

## Effects of Chemical Combination on the X-Ray Emission Spectrum of Sulphur

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With an improved method to eliminate the effects of chemical reactions with the target material, the wave-lengths of the sulphur  $K\alpha$  and  $\beta$ -lines were measured for the following substances: S, FeS, CoS, NiS,  $\text{Cu}_2\text{S}$  and ZnS. The superiority of the new technique over that usually employed is particularly evident in the spectrum of ZnS in

which the  $K\beta$ -line is observed as a triplet instead of the single broad line heretofore observed. This result is independent of the target material. The  $K\beta$ -lines of CoS and NiS are observed for the first time. Two crystal modifications of ZnS, namely, zinblende and wurtzite, gave spectra which showed no appreciable differences.

THE first observations showing that the x-ray emission spectrum of an element depends on chemical combination were made in 1924 by Lindh and Lundquist. The effect is very small except in the case of the lighter elements, such as silicon, phosphorus, sulphur and chlorine. A summary of the work up to 1928 may be found in Lindh's book on *Roentgenspektroskopie*. Recent studies of the subject are those due to Lundquist,<sup>1</sup> Faessler,<sup>2</sup> Deodhar<sup>3</sup> and Svensson.<sup>4</sup> Deodhar, in particular, finds several new lines which are emitted by some compounds and not by others, indicating the creation of new energy levels in an atom when it is combined with one or more other atoms. In addition to this appearance of more or less characteristic lines, there are often shifts of a few X-units in the wave-lengths of some of the lines.

Although sulphur compounds have been investigated several times, in all but one of these studies,<sup>2</sup> and that one restricted to the intense  $\alpha_1$  and  $\alpha_2$ -lines, the spectrum was excited by direct electron impact on the powdered compound. This was rubbed into scratches on the face of the target. What happens to the compound under these conditions is only now beginning to be clearly understood.<sup>4</sup> The chemical reaction between the substance and the target is evident from the fact that the "same" substance often gives a different spectrum depending on the underlying target metal.

In order to overcome such effects it has been often suggested that the spectrum of the compound should be excited by fluorescence instead of electron impact. This is the procedure followed by Faessler, who used one of the new type of x-ray tubes developed by Coster and Hevesy. In this form of tube, the powdered material is rubbed on a flattened portion of the electron focussing shield which surrounds the filament. However, Faessler's work covers only the intense  $\alpha_1$  and  $\alpha_2$ -lines of sulphur, presumably because the other lines could not be obtained with sufficient intensity.

In order to study the less intense lines, particularly the  $\beta$ -lines which show the greatest dependence on chemical combination, the writer has used the target illustrated in Fig. 1. The sub-

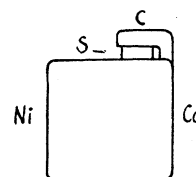


FIG. 1. X-ray target.

stance  $S$  is protected from the direct impact of the electron stream by the copper shield  $C$ . The focal spot is one to two millimeters from the front of the material. This does not give a pure fluorescence spectrum, for many of the electrons no doubt are scattered from the target to the substance. However, the opportunity for chemical reaction is greatly reduced as the results

<sup>1</sup> Lundquist, *Zeits. f. Physik* **60**, 642 (1930).

<sup>2</sup> Faessler, *Zeits. f. Physik* **72**, 734 (1931).

<sup>3</sup> Deodhar, *Proc. Roy. Soc.* **A131**, 647 (1931).

<sup>4</sup> Svensson, *Zeits. f. Physik* **75**, 120 (1932).

show. The spectrum is of fair intensity. The usual exposure for the  $\beta$ -lines was 8 to 10 hours at 10 to 15 milliamperes and 12 to 15 kilovolts. In the case of pure sulphur, the current was reduced to 1 to 2 milliamperes to keep the sulphur from melting and running out onto the target.

A vacuum spectrograph of the Siegbahn type was employed. The crystal was of calcite, the wave-lengths being measured with the aid of comparison spectra. For the sulphur  $K\alpha$ -lines, cobalt  $K\alpha_1$  was used in the third order, while for the  $K\beta$ -lines nickel  $K\alpha_1$  was employed. These lines have been measured with ample accuracy by Eriksson.<sup>5</sup> The Bragg angles for these lines, with Larsson's value for the lattice constant of calcite in the third order,<sup>6</sup> are, at 18°C:

$$\text{Ni } K\alpha_1 \ 55^\circ 0' 25'' \quad \text{Co } K\alpha_1 \ 62^\circ 7' 35''.$$

The angular separations between the reference lines and the sulphur lines were calculated from the distances along the plate as measured by a Gaertner comparator and the radius of the camera measured in the manner outlined by Lindh.<sup>7</sup> Temperature differences between the sulphur and comparison exposures were corrected for by the equation  $\Delta\theta = 2.10'' \Delta T \tan \theta$ . From the glancing angles so found, the wave-lengths of the sulphur lines were calculated with the aid of Larsson's value of the lattice constant for the first order.<sup>6</sup>

The wave-lengths of the various lines in the spectrum of sulphur and the various sulphides studied are given in Table I.

TABLE I. Wave-lengths of the x-ray emission lines of sulphur in X-units.

Line	S	FeS	CoS	NiS	Cu <sub>2</sub> S	ZnS
$\alpha_2$	5363.50	5364.35	5364.16	5364.05	5363.97	5364.27
$\alpha_1$	5360.39	5361.28	5361.34	5361.05	5360.94	5361.29
$\alpha'$	5342.1	5343.0	5342.7	5342.1	5342.4	5342.7
$\alpha_3$	5330.21	5330.75	5330.77	5330.49	5330.39	5330.61
$\alpha_3'$	5327.5	5328.2	5328.4	5328.1	5328.2	5328.1
$\alpha_4$	5323.27	5324.12	5324.04	5323.52	5323.45	5323.89
$\alpha_5$	5284.5	5285.2	5286.0	5284.2	5285.1	5285.4
$\beta_4$	—	5065.24	5065.26	5066.02	—	—
$\beta_5$	—	—	—	—	—	5030.4
$\beta_1$	5020.72	—	5020.89	—	5021.84	5023.77
$\beta_{1x}$	—	5017.3	—	5018.4	—	5016.95
$\beta_x$	5013.35	—	5012.62	—	5013.39	—

<sup>5</sup> Eriksson, Zeits. f. Physik 48, 360 (1928).

<sup>6</sup> Siegbahn, *Spektroskopie der Roentgenstrahlen*, 2nd edition, p. 44.

<sup>7</sup> Lindh, *Roentgenspektroskopie*, p. 63.

The  $\alpha_1$  and  $\alpha_2$ -lines are probably correct within  $\pm 0.1X$ , while the others may be in error by  $\pm 0.1$  up to  $\pm 0.4X$  according to their breadth and intensity. The  $\alpha_5$ -lines were particularly difficult to measure.

Other faint lines which were occasionally observed and seem to be due to sulphur or sulphides are as follows: 5108, 5043, 4953, 4936, and 4900. These values may be in error by  $\pm 2X$ . Of these, the 5108 and 4900 lines were most frequently observed.

The  $\alpha$ -group is seen to change very little from compound to compound. This is surprising in view of the fact that the  $K$  absorption edges shift by 2 to 4X-units.<sup>8</sup> Evidently these shifts are closely paralleled by the shifts in the  $L$  levels.

On the other hand, the  $\beta$ -lines show widely different appearances in some cases. This is clearly illustrated in Fig. 2 which summarizes the re-

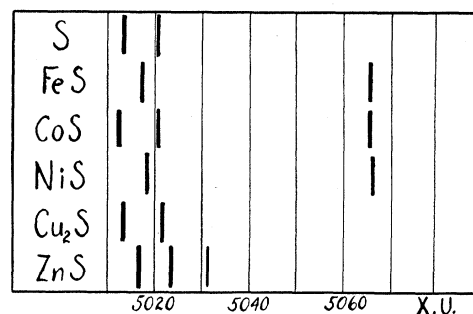


FIG. 2. The  $K\beta$ -lines of sulphur and sulphides.

sults for these lines. The spectra of CoS and NiS have not been previously observed. The CoS was prepared by precipitation from cobalt nitrate by ammonium sulphide. The NiS was the mineral, millerite. The spectrum of ZnS is entirely different from the single broad line heretofore described in the literature. The spectrum here obtained was the same when the copper target was replaced by iron. The spectrum of pure sulphur showed only a slight dependence on the target material. This result could not have been obtained by the usual procedure of electron impact directly on the powdered sulphur.

However, extreme care must be exercised if the electrode influence is to be entirely eliminated, particularly if the substance is easily fused or

<sup>8</sup> Lindh, *Roentgenspektroskopie*, p. 291.

volatilized. This is due to the almost unavoidable contamination of the target which usually gives a scarcely perceptible target sulphide spectrum superposed on that of the compound. This can be reduced to negligible proportions by applying proper care. The target must be kept smooth and clean.

It is surprising that the frequently observed  $\beta_3$ -line could only be seen on two of the plates, namely, two heavily exposed ZnS plates, and that on these it was scarcely visible. On the other hand, two of Deodhar's recently discovered "weak" lines, namely  $\beta_4$  and  $\beta_5$ , were quite strong in some cases. The  $\beta_4$ -line is a prominent line in the CoS and FeS spectra, while  $\beta_5$  appeared in the ZnS spectrum.

The reasons for the observed differences in the  $\beta$ -lines of various sulphides are not clear. One may think of a readjustment of the outer energy levels of the combining elements to some common mean value. It would be of interest to study this question by means of the spectra of the

metallic elements in the sulphides. A start has already been made on this problem, and it has been found that the  $K\beta_1$ -line of iron is strongly shifted in the sulphide to 1758.46X, while its wave-length in the spectrum of pure iron is 1753.01X. In energy units, this shift is approximately equal to the difference between the S  $K\beta_4$  and S  $K\beta_{1X}$ -lines and is in the same direction. A further study of these effects is in progress.

The method of examination here described makes it a relatively simple matter to compare the spectra of various crystal modifications of the same compound. Insofar as this has been done, (ZnS as zincblende and wurtzite) there seems to be no appreciable effect of crystal modification on the x-ray spectrum. This study is being continued.

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