X-Ray Emission Spectra of Sulphides and Sulphates

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A target for exciting x-ray emission spectra of chemical compounds is described. The wave-lengths of the $K\beta$ lines of alkaline earth sulphates and of some semiconducting sulphides are given. Using these results and the wave-lengths of the K absorption edges, the energy gap between the occupied and unoccupied zones in these crystals is obtained. The results for the sulphates are compared with the results previously obtained for the corresponding sulphides. In order to account for the changes in emission wave-lengths from compound to compound, a nonuniform displacement of energy levels is needed in addition to the Madelung energy. A recent article by Slater and Shockley suggests one way in which this may be accomplished.

THE effects of chemical combination on x-ray emission spectra have recently received considerable attention.[1] Since the radiation is emitted by solids in the crystalline state, the results lead to a determination of the relative location of some of the energy levels in these crystals. They supplement the results obtained by studies of ultraviolet absorption and photo-electric effect and contribute to a better understanding of this group of phenomena.

The spectra of the compounds were excited by the general method described by the writer in a previous article.[2] An improvement was effected by water-cooling the clamp which holds the pellet of the material on the target just back of the focal spot. The clamp was made of a loop of thin-walled copper tubing through which water is circulated. In this way the materials are kept much cooler and it is possible to use a greater variety of compounds. A Siegbahn vacuum spectrometer with a calcite crystal was employed. The wave-lengths were determined by comparison with those of Ni $K\alpha$ in the third order.

Table I contains the wave-lengths of the S $K\beta$ lines of various sulphur compounds. The previously published values for the alkaline earth sulphides are given again to facilitate comparison with the new results for the corresponding sulphates. The column K_∞ gives the wave-lengths of the principal K absorption edges as measured by Stelling[3] or Lindh.[4] The next column gives the difference between the $K\beta$ and the K_∞ values in x-ray units (10^{-11} cm). The last column gives this difference in terms of electron volts.

The principal energy bands for the S ions in the alkaline earth sulphides, as inferred from x-ray data, are indicated in Fig. 1. Fine structure, occasionally evidenced by the doublet character of the beta lines and the structure of the K absorption edge is not indicated, the lowest level of each kind being shown. The levels X and above, which belong to the sulphur continuum, are normally vacant, while the sulphur $3p$ band is normally completely filled. The K absorption edge marks the beginning of the removal of a K electron to the X continuum. The $K\beta$ line is emitted when one of the $3p$ electrons drops into the vacancy in the K shell. The last column of

TABLE I. *X-ray wave-lengths of sulphur. (a) Relatively narrow β_1, no β_x; (b) indication of β_x but not measurable; (c) very broad β_{1x}, not resolvable.*

Compound	$SK\beta_1$	$SK\beta_x$	$SK\infty$	Diff. X.U.		Diff. volts	
MgS	5018.40	(a)	5005.3	13.1		6.44	
CaS	5019.00	(a)	5006.6	12.4		6.10	
SrS	5019.39	(b)	—	—		—	
BaS	5019.74	(b)	5007.5	12.2		6.00	
MgSO₄	5016.32	(a)	4987.3	29.0		14.3	
CaSO₄	5017.81	(b)	4987.7	30.1		14.8	
SrSO₄	5018.55	(b)	4987.3	31.3		15.4	
BaSO₄	5019.14	5016.0	4987.9	31.2		15.3	
Cu₂S	5020.9	5013.1	—	—		—	
CuS	5020.8	5013.0	5011.3	9.5	1.8	4.66	0.9
Sb₂S₃	5020.8	5015.5	5009.9	10.9	5.6	5.45	2.8
MoS₂	5019.8	(c)	5009.9	9.9	—	4.86	—
Ag₂S	5024.0	5015.0	5010.1	13.9	4.9	6.82	2.4
Bi₂S₃	5018.5	(c)	5010.3	8.2	—	4.02	—

[1] Faessler, Zeits. f. Physik **72**, 374 (1931); Lundquist, Zeits. f. Physik **89**, 274 (1934); Parratt, Phys. Rev. **49**, 14 (1936); McDonald, Phys. Rev. **50**, 694 (1936); Tazaki, Hiroshima J. Sci. **6**, 299 (1936).

[2] Valasek, Phys. Rev. **47**, 896 (1935).

[3] Stelling, Zeits. f. Physik **50**, 506 (1928).

[4] Lindh, Diss. Lund 1928, or Siegbahn, Spekt. d. R. S. 285 (1931).

Table I gives the gap $X-3p$ in electron volts. This is the internal ionization potential of the sulphur ion in the crystal and should give the threshold of the ultraviolet absorption and the photoelectric effect in the sulphides. In the sulphates, the electrons associated with the oxygen atoms will determine this threshold since they will be more loosely held due to the increased screening.

Because of the similarity in electronic and crystal structure, the energy bands of the alkaline earth sulphides must be similar to those of the alkali halides which have been described by Slater and Shockley.[5] Thus one may imagine the highest occupied $3s$ levels of sulphur to be displaced downward by an amount equal to the Madelung energy Ae^2/r and broadened upward. The location of the original level $3s$ of S^{--} (at very large interionic distances) is determined by the electron affinity of this divalent ion. This has never been directly determined but can be obtained by a quadratic extrapolation of ionization potentials in the isoelectronic sequence of which it is a member.[6] This includes K^+, A, Cl^-, S^{--}, the corresponding ionization potentials being 31.7, 15.7, 3.75. The extrapolation leads to an energy of -4.18 electron volts for the removal of one of the two extra electrons of the divalent sulphur ion. The negative sign indicates that the free divalent ion is unstable. Its existence in crystals is permitted by the increased binding contributed by the surrounding lattice. This is equal to the Madelung energy, Ae^2/r, and is quite large, 15.7 to 19.3 electron volts, in the case of the alkaline earth sulphides.

A comparison of Pauling's ideas in regard to the energy levels of crystals[7] with those of Slater and Shockley reveals striking differences, though for alkali halides the experimental data fit either theory. Referring to Fig. 1 of this paper, the energy difference denoted by E_c is given, according to Pauling, by the average potential, or electron affinity, in the crystal and can be calculated from the diamagnetic susceptibility by a simple semi-empirical formula. The values of E_c thus obtained turn out to be rather large: 5.69^v for NaCl and 7.01^v for BaS.

[5] Slater and Shockley, Phys. Rev. 50, 705 (1936).
[6] Glockler, Phys. Rev. 46, 111 (1934).
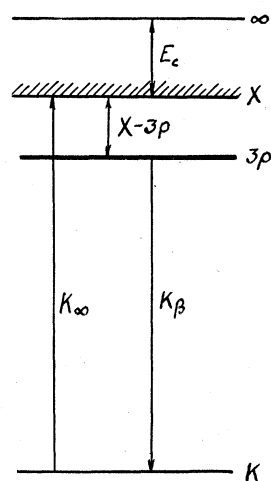[7] Pauling, Phys. Rev. 34, 954 (1929).

FIG. 1. X-ray levels in a crystal.

This would lead to an enormous difference between the internal and external photoelectric effect. Slater does not make E_c so large, for example, about 2 volts for NaCl, but he does not give a clear cut method for calculating this quantity. Another difference lies in the allocation of the occupied levels of the ions inside the crystal with respect to their positions in the free ions. Pauling displaces these occupied levels by only the Madelung energy, the shift being downward for the negative ions, upward for the positive. This equal shift of all levels preserves the differences between them and thus cannot account for the observed changes in wave-length of the x-ray emission lines, particularly those of the anions. While these changes are small in the alkali halides, they become quite large in the sulphates and sulphides, for example, as shown in Fig. 2. The treatment of the energy bands in crystals by Slater and Shockley suggests a possible solution. They consider the displaced levels to be broadened at the close interionic distances prevailing in the crystal, the broadening being in the opposite direction to the shift due to the Madelung term. In the case of the anion, the upward broadening of the $3p$ band and the higher continuum of their picture give nearly the same difference between the nearest edges of the two bands as one obtains by the formula of Pauling. Though Slater and Shockley's picture makes it possible to understand the changes in position and width of x-ray emission
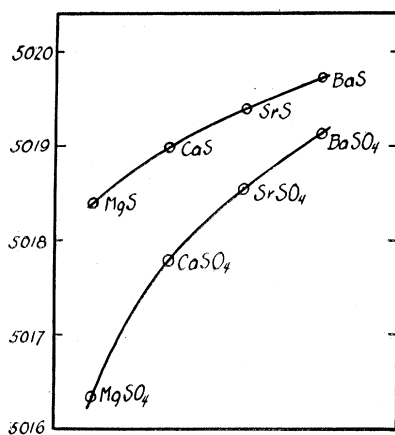
Fig. 2. Wave-lengths of the sulphur $K\beta_1$ lines in compounds.

lines of chemical compounds, the agreement with experiment would be better if the upward turn of the $3p$ band were not accompanied by so much broadening. In the case of NaCl discussed in their paper, the broadening is fully four times that observed.

Molybdenite, MoS_2, argentite, Ag_2S, stibnite, Sb_2S_3, and bismuthinite, Bi_2S_3, are semi-conducting sulphides. Their S $K\beta$ lines are quite broad and consequently difficult to measure accurately. The values given in Table I are probably correct to within 0.4 X.U. while the values for the other sulphides and sulphates are good to 0.15 X.U. Some of the broad lines of the semi-conducting sulphides can be resolved into two lines of approximately the same intensity. The upper level thus obtained is high enough so that its electrons may be raised into the X continuum by visible light. When only one line is observed, it is so broad that the upper edge of its $3p$ band is also close to X.

It is interesting to compare the x-ray spectra of sulphur in the alkaline earth sulphides with the corresponding results for the sulphates. The K absorption edges in the sulphates are harder by about 18.9 X.U. due mainly to the reduced screening resulting from the transfer of electrons from sulphur to the surrounding tetrahedral shell of oxygens. The $K\alpha$ lines are 3.3 X.U. harder in the sulphates.[8] This is an unusually large effect, especially since these are alpha lines. It is rarely surpassed even when the emission is due to a valence electron. On the other hand, the $K\beta$ lines in the sulphates are only 1 X.U. harder, on the average, than in the corresponding sulphides. This is evidence of a rather peculiar deformation.

It is sometimes assumed that sulphur has a valence of plus six in the sulphates. A classical interpretation of this would leave the sulphur with no $3p$ electrons and there would be no ordinary beta line in the x-ray spectrum. The exposure of the $2p$ shell would lead one to expect large shifts in the alpha lines. This agrees with observation, but the beta line appears in nearly its usual place and with fully as great intensity as in the sulphides where the $3p$ group of electrons is completed. It is also interesting that the beta line varies in wave-length from one alkaline earth sulphate to another to even a greater extent than in the corresponding sulphides, as shown in Fig. 2. This is another indication that the outer electron bands of a complex ion belong to the ion as a whole and thus deviate from those of the isolated ion as greatly as the electronic levels of molecules differ from those of the constituent atoms.

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[8] Parratt, Phys. Rev. **49**, 14 (1936).