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Two-Crystal Analysis of *L*-Absorption Limits of Mercury

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An investigation of the shape and width of the *L* II and *L* III absorption limits of mercury has been made with the two-crystal x-ray spectrometer. Mercury was used in the liquid and vapor states and in chemical combination. The absorption limits are found to be asymmetrical. Approaching the limit from the long wave-length side, the intensity of the transmitted beam falls off rather sharply at first. This is followed by a more gradual decrease to the minimum value. The observed curves appear to bear out the suggestion by Kossel that the ejected electron may sometimes not be removed completely from theatom by the absorbed quantum, but only to an unoccupied upper level. The curves for the vapor have an over-all width of 45–50 volts. The curves for the liquid state are practically identical with the vapor curves at the long wave-length side, but fall off in intensity more slowly as the wave-length is decreased. The curves for the compounds are wider than those for the liquid and vapor and some exhibit fine structure.

INTRODUCTION

MOST investigations of x-ray absorption spectra have been concerned with the position and magnitude of the principal absorption edges and with the nature of the associated fine structure and secondary absorption. The single crystal spectrograph has been used in most of these researches. The high resolving power of the two-crystal spectrometer suggests its use in the study of the width and structure of absorption limits. The suitability of this instrument for such investigations was demonstrated by Bergen Davis and Harris Purks.[1]

The present investigation was undertaken to determine the effect of (1) physical state, and (2) chemical combination, upon the structure and width of an absorption edge.

A study was made of mercury in the vapor and liquid states and in compounds. It was observed that the edges were not symmetrical. This lead to a careful study of the shapes of the absorption curves.

The term *fine structure* is used to describe the discontinuities occurring at energy distances from the main edge of less than the ionization potential of the atom in question. The terms *secondary absorption* and *secondary structure* are used to describe discontinuities occurring at distances from the main edge, greater than the ionization potential.

Various investigations have shown that in many cases the main edge was marked by an absorption line followed by one or more regions of weaker and stronger absorption before the continuous absorption region is reached. The work of Kievit and Lindsay[2] in which was reported secondary structure for the *K* absorption spectra of elements calcium to gallium is typical of many researches in this field.

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[1] Bergen Davis and Harris Purks, Phys. Rev. **32**, 336 (1928).

[2] Ben Kievit and George A. Lindsay, Phys. Rev. **36**, 648 (1930).

Secondary absorption edges have been accounted for by Coster,[3] Lindsay and Voorhees,[4] Ray,[5] and others by the assumption of simultaneous transitions of two or more electrons due to the absorption of a single quantum.

More recently Kronig[6] has proposed the following explanation for the existence of secondary structure. The energy spectrum of an electron moving in a determined direction through a periodic potential field consists of permitted and forbidden zones of finite width. The energy of the electron at the end of the absorption process therefore lies within these permitted zones. Kronig also shows why such secondary structure occurs not only in crystals consisting of a large number of atoms, but also in polyatomic molecules, while it is absent in isolated atoms.

Kossel[7] predicted that a fine structure near the main edge should be found corresponding to the removal of the electron to the various permissible unoccupied optical orbits. While Kossel's interpretation is generally accepted, there is a lack of accurate correlation between it and the fine structure actually observed.

E. C. Stoner[8] considers the shape of an absorption edge on the basis of Kossel's suggestion. By analogy with optical spectra, the probability of absorption of the first line should be much greater than that of the higher members. The width of the fine structure range and the resolving power of the spectrometer would determine in the particular case whether the observed edge would be smooth or exhibit discontinuities. As Stoner points out, the fine structure range would be much increased in the case of ionized atoms.

A complete account of the work in this field up to 1930 is given by A. E. Lindh.[9]

The effect of chemical combination and physical state on the L absorption limits of mercury has recently been investigated by Hanawalt[10] with the single crystal spectrograph. His data show that secondary absorption exists for the compounds but not for the liquid or vapor mercury. It was found that the edges of Hg are simple with no indication of a white line. Hanawalt points out that his resolution may not have been great enough to observe possible fine structure. A shift of -2.5 volts in the position of the liquid edge with respect to the vapor edge was found. In the case of $HgCl_2$ and HgO in the solid forms, shifts of $+1.2$ and -7.4 volts respectively were reported.

Pauling[11] has recently attacked the problem of the shifts of the x-ray absorption limits due to chemical combination. He gives the following relation

$$h\nu_{\text{abs}} = h\nu_0 + e\Phi - E_{\text{crystal}}$$

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[3] D. Coster, Zeits. f. Physik **25**, 83 (1924).

[4] G. A. Lindsay and H. R. Voorhees, Phil. Mag. **6**, 910 (1928).

[5] B. B. Ray, Nature **122**, 771 (1928).

[6] R. de L. Kronig, Zeits. f. Physik **70**, 317 (1931).

[7] W. Kossel, Zeits. f. Physik **1**, 119 (1920).

[8] E. C. Stoner, Phil. Mag. **2**, 97 (1926).

[9] Handbuch der Experimental Physik **XXIV 2**, Teil (1930).

[10] J. D. Hanawalt, Phys. Rev. **37**, 715 (1931).

[11] Linus Pauling, Phys. Rev. **34**, 954 (1929).

in which ν_{abs} is the frequency of an absorption edge for an ion in a crystal and ν_0 that for a free ion. Φ is the potential at the center of an ion in a crystal due to all other ions. E_{crystal} is the electron affinity which may be calculated in terms of the magnetic susceptibility. Φ is positive for anions and negative for cations. E_{crystal} has the same effect for both. The agreement between theory and observed values in the case of the chlorine K edge in chlorides and the potassium K edge in various halides is very good. The shift of the potassium K edge is in the direction of longer wave-length and that of the chlorine K in the direction of shorter wave-length.

APPARATUS

The double x-ray spectrometer was of the type described by Davis and Purks.[12] The ionization current was amplified by an F. P. 54 pliotron and read on a Leeds and Northrup type R galvanometer. Methyl bromide was used in the ionization chamber. The Pyrex vapor cell V, with thin windows W, was 22 cm long. It was provided with a side tube for holding the liquid Hg. The arrangement was such that the vapor could be superheated in the main part of the tube. The heat was supplied by the coils H. These coils were wound on cylindrical forms which were placed over the ends of the vapor cell. This arrangement prevented condensation on the windows. In actual operation a temperature of about 310°C was maintained in the side furnace. The main furnace was held about 25°C higher. The temperature could be maintained to ± 1°C. The absorption under these conditions afforded the maximum contrast consistent with a reasonable amount of transmitted energy. The slits S were 8 mm wide and 10 mm high. X-ray tubes with molybdenum and tungsten targets were used. The observed curves were always corrected for the variations in the intensity of the spectrum obtained without the absorber. The correction was made in the following manner. A reference point was chosen on the energy-wave-length curve (without absorber). The energies at all other wavelengths were compared with that at the reference point. This correction in percent was then made in the observed curves. The x-ray tube was usually operated at 40 k.v. and 50 m.a.

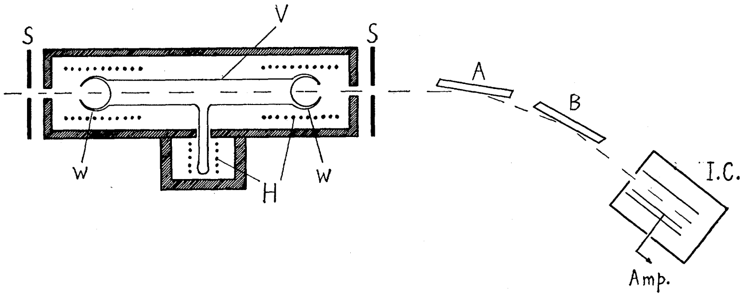

Fig. 1. Apparatus.

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[12] Bergen Davis and Harris Purks, Proc. Nat. Acad. Sci. **13**, 419 (1927).

Preparation of Materials

To observe the absorption edges of liquid Hg in about the same contrast as in the case of the vapor requires a film about 0.003 cm thick. Many methods were tried in an attempt to obtain a uniform film of this thickness without success. Finally a suitable suspension of Hg was found. Its composition is as follows:

Mercury	500 gm	Prepared suet	230 gm
Oleate of mercury	20 gm	Benzoinated lard	250 gm

A very satisfactory absorbing sample may be made from this preparation by mixing it with additional lard. This allows the use of a sample of sufficient thickness to insure uniformity in absorption over the exposed area. Upon dissolving out the fat it was possible to recapture the mercury in the metallic form.

Attention should be called to the fact that with the double x-ray spectrometer used in this investigation, the point at which the beam of x-rays of given λ strikes crystal *A*, moves as crystal *B* is rotated. This means that the beam will shift across the absorbing sample slightly as crystal *B* is rotated. By placing the sample near the x-ray tube this effect may be minimized.

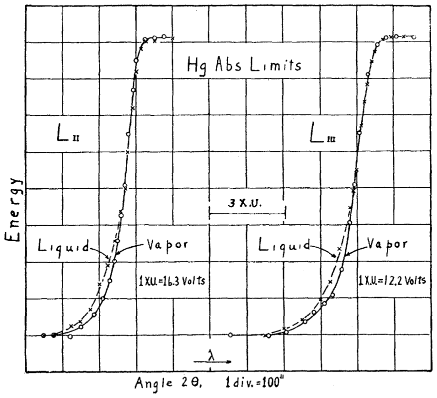

Fig. 2. Hg *L* II and *L* III absorption limits for the vapor and liquid states.

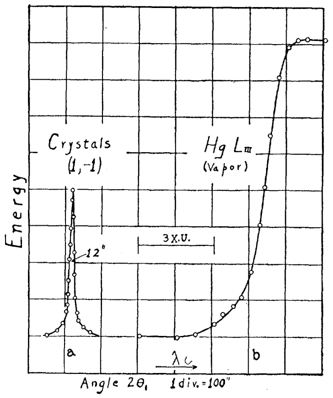

Fig. 3. (*a*). Rocking curve for crystals in the parallel position (1, −1). (*b*), Hg vapor *L* III absorption limit.

Samples of $Hg(NO_3)_2$ and $HgCl_2$ were obtained by dipping cigarette papers in the solutions of these salts. Several of these sheets were superposed in making up the samples. HgO and HgI_2, which were in powder form, were rubbed on cigarette papers, many sheets being used to obtain uniformity in the thickness of compounds in the sample. To test the uniformity, absorption curves were taken with the samples in many different positions.

EXPERIMENTAL RESULTS

Liquid and vapor curves

Fig. 2 shows the absorption curves for Hg *L* II and Hg *L* III in the liquid and vapor states. The intensity of the transmitted radiation is seen to fall off sharply at the long wave-length side of the curves. The decrease is more gradual at the short wave-length side. In the upper part, the liquid curve is practically identical with the vapor curve but a departure is observed in the lower part. The intensity falls off more slowly in the case of the liquid as the wave-length is decreased.

In Fig. 3 a rocking curve taken with the crystals in the parallel (1, −1) position is shown together with that of the vapor Hg *L* III (1, 1). The resolving power of the instrument depends upon the half maximum width of the curve in Fig. 3 (a). This is observed to be 12″ and is equivalent to 2.1 volts. In taking this curve, the slits were of the same width as in the absorption measurements. The same part of the surface of crystal *A* was used in both cases, since crystal *A* remains fixed in position. Although crystal *B* must be reversed in changing from the (1, 1) position to the (1, −1) position, the portions of its surface used in each case can be made very nearly the same.

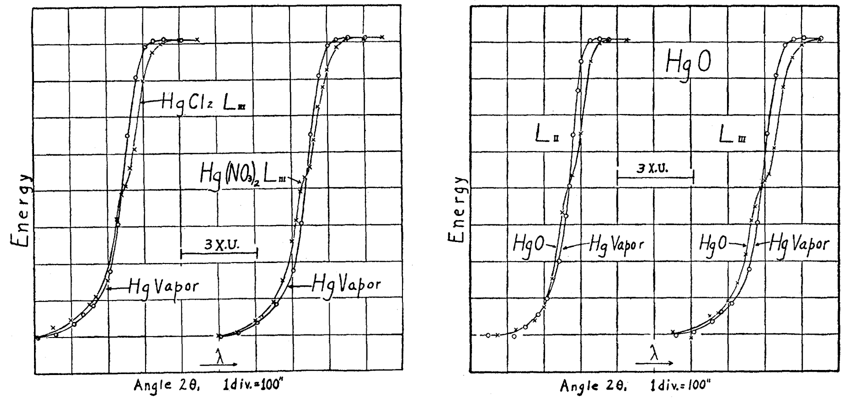

Fig. 4. *a*. HgO *L* II and *L* III limits. *b*, $HgCl_2$ and $Hg(NO_3)_2$ *L* III limits.

The absorption curves for HgO (yellow), $HgCl_2$ and $Hg(NO_3)_2$ are shown in Fig. 4. The Hg vapor curves are plotted for comparison. HgO (see Fig. 4a) shows a definite break in *L* II and *L* III. $HgCl_2$ *L* III and $Hg(NO_3)_2$ *L* III (see Fig. 4b) exhibit this structure also. In each case the main edge comes at a longer wave-length than that for the vapor with the additional break displaced to the short wave-length side of the vapor edge. No evidence of fine structure was found in $HgCl_2$ *L* II and $Hg(NO_3)_2$ *L* II. However these curves were none too reliable. The decrease in intensity from the long wave-length side to the short wave-length side was usually only 25 to 30 percent in the case of *L* II. In the case of *L* III the decrease in transmitted energy was about 50 percent.

There is no evidence of fine structure in the *L* II and *L* III curves of HgI_2 (red), (see Fig. 5).

The *L* II and *L* III curves were plotted to the same scale for purposes of comparison. The absorption curves for the compounds show the gradual sloping off at the high energy (short wave-length) side in common with the liquid and vapor curves.

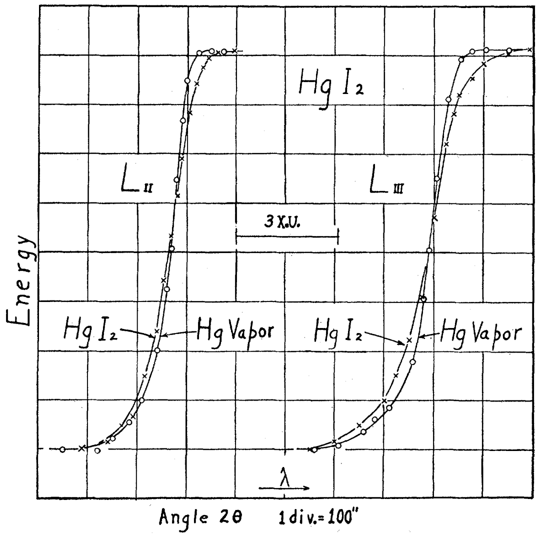

Fig. 5. HgI_2 *L* II and *L* III limits.

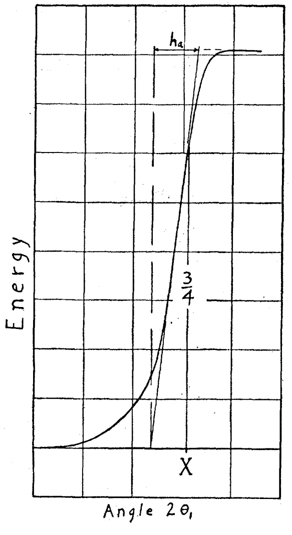

Fig. 6. Absorption limit showing method of estimating angular position and h_a width.

DISCUSSION OF EXPERIMENTAL RESULTS

To determine whether or not a shift in the position of the limit occurs between the liquid and vapor states, all of the observed curves were examined in the following manner. A point whose ordinate (see Fig. 6) is 3/4 of the value of the maximum ordinate is chosen. The abscissa of this point (x) which gives the angular setting on crystal $B(2\theta_1)$ is then read off. These angles were tabulated for all of the liquid and vapor curves. In the case of L III the mean for the liquid curves lies 4 seconds to the long wave-length side of the mean for the vapor curves. In the case of L II the mean for the liquid curves falls within one second of that for the vapor curves. Consideration of the data does not justify specifying these means to better than 5 seconds. It must be concluded that within the limits of the accuracy of the present measurements, the L II and L III absorption edges have the same energy value for both the liquid and vapor states. In the L III position, 5 seconds is equivalent to 0.88 volts. Hanawalt reported a shift of -2.5 volts but did not estimate the precision of his measurements. He states that his dispersion was 70 to 90 volts per mm (on photographic plate) in this wave-length region. A shift of 2.5 volts is equivalent to 14 seconds on crystal B.

Schwarzschild[13] has calculated the correction for the observed breadth of an absorption edge in terms of the width of the curve with the crystals in the $(1, -1)$ position (see Fig. 3). The calculation is for a symmetrical absorption limit. The quantity h_a (see Fig. 6) is taken as a measure of the diffuseness of the absorption edge. If H_c is the half maximum width of the $(1, -1)$ curve it is shown that

$$h = (h_a^2 - 1.13H_c^2)^{1/2}.$$

The quantity h is the corrected width of the absorption edge. All values are expressed in seconds of arc for convenience.

In the present case where the absorption discontinuities are not found to be symmetrical, this correction would not be expected to apply rigorously. If h_a is estimated for the L III curves it is found that the mean is 86″. H_c is 12″. Upon substitution in Schwarzschild's formula it is found that h is 85″. It is thus seen that the correction is negligible.

It is of interest to note that h_a for the L III edge when expressed in volts is nearly the same as h_a for L II expressed in volts.

h_a for L III vapor $= 86'' \backsimeq 15.2$ volts
h_a for L II vapor $= 67'' \backsimeq 15.8$ volts

The over all width of the L II and L III discontinuities is about 45–50 volts.

When an electron is removed from one of the L shells of mercury (80), the resulting configuration resembles a thallium atom. Thus the possible optical levels will be those of Tl and not those of Hg. The International Critical Tables give for the resonance potentials of thallium 0.96, 3.27, and 4.47 volts. The first ionization potential is given as 6.08 volts. The resolving power of the spectrometer as used was about 2 volts. This might explain why the observed vapor curves are smooth. However there seems to be no ready explanation of the width (45–50 volts) on this simple basis.

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[13] Myron Schwarzschild, Phys. Rev. **32,** 162 (1928).

In the compound curves it is found that the main edges for HgO, Hg $(NO_3)_2$ and $HgCl_2$ are shifted −4.8 v, −2.8 v and −3.5 v respectively. They are all shifted in the direction of longer wave-length. Hanawalt found a shift of −7.4 v for HgO and a shift of +1.2 v for $HgCl_2$.

In conclusion the writer wishes to thank Professor Bergen Davis for suggesting this problem and for the many privileges enjoyed in his laboratory.