cate the approximate shape of the transition curve for bursts of more than 100 particles at an altitude of $h=7$ r.u. The fact that the t_μ-burst frequency for such a transition curve is very small compared with the t_0- and t_m-burst frequencies shows that the great majority of the extensive atmospheric showers at higher altitudes do not contain electrons or photons of energies sufficient to create high multiplication under 20 r.u. (i.e., $E>10^{11}$ ev).

It is with sincere gratitude that the writer acknowledges the counsel of Professor Marcel Schein who suggested the problem and guided all phases of the investigation. The author is also grateful to Chancellor A. H. Compton for his support and advice. The work was facilitated by a fellowship granted by the Henry Strong Educational Foundation. Appreciation is likewise expressed to the Carnegie Institution of Washington for its cooperation.

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Structure in the X-Ray K Absorption Edge of Metallic Potassium

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For the alkali metals sodium and potassium the free electron approximation should give the energy states in the conduction band closely. Calculations based on this approximation predict an arctangent shape for the potassium K absorption edge. By use of a two-crystal vacuum x-ray spectrometer, the absorption edge of metallic potassium has been explored with high resolving power. Details of the experimental procedure are given. The shape of the absorption edge is in satisfactory agreement with the theoretical arctangent curve, and the width of the edge agrees with the predicted value. Some evidence is found of a secondary structure not given by the simple theory and the free electron approximation. The wave-length of the midpoint of the edge has been redetermined.

INTRODUCTION

RECENT theories of the solid state have predicted the distribution in energy of the conduction electrons in metals. Knowledge of the electronic energy states in the conduction band of a metal makes possible a theory of the structure to be found in the neighborhood of an x-ray absorption edge for that metal, and this derived theory can be tested experimentally. The photoelectric ejection of an electron from the K state of the metal atom, with absorption of the quantum, is permissible if the quantum has sufficient energy to raise the electron to the lowest unoccupied state in the conduction band. Variation of the absorption coefficient for quantum energies starting at this critical value and increasing by a few ev must be due to the nature and density of the energy states in the conduction band.

The experimental requirement is that the absorption coefficient of the metal be investigated carefully over a range of quantum energies of several electron volts including the absorption edge. Since the energy of the absorption edge itself is in general of the order of electron kilovolts, this puts a stringent requirement on the resolving power of the apparatus used. Such resolving power can be obtained without prohibitive loss in x-ray intensity with the two-crystal x-ray spectrometer. A number of investigators have used this research tool to study the structure of absorption edges in metals.[1,2]

The alkali metals, and especially sodium and potassium, are of particular interest because the theory of their solid state has been developed in some detail. The present study is of the absorption structure in the region of the potassium K

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[1] H. Friedman and W. W. Beeman, Phys. Rev. **58**, 400 (1940).
[2] L. G. Parratt, Phys. Rev. **54**, 99 (1938).

edge. Sodium, on which the most complete theoretical work has been done,[3] has recently been reported on by another investigator.[4]

THEORY OF ABSORPTION STRUCTURE IN POTASSIUM *K* EDGE

The methods of wave mechanics have been used to study three questions which are of interest in predicting the variation of the absorption coefficient of potassium in the region of the K edge. The first of these questions is the determination of the density of energy states, within the conduction band, to which an electron may be ejected. The second is the behavior of the probability of a transition from the K shell to one of the states in the conduction band. The third is the "smearing" of the detail of the absorption curve caused by the fact that the energy of the atom in a state of K excitation is not exactly defined.

Density of Energy States

The Schroedinger equation for the wave function of an electron is

$$\frac{\hbar^2}{2m}\nabla^2\psi+(E-V(\mathbf{r}))\psi=0,$$

where E is the total energy of the electron and $V(\mathbf{r})$ is its potential energy. For a conduction electron in potassium metal, the potential function $V(\mathbf{r})$ is nearly constant over most of the volume within the lattice (the volume outside the ionic cores). To a first approximation $V(\mathbf{r})=0$, if the zero of energy be taken as the mean potential energy of a conduction electron. This leads to the "free electron" solution

$$\psi=\exp\left[i\mathbf{k}\cdot\mathbf{r}\right],$$

where $\mathbf{r}$ is the position vector of the electron, and the wave vector $\mathbf{k}$ has the magnitude $(2mE/\hbar^2)^{\frac{1}{2}}$. For this solution, the number of electronic energy states between E and $E+dE$ is proportional to $E^{\frac{1}{2}}dE$. The energy of the highest occupied state in the conduction band is

$$E_{\max}=\frac{\hbar^2R_{\max}^2}{2m}=\frac{\hbar^2}{2m}\left(\frac{3\pi^2}{\Omega}\right)^{\frac{2}{3}},$$

where Ω is the volume occupied by one atom. For potassium the value of $E_{\max}$ is 2.06 ev.

In second approximation one includes in the potential term $V(\mathbf{r})$ the part of the potential that is not constant. A good deal of information may be secured without knowing the exact variation of the potential simply from the fact that the potential must be identical at corresponding points within the lattice. $V(\mathbf{r})$ may therefore be expanded in a three-dimensional Fourier series the fundamental space periods of which correspond to the lattice vectors for metallic potassium. The problem may then be treated by perturbation methods, in which the "free electron" solutions are taken for the unperturbed wave functions. The result is that the electron energies are very closely those of the unperturbed case except for values of the wave vector $\mathbf{k}$ which fall near the boundary of one of the Brillouin zones in $\mathbf{k}$ space. If these zones were bounded by spherical shells, there would be certain energy values within the electron energy spectrum which would not occur. Since the zones are actually bounded by polyhedra, one can say only that there will be regions in the energy spectrum for which the $E^{\frac{1}{2}}$ law will not be obeyed. In the case of metallic potassium, one expects deviations from the $E^{\frac{1}{2}}$ law in the region from three to five ev, due to the influence of the boundary of the first Brillouin zone. The extent of these deviations should be small if the approximation of constant potential (unperturbed theory) is nearly valid. Effects due to other Brillouin zones than the first should be greatest in the energy regions of 10 ev and 36 ev, and should be smaller than those at the first boundary.

Transition Probability

The variation in absorption coefficient depends not only on the density of states within the conduction band to which the electron can be ejected, but also on the probability than an electron makes the transition from the K shell of the atom to a particular state in the conduction band, under the influence of the radiation.

[3] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934).
[4] K. C. Rule, Phys. Rev. **66**, 199 (1944).

The probability of transition from a state in which the wave function of the electron is ψ_i to a state in which the wave function of the electron is ψ_f is proportional to the absolute square of the matrix element $\mathbf{M}$,[5] where

$$\mathbf{M}=\int \psi_i \mathbf{r} \psi_f^* dv.$$

Here $\mathbf{r}$ is the coordinate vector with respect to which the integration is performed, and dv is an element of volume. Exact evaluation of the matrix element involves the precise functional form of ψ_i and ψ_f. A good deal of information may be secured, however, merely from a qualitative knowledge of the behavior of the wave functions.

It suffices to note that $r\psi_i$, where ψ_i is the wave function of the K electron, varies with the increasing distance from the nucleus roughly as shown in Fig. 1.[6] The maximum occurs at a distance of about 2.5×10^{-10} cm from the nucleus, and from this region on the wave function decreases rapidly with increasing distance. The quantity $r\psi_i$ is only appreciable for a radial distance between 5×10^{-11} and 10^{-9} cm.

To find the behavior of the wave function ψ_f of the ejected electron one makes use of an approximate solution of the Schroedinger equation. As previously, one may neglect in first approximation the periodic variation in the potential of an electron within the lattice. There is one deviation from constant potential, however, which may not be neglected. Upon ejection from the K shell the photoelectron leaves behind it an atomic core which is ionized in the K shell. In the neighborhood of the ion from which it was ejected, then, the electron moves in a potential due to one positive charge. One must add to the expression for the potential a term $-Z'e^2/r$, where Z' has the value unity for large r, and has the value of the effective atomic charge for r within the ion itself. The Schroedinger equation becomes

$$\frac{\hbar^2}{2m}\nabla^2\psi_f+\left(E+\frac{Z'e^2}{r}\right)\psi_f=0.$$

The solution is most conveniently obtained in terms of spherical coordinates since the potential term is spherically symmetric. It is readily shown that the solution may be written

$$\psi_f(r)=A_0\frac{R_0(r)}{r}+\frac{R_1(r)}{r}\sum_{m=-1}^{1}A_{1m}P_{1m}(\phi,\theta)+\frac{R_2(r)}{r}\sum_{m=-2}^{2}A_{2m}P_{2m}(\phi,\theta)+\cdots$$

where the A_{jm} are constants, the $P_{jm}(\phi,\theta)$ are spherical harmonics, and the $R_j(r)$ are solutions of the radial equation

$$\frac{d^2R_j(r)}{dr^2}+\left[\frac{2m}{\hbar^2}\left(E+\frac{Z'e^2}{r}\right)-j\frac{(j+1)}{r^2}\right]R_j(r)=0.$$

The boundary condition to be imposed on the solution $\psi_f(r)$ is that for large values of r, i.e., large distances from the ionized atom, the wave function must be identical with the previous solution,

$$\psi_f(r)=\text{constant}\cdot\exp(i\mathbf{k}\cdot\mathbf{r}).$$

This is equivalent to requiring the electron to assume its normal role in the lattice once it is removed from the influence of the ion. This requirement makes one simplification immediately possible, for, if the polar axis (z axis) of the spherical coordinates be chosen parallel to $\mathbf{k}$, only those spherical harmonics for which m is zero can appear in the expression for $\psi_f(\mathbf{r})$.

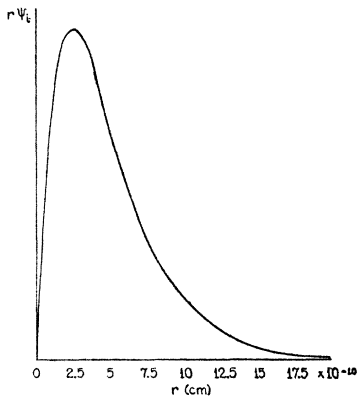

FIG. 1. $r\psi_i$ as a function of the radial parameter r for the potassium K electron.

[5] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 219.

[6] H. A. Bethe, *Handbuch der Physik* (Verlagsbuchhandlung, Julius Springer, Berlin, 1933), Vol. 24/I, p. 285.

A further simplification results from the fact that the wave function ψ_i of the electron in the K shell is spherically symmetric. It can be shown[6] that under this condition the only spherical harmonics in $\psi_f(\mathbf{r})$ which contribute to the matrix element are those for which j is unity. In this problem one is interested only in the coefficient of $P_{10}(\phi, \theta)$.

An approximate method of solving the radial equation has been developed by Wentzel, Kramers, and Brillouin.[7] If one makes the substitution for the case $j=1$,

$$\Phi(r)=\frac{2m}{\hbar^2}\left(E+\frac{Z'e^2}{r}\right)-\frac{2}{r^2},$$

the radial equation becomes

$$\frac{d^2R_1(r)}{dr^2}+\Phi(r)R_1(r)=0,$$

the approximate solution of which is

$$R_1(r)=C\Phi^{-\frac{1}{4}}(r)\cos\left(\int_{r_0}^{r}\Phi^{\frac{1}{2}}(\lambda)d\lambda-\pi/4\right)+\cdots$$

where the constant C is independent of r, and $\Phi(r_0)=0$. The solution holds for r greater than r_0. If we assume $E=10$ ev and $Z=19$ for potassium, then we find r_0 is in the region of the K shell. Thus the W-K-B method leads to the solution

$$\psi_f(r)=\cdots+P_{10}(\phi, \theta)\times(C/r)\Phi^{-\frac{1}{4}}(r)\cos\left(\int_{r_0}^{r}\Phi^{\frac{1}{2}}(\lambda)d\lambda-\pi/4\right)+\cdots.$$

This must be identical with $\exp[i\mathbf{k}\cdot\mathbf{r}]$ for large r. The expansion of this function in spherical harmonics approaches for large r the value

$$\exp_{r\to\infty}[i\mathbf{k}\cdot\mathbf{r}]=\frac{\sin kr}{kr}+P_{10}(\phi, \theta)\left(\frac{\cos kr}{kr}-\frac{\sin kr}{(kr)^2}\right)+\cdots.$$

To compare the two expansions, one notes that for large r, $\Phi(r)$ approaches $2mE/\hbar^2$. Writing the energy E as $\hbar^2k^2/2m$, one finds for large r

$$\Phi(r)=k^2,\quad \int_{r_0}^{r}\Phi^{\frac{1}{2}}(\lambda)d\lambda=kr+\text{constant},$$

$$\psi_f(r)=\cdots+P_{10}(\phi, \theta)\times(C/r)k^{-\frac{1}{2}}\cos(kr+\text{constant})+\cdots.$$

Comparing, we find that in order for the two expressions to be identical, C must be proportional to $k^{-\frac{1}{2}}$.

For small values of r, in the region of the K shell of the ion where the major contribution to the matrix element occurs, $\Phi(r)$ is practically independent of k, since the term involving E is negligible compared to the other two terms. Over this region ψ_f involves $\mathbf{k}$ only in the normalization constant C. The matrix element is therefore proportional to $k^{-\frac{1}{2}}$, and the transition probability is proportional to k^{-1}, or $E^{-\frac{1}{2}}$. Thus the probability of an electron transition from the K state to a state in the conduction band in which it has the kinetic energy E is inversely proportional to the square root of E.

Effect of Radiation Width of K State

The effect of radiation width of the K state must also be taken into account in predicting the variation of the absorption coefficient. Consider a photoelectric process in which the atom initially has the energy E_i. Upon absorption of a quantum of energy $h\nu$, an electron is ejected from the K shell of the atom to some unoccupied electron state. Let the energy of the new state of the atom be E_f. The following energy equation holds:

$$h\nu=E_f-E_i.$$

If the energy of the atom before and after the absorption act could be known exactly, the frequency of the absorbed quantum could be specified exactly.

Actually, however, the energy E_f cannot be known precisely. The reason is that the atom does not remain long in a state of K excitation because of the high probability of the subsequent emission of a K series quantum. According to the Heisenberg uncertainty principle, one cannot know simultaneously the energy of a system and the time at which it has this energy. The product

[7] W. Voss, Zeits. f. Physik **83**, 581 (1933).

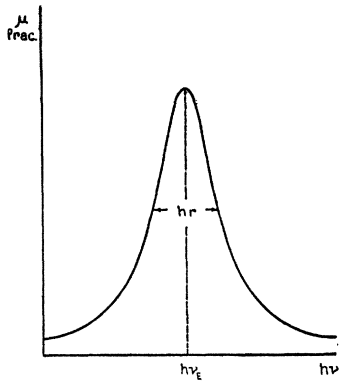

FIG. 2. Fractional absorption coefficient as a function of the energy of the absorbed quantum.

of the uncertainties in these two variables must be of the order of Planck's constant. The energy E_f is therefore uncertain by an amount which is inversely proportional to the lifetime of the atom in a state of K excitation.

Weisskopf and Wigner[8] have shown that the probability of absorption of a quantum of frequency between ν and $\nu+d\nu$, causing transition of an electron between two states whose energy separation is $h\nu_E$ is given by

$$P(\nu)d\nu=\frac{C_1\Gamma d\nu}{(\nu-\nu_E)^2+(\Gamma/2)^2}.$$

Here C_1 is a constant, and $2\pi\Gamma$ is the reciprocal of the mean lifetime of the atom in the excited state.

The fraction of the absorption coefficient for the atom due solely to transitions between these two states, which is proportional to this probability, is therefore given by a classical dispersion curve (Fig. 2) with a peak at $h\nu_E$ and a full width at half-maximum equal to $h\Gamma$.

For K absorption in metallic potassium, the total absorption coefficient $\mu(\nu)$ is simply the sum of these fractional absorption coefficients for transitions from the K shell to the various unoccupied states in the conduction band, if each fractional absorption coefficient is weighted by its relative probability.

$$\mu(\nu)=C_1\sum_i\frac{P(i)\Gamma}{(\nu-\nu_i)^2+(\Gamma/2)^2},$$

where the index i denotes the particular state in the conduction band, and $P(i)$ is the relative probability of an electron transition from the K state to the ith band state. Γ is the same for all band states.

There are actually a great number of states in the conduction band, and the energy gap between any two states is very small, so the summation may be replaced by an integral. If the zero of energy be taken as the energy of the initial state, let $h\nu_i$ be the energy of the atom with a K electron ejected to the ith band state. Let $N(h\nu_i)$ be the number of states per unit energy interval in the neighborhood of the ith band state, and the summation may then be written

$$\mu(\nu)=C_2\int\frac{P(i)N(h\nu_i)d\nu_i}{(\nu-\nu_i)^2+(\Gamma/2)^2},$$

where C_2 is another constant. The integration extends over all unoccupied band states. It has been shown, however, that for metallic potassium in the approximation of constant potential within the lattice, the quantity $N(h\nu_i)$ is proportional to the square root of the kinetic energy of the ith electron, and the square of the matrix element is inversely proportional to the same quantity. The transition probability $P(i)$ is proportional to the square of the matrix element and to the quantity[9] $(\nu_0/\nu_i)^{8/3}$ where $h\nu_0$ is the energy of the electron of lowest energy in the conduction band. Thus the product $P(i)N(h\nu_i)$ is simply proportional to $(\nu_0/\nu_i)^{8/3}$. This quantity varies very slowly over the region where the integrand is appreciable, and is essentially equal to unity over the entire region of the absorption edge. The integral therefore becomes

$$\mu(\nu)=C_3\int_{\nu_F}^{\infty}\frac{d\nu_i}{(\nu-\nu_i)^2+(\Gamma/2)^2},$$

where C_3 is another constant. The integration extends from ν_F, where $h\nu_F$ is the energy of the electron in the highest occupied state, to infinity. It was shown above that $h(\nu_F-\nu_0)$ is about 2.06 electron volts.

Carrying out the integration, we find the following expression for the absorption coefficient:

$$\mu(\nu)=C_4\left\{\frac{\pi}{2}+\tan^{-1}\frac{(\nu-\nu_F)}{\Gamma/2}\right\}.$$

[8] V. Weisskopf, Physik. Zeits. **34**, 1 (1933).

[9] Reference 6, page 475.

Additional Absorption Processes

These calculations deal only with the fraction of the absorption coefficient caused by transitions from the K shell to the conduction band. There is a further contribution due to ejection of electrons from the L and M shells. This contribution, small compared to the K absorption and practically constant over the region of the K edge, may be included by adding a constant term to the expression for the absorption coefficient. A slight diminution of the transmitted beam, and hence a slight addition to the measured absorption coefficient, is caused by scattering of radiation in other than the forward direction. This effect may also be accounted for by the use of an additive constant. The value of the total additive constant may be determined from experimental data. No such data are available for metallic potassium, but for neighboring elements in the periodic table this constant, representing an unchanging background of absorption, is about one-tenth of the maximum value of $\mu(\nu)$ over the immediate region of the K absorption edge. Upon adding such a term to the expression previously derived for the absorption coefficient of metallic potassium, one obtains:

$$\mu(\nu)=C_4\left\{\frac{11\pi}{18}+\tan^{-1}\frac{(\nu-\nu_F)}{\Gamma/2}\right\}. \qquad (I)$$

Summary of Theoretical Predictions

An expression may be obtained for the absorption coefficient of metallic potassium in the region of the K edge if the conduction electrons are assumed to move in a region of constant potential within the lattice. Under these circumstances the density of states to which an electron may be ejected is proportional to the square root of its kinetic energy, and the probability of a given transition is inversely proportional to the square root of this kinetic energy. Upon including the effect of the radiation width of the K state, an analytic expression was derived for the absorption coefficient due to transitions from the K state to the conduction band. An additive term was inserted to include the effect of other absorption processes.

The approximation of constant potential within the lattice, under which the analytic expression was derived, should be poorest for energies corresponding to electron momenta which give rise to Bragg reflection of the electron within the lattice.

EXPERIMENTAL MEASUREMENTS

The apparatus used in the measurements consisted of an x-ray tube and power supply, a two-crystal vacuum x-ray spectrometer, an ionization chamber and d.c. amplifier, and a number of thin potassium foils.

The power supply was of the standard full-wave rectifier type with filtered output. The voltage output of the power supply was stabilized by an electronic device reported elsewhere.[10] This device not only reduced voltage fluctuations caused by "ripple" but also those due to change in the primary voltage and to variations in characteristics of circuit elements. The voltage across the x-ray tube was found to be constant to within 0.1 percent over the eighteen hour period of the average "run." The tube was operated at 10 kv and 100 ma. Over the same period of time the maximum variation in the tube current was one milliampere.

The x-ray tube has been described elsewhere.[11] The focal spot was rectangular, 3 mm×6 mm. The target was made of an alloy of 12 percent antimony and 88 percent lead. The alloy was "tinned," or coated, on the copper face of the target carrier. The lead gave rise to a high background of continuous radiation, needed for measurements distant from the edge, and the strong antimony $L\alpha_1$ line at 3432 x.u. gave high intensity in the immediate region of the potassium K edge (3429 x.u.).

The absorbers were prepared by the evaporation method. The backing material was Kodapak, 2×10^{-3} cm thick. A protective layer of aluminum, 2×10^{-6} cm thick, was condensed on the Kodapak. Next, a layer of metallic potassium, 8×10^{-4} cm thick, was condensed on the aluminum. Lastly, a protective coating of ceresine was condensed over the metallic potassium surface. The techniques used have been described in some detail elsewhere.[12]

[10] J. W. Trischka and L. G. Parratt, Rev. Sci. Inst. **13**, 17 (1942).
[11] L. G. Parratt, Phys. Rev. **54**, 99 (1938).
[12] J. B. Platt and D. H. Tomboulian, Rev. Sci. Inst. **12**, 612 (1941).

Data were taken with three of the absorbers. Uniformity of thickness of the absorbers was checked by measuring percent transmission at a fixed wave-length for each of several areas of a typical absorber. The wave-length used was on the high energy (and hence the high absorption) side of the potassium *K* edge. No variation as large as 1 percent of the incident intensity was found. A sample of the potassium metal used, analyzed spectroscopically,* contained an impurity of 0.2 percent of sodium. No detectable trace of other impurities was found. Since the evaporation process was completed in fifteen minutes in a vacuum system maintaining a pressure of 10^{-5} mm Hg, no appreciable oxygen contamination was possible.

The spectrometer was of the two-crystal type, with calcite crystals. A vacuum instrument was used to eliminate air absorption of the x-ray beam. Details of the construction have been given elsewhere.[13] A study was made of the physical resolving power of the crystals. It was found that at 710 x.u. the width of the $(1, -1)$ rocking curve was 5.2 seconds of arc, and the $(1, -1)$ percent reflection was 61 percent. At 3598 x.u. the $(1, -1)$ width was 26 seconds of arc, and the $(1, -1)$ percent reflection was 60 percent. In the spectral region in which the potassium *K* edge occurs, the spectrometer had a computed physical resolving power of 11,700. This is the limiting factor in the resolving power of the instrument, since the geometrical resolving power is approximately 60,000.

Changes in the angular position of each of the crystals could be read to the nearest fifth of a second of arc, which corresponds at the wave-length of the potassium *K* edge to 0.005 x.u.

The determination of intensity was made with an ionization chamber. This was filled with argon at a pressure of 26 cm Hg. Dimensions were so chosen in the design of the chamber that wall effects were negligible and electric fields were intense in the region of maximum ionization, thus insuring satisfactorily linear response of the ionization chamber.

The d.c. amplifier was of the modified Barth[14] type, using a Western Electric D96475 tube. The maximum voltage sensitivity of the amplifying circuit was 142,000 mm/volt, with a scale at a distance of two meters and a galvanometer of sensitivity 2.6×10^{-9} ampere/mm at one meter. With the 3×10^{11} ohm grid resistor with which most of the data were taken, the over-all current sensitivity for the amplifier was 2.3×10^{-17} ampere/mm. Random fluctuations of the galvanometer spot were of the order of one centimeter, and the mean position of the spot could be read to an estimated accuracy of three millimeters.

The ionization current produced by the direct beam of continuous radiation alone (without the contribution from the Sb $L\alpha$ lines) was 9.2×10^{-15} ampere, and could be measured with an error of one percent.

The term "random fluctuations" is not intended to include the slow continuous shift of position of the galvanometer spot which occurred with no signal on the grid. This will be called "zero drift" and was the source of the largest single error in the measurement of ionization current. In the best set of data obtained the zero drifted at the rate of two cm/hour, and a drift of the order of eight cm/hour was more usual.

Method of Making Measurements

Measurements were made in the following manner:

1. The spectrometer was so adjusted that the crystals reflected the particular wave-length desired.
2. A lead stop was inserted in the x-ray beam, and the "zero" position of the galvanometer spot was recorded.
3. The lead stop was removed, permitting the direct beam to enter the ionization chamber, and the galvanometer deflection was noted.
4. The potassium absorber was inserted in the beam, and the position of the galvanometer spot was noted.

For subsequent zero drift correction, the time was noted at which each reading was made. In the spectral region in which the chief contribution to the intensity of the beam was that of continuous radiation, several measurements were made on the absorber for each measurement of the direct beam, and a determination of the zero position of the galvanometer spot was made every twenty minutes.

* The writer is indebted to Professor A. W. Laubengayer of Cornell University for the spectroscopic analysis of the potassium metal.

[13] L. G. Parratt, Phys. Rev. **54**, 99 (1938).

[14] D. B. Pennick, Rev. Sci. Inst. **6**, 115 (1935).

All intensity measurements were corrected for zero drift. The measured intensity of the direct beam was then plotted as a function of wave-length. The curve thus obtained was the contour of the Sb $L\alpha_1$ line and the neighboring spectral region on the short wave-length side. From this curve was determined the intensity incident on the absorber at each wave-length setting.

At the completion of a "run," a plot was made of the negative of the logarithm of the fractional transmission of the absorber, as a function of wave-length. Six runs extending 40 x.u. from the edge, and one run over only the 10 x.u. region including the edge, are included in the data presented here.

Since the thickness of the potassium layer and of the ceresine coating could not be assumed to be the same from one absorber to another, corrections were necessary to eliminate the effect of materials other than potassium in the absorber, and to adjust the results to correspond to the same thickness of potassium in each case. The negative of the natural logarithm of the fractional transmission of the absorber may be written

$$\log_e Q=\mu_1x_1+\mu_2x_2+\mu_3x_3+\mu_4x_4,$$

where the μ's are the linear absorption coefficients, the x's the corresponding thickness in centimeters, and the subscript 1 refers to the Kodapak, 2 to the aluminum, 3 to the potassium, and 4 to the ceresine. Within the spectral region investigated, only one element other than potassium has an absorption edge. That element is palladium, which has its L_1 edge at 3421 x.u. The probability of the existence of a detectable trace of palladium in the absorber is very small, and there is only a 10 percent change in transmission at this edge in any case, so one would expect no structure to be introduced into the plot by rapid variation in μ_1, μ_2, or μ_4. Furthermore, the fractional change in wave-length over the spectral region investigated was 1 percent, so the variation in each of these μ's, assuming the validity of the λ^3 law,[15] is only three percent over this spectral region. If one writes

$$\log_e Q=\mu_3x_3+C,$$

where C is a constant, the error can be at most three percent of the value of C.

The value of C, or in other words the baseline, was determined for each absorber by adjusting the baseline to give a "jump ratio" of 10 for potassium. The jump ratio is defined as the ratio of the absorption coefficient on the high absorption side of the edge to that on the low absorption side. No data are given in the literature on the jump ratio for potassium, but interpolation between values for elements of near atomic numbers indicates the value 10. For adjusting baselines, the jump ratio was made 10 for quantum energies five electron volts greater and five electron volts less than that of the midpoint of the edge. As a check, "dummy" absorbers, containing no potassium but prepared otherwise in the same way as the actual absorbers, were used for experimental determination of C. The values of C so determined could not, of course, be taken as those for the actual absorbers, but none of the indirectly determined values of C differed by more than six percent from that for the average of the "dummies."

Having determined μ_3x_3 as a function of wave-length for each of the three absorbers, it remained only to adjust these absorption curves for the same thickness of potassium. This was done by multiplying x_3 for two of the absorbers by constants so chosen as to make the curves coincide at a wave-length corresponding to a quantum energy five electron volts greater than that of the edge.

The x-ray spectrometer used in this research is incapable of absolute wave-length measurements but capable of measuring small wave-length intervals with a high degree of precision. For gross adjustment, the calcite crystals could be moved relative to the scales, but once clamped to the scale mechanism further motion of either crystal could be determined to one-fifth of a second of arc. Comparison of data taken in two "runs" between which the position of a crystal was shifted relative to its scale was possible only if some reference point is determined within each "run." The reference point chosen for comparison of data was the midpoint of the absorption edge.

[15] A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment* (D. Van Nostrand Company, Inc., New York, 1936), p. 533.

Errors and Corrections

The largest source of uncertainty in relative wave-length measurements was the determination of reference wave-length positions for successive "runs." This potential error, a possible linear shift of one curve relative to another, is a maximum of two seconds of arc, or 0.05 x.u. Absolute determination of wave-lengths was made by reference to the known wave-length of the peak of the Sb $L\alpha_1$ line. This wave-length is given by Hjalmar[16] as 3431.8 ± 0.1 x.u. It was located to within 0.05 x.u. on each of two "runs," and therefore the wave-length scale on any one "run" is known to within 0.1 x.u. with reference to the Sb $L\alpha_1$ line and to within 0.2 x.u. absolutely. It may be argued that the position of the peak of the Sb $L\alpha_1$ line is in question because the target material was an alloy rather than pure antimony. Detectable shifts of the peaks of lines have been observed due to the presence of other elements in the target.[17] The Sb $L\alpha_1$ line, however, results from an electron transition from the M shell of the atom to the L shell. Since both of these shells lie deep within the antimony atom, the effects of neighboring atoms cannot be expected to shift the energy value of either level, and hence of the emitted quantum, appreciably.

The main source of error in intensity measurements was zero drift. In the best data obtained, the combined effect of zero drift and random fluctuations gave rise to an error in intensity measurements of one percent of the direct beam. For these data, the estimated probable errors caused by zero drift and random fluctuations were each three millimeters. In general, the estimated probable error caused by zero drift was five millimeters. The final results are weighted averages of the data taken on various "runs." Correction was made for the effect of second-order radiation, third and higher orders being ruled out because the tube was operated below the corresponding excitation potentials. The incident beam contained three percent of second-order radiation in the continuum, as determined from absorption measurements on three thicknesses of aluminum foils. A correction was made for second-order radiation in the absorption measurements on potassium. This correction was negligible in the region of the absorption edge because of the high intensity of characteristic radiation.

No correction was attempted for the finite resolving power of the spectrometer. Any such correction for absorption measurements, lacking quantitative knowledge of the diffraction patterns of the two crystals, would be hazardous. Since the measured width of the absorption edge is large compared to the width of the $(1, -1)$ rocking curve at the same wave-length, there is reason to believe that the correction for finite resolving power would be negligible in any case.

The results are presented in Figs. 3 and 4. Figure 3 shows the absorption structure over the entire spectral region investigated, while Fig. 4 includes only the immediate region of the edge. Data were taken every 0.2 x.u. over most of the spectral region investigated, and every 0.07 x.u. over the immediate region of the edge. Probable errors are indicated by vertical lines. The dotted curve is the theoretically predicted absorption structure.

The theoretical curve based on the free electron approximation is in fairly satisfactory agreement with the experimental results. Deviations are less than ± 10 percent and are slightly greater than the experimental uncertainty. The fit is achieved with the aid of two arbitrary constants representing the wave-length of the edge and the thickness of the absorber. The constant determining the width of the edge, i.e., the energy separation between points whose absorption coefficients lie at one-quarter and three-quarters of the height of the absorption edge, is not arbitrary. This is the constant Γ in Eq. (I). It is determined by the mean lifetime of the state of K excitation, and cannot be evaluated theoretically with precision. However, if this constant is known for some neighboring element in the periodic table for which the possible transitions are similar, it can be calculated for potassium. The calculation, based on the Weisskopf-Wigner theory of line widths and the Dirac radiation theory, assumes that Γ is proportional to the square of the energy of the atom due to K excitation. From measurements on argon line

[16] Reference 15, page 528.

[17] A. E. Lindh, *Handbuch der Experimentalphysik* (Akademische Verlagsgesellschaft, M. B. H., Leipzig, 1930), Vol. 24/II, pp. 314–325.

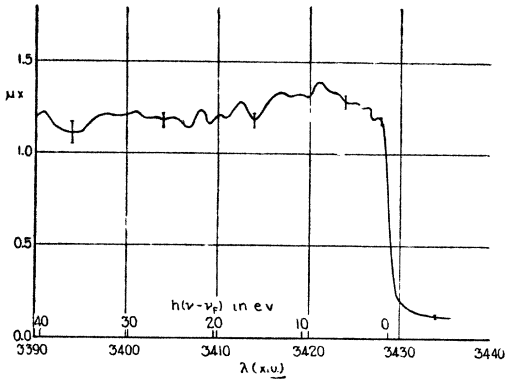

FIG. 3. Absorption coefficient for metallic potassium, in arbitrary units, as a function of the energy of the absorbed quantum. Entire spectral region investigated.

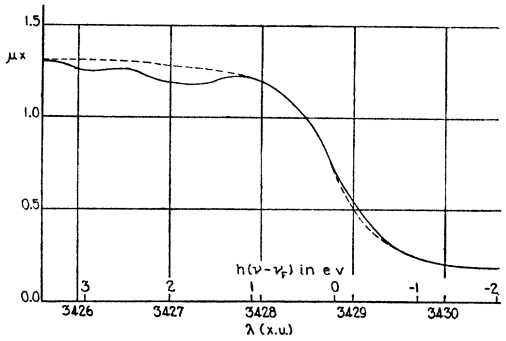

FIG. 4. Absorption coefficient for metallic potassium, in arbitrary units, as a function of the energy of the absorbed quantum. Immediate region of the absorption edge.

widths[18] $\hbar\Gamma$ is known to have the value 0.58 ev for argon. Hence, for potassium, $\hbar\Gamma$ is 0.73 ev. The value found from experimental measurement on the width of the potassium K edge is 0.75 ev.

The experimentally determined values of the absorption coefficient are lower than those predicted on the free electron approximation in just the region (one to three electron volts) corresponding to the first Brillouin zone. The deviation may or may not be meaningful, but should be pointed out.

The wave-length of the midpoint of the absorption edge, where the midpoint is defined to have an absorption coefficient equal to the average of the mean absorption coefficients on the two sides of the edge, has been found to be 3428.8 $\pm$0.2 x.u. This does not agree with the value of 3431.0$\pm$1.0 x.u. given by Lindh.[19]

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[18] L. G. Parratt, Phys. Rev. **56**, 295 (1939).

[19] A. E. Lindh, Ark. Mat., Astr. o. Fys. **18**, 14 (1924).