edges, and the *a* and *b* axes along the perpendicular cubic face-diagonal directions. The magnetic anisotropy energy gives convincing evidence for orthorhombic symmetry. The anisotropy of the conductivity agrees well with that to be expected from Verwey's ordered structure. The increase in conductivity anisotropy with decreasing temperature (Table III) appears to be directly related to the increase in long-range order.

In addition to accounting for the anisotropic properties below the transition, Verwey's model explains the influence of a magnetic field applied during cooling on the properties of the crystal below the transition. The axis-switching effect, not previously predicted, can be readily explained. Twinning at the transition greatly complicates the magnetic behavior at lower temperatures because the different regions of a twinned crystal interact in a complex way. These interactions are quite large in special cases and probably account for the failure of the static anisotropy constants to predict quantitatively the microwave resonance frequencies.

ACKNOWLEDGMENTS

The author is greatly indebted to Professor A. von Hippel for his guidance and encouragement during the course of this research; to B. Frackiewicz for his assistance with the B-H loop tracer measurements; to many members of this laboratory, in particular, D. J. Epstein, D. O. Smith, and L. B. Smith, for the many discussions and helpful suggestions made during the course of this work. The author wishes also to thank R. P. Teele of the National Bureau of Standards for the loan of a "thermo-free" reversing key, and L. R. Bickford, Jr., and R. M. Bozorth for the privilege of seeing their results prior to publication.

PHYSICAL REVIEW VOLUME 94, NUMBER 6 JUNE 15, 1954

Absorption Spectrum of Beryllium in the Neighborhood of the *K* Edge*

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(Received March 3, 1954)

The absorption spectrum of metallic Be has been investigated in the soft x-ray region extending from 60A to 250A. The *K* discontinuity appears at 111A and coincides with the *K* edge observed in the emission spectrum. Over the spectral range studied, the values of the linear absorption coefficient range from 0.25×10^6 to 2.8×10^5 cm^{-1}. Characteristic secondary structure is also noticeable on the short wavelength side of the edge. The positions of secondary absorption maxima are compared with those previously found in the *K* absorption spectrum of Al and with theoretical calculations based on the Hayasi model. The absorption spectrum has also been studied by irradiating Be absorbers with the continuous far ultraviolet radiation emitted by relativistic electrons accelerated in the Cornell synchrotron. Partial reduction of the data indicates good agreement with determinations based on the use of line spectra as the incident radiation.

INTRODUCTION

THE electronic structure of Be ($1s^22s^2$) indicates that the initial state in an absorption transition must either be a *K* level or a level belonging to the filled portion of the conduction band. A study of the *K* emission band of Be shows that the photon energy required for the ejection of a *K* electron should be nearly 112 ev. In the absence of previous information on the absorption spectrum of this metal, an investigation was undertaken to measure the absorption in the spectral region extending from 60A to 250A. The energy of photons in this wavelength region ranges from 50 to 200 ev. Thus, a sample of Be irradiated by photons possessing the above energy spread, should reveal the behavior of the spectrum in the region of the *K* discontinuity. The present paper offers an extension of the preliminary measurements reported on previously.[1]

EXPERIMENTAL

A large portion of the experimental work was carried out by following the general method described in an earlier paper.[2] The dispersing instrument was a grazing incidence spectrograph, equipped with a lightly ruled glass grating having 30 000 lines per inch and a radius of 1.5 m. The grazing angle of incidence was set at 4.5°. The instrument was adjusted carefully in order to insure satisfactory definition in the short wavelength region approaching the cut-off wavelength whose calculated value was 30A. Lines of reasonable intensity were observed down to about 60A.

Absorbers were prepared either by depositing Be directly on a thin substrate of Zapon or by evaporating the metal on a glass surface treated with "Victawet."

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* Supported in part by the Office of Ordnance Research, U. S. Army.

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[1] D. H. Tomboulian and R. W. Johnston, Phys. Rev. 83, 220 (1951).

[2] D. H. Tomboulian and E. M. Pell, Phys. Rev. 83, 1196 (1951).

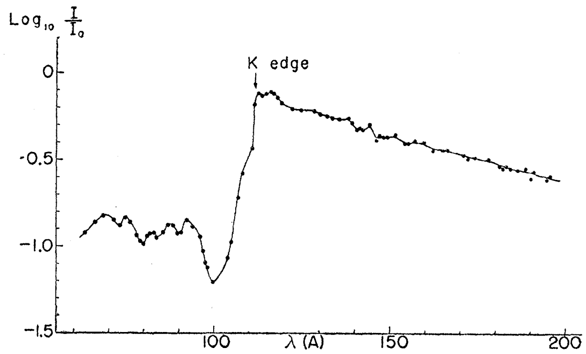

FIG. 1. A typical absorption curve of a metallic Be absorber 1000A in thickness.

The film so condensed was subsequently floated off and mounted on suitable holders. The second procedure resulted in unusually good samples with a bright metallic sheen remarkably free from pin-holes. In all evaporation processes, great care was exercised to prevent contamination.

Thicknesses of the foils were arrived at by taking into account the mass of the metal evaporated and the geometry of the arrangement. The foil density was assumed to be that of the bulk material. It is known that this procedure results in thickness determinations which agree within 5 percent with those obtained by direct weighing on a microbalance when the foil thickness exceeds 3000A. Since the errors in the photometric reductions are of this order, more refined measurements of thickness were not attempted.

The spectrograms consisted of three juxtaposed spectra. One was taken without an absorber while the remaining two represented the spectra transmitted by the absorber under varying times of exposure. This procedure enables one to calibrate each individual plate and to obtain two determinations of the absorption curve. Admittedly a more desirable procedure would have consisted in obtaining contiguous spectra of two absorbers which are prepared under identical conditions but differ in the thickness of the deposited layer. Measurements based on such absorbers would be free from effects due to interface penetration or surface contamination. Since the differential thickness of absorbing material is not readily available, this scheme is not suitable for testing the consistency of a series of measurements or for evaluating the absorption coefficient. However, it affords a means for detecting in an absorption curve those features which are due to surface effects.

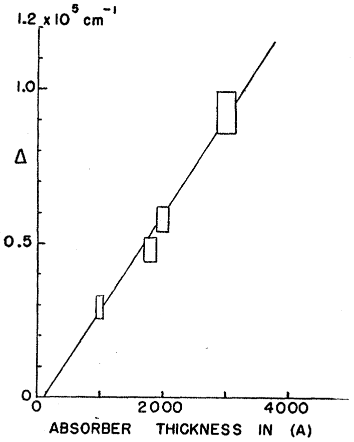

FIG. 2. A graph which shows Δ, the change in $\log_{10}(I_0/I)$, as a function of absorber thickness. The change was evaluated between two wavelengths located respectively on the short and long wavelength side of the edge.

The continuum emitted from targets is very feeble in the soft x-ray region, and until recently one was limited to the use of line spectra as a source of incident radiation. However, within the past year, the continuous electromagnetic radiation emitted by relativistic electrons accelerated in the Cornell synchrotron has been investigated[3] and found to be sufficiently intense to serve as a suitable source. Though the major portion of the data reported in this paper is based on the radiation emitted by condensed spark discharges, an absorption spectrum of Be has also been obtained using the synchrotron radiation as a source. The possibility of utilizing this remarkable source as a tool in absorption spectroscopy shows promise. The details of the method will be published at a later date. Microphotometer traces showing the incident intensity distribution as well as the absorption by Be are included. Complete reduction of the traces is not possible at the present time for reasons to be offered later.

RESULTS

The Absorption Curve

Figure 1 shows the $\log_{10}(I/I_0)$ curve for a sample whose thickness was 1000A. (Here, I_0 is the incident intensity and I that transmitted by the absorber.) An application of the relation $I=I_0e^{-\mu x}$, indicates that the greatest difference in transmitted intensity on either side of an absorption edge occurs when the absorber thickness x has the optimum value given by

$$x_{\text{opt}}=(\ln\mu_1-\ln\mu_2)/(\mu_1-\mu_2),$$

where μ_1 and μ_2 represent the linear absorption coefficients on the short and long wavelength side of the edge. For Be, $x_{\text{opt}}=1100\text{A}$, hence a considerable part of the measurements were carried out with samples having this thickness. The values of $\log_{10}(I/I_0)$ represent weighted averages of the results of several spectrograms taken with different samples and exposure ratios. The K edge appears at 111A. As in the case of other light metallic elements, such as Li, Mg, Al, a secondary structure is also observable. The intense absorption dip at 100A appeared on all spectrograms including

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[3] P. L. Hartman and D. H. Tomboulian, Phys. Rev. **91**, 1577 (1953).

those obtained with absorbers free from Zapon. Except for the small likelihood of an interface effect at the metal "Victawet" boundary, this feature of the absorption curve may be regarded as characteristic of the metal. As a check on the consistency of the measurements, the magnitude of the change in $\log_{10}(I_0/I)$ at the K edge was plotted as a function of absorber thickness. The change was measured between the wavelength $\lambda = 110$A and $\lambda = 118$A, located respectively on the high- and low-energy side of the edge. The plot is shown in Fig. 2, where the sides of the rectangles indicate the estimated errors in thickness x and in $\log_{10}(I_0/I)$. If the four different samples were free from a layer of BeO, then the linear plot should go through the origin and possess a slope proportional to the change in the absorption coefficient between the wavelengths mentioned above. On the other hand if a surface layer of thickness x_0 is oxidized, and if this thickness is the same for all absorbers, the straight line should yield an x-intercept equal to x_0. Due to appreciable errors as indicated it is not possible to estimate x_0 with certainty. However, inspection reveals that the oxide thickness cannot be in excess of a few hundred angstroms.

The linear absorption coefficient μ was determined for a number of wavelengths on the basis of the absorption data given in Fig. 1. A plot of these results appears on the graph of Fig. 3. The values of μ range from 2.8 $\times 10^{+5}$ to 0.25×10^5 cm^{-1}.

The K-emission band of Be has been studied by Skinner and O'Bryan.[4] The intensity distribution in this band shows a sharp emission edge at 110.9A, corresponding to a photon energy of 112 ev, the latter being emitted when an electron makes a transition from the Fermi level to a vacant K state. The present measurements yield the value of 111A for the position of the K absorption edge, that is, the emission and absorption edges coincide. This result is in agreement with expectation, since in a metal like Be, there should be no forbidden zone of energies between the filled and unfilled portions of the valence band. On the theoretical side, Herring and Hill[5] have applied the method of orthogonalized plane waves to beryllium and have calculated the level density curve for energies up to and somewhat in excess of the Fermi energy.

The experimental emission curve, and the theoretical level density curve are reproduced in Fig. 4, which also shows the new measurements of $\log_{10}(I_0/I)$ here plotted as a function of the energy of incident photons. The agreement between the shape of the observed emission curve and that of the level density curve is good. Also, the theoretical curve, suggests a rapid rise in the density of unoccupied states. This feature of the theoretical curve may have its counterpart in the intense absorption that is observed to the high-energy side of the edge.

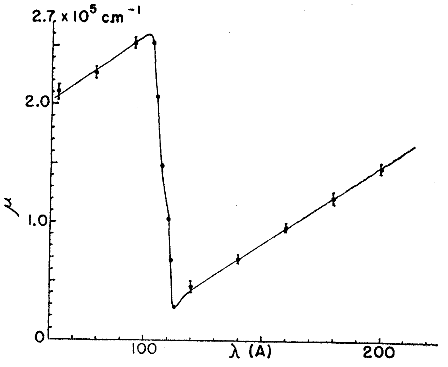

FIG. 3. A plot of linear absorption coefficients as determined from the curve shown in Fig. 1.

Secondary Structure

In common with other studies of this type, a series of secondary absorption maxima are observed on the high energy side of the K edge. The observed energy differences between the edge and the various peaks are given in the second column of Table I. The Be lattice is of the hexagonal close-packed variety. Coster[6] has pointed out that a correlation should exist in the secondary structure exhibited by elements having this symmetry and those which possess a face-centered cubic lattice. It is therefore of interest to compare the fine structure found in the case of Be with the corresponding structure associated with the K edge of an element such as Al which has a face-centered cubic lattice. The fourth column lists the energy differences between the K edge and secondary maxima as found in the K absorption spectrum of Al.[7]

For the ideal close-packed hexagonal lattice the axial ratio (c/a) should be 1.63. In Be, $c/a = 3.59/2.28$

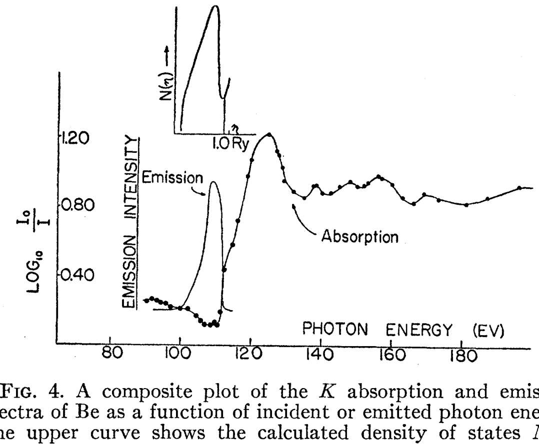

FIG. 4. A composite plot of the K absorption and emission spectra of Be as a function of incident or emitted photon energy. The upper curve shows the calculated density of states $N(\eta)$ as a function of the energy parameter η expressed in Rydbergs.

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[4] H. W. B. Skinner and H. M. O'Bryan, Trans. Roy. Soc. (London) **239**, 95 (1940).

[5] C. Herring and A. G. Hill, Phys. Rev. **58**, 132 (1940).

[6] D. Coster, Physica **2**, 606 (1935).

[7] Munier, Bearden, and Shaw, Phys. Rev. **58**, 537 (1940).

$=1.58$, indicating a departure from the ideal lattice. Upon reducing Be to the ideal close-packed hexagonal lattice, the axial constants are found to be $a_1=2.24$A, $c_1=3.65$A. (These are obtained from the relations $c_1/a_1=1.63$ and $2a_1^2+c_1=2a^2+c^2=23.3$.) The present observations of the secondary structure of Be may be compared with those of Al by multiplying the values given in the second column by $(2.24/2.86)^2$, where 2.86 is the distance (in angstroms) to the nearest neighbors in the Al lattice. The results are shown in the third column.

To account for the observed structure on the high-energy side of an edge, Hayasi[8] has suggested that the structure may be considered as a series of absorption maxima superimposed on the absorption curve as a background. According to this view, the secondary maxima represent transitions in which the final state of an electron ejected photoelectrically from a sharp inner level is a so-called quasi-stationary state. Hayasi points out that such energy states are produced when the waves associated with the ejected electron form a standing wave pattern in the immediate vicinity of the atom from which the electron was emitted.

In the case of an electron ejected from a K shell, the specification of the final state ($l=1$) requires that the wave function shall have a twofold axis of symmetry. This consideration imposes a condition on the propagation sphere in the reciprocal lattice. Such a sphere must pass through two points so located that the sum of the propagation vectors is zero. Thus, the requirement in the case of K absorption is that the ejected electron shall move at right angles to a set of parallel crystal planes and undergo 90° Bragg reflection.

The comparison with experiment is facilitated, since on the basis of this model it becomes possible to select a relatively small set of absorption maxima which are expected to be most intense. The selection is carried out by estimating the relative amplitude of waves backscattered from nearby atoms. The relative intensity is found to depend on (1) the number of equivalent neighboring atoms (2) the magnitude of the distance of such atoms from the one which has lost a photoelectron and (3) the coherence of the scattered waves.

TABLE I. A comparison of the secondary structure in the K absorption curve of Be with the corresponding structure observed in Al. For Al, the predictions based on the Hayasi model are given in column 1. These represent positions of peaks as measured from the average inner potential. For Be and Al the experimentally determined positions of maxima as measured from the K edge are shown in columns 2 and 4, respectively. All quantities are expressed in ev.

V calc	Be observed	Be reduced	Al observed	V corrected
9.2	13.4	8.3	8.0	6.2
18.4	25.9	15.9	15.0	15.4
···	35.8	22.0	···	···
27.6	43.1	26.4	24.5	24.6
36.8	56.9	35.0	34.0	33.8
46.0	···	···	42.0	43.0
55.2	85.0	52.1	52.0	52.2
Av. diff.		8.8	9.0	9.2

The energy, in ev, of electrons reflected normally from crystal planes in a cubic lattice is given by $V=150(\alpha^2+\beta^2+\gamma^2)/4a^2$, where α, β, γ are the reflection indices of cooperating planes, and a is the lattice constant in A. The relation follows directly from the particular Bragg condition $n\lambda=2d$ which must be satisfied in the case of the K absorption spectrum.

The first column in Table I gives the magnitudes of V calculated for the Al lattice corresponding to absorption peaks of high intensity. (The values of the reflection indices are subject to the appropriate condition for the nonvanishing of the atomic structure factor. For a face-centered cubic lattice α, β, γ must be all even or all odd.) The calculated values of V are measured from the average inner potential V_0. The tabulated position of observed peaks represent energy differences from the K edge and correspond to $(V+V_0)-V_K$ where V_K is the energy of the final state corresponding to the K absorption edge. Since V_0 and V_K are not equal the calculated values should be corrected by (V_K-V_0) before comparison with the observed values listed in the fourth column. The value of the inner potential for Al is not known reliably. In any case the correction should be a constant not exceeding a few ev. The last column in the table gives the calculated values corrected by (V_K-V_0). The constant difference of 3 ev was estimated from the observed and calculated values for Al.

Due to the thermal vibrations of the lattice and the natural width of the stationary states[9] a secondary absorption band possesses considerable width. Accordingly, it is not possible to determine the positions of individual absorption peaks very accurately from the experimental observations. The average energy difference between successive peaks as obtained from a sequence should be a more reliable basis for comparison between theory and experiment. This difference should be constant and is found to be equal to 9.2 ev from the values of V calculated for the Al lattice. The corresponding differences obtained from the observations on Be and Al are also given at the bottom of Table I. As in the case of the K spectrum of Mg (see reference 7), the presence of additional peaks is not surprising on account of the more complex hexagonal structure of these elements. One such peak is detected in Be over the present range of measurements. The missing peak in Be falls in the very short wavelength region where the available data are inadequate.

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[8] T. Hayasi, Sci. Repts. Tôhoku Univ. **33**, 123 (1949).

[9] See T. Hayasi, Science Repts. Tôhoku Univ. **34**, 185 (1951) for a determination of these widths in connection with the fine structure of the K absorption edge in Li.

The Use of Synchrotron Radiation

The top curve in Fig. 5 is a reproduction of the microphotometer trace of the absorption spectrum of a 1000A Be foil in the vicinity of the *K* edge. The spectrogram was taken in connection with a study of the properties of the radiation emitted by electrons of maximum energy equal to 321 Mev. Due to the continuous nature of the incident radiation, the reduction of the trace involves a consideration of the energy distribution among the various orders produced by the grating.

In the spectral distribution of the radiation emitted by the source, let $P_0(\lambda)$, $P_0(\lambda/2)$, $P_0(\lambda/3)$, etc. represent the intensity per unit wavelength band centered at λ, $\lambda/2$, $\lambda/3$, etc. Radiation of each of these wavelengths will be brought to a focus on the Rowland circle at the same position x measured from the central image. The contribution to the photographic density at x will be determined by the manner in which the component incident intensities are modified by the absorber and by the grating response. The latter is defined as the fraction of the intensity incident on the grating diffracted into a given order. If $P(x)$ is the intensity per unit distance interval centered at x, we may write

$$P(x)dx/d\lambda = P_0(\lambda)e^{-\mu(\lambda)t}R(\lambda) + \tfrac{1}{2}P_0(\lambda/2)e^{-\mu(\lambda/2)t}R(\lambda/2)+\cdots,$$

where only two spectral orders have been taken into account. In this expression t is the absorber thickness, and μ, the linear absorption coefficient. The grating response is introduced through the factors $R(\lambda)$, and $R(\lambda/2)$, while $dx/d\lambda$ is the reciprocal instrumental dispersion. The factor $\frac{1}{2}$ which appears in the second term on the right is due to the change in dispersion with order.

It is possible to determine $P(x)$, $P_0(\lambda)$, $P_0(\lambda/2)$, and $dx/d\lambda$ experimentally. For a complete reduction of the trace the grating efficiency factors $R(\lambda)$ and $R(\lambda/2)$ must also be known. Our present knowledge[10] of the grating efficiency is very meager. However, in the immediate region of the edge, the absorption by the sample affects primarily the transmitted intensities associated with the first-order radiation and photometer deflections may be converted into relative intensities. In so doing, one neglects the variation of $R(\lambda)$ with wavelength and regards the second- and higher-order intensity components to be free from large changes over the narrow spectral range centered at the *K* discontinuity.

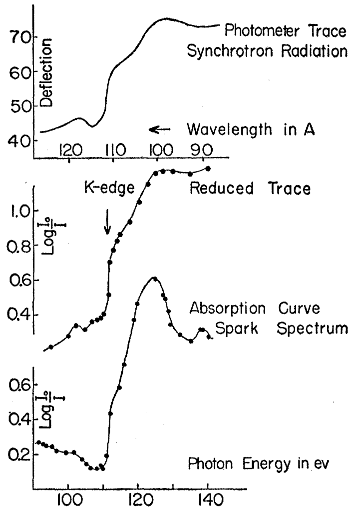

FIG. 5. The absorption curve of Be in the neighborhood of the *K* edge based on measurements using the far ultraviolet continuous radiation from the Cornell synchrotron.

The result of a partial reduction of this sort is shown in the middle curve of Fig. 5. The corresponding portion of the absorption curve as determined by the use of spark spectra is also reproduced in the lowest graph in Fig. 5. A comparison indicates that the shapes of the two curves in the region of the edge are in good agreement. In the case of the middle curve, the less rapid drop in the low-energy side of the edge is most likely due to second order spectra of short wavelength radiations (55 to 70A) which are present in the incident beam and contribute to the observed intensity above the edge. Third-order contributions are not expected since the intensity of the incident radiation below 55A is negligible.

Additional measurements using Al indicate that the absorption curves determined by the use of the synchrotron radiation compare favorably with those obtained by the use of spark spectra. It is gratifying that two radically different types of incident radiation yield similar results. This enhances our confidence in procedures previously used in soft x-ray spectroscopy of the solid state.

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[10] Experiments utilizing various monochromatic radiations in the soft x-ray region and aimed at the determination of the grating response are now in progress.