nuclei are known whose angular momentum is 9/2 in the ground state.

DISCUSSION

In order to avoid the large Δl calculated above, the 8.2-day period might be assigned to Ag^{105}. If this new assignment be made, a n-$3n$ reaction would be involved instead of the n-$2n$ process. Since neutrons of 6 to 10 Mev are more abundant in the $Li+d$ source than those of higher energies, the number of n-$2n$ reactions should in general, on purely energetic grounds, exceed the number of n-$3n$ reactions.[8] But the observations show that the 8.2-day silver is formed at a much greater rate than the 24.5-min. silver. Therefore the assignment to Ag^{105} seems unlikely. The most serious obstacle of all to this assignment is that the negative β-spectrum, which shows a normal energy distribution, would have to be attributed to Compton recoil electrons or that a new stable isotope Cd^{105} would have to be postulated.

Instead, the 24.5-min. period might be assigned to Ag^{105}. This period, however, has been obtained with neutron bombardment at energies as low as 10 Mev and the n-$3n$ reaction necessary in this case would be quite unlikely. Furthermore, one must assume that the 24.5-min. period is obtained from the reactions Cd-n-d and Rh-α-$2n$ instead of the suggested reactions Cd-n-p and Rh-α-n. Reactions of the types α-$2n$ and n-d have not so far been experimentally established.

Consequently, the data at present suggest more strongly that both the 24.5-min. and the 8.2-day periods should be assigned to Ag^{106}. If a very much stronger source were available, the 8.2-day γ-ray and positron spectra could be more accurately measured. The branching ratio of 20, obtained from the reactions Ag-n-$2n$, could then be checked by the following reactions: Cd-n-p, Pd-d-p and Rh-α-n. In the latter three reactions the 24.5-min. period and a long period (presumably the 8.2-day period) have been found but the intensity of the long period was too small to permit a reliable estimate of the branching ratio. However, the experiments are not in disagreement with the hypothesis that the branching ratio is about the same in all three reactions as would perhaps be required for the two periods to be isomeric.

The authors wish to thank Professor L. H. Thomas and Professor H. A. Bethe for helpful discussions regarding the theoretical aspects of this work.

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[8] Pool, Cork and Thornton, Phys. Rev. 52, 41 (1937); Walke, Phys. Rev. 52, 669 (1937).

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X-Ray Spectroscopic Data in Regard to the Electronic Energy Bands in Potassium and Sodium Chlorides

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The wave-lengths of several lines in the $K\beta$ group of Cl in NaCl and KCl, and of K in KCl, have been measured in the secondary radiation from pressed blocks of the salts. The results are discussed in terms of the electronic energy bands in these crystals. It is shown that certain of the weaker lines arise from transitions of valence electrons belonging to one of the ions into a K shell vacancy in the other ion. Some of the residual nondiagram lines seem to be related to the excited levels in irradiated crystals.

RECENT discussions of the electronic energy bands in crystals, of which NaCl has been treated in greatest detail,[1] make it of interest to examine the x-ray spectrum of compounds more closely in the light of these results. One obtains in this way supplementary information on the locations of the principal energy bands and the transitions which take place. There are, however,

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[1] Pauling, Phys. Rev. 34, 954 (1929); Slater and Shockley, Phys. Rev. 50, 707 (1936).

more lines than can be accounted for by the use of the energy diagram which has been given, and these indicate a needed extension of the theory.

Some time ago the writer measured the $K\beta_1$ lines of a series of alkali halides[2] using a secondary radiation method for producing the radiation. An application of Pauling's theory of the energy bands in solids left no doubt as to the origin of these lines. The present work is principally concerned with the weaker satellites which accompany the $K\beta_1$ line. The source of the radiation was improved somewhat by the use of a water-cooled clamp to hold the pressed pellet of salt just back of the focal spot on a water-cooled target. A tungsten screen in front of the target prevented direct x-rays from the focal spot from entering the spectrograph.

The exposures usually amounted to 100 hours at 5–10 ma and 15 kv which resulted in good intensity of the two satellites on the immediate short wave side of $K\beta_1$. In addition a number of very weak lines were observed. The locations of the three strongest lines $K\beta_1$, β_x, and β_5, were measured with respect to tungsten $L\alpha_1$ in the third order. In this way a redetermination of $K\beta_1$ was obtained as well as the new values for the other two lines. The results now given for $K\beta_1$ differ somewhat from those previously reported.[2] The present values are based on more measurements and on better exposed plates and were obtained by the use of two different calcite crystals.

Many weak lines were observed in addition to the three principal lines referred to above. These were difficult to measure accurately because they usually disappeared into the granular background when observed under the measuring microscope even when the lowest available magnification was used. Chemical intensification of the plates was attempted but did not prove to be satisfactory. It seemed best to locate these lines under a hand lens and to indicate their position by marking on the plate with a sharp pencil. These marks were carefully examined with the hand lens and only those which were apparently on the line were then measured with the micrometer microscope. The wave-lengths of these lines are probably correct to within 1 x.u. and they agree as well as can be expected with the values given by Tazaki[3] for the corresponding lines obtained by direct impact on a thin layer of the salt on an aluminum target. It was found that direct impact of electrons on powdered NaCl on Al gave a wave-length for Cl $K\beta_1$ which was less by about 0.5 x.u. than the values obtained from the secondary radiation. However, when lines other than β_x, β'', and β_5 were measured relative to $K\beta_1$ any shift with respect to this line due to the method of excitation was less than the experimental error in measuring these weak lines. Hence in order to obtain better values for these lines some plates were exposed to the direct radiation produced by direct electron impact on a salt coating over an aluminum target. These wave-lengths were then measured relative to the value for $K\beta_1$ as given by the secondary radiation method. The best plates were obtained when the current was reduced to one-half of a milliampere, the salt being changed after each two hours of exposure time. The total exposure was about forty hours.

TABLE I. *Wave-lengths of Kβ lines of Cl in NaCl.*

LINE	EXC.	WAVE-LENGTH x.u.	$\Delta\lambda$ x.u.	ΔV ev
η	*b*	4437	53	34
β'	*b*	4421	37	24
β_1	*a*	4394.90	11.0	7.1
β_x	*a*	4391.34	7.4	4.7
β_5	*a*	4385.6	1.7	1.1
β_{I}'''	*b*	4336.5		
β_{II}'''	*c*	4332		
β_{I}''''	*c*	4325		
β_{II}''''	*c*	4320		

The wave-lengths are given in Table I with the designations of lines following Siegbahn[4] and Tazaki.[3] The letters in the second column refer to the nature of the source used. The letter *a* indicates that the wave-lengths of the lines so marked were determined solely by measuring spectrograms of the secondary radiation from pressed blocks of the salt. Those marked *b* are averages derived from the former type of exposure supplemented by others in which direct electron bombardment of a salt film over an aluminum target was also used. The lines marked *c* were found only in the spectrum of the radiation from the latter type of source. Accord-

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

[3] Tazaki, Hiroshima J. Sci. **6**, 299 (1936).

[4] Siegbahn, *Spektroskopie der Roentgenstrahlen*, second edition (1931), p. 169.

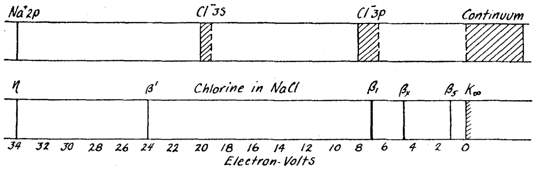

FIG. 1. Upper: electron energy bands of NaCl. Lower: K series emission lines of chlorine in NaCl on energy scale relative to the K absorption edge.

ingly these c values are repetitions of Tazaki's measurements and will be found to agree with them to better than one x.u., the estimated error. However, because of the nature of the source it is not certain that some of these lines may not be due to reaction products of the salt with the aluminum target. The chlorine $K\beta'$ line is so near tungsten $L\alpha_1$ in the third order (corresponding to $\lambda = 4420.08$) that it is no doubt shifted due to the slight amount of overlapping tungsten radiation. This line appears to be a bona fide chlorine line as measurements in the spectra of chlorine in both NaCl and KCl indicate characteristic differences.

The probable errors of the wave-lengths of the $K\beta_1$ lines are 0.07 x.u. for $K\beta_1$ of K, and of Cl in NaCl, and 0.14 for $K\beta_1$ of Cl in KCl. The wave-lengths given to tenths of x.u. are probably correct to 0.3 x.u. and the other weak lines are estimated to be within one x.u. of the correct value.

The column of differences $\Delta\lambda$ gives the distances of the lines from the K absorption edges of the elements considered. These differences were obtained by using Stelling's values:[5] 4383.9 for the K edge of Cl in NaCl, 4385.1 for Cl in KCl, and 3427.9 for K in KCl. The final column gives these differences in electron volts which is of convenience in discussing the energy levels.

Since the location of the K absorption edge is just beyond the $K\beta_5$ line, β''' and β'''' must be spark lines. These are most probably of the $KL-ML$ type analogous to those which are prominent as satellites of the $K\alpha$ lines of these elements. However, there is at present no satisfactory theory for these $K\beta$ satellites comparable to that which has been given by Wolfe[6] for the $K\alpha$ satellites. On the experimental side, Tazaki has shown that they fit the same semi-Moseley curves as the similar lines measured by Ford[7] and others in the spectra of the heavier elements.

The remaining lines are plotted on an electron-volt energy scale in Fig. 1 with the absorption edge as origin, from the values of ΔV of Tables I–III. In the case of those lines which arise from transitions in an atom originally lacking only a K electron, the locations of the lines on such a plot indicate the energy levels from which the radiating electrons come. These levels can then be compared with the calculated energy bands for the crystal. Accordingly, the x-ray emission spectrum is accompanied by an energy band spectrum for NaCl similar to that given by Slater and Shockley.[1] It is evident that the Cl $K\beta_1$ line must result from a $\text{Cl}^-\,1s-\text{Cl}^-\,3p$ transition so that the two spectra are made arbitrarily to coincide at this point. A very rough estimate of the width of the Cl $K\beta_1$ line is only one electron-volt, which is much less than the width of the $\text{Cl}^-\,3p$ level indicated by Slater and Shockley. The width shown in Fig. 1 agrees better with experiment. In addition to Cl $K\beta_1$ there is only one other possible diagram line, Cl $K\eta$, a very weak line, which is apparently due to the transition $\text{Cl}^-\,1s-\text{Na}^+\,2p$, i.e., due to a sodium $2p$ electron falling into a vacancy in the chlorine K shell. This improbable occurrence may be understood by consideration of the quantum-mechanical picture of the energy bands of the valence electrons as extending continuously through the lattice though naturally the wave-function has much higher values in the vicinity of ions of the class to which it belongs.

TABLE II. *Wave-lengths of Kβ lines of Cl in KCl.*

LINE	EXC.	WAVE-LENGTH x.u.	Δλ x.u.	ΔV ev
η	b	4437	52	33
β_{II}'	b	4424	39	25
β_I'	b	4418	33	21
β_1	a	4394.91	9.8	6.2
β_x	a	4391.16	6.1	3.9
β_5	a	4385.3	0.2	0.1
β_7	c	4375		
β_6	b	4368		
β_8	c	4359		
β_I'''	b	4438		
β_{II}'''	c	4333		
β_I''''	c	4326		

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[5] Lindh, *Roentgenspektroskopie* (1930), pp. 298–9, 302.

[6] Wolfe, Phys. Rev. **43**, 221 (1933).

[7] Ford, Phys. Rev. **41**, 577 (1932).

An examination of the K^+ and Cl^- spectra of KCl shows lines which support this conclusion. In Fig. 2 it is noted that the Cl $K\beta_I'$ line results from a $Cl^-\ 1s-K^+\ 3p$ transition and that the K $K\beta_5$ line is due to a $K^+\ 1s-Cl^-\ 3p$ transition. The superposition of corresponding lines in the two spectra is not exact. This seems to be principally due to the fact that they are plotted relative to Stelling's values for the respective absorption edges and that one of these, at least, should be revised. This is most probably that of Cl in KCl for which Stelling gives a wave-length of 4385.1 x.u. This value is out of line with those for Cl in the chlorides of the lighter and the heavier alkalis. An older measurement by Lindh[5] is 4382.9 which is correspondingly too low. An average of these two determinations gives very good agreement between the two spectra of Fig. 2.

The line in the spectrum of Na in NaCl which corresponds to K $K\beta_5$ is in a very different part of the x-ray spectrum but has been observed by Wetterblad.[8] Backlin[9] designated this line Na $K\beta_1$ and considered it to be of "semi-optical" origin, due to a combination between some excited optical level of Na^+ with its K level. He pointed out that normally Na^+ $(1s^2\ 2s^2\ 2p^6)$ has no occupied M level which is needed for the emission of the ordinary $K\beta_1$ line. The fact that this line appears was taken to indicate that transitions occur from a virtual or optical state. The marked deviation of the frequencies of this line from Moseley's law at Na, and also Mg, supports the anomalous origin of this x-ray line. The writer considers that the "optical state" postulated by Backlin is to be identified with the $Cl^-\ 3p$ electron energy band of the NaCl crystal and that Na $K\beta_1$ is a $Na^+\ 1s-Cl^-\ 3p$ transition analogous to the $K\beta_5$ line of potassium in KCl. Since the sodium ion has no M shell, this line becomes the principal line in the $K\beta$ group of Na in NaCl.

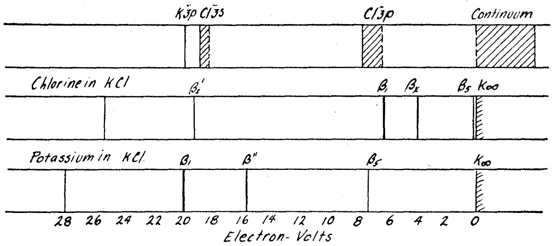

FIG. 2. Top: electron energy bands of KCl. Center: K series emission lines of chlorine in KCl on energy scale relative to the K absorption edge. Bottom: ditto, potassium in KCl.

TABLE III. *Wave-lengths of $K\beta$ lines of K in KCl.*

LINE	EXC.	WAVE-LENGTH x.u.	$\Delta\lambda$ x.u.	ΔV ev
η	*c*	3490	61	63
β'	*b*	3476	49	51
β_1	*a*	3447.00	19.1	19.9
β''	*a*	3442.95	15.0	15.6
β_5	*a*	3434.97	7.1	7.4
β_6	*c*	3416		
β_I'''	*b*	3404.5		
β_{II}'''	*b*	3396.4		
β''''	*c*	3375		

The remaining lines belong to the general class of "nondiagram" lines. They are not necessarily due to double ionization, though this is needed to account for the lines at shorter wave-lengths than $K\beta_5$. Optical absorption studies[10] support the conclusion that the transparent, perfect crystal has no other levels than the present theory indicates. However, by the action of radiation or other ionizing agents, it is possible to produce coloration[11] which indicates that new discrete energy bands arise from the neutralization of the charges on some of the ions in the crystal. Such bands may be involved in the emission of the $K\beta_x$ line of Cl and K, and of the $K\beta_5$ line of Cl. Since selection rules will permit only the combination of P and S states, the x-ray lines cannot be identified in Figs. 1 and 2, with the ground states for the F and U absorptions which must be S-like levels, though they may originate in the same general process. This interpretation requires further investigation.

The writer expresses his thanks to the Graduate School of the University of Minnesota for its generosity in supporting this investigation, and to Mr. Rolf Landshoff for his assistance with a considerable part of the laboratory work.

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[8] Wetterblad, Zeits. f. Physik **42**, 603 (1927).

[9] Backlin, Siegbahn and Thoraeus, Phil. Mag. **49**, 1320 (1925).

[10] Schneider and O'Bryan, Phys. Rev. **51**, 293 (1937).

[11] Hilsch and Pohl, Zeits. f. Physik **59**, 812 (1930); **64**, 606 (1930). Hughes, Rev. Mod. Phys. **8**, 294 (1936).