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Effects of Chemical Binding on the X-Ray $K\alpha_{1,\,2}$ Doublet Lines of Sulphur Studied with a Two-Crystal Spectrometer

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Ionization curves of the $K\alpha_{1,\,2}$ doublet lines of sulphur have been recorded with the two-crystal spectrometer. Several sulphides and sulphates were used as targets. The effects of the chemical binding on the wave-length, on the $\alpha_1\rightarrow\alpha_2$ separation and on the doublet contour were measured. With suitably chosen targets, the wave-length shift of the S $K\alpha_{1,\,2}$ lines from sulphates to sulphides was observed in the process of shifting.

SINCE first noticed in 1924 the effects of chemical binding on x-ray emission spectra have attracted the attention of numerous investigators.[1] Four of these effects have been studied: (1) The wave-length shift of the emission lines of light elements;[2, 3, 4, 5] (2) the different relative intensities;[6] (3) the possibly new lines with certain compounds;[6] and (4) the change in the line contours, particularly in the line widths at half-maximum intensity.[6, 7, 8] All of these effects have been investigated with the vacuum spectrograph by using the photographic method. The uncertainties in the photographic method of measuring intensities, especially of intensity distributions in wave-length (line contours), are well known and quantitative measurements require the ionization method and the high resolving power of the two-crystal spectrometer.[8] The present paper reports observations on the contour shape and the wave-length shift of the $K\alpha_{1,\,2}$ lines of sulphur with a two-crystal spectrometer.[9] With suitably chosen targets, the wave-length shift can be observed in the process of shifting.

Targets of several sulphur compounds were used. FeS, Cu_2S, $MgSO_4$ and $BaSO_4$, in powdered form, were pounded onto a roughened copper or aluminum water-cooled target. PbS was soft-soldered to copper. With the x-ray tube at low power, 10 kv and 10 to 15 ma, with the focal-spot about 2 mm in diameter, these targets operated satisfactorily, although, were the power increased, the powder substance would either change chemically or disappear from the target surface. FeS, by far the best target, would dissipate about 700 watts. The making of satisfactory targets for ionization recordings of intensities is a different problem than is the case for photographic measurements—the emitted intensity must remain constant (within 1 or 2 percent) throughout the time required to record a complete curve, about 30 minutes in the present work. Several sulphur compounds in addition to the ones mentioned above were tried but were found to be unsatisfactory.

In Fig. 1 are plotted the ionization curves of the S $K\alpha_{1,\,2}$ doublet lines with different targets—compounds and mixtures of compounds. These various targets are described in the caption to the figure. There can be no doubt that under the stress of the electron bombardment the sulphates decompose or react chemically, either by simple reduction or with the target material or both, and yield the spectra characteristic of the sulphides. In a sense these curves may be interpretated as x-ray pictures of the chemical reaction, each curve giving a quantitative measure, in fractions of the total number of molecules, of the extent of the reaction. The wave-length shift is clearly shown and differences in the widths of the lines and in the overlapping factor[10] are also evident. It so happens that the

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[1] See Lindh, *Handbuch der Experimentalphysik* (1930), XXIV, part 2, pp. 314–325.

[2] Lundquist, Zeits. f. Physik **60**, 642 (1930); **77**, 778 (1932); **89**, 273 (1934).

[3] Faessler, Zeits. f. Physik **72**, 734 (1931).

[4] Svensson, Zeits. f. Physik **75**, 120 (1932).

[5] Valasek, Phys. Rev. **43**, 612 (1933); **47**, 896 (1935).

[6] Deodhar, Proc. Roy. Soc. **A131**, 647 (1931).

[7] Siegbahn and Magnusson, Zeits. f. Physik **96**, 1 (1935).

[8] Parratt, Phys. Rev. **45**, 364 (1934); Wilhelmy, Zeits. f. Physik **97**, 312 (1935).

[9] This instrument has been described in previous reports, Phys. Rev. **41**, 553 (1932); Rev. Sci. Inst. **5**, 395 (1934).

[10] This factor, a measure of the degree of overlapping of the two $K\alpha$ components, is defined as twice the ratio of the minimum ordinate between the lines to the maximum ordinate of the α_1 line. See Allison, Phys. Rev. **44**, 63 (1933); Parratt, Phys. Rev. **44**, 695 (1933).

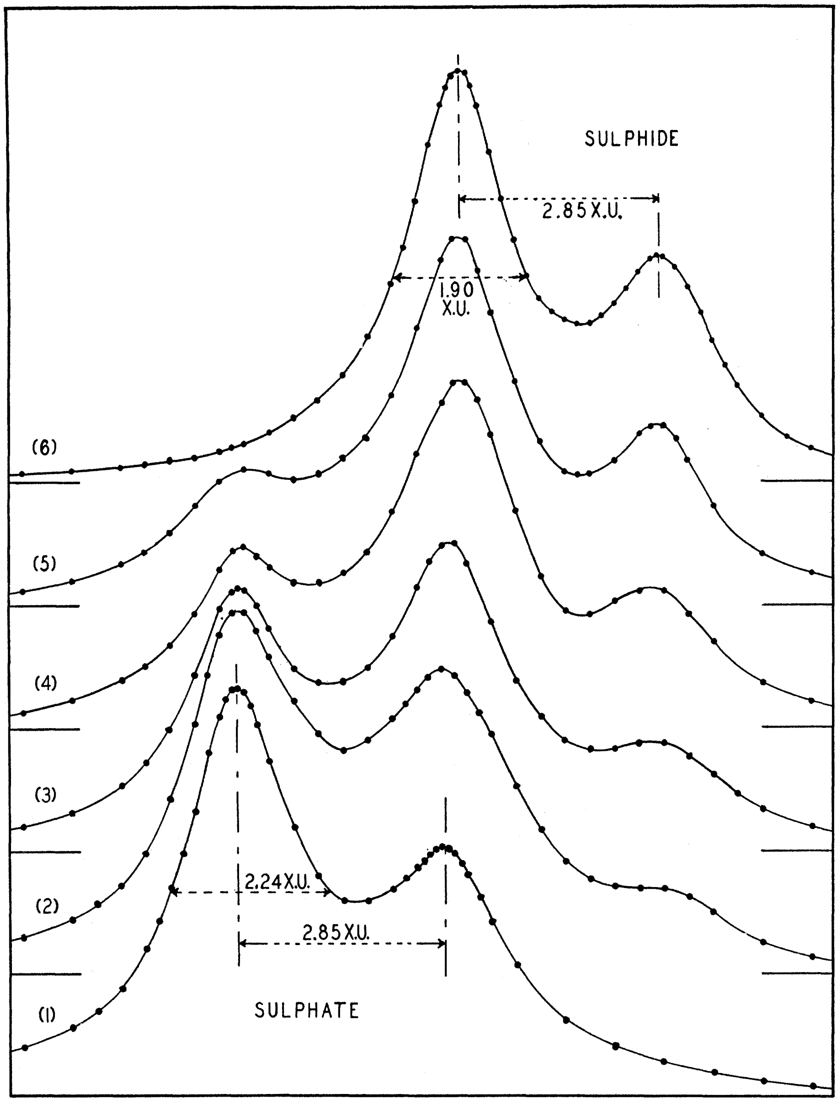

FIG. 1. Ionization curves of the S $K\alpha_{1,2}$ doublet lines. All six curves are plotted on the same abscissae scale. The targets used in recording these curves are:

Curve (1)—$BaSO_4$ on Al. The curve was recorded as soon as possible after applying the voltage to the tube, 8 kv and 8 ma.

Curve (2)—Same target as with curve (1) after the tube had been operating at 16 kv and 15 ma for two hours. After this "seasoning" the tube power was reduced to 10 kv and 15 ma and the curve recorded.

Curve (3)—$MgSO_4$ on Al. The curve was taken at 10 kv and 15 ma after the tube had been operating one hour at 15 kv and 15 ma.

Curve (4)—$MgSO_4$ on Cu. The curve was taken at 10 kv and 15 ma after the tube had been operating one hour at 15 kv and 15 ma.

Curve (5)—$MgSO_4$ on Cu. This target was the same as with curve (4) after three additional hours of operation at 15 kv and 25 ma. The curve was taken at 12 kv and 15 ma.

Curve (6)—Cu_2S on Cu. Taken at 10 kv and 10 ma. The target of curve (5) after 10 hours additional operation at 15 kv and 20 ma yielded a curve identical with curve (6) within the experimental error. Evidently after being subjected to the electron bombardment with the attending heat of the focal spot the $MgSO_4$ goes, with sufficient time, completely over to the sulphide, either Cu_2S or MgS or both.

Although an effort was made to record the intermediate curves in a minimum of time it is no doubt true that the chemical change was going on at the time of the recordings and the curves obtained do not represent truly static stages of the process.

wave-length of the α_2 line of the sulphates is in near coincidence, though not quite, with the wave-length of the α_1 line of the sulphides: There are actually four lines in the intermediate curves of the figure instead of the obvious three.

Measurements were made on the wave-length shifts, the wave-length interval $\alpha_1 \rightarrow \alpha_2$, the line widths at half-maximum intensity, and on the overlapping factors. Free sulphur was not used as a target so the wave-length shifts are referred to the position of the peak of the α_1 line of FeS. These data are given in Table I. The estimated maximum error in these measurements is indicated in the table.

A test with the FeS target showed no variations in the shape of the doublet contour as the tube voltage or current was altered. The voltage range in this test was 5 to 30 kv. This confirms and extends the results of similar tests by many investigators in the shorter wave-length regions.

TABLE I. *Measurements of the $S\,K\alpha_{1,\,2}$ doublet lines (5.36A) from various sulphur compounds as determined with the two-crystal spectrometer in the (1, +1) position.* (The width data are not corrected for overlapping of the α_2 line.)

TARGET	FULL WIDTH OF α_1			SEPARATION $\alpha_1 \rightarrow \alpha_2$		SHIFT OF α_1 MAX. ORDINATE (X.U.)	OVERLAPPING FACTOR
	(sec.)	(X.U.)	"true"	(sec.)	(X.U.)		
FeS on Cu	275±5	1.88	1.63	416±3	2.85	0	0.77
Cu_2S on Cu	280±5	1.91	1.67	416±3	2.85	0.27±0.03	0.78
PbS	278±5	1.90	1.65	412±4	2.82	—	0.79
PbS*	144±3	2.30	(2.13)*	182±3	2.81	—	0.91
$MgSO_4$ on Cu after 12 hours of operation	282±7	1.93	1.68	415±3	2.84	0.27±0.03	0.78
$MgSO_4$ on Al taken as soon as possible with low power	326±10	2.24	1.99	415±4	2.84	3.28±0.04	0.93
$BaSO_4$ on Al taken as soon as possible with low power	327±6	2.24	1.99	416±4	2.85	3.28±0.04	0.91

* These data with PbS were recorded with quartz crystals, (10·0) planes, ground and etched. These quartz crystals, compared with calcites, have considerably less effective resolving power at this wave-length (5.36A) as determined from the (1, +1) width measurements; however, the (1, −1) width of the quartz specimens at this wave-length is less than the corresponding width with the calcites. The shape of the (1, −1) curve with quartz crystals is markedly different from the shape of the same curve with calcites. See Rev. Sci. Inst. **6**, 113 (1935) and **5**, 395 (1934). The relative effective resolving powers of these quartz and calcite crystals are in agreement with the discussion in Rev. Sci. Inst. **6**, 387 (1935). It should also be pointed out that, in view of the great difference in the (1, −1) shapes with two types of crystals, the correction Eq. (1) will not apply to the width measurements with quartz—rather the correction should be greater than this equation gives. Furthermore, as pointed out in the last reference, the validity of the correction in the case of calcite is somewhat doubtful at this wave-length.

All the data in the present report, except those with the PbS target, were taken with calcite crystals $A_4\,B_4$ which have been studied in other reports, Parratt, Rev. Sci. Inst. **6**, 387 (1935) and Parratt and Miller, Phys. Rev. in press (1936).

The observed contours have not been resolved into the α_1 and α_2 components—the uncertainty of how this resolution should be made (due to our lack of knowledge of the true shapes of the individual lines) is too great to warrant the attempt at the present time. Hence, width measurements of the α_2 line and of the degrees of asymmetry of the lines are not given. The "true" widths of the α_1 line are obtained by applying to the observed widths the empirical correction for the finite resolving power of the crystals of the spectrometer as discussed in another article.[11] This correction is

$$W_T = W_0 - 2.9 W_C^{1.7}, \tag{1}$$

where W_T is the true width, W_0 is the observed (1, +1) width and W_C is the observed width when the crystals are in the (1, −1) position. All the widths in Eq. (1) must be expressed in X.U. The (1, −1) width with calcites is 0.437 X.U. and with the quartz crystals is 0.353 X.U.

The measurements of the wave-length intervals are in good agreement with those obtained photographically. The photographic measurements, however, vary among themselves considerably. The $\alpha_1 \rightarrow \alpha_2$ separation of FeS, for example, is reported as 2.81 X.U. by Faessler[3] and 3.07 X.U. by Valasek[5]; and of $BaSO_4$ as about 2.84 X.U. by Faessler[3] and 3.00 X.U. by Lundquist.[2] The shift of the α_1 line, referred to FeS, of Cu_2S is given by Lundquist[2] as 0.05 X.U. and by Valasek[5] as 0.34 X.U.; of $BaSO_4$ by Lundquist[2] as 3.04 X.U. and by Faessler[3] as about 3.65 X.U. Such variations in the photographic measurements are not surprising when one considers the large widths of these doublet lines and the lack of resolution. Because of the higher resolving power of the two-crystal instrument and because of the greater accuracy of the ionization method in recording the intensity distributions in wave-length, the present measurements are more reliable.

The author is indebted to the University of Chicago for the loan of the double spectrometer with which these data were obtained.

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[11] Parratt, Rev. Sci. Inst. **6**, 387 (1935).