AN EFFECT OF TEMPERATURE ON X-RAY ABSORPTION

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Abstract

The effect of temperature on the average atomic absorption coefficients for x-rays.—The variation with temperature of the absorption by sheets of Al, Cu, Fe, Ni, Ag, and Pb of the total x-radiation from a tungsten x-ray tube operated at 50 kv has been studied. The measurements were made by balancing the ionization currents produced by two x-ray beams from the same tube, one of which passed through the absorber. After proper corrections are made for changes in the density of the absorber and of the air in the path of the beam, there remains a residual effect indicating a true variation of the atomic absorption coefficient with temperature. The results indicate that for all absorbers used the average atomic absorption coefficients for the total x-radiation from the tungsten target increased nearly linearly with the temperature by about 0.2 percent per 100°C up to temperatures near the melting point of the absorber. The work is being continued to determine the magnitude of the effect at different wave-lengths.

THE statement has been made,[1,2,3] and is generally accepted, that heating a crystal affects measurably its ability to reflect x-rays. Also it has been stated[4] that x-ray absorption is independent of all physical conditions, and specifically, independent of temperature. The critical analysis of x-ray phenomena show such close relations between transmission, reflection, scattering, and absorption that they appear to be consequences of one or two more fundamental phenomena. The object of the present work was to search for an effect of temperature on x-ray absorption by the metals, Al, Fe, Ni, Cu, Ag, and Pb.

A small temperature effect has been found and measured. Although this preliminary work does not give the accurate value of the small effect, it shows the existence of the temperature effect and the experiments are being continued to determine the value for the different wave-lengths.

Method and Apparatus

A balance method of measurement was used. Two beams from one Coolidge tungsten x-ray tube (Fig. 1) were isolated by four pairs of lead slits and a Bumstead electroscope indicated their balance in two ionization chambers containing methyl bromide. An absorber in one beam was

[1] W. H. and W. L. Bragg, X-rays and Crystal Structure, 1st ed., pp. 190, 196.

[2] C. G. Darwin, Phil. Mag. **27**, 325 (1914).

[3] P. Debye, Ann. d. Physik **43**, 49 (1914); Vehr. d. D. Phys. Ges. **15**, 678, 738, 857 (1913).

[4] W. H. and W. L. Bragg, X-rays and Crystal Structure, 1st ed., p. 46.

heated by raising up an electric furnace with a narrow slot for the absorber holder. The furnace was 20 cm long, 8 cm inside diameter, and to prevent air currents was closed at the ends by Al sheet .001 cm thick. After raising the furnace the balance was found to be destroyed and the small amount that the adjustable slit in the other beam was changed in order to regain a balance, was recorded. All records and computations were made in terms of the adjustable slit width. Seven or nine trials, alternately hot and cold, were made and the difference between the averages computed. This difference was the uncorrected measure of the temperature effect.

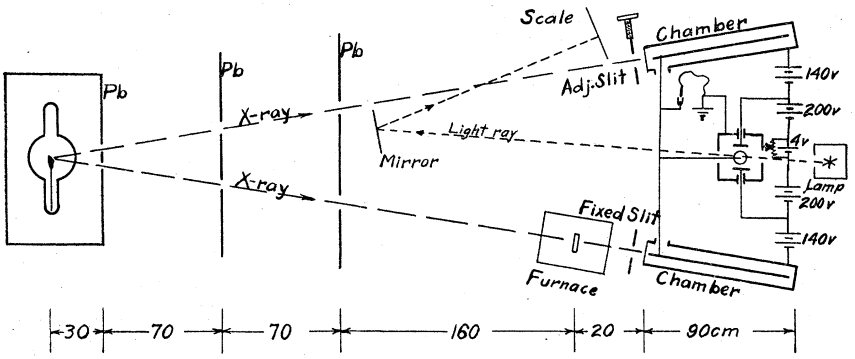

Fig. 1. Arrangement of apparatus.

Six 100 ampere-hour storage batteries were soldered together for a 12 volt source for the tube filament. Over one hour was allowed for the battery to approach a constant discharge current. After that time the tube electron current decreased very steadily at a rate of nearly 0.2 milliamperes per hour. A source of alternating current was obtained by running a compound wound rotary converter on a Terrill regulated d.c. generator. Voltage fluctuations larger than one percent would have been detected on the voltmeter.

The steadiness of operation is measured by the facts that the adjustable slit could be set to 1.0×10^{-4} inch, and when set the electroscope deflection did not change over 1 mm in 10 seconds. However, some unknown cause gave variations as large as 30×10^{-4} inch from day to day. The total absorption of the metals used was equivalent to 6000 to 9000×10^{-4} inch and the temperature effect was from 0 to 200×10^{-4} inch. The maximum slit opening was 1.2400 inch.

An improved Bumstead electroscope was used to indicate the balance between the ionization currents in the two chambers. The sensitivity used was about 150 mm per volt of leaf potential. The possible greater

sensitivity[5] would not have increased the accuracy proportionately because errors in single slit settings were smaller than other errors.

A correction for the smaller density of hot air in the x-ray path and for the Al furnace windows was made by measuring the effect of raising the furnace up around the empty holder while the absorber was across the x-ray beam but beyond the furnace. This was done for each absorber at each temperature used and the correction obtained was appropriate for the particular x-rays transmitted through the sample and for the particular furnace temperature. Since the order of position of successive, relatively thin absorbers does not affect much the total absorption, the different location of the absorber for the air correction observations caused no error.

Switching on and off the full load current in the furnace did not give any observable unbalance and consequently it was assumed that the fields of the furnace current did not cause any of the effect found.

The temperatures of the absorbers were measured in arbitrary units by a chromel-alumel thermocouple inside and near the wall of the furnace. Later this couple was calibrated in terms of a standardized Pt-Pt Rh couple, one junction of which was placed between two similar layers of the various absorbers.

Effect of Heat Expansion

The measured change of x-rays transmitted was an absorption and a scattering effect. The latter is not easily computed and was not measured. However it probably was smaller than the absorption effect. For example Kaye[6] says that for the copper group the scattered is sometimes less than 1/200 of the total radiation and A. H. Compton[7] shows that scattering of other elements is of the same order of magnitude or less. And, since the absorber in the furnace covered the beam there and had about twice the area of the final slit the scattering into the beam partly compensated scattering out of the beam. No correction was made for scattering or reflection.

A correction was made for the thermal expansion of the absorber, an appreciable part of which expanded out of the path of x-rays. The beam was defined by a fixed slit, the projected area of which, at the absorber was an area B. Let n represent the number of atoms per cc in the cool absorber, x the cool absorber thickness, a and a' the average atomic ab-

[5] K. Cole has recently calibrated a Bumstead electroscope up to 37,000 mm per volt. J. Optical Soc. of America **10**, 99 (Jan. 1925).

[6] Kaye, X-rays, 4th ed., p. 114.

[7] A. H. Compton, National Research Council Bulletin **4**, Part 2, No. 20, p. 5 (1922).

sorption coefficients for the absorber cool and hot respectively, I_0 the incident intensity, and I the transmitted intensity. For room temperature the transmitted energy is

$$W_1 = BI = BI_0 \exp\,[-anx] \tag{1}$$

and for the heated absorber is

$$W_2 = BI_0 \exp\left[-a'\frac{n}{(1+g)^3}(1+g)\right] = BI_0 \exp\left[\frac{-a'nx}{(1+g)^2}\right] \tag{2}$$

where $(1+g)$ is the usual thermal expansion coefficient for the absorber, values of which for the temperature ranges used were obtained from tables of Landolt and Bornstein, 5th edition, p. 1228. The percentage increase in transmitted energy due to heating is given by

$$K_c = \frac{W_2 - W_1}{W_1} = \exp\left[anx - \frac{a'nx}{(1+g)^2}\right] - 1\ . \tag{3}$$

Since the largest value of $2g$ used was .0388 and of anx was 1.69 this expression reduces approximately to

$$K_c = (a-a')nx + 2ga'nx \tag{4}$$

TABLE I

Computed results

			20°	190°	320°	475°	630°	880°	1080°
Al	anx	:	.66						
.102 cm	K_m	:	.0003	.0062	.0035	.0060	.0085		
thick	K_c	:	.0000	.0054	.0102	.0195	.0235		
	$K_m - K_c$	:	0003	.0008	−.0060	−.0135	−.0150		
Fe	anx	:	.914						
.014 cm	K_m	:	.0000	.0025	.0043	.0050	.0075	.0134	
	K_c	:	.0000	.0038	.0073	.0117	.0164	.0254	
	$K_m - K_c$	:	.0000	−.0013	−.0030	−.0067	−.0089	−.0120	
Ni	anx	:	1.14						
.008 cm	K_m	:	.0014	.0023	.0046	.0071	.0106	.0089	.0190
	K_c	:	.0000	.0053	.0103	.0150	.0214	.0319	.0410
	$K_m - K_c$	:	.0014	−.0030	−.0057	−.0079	−.0108	−.0408	−.0220
Cu	anx	:	1.14						
.009 cm	K_m	:	−.0002	.0024	.0051	.0078	.0068	.0023	
	K_c	:	.0000	.0066	.0119	.0187	.0258	.0386	
	$K_m - K_c$	:	−.0002	−.0065	−.0068	−.0109	−.0190	.0363	
Ag	anx	:	.95						
.005 cm	K_m	:	.0002	.0023	.0054	.0087	.0117	.0171	
	K_c	:	.0000	.0063	.0112	.0176	.0245	.0368	
	$K_m - K_c$	:	.0002	−.0040	−.0058	−.0089	−.0128	−.0197	
Pb	anx	:	1.69						
.004 cm	K_m	:	.0019	.0115	.0169				
	K_c	:	.0000	.0166	.0301				
	$K_m - K_c$	:	.0019	−.0051	−.0132				

The atomic absorption coefficient is not generally assumed to change with any physical or chemical condition but the measurements reported here indicate that it is approximately proportional to the temperature. To show this first assume $a=a'$, giving $K_c=2ganx$. Because K_c is positive the transmission should be greater when the absorber is hot. The observed values, K_m, of the percentage increase in transmitted x-rays due to heating the absorber together with the values, K_c, calculated on the assumption that the change is due to the usual thermal expansion only, are given in Table 1 and are presented graphically in Fig. 2.

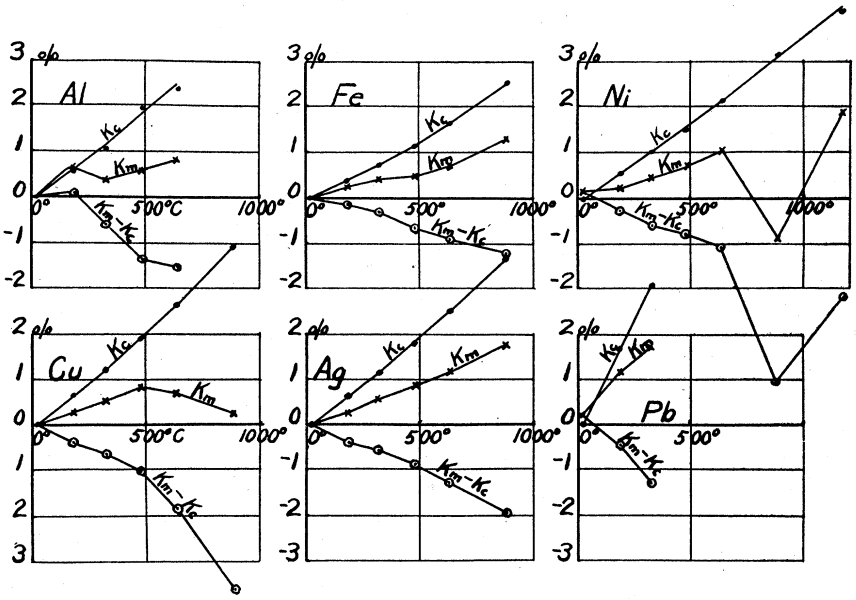

Fig. 2. Variation with temperature of the percent increase in transmission. K_m is observed and K_c calculated on the assumption that there is no variation of the atomic absorption coefficient with temperature.

To express the percentage decrease in transmission in terms of the percentage increase in absorption (L_m-L_c) simply multiply by the ratio of transmitted to absorbed energy.

$$(L_m-L_c)=\frac{W_1}{W_0-W_1}(K_m-K_c) \tag{5}$$

It will be noted that the measured change K_m was smaller than the calculated change K_c. In fact K_c was approximately twice K_m, except for a few temperatures. Therefore a' is not equal to a. These results suggest that the average atomic absorption coefficient depends on the

temperature of the absorber in the following manner. Within the experimental error and for most of the temperatures and metals used

$$K_m = ganx \tag{6}$$

The true K_c given by Eq. (4) should equal K_m

$$ganx = (a-a')nx + 2ga'nx \tag{7}$$

The largest value of g was .0194 which may be neglected here when added to unity and Eq. (7) reduces approximately to

$$a' = (1+g)a\ . \tag{8}$$

This relation may be very important in the application of x-ray data to atomic structure studies. It should be confirmed by independent further measurements but unfortunately x-ray intensity measurements cannot, in the present state of the art, be measured much more accurately than was done for this work. The art of making accurate intensity measurements should be developed or new methods used for such work. Absorption coefficients are now known to three significant figures and as soon as they are measured to four figures a temperature correction will be necessary. It must be remembered that the a used above is not the usual coefficient, for a has widely different values for different wave-lengths. Only an effective value is used here. The work is being continued using narrow bands of wave-lengths and the smaller intensity of reflected x-rays makes it more difficult but not impossible to get sufficiently accurate results to show the temperature effect on absorption.

Sample of Data and Computation

A complete set of observations and computations is given below:

Primary, 61.0 volts, 2.8 amps.; tube current, $3.1 \pm .1$ m.amps.; tube filament current, 3.75 amps.; electroscope sensitivity, 173 mm per volt; temperature in the furnace, 475°C.

Run 1. Air effect, x-rays filtered through the Ag strip.

					Ave.	Diff.
Slit reading (cold):	.7812″	.7806″	.7800″	.7797″	.7804″	
						+.0072
Slit reading (hot):	.7882	.7875	.7870		.7876	

Run 2. Ag absorber (0.5 min. allowed to heat or cool off)

Slit reading (cold):	.7811	.7897	.7798	.7801	.7801	
						.0032
Slit reading (hot):	.7834	.7832	.7832		.7833	

The difference, $W_2 - W_1 = .0072'' - .0032'' = .0040''$ of the adjustable slit measures the effect of mass expanding out of the beam and any change

in absorption coefficient. $(W_2-W_1)/W_1$ is the measured percentage increase in transmission due to the heating.

No absorber in balanced a slit setting of .0405''. Complete absorption by a strip of Pb balanced 1.2400''. The W_0 incident on the absorber was $1.2400-.0405=1.1995$. The Ag transmitted

$$W_1=1.2400-.7804=.4596'' \tag{9}$$

Thus

$$K_m=\frac{W_2-W_1}{W_1}=\frac{.0040}{.4596}=.0087 \tag{10}$$
$$=0.87\% \text{ change}.$$

Since

$$\frac{I_0}{I}=\frac{1.2400-.0405}{1.2400-.7804}=2.61$$

$$anx=2.30\log\frac{I_0}{I}=0.95 \tag{11}$$

and, since for Ag $2g=16.8\times10^{-3}$,

$$K_c=2ganx=.0176 \tag{12}$$

$$K_m-K_c=-.0087+.0176=+.0089 \tag{13}$$

The Ag transmitted .89 percent less at 475°C than at 20°C or by Eq. (5) the Ag absorbed

$$\frac{.4596}{.7804-.0405}0.89\%=0.53\%$$

more at 475°C than at 20°C.

Criticism

The increase in absorption due to heating was somewhat of a surprise and it seems appropriate to criticise the method and results as follows. The balance method is good for such work but the two x-ray beams were not exactly alike, and the absorber filtered one beam.

Total radiation used had a limiting wave-length of about 0.25A. The value of anx used in computing K_c is only an effective value and the approximation

$$\exp[2ganx]=1+2ganx \tag{14}$$

may not be close enough for all wave-lengths present. If the result, K_m-K_c, were small compared to K_m more terms of the expansion should be used.

The value of K_c depends on the expansion coefficients but it is improbable that there is the 50 percent error in the latter which would be needed to make the temperature effect zero.

The absorber and the absorber holder must have warped slightly on heating. To calculate the angle of warping which would just account for the effect simply remember that approximately $K_m = 2/3K_c$ and that K_c is about 3 percent at 1000°. Thus an increase of 1 percent in the transmitted intensity when hot would make $K_m = K_c$. This requires 1.7 percent increase in anx for Al, 0.7 percent for Pb, and intermediate values for the other metals. A warping of 8° would increase x by 1 percent but that much of an angle seems improbable. No warping was observed.

No way was found to separate the effects of temperature on absorption, reflection and scattering; all are combined here.

The Braggs[8] show that the small amount of x-rays reflected from a crystal changes measurably with temperature of 370°. Collins[9] says that temperature has a marked effect on the scattered x-rays. It is suggested but not proved that the measured effect is larger than all the x-rays reflected and scattered and thus is larger than any probable change in reflection and scattering.

I wish to express my thanks to Professor F. K. Richtmyer for his pleasant interest and very generous aid. He suggested this study.

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CORNELL UNIVERSITY,
February, 1924.

[8] W. H. and W. L. Bragg, X-rays and Crystal Structure, 1st ed., p. 196.
[9] E. H. Collins, Phys. Rev. **23**, 105 (1924).