than the K absorption limit the mass absorption coefficient μ/ρ is given by the empirical equation

$$\mu/\rho = F\lambda^3 + \sigma/\rho \tag{1}$$

where μ is the exponent in the ordinary absorption law $I = I_0 e^{-\mu x}$, ρ is the density of the material, σ/ρ is a constant which is frequently identified with the scattering, and F is a constant (very nearly). By dividing both sides of this equation by the number of atoms per gram, equal to n/A where n is Avogadro's constant and A the atomic weight, one obtains

$$\frac{\mu}{\rho}\ \frac{A}{n} = \mu_a = F\ \frac{A}{n}\ \lambda^3 + \frac{A}{n}\ \frac{\sigma}{\rho} = F_a\lambda^3 + \sigma_a \tag{2}$$

where μ_a is the atomic absorption coefficient and F_a and σ_a are constants.

In the previous experiments above referred to,[5] a curve plotted between log F_a and log N, where N is the atomic number, for the four elements Al, Cu, Mo and Ag gave a straight line with a slope 4.00; i.e.

$$F_a = kN^4 \tag{3}$$

If, however, a curve be plotted with log F_a and log A as coordinates, a straight line nearly as good results, with a slope 3.7. So that one might write

$$F_a = kA^{3.7} \tag{4}$$

It is of importance to decide whether (3) or (4) is correct. A determination of the value of F_a for the series of elements Fe, Co, Ni and Cu should answer the question since the order of atomic number and of atomic weight in Co and Ni is inverted.

APPARATUS AND METHOD

The absorption measurements were made by use of an x-ray spectrometer of the Bragg type specially constructed[6] in the instrument shop of the Department. Since instruments of this type are so well known, no description need be given, excepting as regards a few minor points. The x-ray beam was limited by two bilaterally and independently adjustable micrometer slits, 2.5 cm long, and 37 cm apart placed *between* the crystal and the x-ray tube. These slits were, for most of the measurements, kept at widths between .015 cm and .025 cm, thus giving a very

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[6] The writers' thanks are due to Mr. F. E. Miller, whose skill as an instrument maker and ingenuity as a designer made possible the spectrometer by which these measurements were made.

narrow beam. The crystal was the split (and not polished) calcite crystal No. A_3 described by Bergen Davis[7] and used by him in his measurements on the monochromaticity of beams reflected by various crystals. This particular crystal when used with the very narrow slit system above mentioned gave a beam of exceptional purity. The ionization chamber was of the usual type, filled with methyl bromide, the ionization currents being measured by the rate of drift of a Compton electrometer, reconstructed in the Department shop, and operated at a sensitivity of approximately 1500 mm per volt.

The x-ray tube[8] was a tungsten target tube, of the radiation type, capable of operating at 200,000 volts (peak). Special attention was paid to keeping the voltage applied to the tube and the current through it constant. Neither varied by as much as $\frac{1}{2}$ per cent during a run.

The leakage current through the ionization chamber was almost entirely compensated by connecting an opposing voltage, the best value of which was determined by trial, to the metal tube forming part of the electrostatic screening of the wire connecting the rod of the ionization chamber to the electrometer. Correction was made for any residual drift.

In making precision measurements of x-ray absorption coefficients, not so much difficulty is experienced in making the x-ray measurements as in getting chemically pure materials sufficiently homogeneous and of uniform thickness. The matter of purity is particularly important in measuring the absorption coefficients of the light elements. Consider, for example, carbon, with iron as an impurity. At $\lambda = .5$ A the mass absorption coefficient of carbon is approximately .30; that of iron approximately 15.0. The mass absorption coefficient of carbon containing 0.1 per cent of iron would differ from that of *pure* carbon by 4.5 per cent. At $\lambda = 1.0$ A the error would be 6.5 per cent. However, an impurity of low atomic number in a substance of high atomic number will cause no greater proportionate error than is made in getting the density of the sample. Thus the absorption coefficient of iron containing 0.1 per cent of carbon would differ from that of pure iron by only about 0.1 per cent.

Homogeneity and uniformity of thickness are, in some substances, very difficult to secure, particularly in elements of high atomic number, where one must work with samples only a fraction of a mil thick. Even

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[7] Davis, Phys. Rev. **17**, 608 (1921). The crystal was kindly loaned to one of the writers (F. K. R.) by Dr. Davis.

[8] For this tube the writers are indebted to Dr. W. D. Coolidge of the General Electric Co. Also the 150,000 volt 10 kv-a transformer used with the tube, was loaned by the General Electric Co.

though one can secure the pure material in this thin form, one must measure its thickness to, say, one-half per cent, or determine the mass per square centimeter with that precision. The *average* mass per square centimeter can readily be obtained by weighing a strip of the material of known area, but this does not necessarily give the mass per square centimeter at *every* point unless the specimen be of uniform thickness.

The iron used in the present investigation was electrolytic iron obtained from the General Electric Company. The nickel and the copper were obtained from Eimer and Amend. Much difficulty was experienced in obtaining the cobalt in the form of a thin strip. The pure metal could be obtained from several sources but it could not be worked. Electroplating cobalt onto aluminum, and stripping off the cobalt layer was tried, but without success. The writers are indebted to Mr. C. J. Kayko for the final solution of the problem. Working at the General Electric Research Laboratory, in Schenectady, he took chemically pure cobalt oxide, bolted it twice through fine silk, and then under a pressure of several tons per square inch pressed it into a thin placque. This was then placed in a furnace in an atmosphere of hydrogen until the oxide was reduced to metallic cobalt. A fine, firm adherent strip of exceptionally uniform composition and thickness was obtained.

Since, for any given substance, the mass absorption coefficient is very

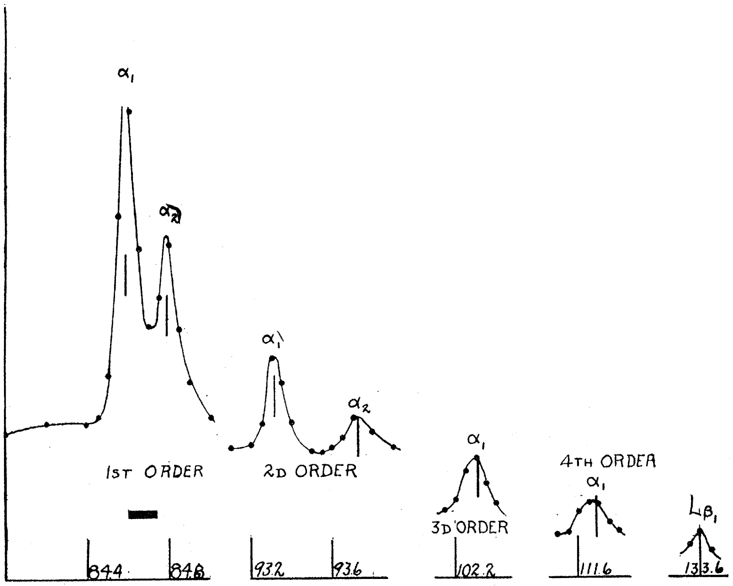

Fig. 1. Calibration of spectrometer.

nearly a linear function of the cube of the wave-length, it is important in determining the value of F in equation (1) that the wave-length measurements be made with as high precision as possible. A calibration curve was computed for the various chamber angles of the spectrometer by means of the known grating space of calcite. This curve was checked by the several orders (first to fourth) of the α lines of tungsten. The check is shown graphically in Fig. 1. The abscissas are sections of the spectrometer scale (arbitrary units). The short vertical lines show, for the several orders, the computed position of the lines, and the full lines indicate the observed position. The agreement is seen to be excellent. The graph also shows the high resolving power of the apparatus, the lines α_1 and α_2, which differ by about .004 A, being well separated in the first order spectrum. The equivalent "slit width" is shown by the small rectangle under the first order, and, at the first order of the α lines ($\lambda = .211$ A) is about .0028 A.

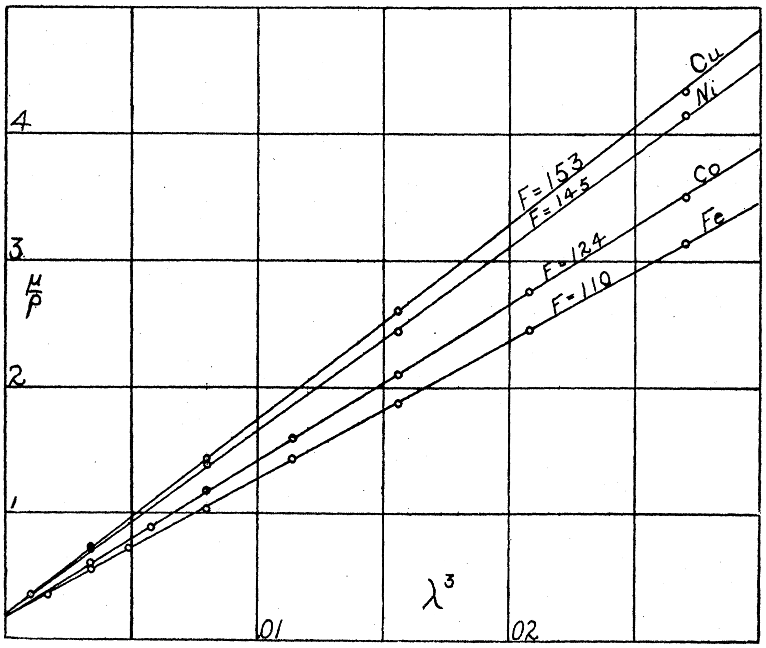

Fig. 2. μ/ρ as a function of λ^3 for Fe, Co, Ni and Cu.

RESULTS

The mass absorption coefficients as a function of the cube of the wave-length, for Fe, Co, Ni and Cu, are shown graphically in Fig. 2 for the wave-length range $.12\text{ A} < \lambda < .30\text{ A}$. Over this range the following equations hold.

$$\begin{aligned}\text{For Fe } \mu/\rho &= 110\lambda^3+.18\\ \text{Co } \mu/\rho &= 124\lambda^3+.18\\ \text{Ni } \mu/\rho &= 145\lambda^3+.20\\ \text{Cu } \mu/\rho &= 153\lambda^3+.20\end{aligned}$$

Wave-length is expressed in angstrom units. If now these several values of F be divided by n/A one obtains. F_a in column four of the following table.

Element	N	F	F_a	$\log_{10}F_a$	$\log_{10}N$
Fe	26	110	101×10^{-23}	-20.006	1.415
Co	27	124	121	.081	1.431
Ni	28	145	140	.148	1.447
Cu	29	153	161	.206	1.462

The relation between log F_a and log N is shown graphically in Fig. 3. The line is drawn to a slope of 4.00. All points fall on this curve within experimental error with the possible exception of that for iron, for which the mass absorption coefficient would have to be increased by about 3 per cent. Whether this difference for iron is real or is the result of some as yet undetected experimental error remains to be determined. The agreement in the case of cobalt and nickel is so excellent as to leave no room for doubt as to the correctness of Eq. (3) as contrasted with (4).

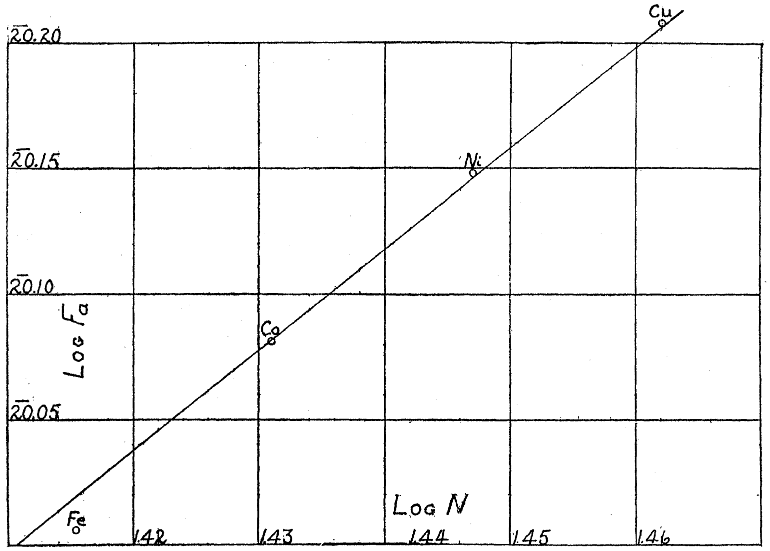

Fig. 3. Log F_a as a function of log N.

To bring out more clearly the correctness of Eq. (3) there is collected in graphical form in Fig. 4 the results recorded in this paper for Fe, Co, Ni and Cu and also some previous data.[5] This curve, like Fig. 3, is drawn to a slope of 4.00. The values for carbon, lead and tungsten are from unpublished data. That for carbon has been corrected for a slight impurity; that for tungsten as well as for lead is somewhat in doubt because of the difficulty of getting the material in thin enough strips. On the basis of this curve one may make a slight correction to the empirical equation for atomic absorption coefficients previously given,[9] viz.

$$\mu_a = 22.4 \times 10^{-27} N^4 \lambda^3 + \sigma_a$$

The numerical factor previously given was 22.9×10^{-27}.

It should be borne in mind that this equation holds only for wave-lengths considerably below the K absorption limit, since further and more careful observations have confirmed the previous conclusion that there is a real departure from the λ^3 law in the neighborhood of the K limit. The *exact* value of F and of F_a will therefore depend somewhat on the wave-length range used. This may in part explain the low values for tungsten and for lead.

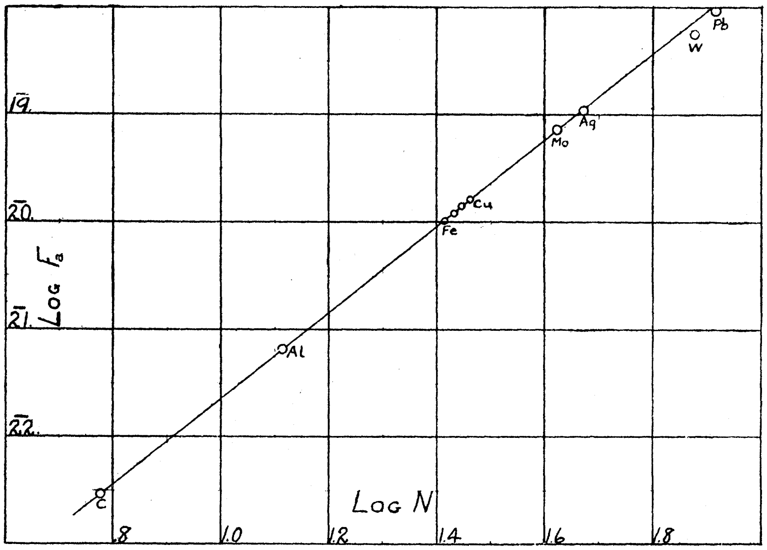

Fig. 4. Log F_a as a function of log N.

On the basis of present data it seems unlikely that there is any periodicity in the values of F_a in the atomic number series, but the number of elements for which careful measurements are available is insufficient to decide the question beyond doubt. Work is in progress to test this point and to ascertain the change in F_a on passing the K limit, as a function of atomic number.

Cornell University,
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[9] Loc. cit.[5] Eqs. 6 and 6′ in this former paper unfortunately contain as an error a factor 10.