Effect of Chemical Combination on the $K\beta_1$ Lines of Sulphur, Chlorine and Potassium*

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By using a special form of target, the $K\beta_1$ lines in the spectrum of the secondary x-radiation from a series of alkali halides and some alkaline earth sulphides have been measured. Combining the results with Stelling's values for the K absorption edges one readily finds values for the electron affinities of Cl^- and S^{--} and for the ionization potentials of K^+ as they exist in the respective crystals. Pauling's theory is used to reduce these values to those for the free ions. Good agreement with other data is obtained in the case of the chlorides, fair agreement in the case of the potassium compounds, and poor results in the case of sulphur. Possible causes for these discrepancies are suggested. The general method used in this work to obtain the spectra of compounds may find useful application in methods of chemical analysis by means of x-ray spectra.

THE change in wavelength of an x-ray emission line as a result of the state of chemical combination is usually very small even when the line involves the "optical" energy levels. The effect is best observed in the $K\beta$ lines of light elements such as sulphur, chlorine and potassium. However, practically all but the most recent data on this point are unreliable. This results from the use of the powdered substance rubbed into fine scratches on the surface of the target as the source of the radiation. Under the intense heat in the focal spot, the material reacts with the target metal and one thus observes the spectra of the products of the reaction. This difficulty can be overcome to a large extent by using a fluorescence method and by changing the substance frequently since even the x-rays dissociate the material in many cases. However, most of the recent investigations[1,2,3] employing a strict fluorescence method have been necessarily restricted to the strong $K\alpha$ lines. These do not show much displacement as a result of chemical combination and are not fundamentally as interesting as the $K\beta$ lines which are radiated when the most loosely bound electrons in the compound fall into a vacancy in the K shell.

The writer has been experimenting with a method which excites the spectra with sufficient intensity so that the $K\beta$ lines can be studied without much difficulty. As first developed and described,[4] the target was simply provided with a clamp which held the substance to be studied within a millimeter or two of the focal spot. The substances used at first were pieces of single crystal or mineral. Because of the difficulty in obtaining the materials and the purity desired, the compounds have lately been obtained as pure chemicals or prepared by precipitation from solution. The slightly damp powder is pressed into a semi-cylindrical "pill" and dried in vacuum. The compound is then placed under the clamp with its flat side toward the focal spot. With the form of target described, there is a troublesome background of direct radiation from the target which, in spite of care, becomes more or less contaminated with the material being studied. Consequently there is always at least a weak spectrum of the products of reaction with the target metal superposed on the spectrum it is desired to observe. To overcome this difficulty, the target was remodeled as shown in Fig. 1. The shield, *a*, attached to the side facing the spectrograph effectively prevents any radiation

Table I. *Wavelengths of reference lines.*

Line	Reference	Wavelength	Order
S $K\beta$	Ni $K\alpha_1$	1654.50	3
	Ni $K\alpha_2$	1658.35	3
Cl $K\beta$	W $L\alpha_1$	1473.36	3
K $K\beta$	Ni $K\alpha_1$	1654.50	2
	Ni $K\alpha_2$	1658.35	2
	Co $K\alpha_1$	1785.29	2
	Co $K\alpha_2$	1789.19	2

* A preliminary report was made at the Pittsburgh Meeting of the American Physical Society, December 28–29, 1934.

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

[2] Lundquist, Zeits. f. Physik **77**, 778 (1932); **83**, 85 (1933); **89**, 273 (1934).

[3] Yoshida, Inst. Phys. Chem. Research Tokyo, Sci. Rep. **421**, 298 (1933).

[4] Valasek, Phys. Rev. **43**, 612 (1933).
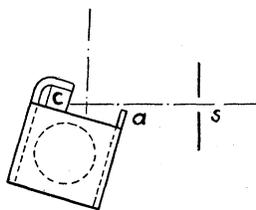
FIG. 1. X-ray target. c is a pressed block of the compound; a is a metal shield which screens the spectrograph slit s from the direct radiation from the face of the target.

except that from the compound, c, from entering the spectrograph, s. The spectrograph was of the Siegbahn vacuum type with a calcite crystal. The wavelengths were determined by measuring their distances from certain selected standard lines. These lines and their assumed wavelengths are given in Table I.

The results of measurements of the principal beta-lines are given in column four of Table II. In several cases weak satellites were observed and measured, but the data are as yet incomplete and not very accurate because of the faintness of these lines. It is planned to use a concave crystal spectrometer to finish the study of these weak lines. The compounds listed are all of the rare gas electron shell type and, except for CsCl, they all form crystals of the familiar NaCl type with the interionic distances given under R. The column headed K_∞ gives the wavelengths of the principal K absorption edges as measured by Stelling.[5] The fifth column gives the difference between K_∞ and $K\beta_1$ in X. U. $(10^{-11}$ cm), while the last column gives this difference expressed in electron volts.

These results give information in regard to the energy levels and photoionization frequencies of solids. If we let ν_K represent the K absorption frequency, and ν_β the frequency of the beta-line, then the difference

$$h\nu_K - h\nu_\beta = eV_M = h\nu_M$$

represents the energy required to remove an M electron from the ion in the crystal. These M electrons, it might be noted, constitute the outermost or rare gas shell of the ion. Thus one obtains a measure of the ionization potential or electron affinity of the ion in the crystal. Furthermore, the most easily removed electron which will belong to the negative ion, should determine

TABLE II. *Interionic distances and x-ray wavelengths.*

Compound	R	K_∞	$K\beta_1$	Diff. X. U.	Diff. volts
Sulphides					
MgS	2.595	5005.3	5018.40	13.1	6.5
CaS	2.84	5006.6	5019.00	12.4	6.2
SrS	2.935		5019.39		
BaS	3.175	5007.5	5019.74	12.2	6.1
Chlorides					
LiCl	2.57	4383.8	4394.57	10.8	6.9
NaCl	2.814	4384.1	4395.36	11.3	7.2
KCl	3.14	4385.0	4395.44	10.4	6.6
RbCl	3.285	4385.3	4395.24	9.9	6.3
CsCl	3.55	4387.4	4394.77	7.4	4.7
Potassium halides					
KF	2.665	3427.7	3447.16	19.5	20.3
KCl	3.14	3427.9	3446.98	19.1	19.9
KBr	3.289	3427.9	3447.34	19.4	20.3
KI	3.526	3427.7	3447.43	19.7	20.5

the photoelectric threshold of the crystal. There are presumably no free electrons in these crystals.

The values listed in the last column of Table II are these ionization potentials for the ions in the crystals. In most cases it is possible to reduce these values to those pertaining to the free ions and to compare the results with those obtained by independent methods. In order to make this reduction we will use Pauling's theory[6] on the effects of chemical combination on x-ray absorption edges and on photoelectric thresholds. According to Pauling, if the energy required to remove an electron from a free ion is represented by $h\nu_0$, then the energy required to remove the same electron when the ion is in a crystal lattice is

$$h\nu = h\nu_0 + e\phi - E_c.$$

Here $e\phi$ is the increase in binding energy of an electron due to the external screening effect of the surrounding ions and is approximately equal to the lattice energy. E_c is the electron affinity of the crystal and is proportional to the magnetic susceptibility of the crystal. It is closely related to the inner field in the Sommerfeld theory of electrical properties of metals. The sign and magnitude of E_c is the same for both ions in the crystal, while $e\phi$ is positive for a negative ion and negative in the case of the positive ion. Pauling[6] finds that the photoelectric threshold of the crystal, which is the energy required to remove an electron from the negative ion, is

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

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

affected by chemical combination to exactly the same extent as the K absorption edge of the negative ion. Thus there is no appreciable ionic deformation even in the ion in which it would most likely occur. However, most of the data on the wavelengths of the x-ray emission lines, Table II, show that there is some differential shift in the various energy levels but that this is small compared to the shift in the levels themselves.

As a specific example of the relation of Pauling's theory to the data given here, consider the Cl^- ion in KCl. The value of $e\phi$ is 7.98 electron volts and E_c is 5.2 volts. Thus the x-ray energy levels are shifted upward by $+2.8$ volts with respect to their locations for the free Cl^- ion. The emission of a $K\beta$ line by the K shell ionized Cl^- ion brings it to within 6.6 volts of its ground state, that is, to its M level. (Table II, last column.) This is the energy required to remove an electron from the outer rare gas shell of the Cl^- ion when it is in the crystal. If this state is also 2.8 volts higher than it would be in the case of free Cl^-, the electron affinity of free Cl is $6.6 - 2.8$ or 3.8 electron volts which is in good agreement with the accepted value of 3.7 volts. The other chlorides give equally good agreement as is shown in the last column of Table III where results of similar calculations are given.

In the case of the K^+ ion in KCl, the energy levels are all displaced by $-e\phi - E_c$ according to Pauling, or by 13.2 electron volts. This is a downward displacement of the levels for the ions in the crystal with respect to their positions for free ions. Now the x-ray data give 19.9 volts as

the ionization potential for the K^+ in KCl; consequently the ionization potential of free K^+ ions turns out to be 33.1 volts. This is farther from the accepted value of 31.7 for the second ionization potential of potassium than one may account for by experimental error in the x-ray data. It seems significant that all the values obtained in this way are quite uniformly high by about 1.5 volts.

In the case of the only sulphide for which the magnetic susceptibility could be found, namely BaS, the electron affinity of S^{--} comes out much too high, as is shown in Table III.

Several causes for these discrepancies may be suggested. In the first place, a point lattice of positive and negative charges is assumed in the derivation of the formula for the crystal potential $e\phi$ which contributes to the energy level shifts. A formula based on a distribution of electrons throughout space, which is more in accord with that existing, may give better results. Secondly, the M levels are not single levels and the use of only the strongest $K\beta_1$ line may lead to a calculated M level which is consistently higher than the lowest level. The multiplicity or fine structure of the M level may be partly due to the fields of the neighboring ions and thus be different for the different types of compounds. Previous study of the sulphur $K\beta$ lines[4] demonstrates the existence of such an effect. A more complete study of the entire pattern of the beta-lines of the compounds reported on here will be made with a focusing spectrograph.

The method described here for obtaining the x-radiation from compounds may find useful application in problems of chemical analysis along lines given by von Hevesy.[7] It seems to be an advantage to work with a pressed block of the material instead of a thin layer of the powder in intimate contact with a metallic background. The spectra obtained are more intense when the block is used, and one avoids the risk of chemical reaction with the metallic surface.

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TABLE III. *Electron affinities and ionization potential of ions.*

Substance	$e\phi - E_c$	$h\nu_K - h\nu_\beta$	El. Aff. (calc.)
Chlorine ion. Electron affinity $= 3.7$ volts			
LiCl	$+3.5$ v	6.9 v	3.4 v
NaCl	3.3	7.2	3.9
KCl	2.8	6.6	3.8
RbCl	2.6	6.3	3.7
CsCl	1.2	4.7	3.5
Potassium ion. Ionization potential $= 31.7$ volts			
KF	-13.0	20.3	33.3
KCl	13.2	19.9	33.1
KBr	12.9	20.4	33.3
KI	12.7	20.5	33.2
Sulphur ion. Electron affinity $= 2.06$ volts			
BaS	$+0.9$	6.1	5.2

[7] v. Hevesy, *Chemical Analysis by X-Rays and its Applications*, McGraw-Hill Book Company.