

The K X-Ray Absorption Edge of Silicon

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(Received December 26, 1946)

The K absorption edge of silicon was measured in silicon metal and in the following compounds: quartz, sodium silicate, muscovite, biotite, phlogopite, lepidolite, carborundum, and an organic compound, mono ethyl siloxane. It was found that the quartz, sodium silicate, and the four micas all gave approximately the same wave-length for the absorption edge, namely, about 6700 x.u., while for the siloxane the value was 6706 x.u., and for the silicon metal and for carborundum it rose as high as 6718 x.u. It is to be noted that the surroundings of the silicon atom are the same for all those compounds which gave an edge at 6700 x.u. In the organic compound one oxygen has probably been replaced by the group C_2H_5 , while for carborundum and for silicon metal all four oxygens of the tetrahedral group surrounding the silicon atom have been replaced by carbon and by silicon, respectively.

THE K absorption edge of silicon in the x-ray spectrum has not been measured very thoroughly up to the present time. In 1920 Fricke¹ photographed and measured the K edges of several elements from Na(11) to Cl(17). Although he found the edge for the lighter elements Na(11), Mg(12), and Al(13), the edge of silicon failed to appear. Fricke attributed the difficulty to the presence of an M emission line of tungsten which lies in the immediate neighborhood of the silicon edge. The undesirable tungsten line, however, which was caused by the tungsten filament of the x-ray tube, is in the first order, and hence should be absorbed the same as any other radiation of the continuous spectrum. Realizing this fact, Lindh,² in 1925, showed that the absorption edge could be observed on the short wave-length side of the broad emission line of tungsten. Lindh used screens of silicon metal and several compounds. His values were:

Substance	λ of edge in x.u.
Si	6731.0
SiO ₂	6707.5
Na ₂ SiO ₃	6707.3
K ₂ SiO ₃	6707.7

The only other measurement which has come to the attention of the authors was by Deodhar³ in 1930. In his work the absorption occurred in the quartz crystal used as a grating, while Lindh

used absorbing screens with a gypsum crystal as reflector. Deodhar's value for the Si K edge was 6705 x.u. Neither of these workers made any correction for refraction of the x-rays in the reflecting crystal. In fact, at the time when these measurements were made the indices of refraction were not well known and it was not customary to attempt to make such corrections. The correction, however, amounts to several x.u.—in some of the present work to as much as 10 x.u.—and hence it should be made to compare works of different authors as well as to obtain a better absolute value.

In the present work both the methods of absorption in the crystal and in absorbing screens were used. Since in either method the grating space of the reflecting crystal must be more than one half the wave-length to be measured, this requirement immediately rules out the possibility of the first method for those substances which do not have a large enough grating space. The grating spaces of the cleavage faces of the micas are all large enough and to spare, while in quartz the prism face has a value of d about 4246 x.u., and hence is qualified to reflect a wave-length of 6700 x.u. The rhombohedral face, although usually better than the prism face, has a d of about 3336 x.u. Since this is less than one half the wave-length desired, only the prism face of quartz can be used. Obviously the first method also requires a fairly good crystal. In view of these requirements, quartz and the micas were used as

¹ Hugo Fricke, *Phys. Rev.* **15**, 202 (1920).

² Axel E. Lindh, *Zeits. f. Physik* **31**, 210 (1925).

³ G. B. Deodhar, *Nature* **125**, 777 (1930).

gratings, and so gave the silicon edge without any further absorber, while for sodium silicate, carborundum, the siloxane, and silicon metal a gypsum crystal was used as reflector with absorbing screens of the substance desired. A very fine grade of carborundum was moistened, then allowed to dry on a thin collodion membrane, thus forming the carborundum absorber. Finely powdered sodium silicate and silicon were placed wet on the face of the gypsum crystal in a very thin layer, while the mono-ethyl siloxane was dissolved in isopropyl ether and a few drops of the liquid placed on the surface of water. The thin rubbery layer thus obtained could then be used as an absorbing screen. The radius of the spectrometer was 180.2 mm and the photographic method was used throughout.

As reference line with the micas we used the $K\beta_1$ -line of copper in the 5th order which came on during the exposure without moving the film. For the other substances the $K\alpha_1$ -line of copper in the 4th order was used, the film being turned through an accurately determined angle between the exposure of the reference line and the exposure of the edge. With the latter procedure the method of calculating the wave-length of the edge was as follows. From the known wave-length of the reference line the actual Bragg angle θ was calculated by using the grating space for the 4th order as determined by Larsson⁴ and given by Siegbahn in his *Spektroskopie der Röntgenstrahlen*. Then the angle through which the plate was turned between the exposures for the reference line and the edge was added to 2θ , thus giving the Bragg angle corresponding to the point in the spectrum where the reference line lay while the edge was being photographed. Then the angle corresponding to the position of the edge was calculated by subtracting the angle at the crystal whose arc is the distance on the film from the edge to the reference line. When the Bragg angle for the edge is thus found the grating space for the first order is used to calculate the wave-length of the edge. By thus using the two values of the grating space in the different orders only correction for normal refraction in the crystal is made.

Some trials were made of the effect of anomalous refraction on the position of the edge for

⁴ Larsson, Uppsala Univ. Årsskrift 1929.

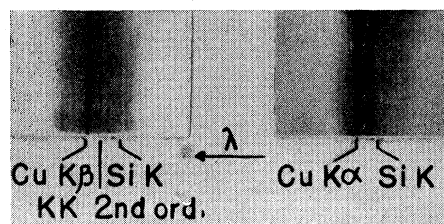


FIG. 1. K absorption edge of silicon. Muscovite, left; carborundum, right.

those reflecting crystals which contained silicon. Finely powdered quartz was put on the face of a gypsum crystal and the wave-length of the edge so obtained was compared with that from the quartz as a reflecting crystal. No difference between the two could be definitely established, and since a calculation⁵ of the anomalous refraction including the effect of absorption shows that the anomalous refraction is rather small, it was neglected entirely and only the normal refraction was used as indicated above.

The grating space of muscovite has been determined accurately; those of the other micas only approximately. The constants for biotite, phlogopite and lepidolite were accordingly measured with the following results:

Crystal	d (x.u.)
Biotite	10006
Phlogopite	10015
Lepidolite	9923

In determining these values the $Cu K\alpha_1$ -line was photographed in different orders from the third to the sixth. Since the error in the observed d , due to refraction, is only $\frac{1}{5}$ as much in the third order as in the first order, and still less in higher orders, the values obtained were considered to be those for the high orders, and the value for the first order was assumed to be smaller in the same proportion as that found accurately for muscovite by Larsson. This procedure is justified from the consideration that the index of refraction is much the same for all the micas, and because in the reference method used an error in the value of d of as much as 10 x.u. would cause a corresponding error in the wave-length of the edge of only 0.3 x.u.

Figure 1 shows two absorption edges, one

⁵ See Compton and Allison, *X-Rays in Theory and Experiment*, page 294.

TABLE I. Wave-lengths of the K absorption edge of silicon in various substances.

Substance	λ of edge (x.u.)	Crystal used
Muscovite	6703.0	Muscovite
Phlogopite	6703.2	Phlogopite
Biotite	6703.7	Biotite
Lepidolite	6699.0	Lepidolite
SiO ₂	6702.7	Quartz
Na ₂ SiO ₃	6698.4	Gypsum
Si Metal	6715.2	Gypsum
SiC	6717.9	Gypsum
C ₂ H ₅ SiO _{1.5}	6706.2	Gypsum

taken by a muscovite crystal, the other by a screen of carborundum, using a gypsum crystal. At least three good films were taken for each substance used.

The results of the measurements of the K absorption edge of silicon are set forth in Table I. Each value is the average of at least three good films for that particular substance. The results are corrected for normal refraction in the various crystals used in the manner described above. It will be observed that the wave-length of the edge is nearly the same for all the micas, quartz, and sodium silicate, although for lepidolite it is unexpectedly lower than for the other micas. An extra number of trials was made for lepidolite with independent adjustments of the crystal, but the results had persistently the lower value.

When one considers the crystal structure of the different substances it is easy to see why the first six should be so nearly alike. In all of them the silicon atom is considered to be at the center of a tetrahedron having an oxygen atom at each of the four corners. Any other atoms in the molecule should have little influence on the silicon energy levels, hence one might expect little difference in

the wave-length of the edge. In the silicon metal there are also tetrahedrons, but each silicon atom at the center is surrounded by four other silicon atoms instead of oxygens. In carborundum the silicon is surrounded by four carbon atoms. The silicon or carbon atoms would disturb the energy levels of the silicon atoms less than the more negative oxygen atoms would. The result is some 17 x.u. greater wave-length for the silicon metal and the carborundum.

The structure of the silicone is not known, but the formula indicates that one of the oxygen neighbors has been replaced by the ethyl group C₂H₅ so that one might expect the wave-length of the edge to lie between that for the micas and that for the silicon metal or carborundum, but nearer that for the micas. The table shows agreement with this assumption. The difference in the values of the edge for the micas and for silicon or carborundum is about one electron volt, while between the micas and the siloxane it is about $\frac{1}{3}$ volt. This difference in the position of the edge really represents the variation of the difference between the initial and final levels concerned in the absorption process when a change occurs in the neighbors of the silicon atom.

No attempt was made to investigate the fine structure of the edge although such structure could be observed, especially with the carborundum, where it consisted principally of two strong white lines.

Other silicones containing a different proportion of oxygen atoms might well give more information concerning the dependence of the position of the absorption edge on the neighbors of the silicon atom.

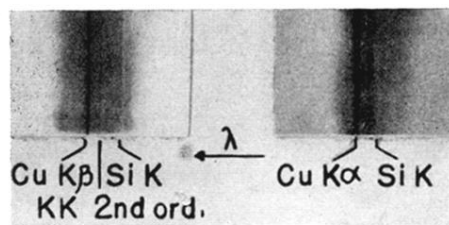


FIG. 1. *K* absorption edge of silicon. Muscovite, left; carborundum, right.