

K Absorption Edge of Selenium

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Use of thin unsupported selenium absorbers has permitted observation of significant structure in the K absorption spectrum. Observations of the $K\beta_2$ emission and the fundamental optical absorption of similar samples have been made and used to assist in the interpretation of the K edge structure. It is suggested that the prominent absorption maximum at the experimentally determined "edge" arises from transitions to an x-ray excitation state or states in the region of the forbidden energy gap. The following general absorption is attributed to transitions to the conduction band. The gap energy required in this interpretation is approximately 4 electron volts, indicating that the lower part of the conduction band contains little p -type symmetry.

1. EARLIER WORK

THE K absorption spectrum of selenium has been obtained by several investigators. Kievit and Lindsay,¹ Idei,² and Hanawalt³ used single-crystal spectrometers and photographic detection. Kievit and Lindsay observed no structure; Idei reported a broad (30 ev) maximum of absorption at the K edge of selenium in some of its compounds, and Hanawalt found evidence for a narrower (reportedly 4 ev) maximum of absorption at the K edge of solid selenium.

Hulubei and Cauchois⁴ observed an absorption maximum (12.8 ev) at the K edge of solid selenium, using a curved-crystal spectrometer with photographic detection. Zinn⁵ observed fine structure in the K edge of selenium and two of its compounds. He used a double-crystal spectrometer with ionization chamber detection. His transmission curves are in general agreement with the data of Hanawalt and Hulubei and Cauchois; but he points out that Idei probably did not resolve the first absorption maximum. His transmission curves show two barely resolved peaks of approximately the same height. Although there seems to be general agreement that there is an absorption maximum at the K edge, it does not seem to have been specified with sufficient detail to permit interpretation.

The inconclusiveness of these earlier measurements may be attributed principally to two causes. In the first place, notorious difficulties are associated with the use of photographic detection where the dynamic range of intensities is large.⁶ Secondly, the techniques used for the preparation of the absorbers used are such that the thicknesses obtained were probably too large. The discrepancies would then arise as a consequence of the washing out of structure associated with the "thickness effect,"⁷ which was unknown at the time of these early measurements.

The L_{II} and L_{III} edges of selenium were obtained by Sandström.⁸ In the reproductions of microphotometer traces of these edges which are shown there is little evidence of appreciable structure and certainly nothing to suggest the results of the present observations. This is somewhat more difficult to attribute to experimental technique since the method of preparation of the absorbing screens used by Sandström is quite similar to that used here. In addition, some of the thicknesses mentioned indicate that the requirement of thin absorbers dictated by the presence of the thickness effect could have been met. It will accordingly be necessary that the interpretation advanced here in connection with the K edge structure be at least in principle compatible with the absence of a similar structure in the L_{II} and L_{III} edges. The recent measurements of the L_I absorption edge by Rudström and Sjöberg⁹ are of special relevance to the present study. Their results will accordingly be discussed in detail later.

2. EXPERIMENTAL TECHNIQUE

(a) The Spectrometer

The measurements reported here were obtained with a two-crystal spectrometer of high resolving power. The crystals were arranged in a Ross mounting. In this the first crystal moves along the perpendicular bisector of the line joining the focal spot of the x-ray tube and the axis of rotation of the second crystal. Small wavelength changes are affected by rotation of the second crystal about its axis by means of a micrometer-driven lever system. With the present spectrometer, absolute wavelength measurements are not possible so that where these are required, they have been taken from other sources. Quartz crystals¹⁰ cut with their reflecting surfaces parallel to the planes $(10\bar{1}\bar{1})$ were used. With this pair of crystals rocking curve widths approximately 30% lower than those reported in the literature¹¹ have been obtained. With the vertical divergence limited to

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¹ B. Kievit and G. A. Lindsay, *Phys. Rev.* **36**, 648 (1930).

² S. Idei, *Sci. Repts. Tôhoku Univ.* **19**, 653 (1930).

³ J. D. Hanawalt, *Phys. Rev.* **37**, 715 (1931).

⁴ H. Hulubei and Y. Cauchois, *Compt. rend.* **211**, 316 (1940).

⁵ W. H. Zinn, *Phys. Rev.* **46**, 659 (1934).

⁶ D. H. Tomboulion, *Handbuch der Physik*, edited by S. Flugge (Springer-Verlag, Berlin, 1957), Vol. 30, pp. 269-270.

⁷ Parratt, Hempstead, and Jossem, *Phys. Rev.* **105**, 1228 (1957).

⁸ A. Sandström, dissertation, Uppsala, 1935 (unpublished).

⁹ L. Rudström and S. Sjöberg, *Arkiv Fysik* **13**, 297 (1958).

¹⁰ Obtained from the Valpey Crystal Company.

¹¹ Adell, Brogren, and Haeggbloom, *Arkiv Fysik* **7**, 197 (1953).

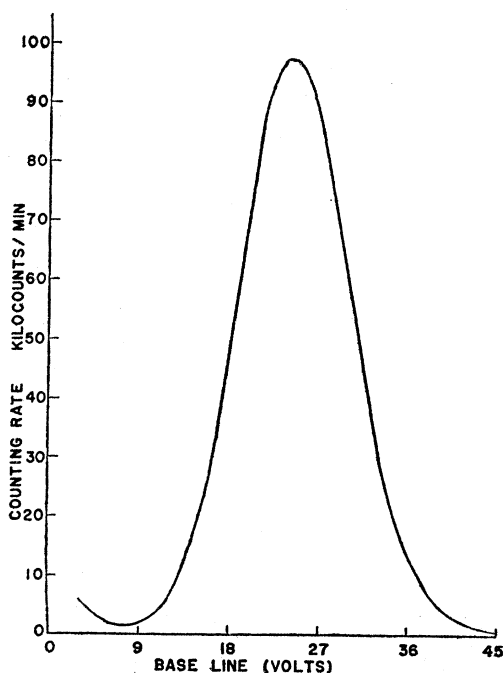


FIG. 1. Pulse-height distribution obtained from the NaI scintillation counter illuminated by an analyzed beam of 10-kev photons. 3-v channel.

0.02 radian, the nominal resolving power is approximately 13 000.

(b) Detection

Photons were detected in a NaI counter,¹² amplified in a conventional linear amplifier, and the signal peak isolated from the noise and higher order radiation by means of a differential analyzer which had been modified to give up to a 24-volt window. A typical pulse-height distribution obtained with 10-kev photons is shown in Fig. 1. With the window edges set well down in the tails of this distribution, counting efficiencies of over 90% are obtained while the background at this energy is generally 1 or 2 counts per minute; this should be compared with Geiger counter backgrounds which generally exceed this rate by a factor of 10 or more. The dead time of this system was about 6×10^{-6} second.

(c) Radiation Sources

For the absorptions measurements, continuous radiation was obtained from a commercial tungsten tube (Machlett AEG-50-A). For the emission measurements, a demountable, continuously pumped tube¹³ was used.

The continuously pumped tube has a four-sided anode structure onto which selenium was deposited by vacuum evaporation. The target thus formed deteriorated rapidly under electron bombardment. Some improvement was obtained by cooling the anode with

¹² Obtained from the North American Phillips Company.

¹³ J. A. Bearden and G. Schwarz, *Phys. Rev.* **79**, 674 (1950).

water refrigerated to 2°C. Even so, measurements taken more than 10 minutes after commencing bombardment at very low beam currents (2 ma) were no longer reproducible. Accordingly, emission data were taken only during this period.

Voltage and current supplied to these tubes were highly stabilized. The voltage stabilizer is a modified version of the inductively coupled degenerative circuit of Pepinsky and Jarmotz.¹⁴ Performance tests indicate drifts of the order of a few parts in 10^5 per hour or about what would be expected from drifts in the reference batteries. The current regulator is of the controlled-reactance type due to LeMieux and Beeman.¹⁵ After suitable aging of components, drifts are generally below a part in 10^3 .

(d) Data Accumulation

For the absorption measurements, runs were programmed for automatic execution by means of simple circuitry.¹⁶ With this circuitry and servo devices for changing absorbers and wavelengths, the only manual operation necessary was establishing the initial wavelength for a scan. Scans were interlaced during separate 12 hour runs so that adjacent points in the absorption spectrum were obtained from different runs.

(e) Absorber Preparation

Selenium films were deposited on fresh cleavage faces of rocksalt single crystals. The crystals were masked by a plate containing circular holes approximately $\frac{7}{8}$ inch in diameter. Selenium powder was placed in a tantalum boat and heated slowly to the melting point. Thereafter, it was attempted to raise the temperature rapidly and complete the deposit as quickly as possible. Unfortunately, in order to avoid a tendency for the selenium to be ejected violently from the boat, it was necessary to allow about 5 minutes for completion of the deposit. The rocksalt was then dissolved in water and the resulting selenium disk picked up from the water surface, weighed, and placed in an aluminum mounting ring. The free area of the resulting absorber was a disk approximately $\frac{3}{4}$ inch in diameter. Absorber thicknesses were generally about 5 mg/cm².

Foils prepared in this way are reported to consist largely of amorphous selenium.¹⁷ To verify this, measurements were made of the fundamental optical absorption edge in similarly produced samples using a Beckman DK-1 spectrophotometer.¹⁸ In order to eliminate

¹⁴ R. Pepinsky and P. Jarmotz, *Rev. Sci. Instr.* **19**, 247 (1948).

¹⁵ A. F. LeMieux and W. W. Beeman, *Rev. Sci. Instr.* **17**, 130 (1946).

¹⁶ R. D. Deslattes and D. L. Clemmons, Air Force Technical Report No. 3, Florida State University, 1958 (unpublished).

¹⁷ T. S. Moss, *Photoconductivity in the Elements* (Academic Press, Inc., New York, 1952), p. 189.

¹⁸ The authors are indebted to Mostafa Amr El Sayed for his assistance in these optical measurements.

the effects of reflectivity changes, two specimens of differing thickness were prepared in the same evaporation and one introduced into the reference path of the spectrophotometer. The resulting value of the absorption edge energy agreed with that given for amorphous selenium.¹⁹ In attempting to convert the absorber to metallic selenium, considerable difficulty was experienced with tearing resulting from the dimensional changes. Although a successful conversion to the metallic state would have been desirable, our conclusions may be applied qualitatively to this state on account of the similarity of the band structure in the two and the insensitivity of x-ray measurements carried out at these energies to small changes in this structure.

(f) Absorber Position

It has recently been pointed out that the position of an absorber with respect to a spectrometer having the high angular resolution of a two-crystal instrument influences the apparent value of the absorption coefficient as well as the extent to which a complex spectrum may be resolved.²⁰ It is suggested that the absorber be placed between the x-ray source and the spectrometer in order to minimize the effects of small-angle scattering, avoid alteration of the spectrometer's window function, and secure adequate rejection of fluorescent radiation. This absorber position has accordingly been employed in the present measurements.

3. EXPERIMENTAL RESULTS

Figure 2 shows the K absorption edge and the $K\beta_2$ emission band of selenium as obtained in the present study. The insert to this figure gives the spectral window at the edge energy. It was obtained from the $(1, -1)$ rocking curve which is shown by Parratt and Porteus²¹ to approximate the window function fairly well except in the distant tails. Measurements in the case of the absorption curve are at intervals of approximately 1 electron volt. On account of the difficulty of maintaining a stable target for the emission spectrum, it was only possible to make measurements at intervals of about 2 electron volts, and these with very poor statistics.

The absorption data indicate the possibility of faint structure both at the foot of the edge and beyond the second absorption maximum. Deviations from the smooth curve drawn are in both cases approximately three times the statistical uncertainties. Since such structure was not of particular interest to the present study, it has not been investigated further. The principal features of the absorption curve are evident. The asymmetry of the first peak is well beyond experimental error. Correction of this curve for the effects of instru-

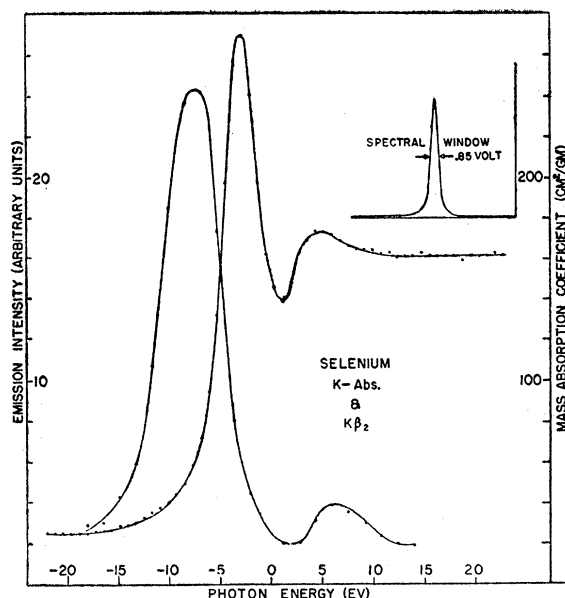


FIG. 2. The left-hand curve is the $K\beta_2$ emission band. It is followed by a prominent satellite. The absorption spectrum is referred to the right-hand ordinate scale. The energy scale refers to a zero taken at the inflection point of the arctangent curve discussed in the text.

mental resolving power would be expected to narrow the first peak by about 20%, increase its amplitude and deepen the following valley. A crude graphical decomposition of this curve is possible, leading one to regard it as the sum of a Lorentzian line (at 3.5 eV on the energy scale of Fig. 2) and an approximately arctangent-type edge whose inflection point occurs at 0 on the energy scale of Fig. 2. The second absorption peak deviates appreciably from this but may also be accounted for (see below).

The emission band shown is considerably broader than the absorption line discussed above. It is possible that the slight asymmetry indicated may be explained by self absorption in the target.²² In order to minimize this effect, the electron beam was brought to the target under a small grazing angle of incidence (about 10°) and the target viewed from close to the normal to its surface. The small grazing angle of incidence tended to reduce the depth from the surface at which the x-rays were produced while the large take-off angle reduced the amount of target material which the x-rays had to penetrate. The effectiveness of these procedures is apparent from the small asymmetry of this line compared to those reported in neighboring elements by Bearden and Shaw,²³ for example, who used a fairly large incidence angle and a small take-off angle. The following weak line is a satellite whose origin will be the subject of brief comment below.

¹⁹ See reference 17, p. 202.

²⁰ Parratt, Porteus, Schnopper, and Watanabe, *Rev. Sci. Instr.* **30**, 344 (1959).

²¹ L. G. Parratt and J. O. Porteus (to be published).

²² H. P. Hanson and J. Herrera, *Phys. Rev.* **105**, 1483 (1957).

²³ J. A. Bearden and C. H. Shaw, *Phys. Rev.* **48**, 18 (1935).

4. INTERPRETATION

In a general way, it may be stated that the absorption spectrum reflects the product of density of unoccupied states times a transition probability while the emission band reflects the density of occupied states times a similar transition probability. Two difficulties intervene in attempts to draw conclusions about the energy band structure in solids from x-ray spectroscopy.

First, there is the effect of the transition probability which is principally to select from the total manifold of available states only those which have nonzero projections on the states of (in the case of K emission and absorption) p -type symmetry which can be constructed about the initial vacancy. Secondly, the states which are available are not characteristic of the unperturbed solid but rather such as are appropriate to the neighborhood of an ionic defect in the lattice.²⁴ The first difficulty, corresponding to the dipole selection rule, is always operative and provides, in principle, an experimental method for obtaining the degree of hybridization in the energy bands. The second is most striking in insulators²⁵⁻²⁷ but suppressed in metals owing to the rapid screening of the ionic defect by the conduction electrons.²⁸ The case of semiconductors is interesting, since according to the carrier density and mobility one might expect either situation to arise.

Since the carrier density is expected to be low at room temperature in the selenium samples used here, x-ray spectra characteristic of an insulator may be anticipated. We have accordingly interpreted the decomposition of the total absorption curve suggested above (Sec. 3) tentatively in the following way. The line absorption is associated with transitions to a bound, hydrogen-like p state produced by the field of the K -shell vacancy. The absorption edge which follows would then represent transitions to the p -type continuum (conduction band). The excess absorption (second peak in the absorption curve) is consistent with the conduction band structure observed by Givens and Siegmund.²⁹

If the midpoint of the upper edge of the emission band is interpreted as yielding the highest filled p -type

state, the gap which is obtained is 4.5 ± 0.3 ev. This is considerably in excess of the gap obtained by optical studies for either amorphous (2.5 ev) or hexagonal (1.6 ev) selenium.¹⁹ Such a situation may arise in several ways. A probable explanation would attribute the larger x-ray gap to the absence of appreciable p -state admixture in the lower 2 ev of the conduction band.

The absence of structure such as observed here in the L_{II} and L_{III} edges reported by Sandström⁴ would seem to require that the state responsible for the line absorption be of strictly p -type symmetry and that there be no neighboring states of s - or d -type symmetry. Such an interpretation suggests that an absorption maximum similar to that reported here in the case of the K absorption limit should also be observed in the case of the L_I absorption edge. Indeed Rudström and Sjöberg⁹ report the appearance of such structure in their preliminary measurements of the L_I edge. They were, however, apparently unaware of the "thickness effect" since, in their final measurements aimed at confirming this structure, they employed an absorber having considerably greater attenuation. This was of course advantageous from a statistical standpoint but was unfortunate in view of the "thickness effect." Their results are thus compatible with the interpretation offered here. It would, however, be most desirable to have measurements on the L_I edge taken with absorbers sufficiently thin to avoid the objections given above.

The satellite observed in the emission spectrum is similar to those observed by Bearden and Shaw²³ in neighboring elements. While there has been general agreement that satellites arise from atomic states involving multiple ionization, there has been little in the way of a satisfactory explanation of how such states are produced in K spectra.³⁰ Parratt²⁴ has recently suggested that the notion of a single valued K state (vacancy in the K shell, electron at rest at infinity) should be dispensed with and replaced (for both emission and absorption) with a multiplicity of states (excitation states) as seems to be required by the absorption data. A suitable elaboration of this idea would seem capable of providing an origin for some of the K satellites in a natural way.

ACKNOWLEDGMENTS

We are indebted to R. A. Kromhout of the Florida State University and L. G. Parratt of Cornell University for helpful discussions.

³⁰ A. Sandström, *Handbuch der Physik*, edited by S. Flugge (Springer-Verlag, Berlin, 1957), Vol. 30, p. 200.

²⁴ L. G. Parratt, Air Force Technical Report No. 8, Cornell University, July 1957, revised October, 1958 (to be published).

²⁵ L. G. Parratt and E. L. Jossem, *Phys. Rev.* **84**, 362 (1951); *Phys. Rev.* **97**, 916 (1955).

²⁶ Korringa, Jossem, Liefeld, Kvarda, and Shaw, Office of Naval Research Technical Report No. 6, The Ohio State University, May, 1957 (unpublished).

²⁷ Y. Cauchois and N. F. Mott, *Phil. Mag.* **40**, 1260 (1949).

²⁸ J. C. Slater, *Phys. Rev.* **98**, 1039 (1955).

²⁹ M. P. Givens and W. P. Siegmund, *Phys. Rev.* **85**, 313 (1952).