

cated. A promising experimental approach to the problem would be to vary the energy of the photoelectron by varying the energy of the x rays and to measure the continuous energy distribution of the electrons emitted during the atomic readjustment. We hope in the future to carry out such investigations.

*Note added in proof.* Most recently, the authors have reexamined the charge distribution of neon ions using a magnetic mass spectrometer. The large extent of ionization observed in the present experiment as compared with theory was confirmed, though the abun-

dances of the more highly charged ions were somewhat lower.

#### ACKNOWLEDGMENTS

The authors wish to thank Professor Bearden for the design of the special x-ray tube and Professor A. L. Wahrhaftig for valuable advice in the design of the spectrometer. We also like to thank Dr. R. A. Mann for discussions on the calculations of Auger transition rates and C. W. Nestor for programming the calculations.

### $K\beta$ Emission Spectra of Argon and KCl. I\*

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Measurements of the  $K\beta$  region of argon gas, and potassium and chlorine in KCl are reported. These spectra were obtained in fluorescence and recorded by means of a vacuum, two-crystal spectrometer using calcite crystals. Under high-energy fluorescent excitation, the chlorine spectrum differs only slightly from that obtained under electron bombardment. Differences, if any, in the potassium spectrum are not apparent. The argon spectrum does not seem to have been previously examined with sufficient resolution and intensity linearity to allow such comparison. The spectra are discussed together in an attempt to clarify some of the problems associated with the chlorine valence emission band.

#### I. INTRODUCTION

THE present work was undertaken in order to clarify certain features of the  $K$ -series valence emission band of chlorine in KCl. The problems of interpretation associated with spectra obtained in KCl have been extensively treated by Parratt and Jossem.<sup>1,2</sup> The extent to which difficulties associated therewith have affected interpretations of x-ray spectra in general may be seen in recent review articles.<sup>3,4</sup> In view of the considerable detail available in the references already cited, the motivation for this research will be only briefly described here.

#### A. The State of the Problem

The valence band in KCl arises principally from  $3p$  electrons associated with the chloride ion. Calculations due to Howland<sup>5</sup> indicate very little admixture of other symmetry types as one passes through the band. It

should therefore be possible to study this band by introducing  $K$ -shell vacancies on the chlorine sites and examining in detail the spectrum of radiation associated with filling of these vacancies by valence electrons. The importance of this spectrum for the understanding of x-ray spectra in solids derives from the simplicity of the theoretical expectations and the position of KCl as a typical ionic crystal.

The required inner shell vacancies can readily be produced by means of photons or electrons of sufficient energy. Electron excitation, by reason of its efficiency, has been used in previous studies involving sufficient resolution to warrant consideration here. In this case, the spectrum is obtained from a thin layer of the salt deposited on a metal anode, typically by vacuum evaporation. Results of such a measurement have been most recently described by Porteus.<sup>6</sup> The data do not differ significantly from those reported in Ref. 1. The results of correction for instrumental and  $K$ -state lifetime broadening are shown in Fig. 1 of Ref. 6. Principal features are the intense line,  $K\beta_{1,3}$  and its smaller companion  $\beta_x$ . Most discussions of this spectrum have considered  $\beta_{1,3}$  as the valence emission band which was sought, and  $\beta_x$  as a satellite or satellite complex.<sup>7</sup>

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<sup>1</sup> L. G. Parratt and E. L. Jossem, *Phys. Rev.* **97**, 916 (1955).

<sup>2</sup> L. G. Parratt and E. L. Jossem, *Phys. Chem. Solids* **2**, 67 (1957).

<sup>3</sup> L. G. Parratt, *Rev. Mod. Phys.* **31**, 616 (1959).

<sup>4</sup> C. H. Shaw, in *Theory of Alloy Phases* (American Society of Metals, Cleveland, 1956), p. 13.

<sup>5</sup> L. P. Howland, *Phys. Rev.* **109**, 1927 (1958).

<sup>6</sup> J. O. Porteus, *J. Appl. Phys.* **33**, 700 (1962).

<sup>7</sup> The term "satellite" is reserved here for those transitions involving multiple vacancy states. This departs slightly from conventional usage (Ref. 3), where this term is reserved for the case of multiple *inner-shell* vacancies.

Alternative identifications have been suggested. One would have it that  $\beta_x$  is the valence band and  $\beta_{1,3}$  an emission from some impurity-type state occasioned by the presence of the inner shell vacancy. Another retains  $\beta_x$  as a satellite complex, but considers  $\beta_{1,3}$  as predominantly an emission from some sort of "excitation state" (in the terminology of Ref. 3, a "vec" state). In this view, the valence emission band, if present, is obscured by these features.

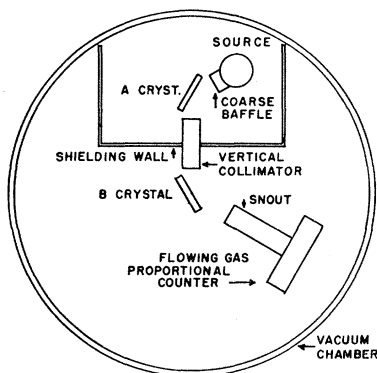
## B. Outline of Present Work

In view of the problems associated with interpretation of the spectrum of KCl, it seemed desirable to reexamine it using fluorescent excitation. In this type of excitation, the target, although certainly subject to radiation damage, is less disturbed than in the case of electron-bombardment excitation.

A qualitative investigation of differences in the electron- and photon-excited radiations from KCl was made by Valasek.<sup>8</sup> His negative result is not sufficiently precise for our purposes. Accordingly, the first experimental investigation reported here repeats Valasek's experiment using a high-resolution instrument and more precise intensity registration. For large photon energies we obtain a small, positive effect distinguishing the over-all spectra as obtained under electron and photon excitation. This, it turns out, is due to multiple vacancy processes and can be made quite large as is shown in the following paper, hereinafter designated II.<sup>9</sup> The results obtained here, however, generally confirm those obtained earlier.

The next question which is raised by the difficulties in interpretation of the observed spectrum is just where the solid-state effects are in the chlorine spectrum as obtained in KCl. We may approach this question by asking what is the spectrum obtained from the corresponding free ion. Careful comparison of these spectra would be expected to be quite informative. The experiment cannot be literally carried out at the present. We can, however, closely approximate it by a study of the corresponding emission spectrum from free atoms of argon

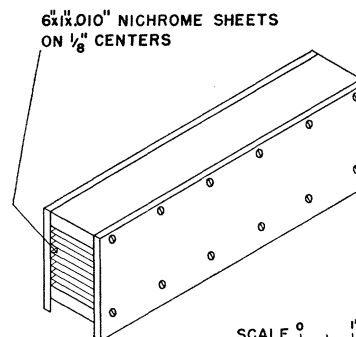
FIG. 1. Schematic diagram of the interior of the vacuum spectrometer. The plane of this figure is the plane of dispersion of the instrument.



<sup>8</sup> J. Valasek, Phys. Rev. 47, 896 (1935).

<sup>9</sup> R. Deslattes, following paper, Phys. Rev. 133, A399 (1964).

FIG. 2. Vertical-divergence-limiting collimator used between the crystals.



which is isoelectronic to the  $\text{Cl}^-$  ion. Results of such measurements are presented below. The similarity of this spectrum to that obtained from chlorine in KCl suggests that we should seek an atomic model for the grosser features of both spectra. For the purposes of testing such a model and for additional reasons indicated below, the isoelectronic sequence is extended by fluorescent measurement of the corresponding spectrum from  $\text{K}^+$  in KCl.

The main conclusion of II is the identification of at least most of  $\beta_x$  as a  $KM$  satellite complex and the probable extension of this identification to the analogous high-energy companions in the argon and  $\text{K}^+$  spectra. Thus, the concluding section of the present report deals with  $\beta_{1,3}$  and its possible relation to the valence band in KCl. In this we consider two additional pieces of evidence regarding its width and shape. The first of these allows us to approach the width question without intervention of an unfolding procedure by a comparison of  $K\beta_{1,3}$  from argon and  $K\beta_{1,3}$  from  $\text{Cl}^-$  in KCl. Small corrections are required to the argon spectrum to allow us effectively to infer that of free  $\text{Cl}^-$ . The second of these follows from identification of the cross transition in which a valence electron fills a potassium inner vacancy; its width and shape are compared with those obtained in the preceding ways.

## II. EXPERIMENTAL ARRANGEMENT

A plan of the experiment is shown in Fig. 1. The fluorescent source is illuminated from above by the primary x-ray beam. The divergence of the fluorescent and scattered radiation directed toward the  $A$  crystal is restricted by a coarse baffle, consisting of a cluster of  $\frac{1}{8} \times \frac{1}{8}$ -in. openings, 1 in. in length. Radiation diffracted and scattered by the  $A$  crystal next encounters the vertical Soller<sup>10</sup> collimator which is indicated.

The primary function of the collimator, Fig. 2, is to permit the use of large area sources while restricting the vertical divergence as is required by consideration of geometrical resolving power.

Radiation from the collimator is analyzed by the  $B$  crystal and detected by a large, flowing-gas proportional counter. The standard argon-methane mix was used

<sup>10</sup> W. Soller, Phys. Rev. 24, 158 (1924).

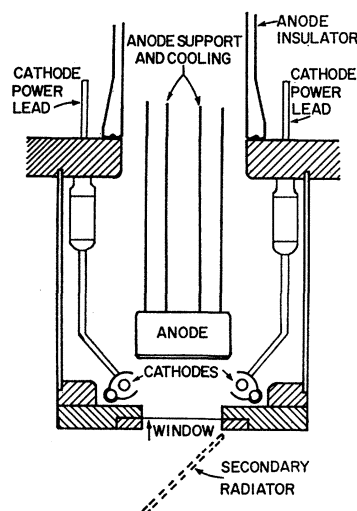


FIG. 3. Cross section of source showing disposition of primary and secondary radiators. The useful beam proceeds from the secondary radiator to the left in the figure.

and subsequent pulse handling was fairly conventional. Since the individual experiments are quite long (typically, 200 h), they were carried out by means of automatic devices, and the results stored in punched tape for subsequent computer reduction. Some of the experimental details are described in the following paragraphs.

### A. The Spectrometer

The vacuum two-crystal spectrometer is an adaptation of the bent crystal instrument (BXI) described by Jossem and Parratt.<sup>11</sup> The internal details of BXI were removed leaving only the precision worm-driven shaft originally used for the counter drive. The *B* crystal is mounted on this shaft. Its angular position can be determined through the worm to an accuracy of  $\pm 2$  sec of arc, but the precision of small motions is better by about an order of magnitude. The *A* crystal is located at the position of the bent crystal in BXI and mounted on a large, precision rollerbearing which has been heavily preloaded. This provides a stable platform but it is driven by only a fairly crude worm. In practice, the *A* crystal is positioned roughly ( $\pm 0.1$  deg) and the parallel position found by rotating the *B* crystal. From this origin, the *B* crystal may then be rotated to the "plus" position and the energy scale is thus established. Thereafter, the *A* crystal cannot be moved without returning to the minus position to see where it is. This cumbersome arrangement was dictated by expediency and places the instrument at a considerable disadvantage relative to a well-designed two-axis<sup>12</sup> or Ross<sup>13</sup> instrument.

The source rotates about the *A* crystal in the manner described in Ref. 10. Detector motion is secured by mounting the counter arm on a double-race ball bearing concentric with the *B* axis. Control of all motion is available from outside the spectrometer vacuum.

<sup>11</sup> E. L. Jossem and L. G. Parratt, *Phys. Rev.* **79**, 210 (1950).

<sup>12</sup> L. G. Parratt, *Phys. Rev.* **54**, 99 (1938); H. Schnopper, dissertation, Cornell University, 1962 (unpublished).

<sup>13</sup> P. A. Ross, *Phys. Rev.* **39**, 550A (1932).

### B. X-Ray Source

The source for the experiments reported here consists of a primary x-ray tube and a secondary radiator. The primary x-ray tube was built by Liefeld.<sup>14</sup> It is shown schematically in Fig. 3. The target is a thin copper disk which is coated, usually by evaporation, with other materials. The focal spot is roughly square (two contiguous rectangles) and has approximately 1-in. sides.

The secondary radiators are mounted below the primary x-ray tube. The dotted lines in Fig. 3 indicate the position of a solid target. In the case of gas spectra, a cell such as shown in Fig. 4 is sealed to the bottom of the primary tube by means of the indicated O-ring. In either case it is necessary that the secondary radiator be as thin as intensity requirements permit in order that the background scattering remain small.

### C. Power Supply

The high-voltage source is that described by Parratt and Trishka<sup>15</sup> except for the following changes: (1) The KC-4 kenotrons were replaced by oil-immersed type ML-141 kenotrons because of a significant radiation hazard at the voltages used in this experiment. (2) The regulator was replaced by a double-loop system. The inner loop, similar to that described by Pepinsky and Jarmotz,<sup>16</sup> uses paralleled 450th tubes for the control element. The outer loop contains a slow servo system (velocity drive) which continuously adjusts the primary voltage to null any control error. This arrangement provides excellent long-term stability and permits the series tubes to be operated at their maximum power dissipation. Over-all performance is such that no variation, short or long term, above 0.01% is experienced.

Power supplied to the x-ray tube cathode is adjusted to maintain constant emission by means of a circuit sim-

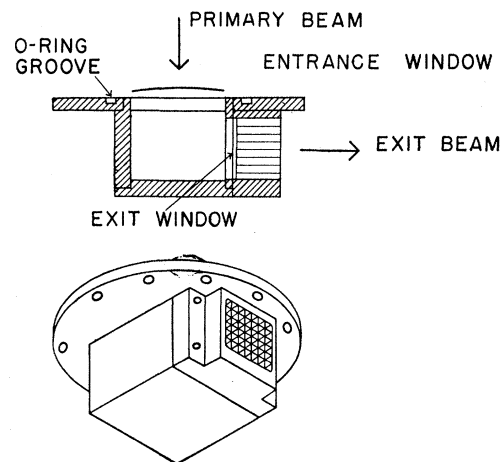


FIG. 4. The gas cell is shown with an attached coarse baffle.

<sup>14</sup> R. J. Liefeld, *Bull. Am. Phys. Soc.* **6**, 284 (1961).

<sup>15</sup> L. G. Parratt and J. W. Trishka, *Rev. Sci. Instr.* **13**, 17 (1942).

<sup>16</sup> R. Pepinsky and P. Jarmotz, *Rev. Sci. Instr.* **19**, 247 (1948).

ilar to that used by LeMieux and Beeman,<sup>17</sup> with the following modifications: (1) Thyatron loading tubes are used as suggested by Allenden<sup>18</sup> in order to retain control at high-power loads. (2) A high-performance operational amplifier<sup>19</sup> with feedback networks providing integral plus derivative control is employed. (3) Reference current is obtained from a cascaded Zener regulator. The performance is such, that when averaged for periods in excess of one second, the changes in current do not exceed 0.1%

#### D. Data Acquisition

The simple, repetitive operations required in point-by-point measurements of x-ray spectra are readily automated. For the case of the emission experiments reported here, it is required only to move alternately the *B* crystal in an incremental fashion and record the counting rate. Selection of these operations is done in a simple sequential programmer. The intensity and angular data are punched into paper tape and the subsequent data reduction accomplished in a computer. In parallel with the punch storage, the count data are displayed on an incrementally advanced strip chart through a digital-to-analog converter. The resulting histogram is a rather effective monitor of the over-all system performance and serves in addition to make preliminary results available at an early stage in the measurement.

#### E. Crystals

A calcite plate of unknown origin was cleaved and chemically polished. The full widths at half-maximum for the various rocking curves are given in Table I.

### III. EXPERIMENTAL RESULTS—TYPICAL SPECTRA AT LARGE EXCITATION ENERGIES

In this section, experimental data are presented for the isoelectronic sequence Cl<sup>-</sup>, Ar, and K<sup>+</sup>. The results chosen for discussion here were obtained with fairly large energy excess over threshold ( $\approx 20$  Ry). There is a general resemblance between such data and that obtained under electron bombardment. The differences, however, are significant as discussed at length in II. It

TABLE I. Experimental conditions.

Spectrum	Cl <sup>-</sup>	Ar	K <sup>+</sup>
Secondary radiator	KCl (0.2 mm)	Gas (150 mm Hg)	KCl (0.2 mm)
Primary anode	Ag	Sn	Ti
Energy of main line (keV)	2.815	3.192	3.589
$W_{1,-1}$ (sec)	41	30	23
Dispersion (sec/eV)	155	107	79
Step size (sec)	8	6	8
XRT voltage (kV)	20	20	20
XRT current (mA)	70	150	135

<sup>17</sup> A. F. LeMieux and W. W. Beeman, Rev. Sci. Instr. **17**, 130 (1946).

<sup>18</sup> D. Allenden, J. Sci. Instr. **36**, 66 (1959).

<sup>19</sup> G. A. Philbrick, Inc., Model U. S. A.—3.

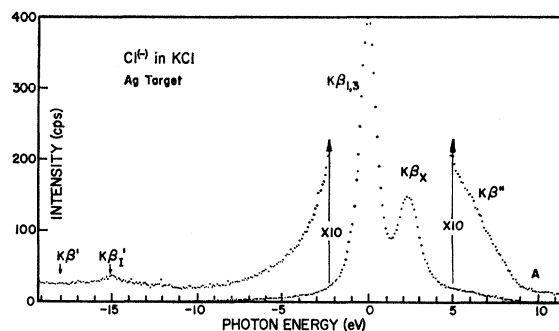


Fig. 5. The  $K\beta$  region of Cl<sup>-</sup> in KCl. Dots represent averaged raw data. The zero of energy coincides with the peak of  $K\beta_{1,3}$ . This spectrum was obtained using a silver primary anode and differs only slightly from that shown in Ref. 1.

is also shown there that, for other choices of primary energy, greater differences in the appearance of these spectra may be expected and such differences demonstrated in the case of the Cl<sup>-</sup> spectrum.

Historical nomenclature is used here for all the spectral features to be discussed. In the case of the argon spectrum a new emission has been observed; its designation is made to conform as closely as possible to such usage.

#### A. Cl<sup>-</sup> $K\beta$ Region in KCl

Experimental results obtained on this spectrum excited by primary radiation from a silver target are shown in Fig. 5. Operating conditions are summarized in Table I.

The main line  $\beta_{1,3}$  is an unresolved doublet arising from the splitting of the  $2P_{1/2}^0$  and  $2P_{3/2}^0$  states of the  $3p^5$  configuration. This splitting amounts to<sup>20</sup> 0.11 eV and is not discerned in the present data. The structure appearing on the low-energy side and designated  $\beta'$  is generally regarded as a satellite. Its origin and relation to other satellites of similar designation are obscure<sup>21</sup>; it will not be discussed further except to note that  $\beta_1'$  appears where one would expect to see the Cl<sup>-</sup> 3s band. The first high-energy companion to the main transition,  $\beta_x$ , is clearly complex (see II). Following  $\beta_x$  there is apparent in Fig. 5 a region in which the intensity does not decrease in a way easily attributable to the combined tails of  $\beta_{1,3}$  and  $\beta_x$ . From this it has been customary to infer the presence of another satellite component designated  $\beta''$ . This region is further investigated in II. The effects of self-absorption are apparent in the region marked *A* and what follows to higher energies.

The statistical precision of the data of Fig. 5 is quite high. There are, for example, in the case of the central region shown in Fig. 5 no statistical uncertainties as large as 1% of the peak intensity. The accuracy of the

<sup>20</sup> C. E. Moore, Natl. Bur. Std. Circ. (U. S.) No. 467, Vol. I, p. 195, June (1949).

<sup>21</sup> The literature on this is extensive but see: K. Tsutsumi, J. Phys. Soc. Japan **14**, 1696 (1959) and references cited therein.

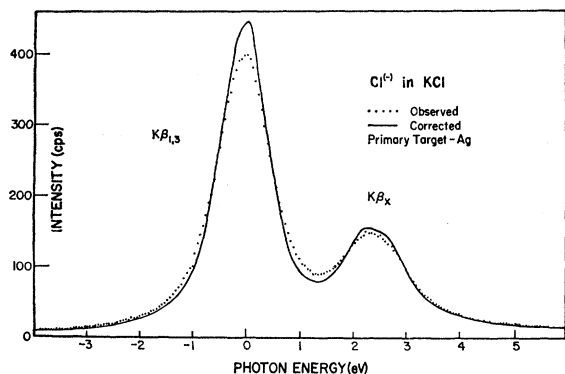


FIG. 6. Central region of Fig. 5. Averaged raw data and results of correction for instrumental broadening are shown.

data is another matter. In the tail region, the response of the instrument falls off due to "beam walking" which distorts the relative intensities of the more remote features. Experimental tests indicated that this effect might give rise to as much as 20% error in the peak height of  $\beta'$  relative to  $\beta_{1,3}$ . Similar considerations also apply at an equal distance to the high-energy side of the main line. Neither effect is of much relevance to the present discussion since at this distance from the main line, statistical uncertainties are already of this magnitude.

Another source of error in the spectrograms arises from the effects of radiation damage. A fresh crystal became heavily colored within a few hours. The more copious production of  $F$  centers at the entrance face for the primary beam resulted in mechanical deformation of the thin sample during the experiment. Careful comparison of spectrograms taken after various periods of irradiation showed differences in the central region which were slightly beyond statistical uncertainties. Hence, the intensity contours of Fig. 5 are those characteristic of a KCl crystal with an equilibrium concentration of defects at room temperature, or slightly above, under the primary beam conditions given in Table I. These contours may differ from a hypothetical contour at zero flux by as much as a few percent. Because of the interpretational difficulties of the spectrum itself, this uncertainty is not considered serious. If there occurs in the future some detailed theoretical model for this emission band, then the measurements must be repeated with frequent or continuous annealing and/or bleaching of the defects.

The dominant residual errors in the spectrogram of Fig. 5 are the effect of instrumental smearing and self-absorption in the target. The required corrections must, of course, be performed in the order just given since the self-absorbed spectrum is that which is seen by the instrument. Correction to the central region of Fig. 5 was carried out by means of a procedure described in the Appendix. The results are shown in Fig. 6. Two features are of special importance. First, the corrected width of the main line at half-maximum is  $1.15 \pm 0.05$  eV. Second, one can observe from the figure the enhanced complexity of  $\beta_x$ .

There is an "excess" intensity between  $\beta_x$  and  $\beta_{1,3}$ . In the past, a presumed symmetrical  $\beta_{1,3}$  has been subtracted from the observed contour and a low-energy protuberance developed on  $\beta_x$ .<sup>1</sup> If, instead a relatively smooth  $\beta_x$  low-energy tail is subtracted from the observed contour, then a high-energy protuberance develops on  $\beta_{1,3}$ . The resulting base width is consistent with the theoretical density of states but the shape and full width at half-maximum are not.

It is necessary to emphasize that this spectrum does not give the most probable representation of the valence emission band (if this is the origin of  $K\beta_{1,3}$ ), due to the presence of almost degenerate satellite radiation as discussed in II. The extent of the differences may be appreciated by comparison with Fig. 7 which was obtained using a palladium target as the source of primary radiation. In this case, the full width at half-maximum, after correction for instrumental broadening, is  $1.00 \pm 0.05$  eV. Figure 7 gives, within present technical limitations, the most probable contour for  $K\beta_{1,3}$ .

### B. Argon— $K\beta$ Region

The spectrum of x-ray fluorescence from an argon gas target at low pressure is shown in Fig. 8. Operating conditions for these measurements are summarized in Table I.

The spectrum of the  $K\beta$  region of argon has been previously observed only in a gas discharge using photographic registration and a bent crystal instrument.<sup>22</sup> The expected doublet separation in the main line is 0.18 eV (Ref. 20, p. 216), and hence, it is not revealed as a doublet in this experiment.

Possible weak emission features were found in the low-energy tail region 17 and 35 eV below the main line. The first feature on the high-energy side of the main line was designated  $\beta^V$  by Nilsson and Slatis.<sup>22</sup> The evident complexity of this feature was not apparent in the earlier observations. As discussed further in II, it seems to be a

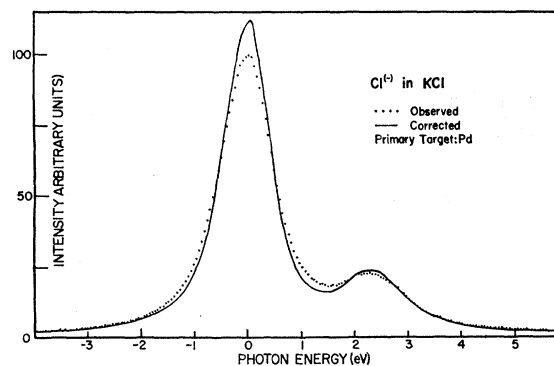


FIG. 7. Same spectrum as Fig. 6, except that the silver target was replaced by palladium. The results of II suggest that if it were possible to reduce the excitation energy still more (while remaining above threshold) further alterations might be observed.

<sup>22</sup> A. Nilsson and H. Slatis, Arkiv Mat. Astron. Fysik, Bd. 31A, 1 (1944).

complex of satellite transitions. The next feature as we proceed to higher energies in Fig. 8 has not been previously reported. It is designated  $\beta''$  on the basis of energy systematics and a consideration of a consensus of the terminology for the satellites at higher atomic numbers.

Evidence for the validity of the argon  $\beta''$  feature may be summarized as follows: It is not precluded by previous observations<sup>22</sup> owing to their lower sensitivity (e.g.,  $\beta^V$  is barely discernible in the spectrograms of Ref. 22). There is no known line (even in second order) in other elements which would not be distinguishable from this one.<sup>23</sup> In the way of positive evidence,  $\beta''$  has appeared in all argon spectrograms recorded in this research. It has appeared with constant intensity relative to  $\beta_{1,3}$  over a range of cell pressure from 100 mm to 1 atm. It appeared again with the same constancy under several different operating conditions for the primary x-ray tube.

The next feature (labeled A in Fig. 8) which is encountered on the high-energy side represents the effect of self-absorption in the gas target. It is a large effect in this case owing to the gas between the effective source position and the cell window.

The statistical precision of the data in Fig. 8 is again quite high—better than 1% of the peak intensity. There are, however, a number of systematic errors which limit the accuracy attributed to this spectrum. The effects of falling off of instrument response are covered by the remarks made in discussing the chlorine spectrum. The radiation damage question however does not arise in the same form. As a caution against building up high concentration of impurities or metastables, the gas was supplied from a continuous flow system. The flow rate was 1 cc/sec and the chamber volume 50 cc so that the target was replenished about once a minute. The pressure stabilization system was not very satisfactory and drifts attributable to this source appear in the data increasing its uncertainty beyond statistical expectations (approximately a factor of 2).

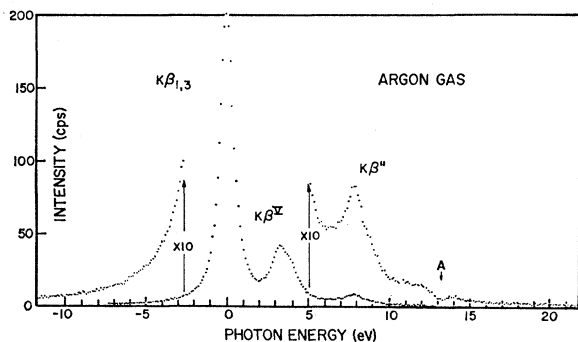


FIG. 8. The  $K\beta$  region of argon gas, averaged raw data. The zero of energy is at the peak of  $K\beta_{1,3}$ .

<sup>22</sup> Y. Cauchois and H. Hulubei, *Tables de constantes et donnees numeriques I. Longueurs d'onde des emissions x et des discontinuités d'absorption x* (Hermann & Cie, Paris, 1947).

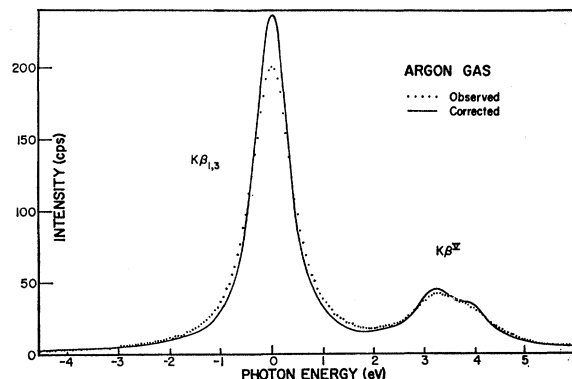


FIG. 9. Central region of Fig. 8. Averaged raw data and the results of correction for instrumental broadening are shown.

Finally, serious objections can be raised to the use of an argon counter in recording this spectrum. Its use was dictated by the requirements of using a flowing gas counter for long-term stability. Economic considerations precluded flowing a more appropriate counting gas. To minimize the effect of changes in counter sensitivity at the absorption edge, it was operated at a high pressure (0.7 atm) where the change in efficiency for the 2-in. counter amounts to only a few percent. This high-pressure operation increases background and sensitivity to second-order radiation. In spite of this precaution, the spectrogram should not be considered accurate in the region of the edge. In the vicinity of the main transition and  $\beta^V$ , there should be no effect except that of increased (uniform) background.

The dominant residual error in the spectrogram of Fig. 8 is the effect of instrumental smearing. Correction for this effect was carried out as discussed in the Appendix. The results are shown in Fig. 9. The resulting full width at half-maximum is  $0.80 \pm 0.05$  eV. This, it must be recalled, included the  $2P_{1/2}^0 - 2P_{3/2}^0$  splitting which amounts to 0.18 eV. Its effect owing to the expected intensity ratio probably accounts for 0.1 eV in the above width. One would therefore estimate the lifetime width of the  $K$  state (that for the  $M_{II,III}$  state being considered negligible) as  $0.70 \pm 0.05$  eV.<sup>24</sup> This is in close agreement with the estimates of  $0.64 \pm 0.03$  eV from the absorption data.<sup>25</sup>

### C. $K^+$ , $K\beta$ in KCl

The x-ray fluorescence potassium  $K$  spectrum from KCl excited by primary radiation from a titanium anode is presented in Fig. 10. Operating conditions are given in Table I. The coarser step size, about 0.1 eV (rather than

<sup>24</sup> Preliminary measurement of the  $K\alpha$  region of the argon spectrum give for  $K\alpha_1$  a full width at half-maximum of  $1.25 \pm 0.05$  eV. This may be compared with the observed width of  $K\beta_{1,3}$  ( $0.98 \pm 0.02$  eV) to obtain an upper bound of  $0.25 \pm 0.1$  eV for the width of the  $L_{III}$  state.

<sup>25</sup> T. Watanabe, *Theory of the X-Ray K Absorption Spectrum of Argon*, Research Rept No. 12, AFOSR-2254, April 1962 (unpublished).

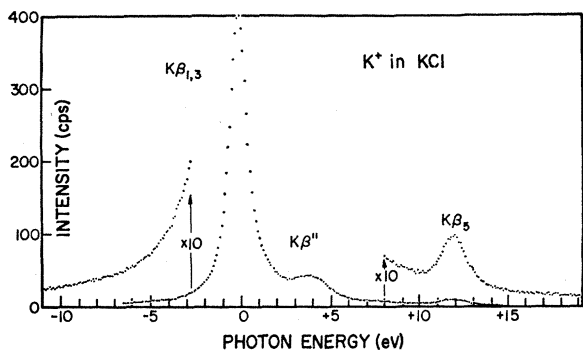


FIG. 10. The  $K\beta$  region of  $K^+$  in  $KCl$ . The zero of energy is at the peak of  $K\beta_{1,3}$ . As discussed in the text,  $K\beta_5$  might be absent in the spectrum of free potassium.

half this as in previously presented data) reflects the lesser amount of interest attached to details of this spectrum.

The main line  $K\beta_{1,3}$  contains a doublet separation for the final-state hole configurations of 0.27 eV.<sup>26</sup> The low-energy tail region appears devoid of structure in the region studied. The first high-energy structure, labeled  $\beta''$  by convention is suggested by the arguments of II to be a satellite complex, similar in origin to  $\beta_x$  and  $\beta^V$  seen in the previous spectra.

The next spectral feature, which is labeled  $\beta_5$  in previous work, requires careful consideration. It is now argued that this feature is due to the cross transition of electrons from the predominantly chlorine  $3p$  band filling  $K$ -shell vacancies on the potassium sites. This identification is in agreement with Valasek's suggestion.<sup>27</sup> Evidence in support of this view is as follows: In the spectrum of metallic potassium, no such line appears<sup>28</sup>; more precisely, if it is present then its peak intensity is no more than 10% of that of the line obtained in  $KCl$ . (The possibility that the transition becomes extremely diffuse in going from  $KCl$  to metallic potassium cannot be ruled out by inspection.) According to the results of II, no satellite is expected there either on the basis of the analysis or a consideration of the empirical results in neighboring elements. The energy of this emission measured from the  $\beta_{1,3}$  peak is in good agreement with Howland's calculation.<sup>5</sup> The observed peak to peak interval is  $12.0 \pm 0.1$  eV, that calculated 11.7 eV. The width at half-maximum is also comparable to Howland's expectations.<sup>5</sup> The intensity expected in the "cross-transition" relative to that in the main band ( $K$ ,  $K\beta_{1,3}$ ) may be readily estimated. According to Howland's calculation for the potassium  $3p$  band, there is very small admixture of other ionic orbitals. On the other hand, there is about 10 to 15% amplitude of  $K$   $3p$  orbitals appearing in the  $Cl$   $3p$  band wave function.<sup>29</sup> If the total relative inten-

<sup>26</sup> Reference 20, p. 232.

<sup>27</sup> J. Valasek, Phys. Rev. 47, 896 (1935); 53, 274 (1938); 58, 213 (1940).

<sup>28</sup> E. L. Jossem and L. G. Parratt, Phys. Rev. 98, 1151A (1958).

<sup>29</sup> L. P. Howland, Ph. D. thesis, Massachusetts Institute of Technology, 1957 (unpublished).

sity for the cross transition is due to this admixture then we would expect it to be 1 to 2% of the parent. This is in quite reasonable agreement with the experimental result of 1.5%.

Precision and accuracy considerations for the  $K^+$  emission spectrum are similar to those given in connection with the  $Cl^-$  spectrum except for the following: there appear in the data no effects which could be attributed to possible radiation damage perturbations of the spectrum. There is no self-absorption shape correction required in the spectral region of Fig. 10.

As in the previous spectra the dominant error in Fig. 10 is caused by instrumental broadening. This effect is removed as described in the Appendix and the resulting spectrum is shown in Fig. 11.

The corrected full width at half-maximum is  $1.03 \pm 0.04$  eV. The profile still includes the  $2P_{1/2}^0 - 2P_{3/2}^0$  splitting of the final state which probably accounts for about 0.2 eV. When this is subtracted from the above one obtains  $0.80 \pm 0.05$  eV for the sum of the  $K$ -state and  $M$ -state widths.

#### IV. DISCUSSION

Anticipating the results of II, this discussion does not consider the high-energy satellite companions of  $K\beta_{1,3}$ . An exception to this is the  $K^+$   $K\beta_5$  in  $KCl$  which, as argued above, is not necessarily a satellite. Our principal concern here will be what can be asserted about the width and shape of the  $3p$  band of  $Cl^-$ .

Evidence purporting to deal with this question is now available from three sources. The first is that given in Ref. 3. According to this source the full width at half-maximum of  $\beta_{1,3}$  corrected for instrumental and lifetime broadening is 0.6 eV. The shape is not that expected on the basis of Howland's calculation.

The next approach follows fairly directly from the present work. The argon band width, corrected for instrumental broadening only, is 0.70 eV. Assuming a  $Z^2$  dependence for the state width and neglecting the change in the  $2P_{1/2}^0 - 2P_{3/2}^0$  splitting from argon to chlorine, we may infer a bandwidth of 0.60 eV for the free ion  $Cl^-$ .

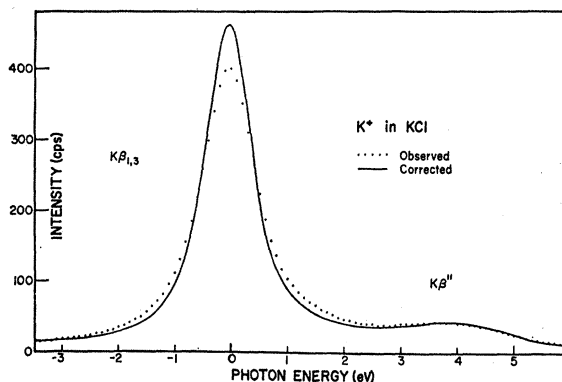


FIG. 11. The central region of Fig. 10. Averaged raw data and the results of correction for instrumental broadening are shown.

When this is compared with the Cl<sup>-</sup> width obtained from the present data after correction for instrumental aberration (viz., 1.0 eV), one obtains an increase of 0.4 eV, presumably attributable to solid-state effects. This is in quite reasonable agreement with the earlier result.<sup>6</sup> These results differ from that expected from Howland's calculation by more than a factor of 2.

Now consider the so-called  $K\beta_5$  line of the K<sup>+</sup> spectrum. We have attempted above to identify it with the "cross-transition," 'valence band'-K<sup>+</sup> 1s. If such is the case, then it should provide another view of the valence band. An attempt was made to resolve this structure from the combined tails of  $\beta''$  and  $\beta_{1,3}$  on which it lies. The result is plotted in Fig. 12. What would be expected is a measure of the admixture of K<sup>+</sup> 3p function in the total density of states. From Howland's calculation this admixture does not vary greatly<sup>30</sup> as one passes through the band so that the result should be roughly proportional to the total density of states. Accordingly, a histogram giving an approximate picture of the total density of states<sup>31</sup> is indicated in Fig. 12. An approximate fold of the histogram with a Lorentzian curve matched at half-maximum to the sum of instrumental and K-state widths, viz., 1.2 eV, is also shown in that figure. In disposing the experimental curve relative to the theoretical expectation, no adjustment of energy scales has been employed. By that statement it is meant that Howland's K<sup>+</sup> 3p band was anchored to the observed K<sup>+</sup>  $K\beta_{1,3}$  line, and the Cl<sup>-</sup> band allowed to fall at the calculated relative energy position. The agreement in energy position, width, and shape is surprising.

It would seem that the interpretations at hand cannot all be valid if the expectation is to be retained that the emission bands reflect simply the symmetry-restricted

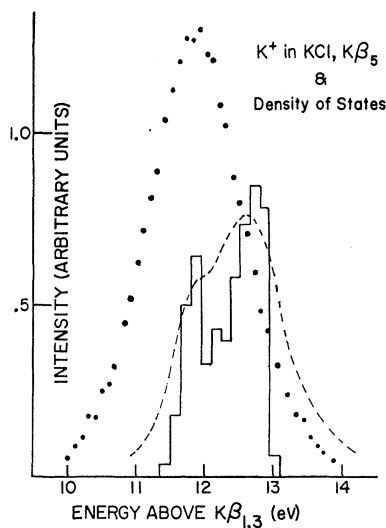
density of states in the valence band. It should be emphasized that the difficulty is independent of the validity of the particular calculation with which we have chosen to compare the experimental results. The difficulty arises from the dissimilarity of K<sup>+</sup>  $K\beta_5$  and Cl<sup>-</sup>  $K\beta_{1,3}$  which, according to the arguments made above, should reflect the same valence-band distribution. Now these arguments were not conclusive in that it is relatively easy to produce other explanations for K<sup>+</sup>  $K\beta_5$ . Let us see, however, where we are led by accepting both Cl<sup>-</sup>  $K\beta_{1,3}$  and K<sup>+</sup>  $K\beta_5$  as arising from the valence band. To retain the identification, we must modify, in some way, our expectation that what is observed is simply the symmetry-restricted density of states.<sup>32</sup> Attention is, therefore, directed to a brief examination of the basis for this expectation.

For the x-ray emission process, the initial state is the target system (e.g., crystal) containing an inner band (shell) vacancy.<sup>33</sup> The process of interest is one in which the final state contains a hole in the valence band. For the moment, suppose that the inner band is narrow and that the effect of lifetime broadening in the initial state is either small or has been removed by a suitable unfolding procedure. In this case, the expectation that the emission band should reflect the symmetry-restricted density of electronic states in the valence band comes from an application of Koopmans' theorem<sup>34</sup> to the final-state hole. Modification of our simple expectation thus seems to require that Koopmans' theorem should fail to apply.

One example of such a breakdown in the application of Koopmans' theorem has been known for some time. This is the Landsberg<sup>35</sup> broadening of the low-energy side of the emission bands of metals. Such an effect is, of course, not expected for the case of KCl since the band is very narrow compared to the gap. Another mechanism which leads to differences between an electronic energy band and the spectrum over which a hole therein may range, has been recently discussed by Nettel<sup>36</sup> with direct application to KCl. This is the interaction of the hole with its polarizable environment. The basic result of such considerations is a flattening of the bands due to crystal polarization which Nettel points out had already been noted in earlier work which he cites.

Lattice polarization and electronic polarization are involved. In the x-ray case, it is customary to neglect lattice polarization by invoking the Frank-Condon principle. The hole is then pictured as making a vertical transition (in configuration space) and its relaxation (since it is otherwise stable) occurs by means of sub-

FIG. 12. The possible cross transition in the K<sup>+</sup> spectrum is shown in relation to Howland's density of states. The result from a somewhat arbitrary separation of  $K\beta_5$  from the tails of  $K\beta_{1,3}$  and  $K\beta''$ . The dashed curve suggests the effects of the combined instrumental and lifetime broadening on the density of states.



<sup>30</sup> The variation is considerably larger than that of the Cl<sup>-</sup> 3p admixture but in view of the remaining divergences it is not thought worthwhile to refine these considerations at present.

<sup>31</sup> L. P. Howland, Quarterly Progress Report, Solid State and Molecular Theory Group, Massachusetts Institute of Technology, 15 January 1958, pp. 50-54 (unpublished).

<sup>32</sup> The details of the required symmetry restrictions are given in a number of places and so will not be repeated here. For a rather careful discussion see, D. H. Tombouli, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. XXX, pp. 255-261.

<sup>33</sup> It is assumed that the photoelectron has been supplied sufficient energy that it is removed from consideration.

<sup>34</sup> T. Koopmans, *Physica* 1, 104 (1933).

<sup>35</sup> P. T. Landsberg, *Proc. Phys. Soc. (London)* A62, 806 (1949).

<sup>36</sup> S. J. Nettel, *Phys. Rev.* 121, 425 (1961).



sequent phonon processes. The transition is, of course, not vertical in  $k$  space since the photon wave vectors involved are of the order of the reciprocal of a lattice constant. Nettel estimates that the narrowing due to electronic polarization would be insufficient to account for the observed width of  $\text{Cl}^- K\beta_{1,3}$  in KCl.<sup>37</sup>

stant would be insufficient to account for the observed width of  $\text{Cl}^- K\beta_{1,3}$  in KCl.

It is possible that the strict application of the Frank-Condon principle is not correct, that is, that some short-range lattice polarization should be included in the description of the final-state hole. A small measure of support for this possibility follows from the observation that Nettel's results for the fully relaxed system produce a narrower band than would be required by the observation on  $\text{Cl}^- K\beta_{1,3}$  in KCl. We proceed then to apply his discussion in a qualitative way to the x-ray situation.

What bears directly on the difficulty of the two experimental valence bands is the necessity found by Nettel<sup>38</sup> of using two distinct environmental configurations for the cases that the extra positive charge is located at positive and negative ions, respectively. In the case that the extra positive charge is located at the negative ion site, Nettel finds self-trapping possible and, more generally, a very narrow band. This presumably is the situation corresponding to  $\text{Cl}^- K\beta_{1,3}$ . In the case that the valence-band hole is placed on the positive-ion site, this does not seem to occur or, more generally, the narrowing is not so great. This seems to be the case of  $\text{K}^+ K\beta_5$ .

Thus, the possibility arises that we can retain the identifications made above regarding these two emission lines. It also seems that there exists a framework in which they may be understood from theoretical calculations. The results are qualitative and much further work is required in order to test adequately these suggestions.

#### ACKNOWLEDGMENTS

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#### APPENDIX: CORRECTION PROCEDURES

The observed spectra were corrected for instrumental broadening by the method of Burger and van Cittert.<sup>39</sup>

<sup>37</sup> Reference 36, p. 433.

<sup>38</sup> Reference 31, p. 430.

<sup>39</sup> H. C. Burger and P. H. van Cittert, *Z. Physik* **79**, 722 (1932); **81**, 428 (1933).

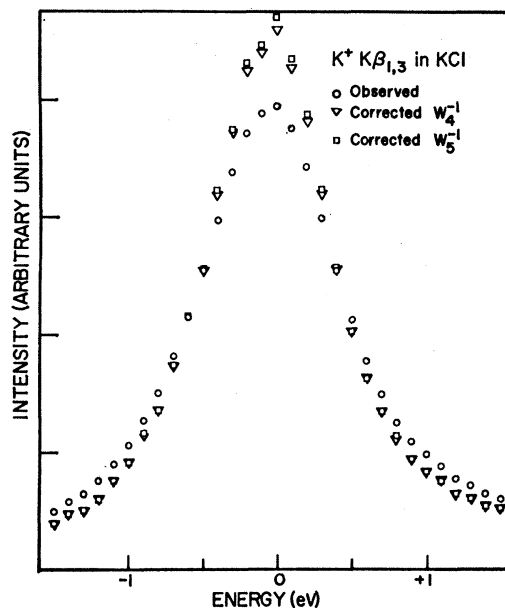


FIG. 13. Comparisons of the results of successive approximations to the unfolding operator.

In the case of the results quoted in the text, the fourth approximation to the unfolding operator was used. This is

$$W_4^{-1}(\nu - \nu_0) = 4\delta(\nu - \nu_0) - 6W(\nu - \nu_0) + 4W^2(\nu - \nu_0) - W^3(\nu - \nu_0),$$

where  $\nu_0$  is the point at which the corrected datum was required, and  $W^n$  stands for the  $n$ -fold autoconvolution of the window function,  $W(\nu - \nu_0)$ . The corrected datum at  $\nu_0$  is the convolution of  $W^{-1}(\nu - \nu_0)$  with the observed spectrum. The window function was taken as the (1, -1) rocking curve,<sup>6</sup> normalized to unit area and cut off at approximately  $\pm 15$  half-widths. No formal smoothing operator was introduced into the correction procedure.

In order to test the adequacy of the above procedure, the fifth approximation to  $W^{-1}$  was constructed, viz:

$$W_5^{-1}(\nu - \nu_0) = 5\delta(\nu - \nu_0) - 10W(\nu - \nu_0) + 10W^2(\nu - \nu_0) - 5W^3(\nu - \nu_0) + W^4(\nu - \nu_0)$$

and folded with the  $\text{K}^+$  spectrum. Figure 13 compares the results obtained with  $W_4^{-1}$  and  $W_5^{-1}$ . The slight change observed is typical of what one would expect of the remaining spectra. The increased statistical uncertainty accompanying use of  $W_5^{-1}$  and higher approximations to  $W^{-1}$  thus indicates that the choice of  $W_4^{-1}$  is reasonable.