

## $K\beta$ Spectra of Argon and KCl. II. Satellite Excitation\*

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A model for double-vacancy, single-jump satellites is considered for the case of the  $K\beta$  spectra of argon, and argon-like ions. The excitation thresholds implied by this model were investigated by quasimonochromatic fluorescence for the  $K\beta$  spectrum of chlorine in KCl. Significant alterations in the spectrum, depending on the character of the primary radiation, are reported for this case. From these observations, the initial states for certain of the more prominent spectral features have been identified as belonging to the configuration  $KM$ .

### I. INTRODUCTION

RECENT measurements of the  $K\beta$  spectra of argon and KCl have been reported.<sup>1</sup> When these spectra are compared, a reasonable "isoelectronic sequence" obtains despite the fact that the  $\text{Cl}^-$  and  $\text{K}^+$  spectra were obtained from a crystalline target. This observation suggests that it may be worthwhile to look for an atomic model on the basis of which at least the grosser features of these spectra might be understood.

If it is assumed, for the moment, that the intense line is in each spectrum  $K\beta_{1,3}$  (viz., the hole transition  $K-M_{\text{II,III}}$ ), then it is natural to try to account for the accompanying high-energy structure in terms of satellite processes. For present purposes, the term satellite is used in a restrictive sense to mean the radiation due to the same hole transition as the parent line except that this is to occur in an atom with one or more electrons removed (or excited).

It is clear from the above that we mean to consider only Wentzel-Druyvesteyn<sup>2</sup> satellites but much further restriction is required. It is a deceptively easy task to account for the energy position of satellite lines in x-ray spectra. In order to restrict somewhat the number of models which might be considered, we must look for other criteria.<sup>3</sup>

Two aspects of these spectra are, under the assumption that the high-energy components are such satellites, quite suggestive. First, these satellites are very close to the parent lines suggesting that the extra vacancy represents a relatively small perturbation on the atomic field, implying that the extra vacancy (or vacancies) lies in the  $M$  shell itself. Second, the principal high-energy line is quite intense. According to the perturbation theoretic treatment of Bloch,<sup>4</sup> one expects that this

high intensity is due to the satellite process having a relatively small excess in threshold energy over the threshold for the parent transition. Again this suggests extra vacancies in the  $M$  shell itself.

According to these suggestions, consideration is here restricted to processes of the character  $KM^n-M^{n+1}$ . It is probably not necessary to examine such processes beyond  $n=2$ . A crude model is developed in the following section which is in accord with these suggestions. It is shown to yield parent-satellite separations which, for some cases, agree roughly with those obtained experimentally. The model is, in this respect, by no means unique.

We are thus led to search for other criteria on which to evaluate this sort of model. The question of relative intensities is currently under investigation<sup>5</sup> but the results are not yet at hand. The threshold energies for satellite production represent another feature of the model which can be investigated. It is toward a study of these thresholds that that experimental work reported here is directed.

The utility of threshold studies in the diagnostics of satellite spectra is well known. Such studies have been carried out in certain cases under both electron excitation<sup>6</sup> and photon excitation.<sup>7</sup> Although, in principle, either technique is capable of yielding values for threshold energies, certain differences must be noted.

In analogy to the relation of excitation functions for single-vacancy processes by electrons and photons, we expect the electron excitation function for two-vacancy processes to rise more slowly above threshold than the photon excitation function. This would suggest that, for a given excess energy above threshold, the two-vacancy to one-vacancy ratio for photons would be higher than for electrons. There is, however, working in the contrary direction, the extra ionizing agent present in the case of electron excitation. If there is a significant contribution to multiple-vacancy production due to Coulomb interaction with the out-going electrons, one would expect, at sufficient energy above threshold, higher multiple to single ratio for electron

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<sup>1</sup> R. Deslattes, preceding paper, Phys. Rev. **133**, A390 (1964). This will be referred to as I.

<sup>2</sup> G. Wentzel, Z. Physik **31**, 445 (1925); M. J. Druyvesteyn, *ibid.* **43**, 707 (1927).

<sup>3</sup> For a summary see, e.g., F. R. Hirsh, Jr., Rev. Mod. Phys. **14**, 45 (1942).

<sup>4</sup> F. Bloch, Phys. Rev. **48**, 187 (1935).

<sup>5</sup> M. Wolfsberg and M. L. Perlman (private communication).

<sup>6</sup> L. G. Parratt, Phys. Rev. **49**, 132 (1936).

<sup>7</sup> K. Tsutsumi, J. Phys. Soc. Japan **14**, 1696 (1959).

bombardment. This last possibility seems to be favored by the data which will be presented here. One would still expect relatively sharper thresholds under photon bombardment as compared with electron excitation.

There are, of course, other reasons for preferring photon excitation for the targets which are of special interest for the present work. These are the fairly obvious technical difficulties in bombarding either a gas target or an insulating solid.

Against the above difficulties associated with threshold measurements by means of electron bombardment must be weighed the, perhaps more obvious, difficulties associated with an attempt to make such measurements under excitation by photons. The problem of merely exciting a fluorescent x-ray spectrum having sufficient intensity to be examined by means of a high-resolution instrument is somewhat formidable. The possibility, therefore, does not likely exist at the moment, with readily available sources,<sup>8</sup> to monochromatize the primary beam and still retain sufficient intensity to examine the spectrum.

Alternatively, one can consider the possibility of using characteristic lines from tractable anode materials and possibly filters to produce an approximately monochromatic excitation source. In the present case, we wish to distinguish excitation thresholds for production of  $KM$  and  $KM^2$  etc., vacancy systems. Such distinctions require the rather fortuitous occurrence of a strong characteristic line of a tractable anode material within an  $M$ -shell energy of the  $K$  limit of the target we wish to study. It is fortunate that this unlikely conjunction occurs in the relation of Pd  $L\alpha$  to the chlorine  $K$  edge. Supply of larger excitations becomes, of course, progressively easier since these need not be so precisely specified. There are, in fact, quite convenient  $L$  series radiations from the elements lying above Pd in the periodic table, and the  $K$  radiation from Ti.

## II. A MODEL FOR $K\beta$ SATELLITES IN THE ISOELECTRONIC SEQUENCE OF ARGON

Our object in this section is to treat the  $K\beta$  satellites in analogy to the work of Langer<sup>9</sup> and Wolfe<sup>10</sup> on  $K\alpha$  satellites. These authors were the first to make quantitative arguments for the importance of exchange interactions in determining the energy levels for doubly ionized systems. Their original work was later refined by Kennard and Ramberg.<sup>11</sup> More recently, it has been extended by Candlin<sup>12</sup> and by Horak.<sup>13</sup> By virtue of this work, those satellites of  $K\alpha$  arising from transitions of the type  $KL-LL$  have been, by now, fairly well identified.

<sup>8</sup> The orbit radiation from a high-energy electron synchrotron may be sufficiently intense.

<sup>9</sup> R. M. Langer, Phys. Rev. **37**, 457 (1931).

<sup>10</sup> H. C. Wolfe, Phys. Rev. **43**, 221 (1933).

<sup>11</sup> E. H. Kennard and E. G. Ramberg, Phys. Rev. **46**, 1040 (1934).

<sup>12</sup> D. J. Candlin, Proc. Phys. Soc. (London) **A68**, 322 (1955).

<sup>13</sup> Z. Horak, Proc. Phys. Soc. (London) **A77**, 980 (1960).

We wish now to consider the energy terms associated with  $KM$  initial states and  $MM$  final states. If we begin with an argon atom and make a  $K$  vacancy and an  $M$  vacancy, the most characteristic feature of the resulting term system is its splitting into singlets and triplets by the exchange interaction of the holes. A similar observation applies also to the  $MM$  configuration. It is possible to write down the term systems for these configurations as linear combinations of one- and two-electron integrals taken over some set of wave functions. For present purposes, it is perhaps simpler to take an approach in which the final-state energies are taken directly from available optical term systems and in which the initial-state energies are obtained, except for the exchange splittings, on the assumption of complete inner screening.

### A. Term Systems for $KM$ Configurations

The configurations symbolized by  $KM$  (viz.,  $KM_I$  and  $KM_{II,III}$ ) are highly degenerate. This degeneracy is lifted in part by the spin-orbit interaction and by exchange. In the region near  $Z=18$ , the spin-orbit interaction is somewhat small compared to the Coulomb interaction. Accordingly, we first neglect spin-orbit interaction and for convenience, take the direct and exchange parts of the Coulomb interaction into account in somewhat different ways. The direct part of the Coulomb interaction between the electrons, together with the nuclear potential, in the above approximation, may be regarded as giving rise to a mean term which is then split into a singlet and a triplet. We may approximate the mean terms for the  $KM$  configurations by the sum of the  $K$  term for the ion in question and the  $M$  terms for the isoelectronic ion having an atomic number that is larger by one.

Since we shall in the end only wish to find the parent satellite separations, the contribution of the  $K$  vacancy can be suppressed. Table I shows the separations  $E(KM) - E(K)$  obtained from the optical data.<sup>14</sup>

TABLE I. Mean terms and exchange splittings for  $KM$  configurations.<sup>a</sup>

	Cl <sup>-</sup>	Ar	K <sup>+</sup>	K <sup>+</sup> (S.C.F.)
$E(KM_I) - E(K)$	29.23	47.99	70.09	
$E(KM_{II,III}) - E(K)$	15.75	31.81	51.20	
$E/2$ (1s,3s)	0.61	0.70	0.81	0.83
$E/2$ (1s,3p)	0.29	0.37	0.44	0.30

<sup>a</sup> All energies in eV; all lengths in atomic units.

The required exchange energies may be estimated in several ways ranging from numerical integration over Hartree-Fock wave functions to use of hydrogenic wave functions with effective charges chosen, for example, by

<sup>14</sup> C. E. Moore, Natl. Bur. Std. Circ. No. 467, Vol. I, p. 195 (1949).

means of Slater's rules.<sup>15</sup> We consider briefly the limitations of these various procedures and then attempt to improve the hydrogenic results.

For hydrogenic wave functions, somewhat different situations may be anticipated for the  $1s^{-1}3s^{-1}$  and  $1s^{-1}3p^{-1}$  configurations. In the former, the use of a fixed screening number will result in too large an amplitude near the nucleus and an overestimate of the exchange. In the latter configuration, the centrifugal barrier will reduce the amplitude near the nucleus, and thus the tendency toward the overestimate mentioned above.

When Hartree-Fock wave functions are used, different objections may be advanced. Most available Hartree-Fock functions were obtained for neutral atoms and not for two-vacancy configurations. This discrepancy can be only partly compensated by scaling. The Hartree-Fock procedure for  $1s3s$  keeps the  $3s$  electrons "farther out" than should be the case when there is a  $1s$  electron missing. This will presumably lead to an underestimate of the exchange splitting.

The remarks pertaining to Hartree-Fock wave functions suggest that a more reasonable estimate could be obtained by using Hartree functions, since, in this case, there is no "exchange hole" associated with the inner shell.<sup>16</sup> Such a procedure was more or less followed, except that an approximation scheme was used in order to avoid numerical evaluation of the two-electron integrals. Hartree functions were directly available for  $\text{Cl}^-$  and  $\text{K}^+$ .<sup>17</sup> For argon, they were derived from the Hartrees' comparison of wave functions with and without exchange.<sup>18</sup>

In brief, the procedure for getting the exchange energies is to begin by calculating those for hydrogenic wave functions. The effective charge for the outer wave function is then fixed by matching the first radial node of the hydrogen function to that for the corresponding Hartree function. Then a graphical comparison is made between the "exchange charge densities" from the hydrogenic functions and from the Hartree results. This comparison gives a scaling factor, the product of whose square with the hydrogenic value constitutes the present estimates of the exchange integral.

Let  $Z$  and  $Z'$  be the effective charges for the inner and outer wave functions, respectively. Following Löwdin,<sup>19</sup> if  $J$  is defined by:

$$J = \frac{1}{2}(^1E - ^3E) \quad (1)$$

since the wave functions are not, in general, orthogonal, then

$$J = \frac{\langle ab | e^2/r_{12} | ba \rangle - |S_{ab}|^2 \langle ab | e^2/r_{12} | ab \rangle}{1 - |S_{ab}|^4} \quad (2)$$

<sup>15</sup> J. C. Slater, *Phys. Rev.* **36**, 57 (1930).

<sup>16</sup> The writer is indebted to Professor J. S. Levinger for this suggestion.

<sup>17</sup> D. R. Hartree, *Proc. Roy. Soc. (London)* **A143**, 506 (1934); **A141**, 282 (1933).

<sup>18</sup> D. R. Hartree and W. Hartree, *Proc. Roy. Soc. (London)* **A166**, 450 (1938).

<sup>19</sup> P. O. Löwdin, *Rev. Mod. Phys.* **34**, 80 (1962).

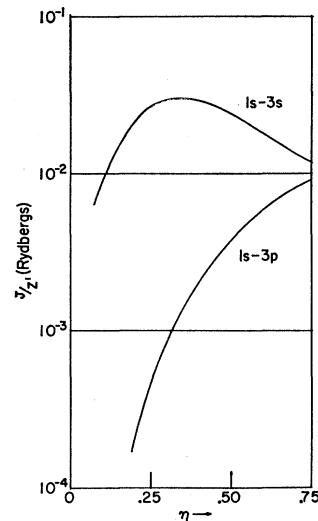


FIG. 1. Exchange integrals for hydrogen wave functions. The effective charge for the outer function is primed.

These two-electron integrals are treated by Condon and Shortley.<sup>20</sup> The letters  $a$  and  $b$  represent the inner and outer wave functions, respectively. For the case of the configuration  $1s^{-1}3p^{-1}$ , the overlap integral vanishes so that only the first term of the numerator of Eq. (2) survives. For  $1s^{-1}3s^{-1}$ , overlap must be considered and, along with it, the direct part of the Coulomb interaction which contributes to the second term in the numerator of Eq. (2).

Expressions for the various two-electron integrals required are readily obtained in closed form. The quantities  $J/Z'$  turn out to be functions of the ratio  $Z'/Z$  alone, and this, most conveniently, through the combination

$$\eta = Z'/Z + \frac{1}{3}Z' \quad (3)$$

The results are plotted in Fig. 1. The limit  $\eta=0.75$  corresponds to equal effective charges for the inner and outer wave functions.

Next, we must choose  $Z'$  to fit the first radial node of the Hartree wave functions. These locations are listed in Table II together with the corresponding values of  $Z'$ .

TABLE II. Parameters for calculation of exchange energies.<sup>a</sup>

	$\text{Cl}^-$	Ar	$\text{K}^+$
$r_0(3s)$	0.121	0.115	0.109
$Z(3s)$	15.5	16.5	17.5
$r_0(3p)$	0.574	0.488	0.450
$Z(3p)$	10.5	12.3	13.3
$g(1s,3s)$	0.485	0.507	0.529
$g(1s,3p)$	0.668	0.664	0.660

<sup>a</sup> All energies in eV; all lengths in atomic units.

Direct use of the hydrogenic exchange energies for these effective charges would lead, of course, to large overestimates especially in the  $1s, 3s$  case so we must

<sup>20</sup> E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1953), Chap. V.

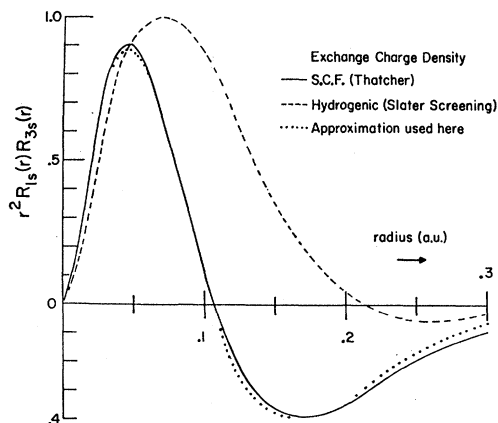


FIG. 2. Exchange charge densities versus radius for the case of potassium.

proceed to the final step of approximating charge densities.

The resulting scale factors,  $g$ , are given in Table II. It will be noted that they are not very sensitively dependent on atomic number. This is fortunate, since the matching has only been carried out for "ground-state" wave functions. To obtain parameters for the excited state, the  $g$  values in Table II were retained, the inner wave function taken as the unscreened hydrogenic 1s function, and the outer function adjusted under the assumption of complete inner screening.

An indication of the effectiveness of this procedure is given in Fig. 2, which shows the result of Thatcher's self-consistent field calculation<sup>21</sup> is compared with the present approximation procedure. To emphasize the difficulties which result from use of hydrogenic wave functions with effective charges fixed by Slater's rules, the corresponding exchange charge density is also shown in Fig. 2. A numerical comparison with Thatcher's results is also indicated in Table I. It suggests that the simple procedure employed here has attained an accuracy which is satisfactory for present purposes.

### B. Final-State Terms and Transition Arrays

It is a fortunate occurrence that the final states for the transitions which we are considering are those of normal optical ions. Since only the parent-satellite splittings are sought, and the  $K$  energy has been suppressed in the consideration above, we now suppress the  $M_{II,III}$  energy in listing the required terms. These values, obtained directly from the optical data,<sup>14</sup> are given in Table III. They are, of course, for the ion in question (not for the next higher species).

The transition arrays allowed by selection rules requiring only one electron to change orbital are indicated in Table IV. For the sake of completeness an average transition energy for  $KM^2-M^3$  has been in-

<sup>21</sup> W. A. Thatcher, Proc. Roy. Soc. (London) **A172**, 242 (1939).

TABLE III. Final-state term values (eV) measured relative to  $M_{II,III}$ .

	$J$	Cl <sup>-</sup>	Ar	K <sup>+</sup>
$M_1 M_{II,III}$	$^1P$	27.34	45.47	67.2
	$^3P$	0	24.70	41.91
		1	24.66	41.85
		2	24.58	41.72
$M^2_{II,III}$	$^1S$	16.47	31.74	50.8
	$^1D$	14.45	29.36	48.3
	$^3P$	0	13.13	27.81
		1	13.09	27.76
		2	13.01	27.62

cluded in Table IV. In addition, the singlet-triplet intercombination line between  $KM_1$  and  $M_1 M_{II,III}$  has been listed.

In Fig. 3 the observed spectra are shown together with the locations of the calculated satellite arrays. Inspection of this figure suggests that the location of the first high-energy satellite and its complexity are fairly well accounted for in terms of the model which has been developed in this section. This does not, however, assure the model's uniqueness. The satellite ( $^1P-^1S$ ) whose energy would be quite close to the parent is not obvious in the data. There is considerable room for argument regarding argon  $K\beta''$  and K<sup>+</sup>  $K\beta_5$  (KCl).

### III. EXPERIMENTAL STUDY OF Cl<sup>-</sup> $K\beta$ UNDER VARIOUS EXCITATIONS

In this section the results of measurements of the  $K\beta$  region of the Cl<sup>-</sup> spectrum in KCl excited near threshold are reported. As discussed in the Introduction, this has been done in fluorescence using characteristic spectra from various anodes. Such a crude procedure is required by intensity considerations and the results cannot claim to represent a satisfactory measurement of the excitation function for this spectrum. They are, however, sufficient to suggest some of its main features.

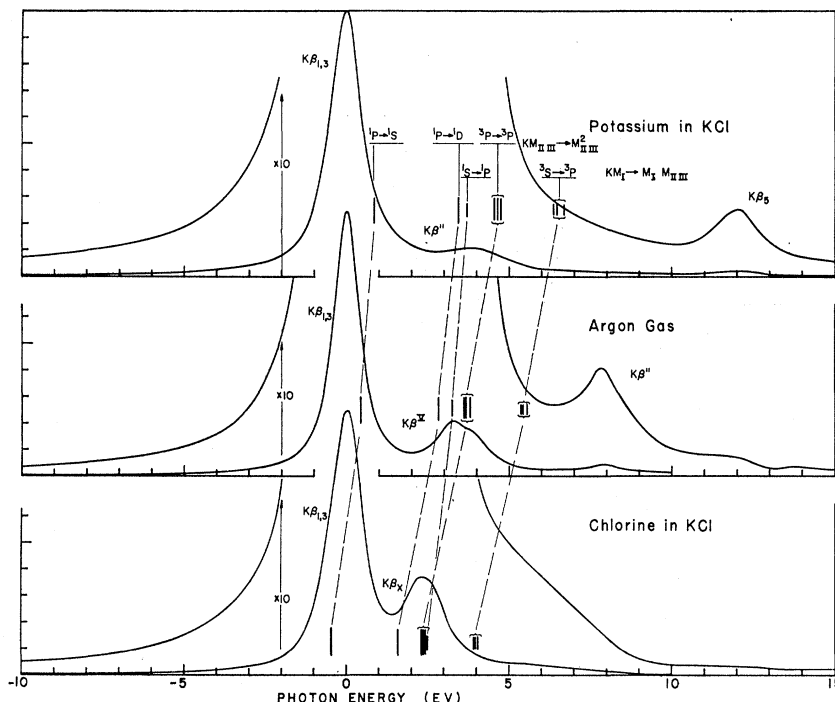
#### A. Experimental Arrangements

The disposition of apparatus was the same as that described in the preceding paper (I) and the secondary

TABLE IV. Calculated satellite-parent separations (eV).

	Cl <sup>-</sup>	Ar	K <sup>+</sup>
$KM_{II,III}-M^2_{II,III}$	$^3P \rightarrow ^3P$	2.45	3.82
		2.38	3.68
		2.34	3.63
	$^1P \rightarrow ^1D$	1.59	2.82
$^1P \rightarrow ^1S$	-0.43	+0.44	
$KM_1-M_1 M_{II,III}$	$^3S \rightarrow ^3P$	4.04	5.57
		3.96	5.44
		3.92	5.38
	$^1S \rightarrow ^1P$	2.50	3.22
	$^1S \rightarrow ^3P$	5.26	6.97
		5.18	6.85
$KM^2-M^3$		5.14	6.74
		6.6	9.3
			11.3

FIG. 3. Experimental spectra and calculated transition arrays. The transitions marked with longer vertical lines are expected to have greater intensity than the others.



emitter was again a cleaved crystal of KCl. The primary anode materials used were Pd, Ag, Sn, Ti, and Pd with a Ru filter. Spectra were measured mostly at 20 kV, 150 mA with the following exceptions: In an attempt to ascertain the effect of the continuum on the observed spectrum, measurements were made with the Pd anode operated at 20, 11.5, and 7.5 kV.

We need now to make some estimates of the excess energies above threshold corresponding to the line spectra employed. (The continuum effects will be discussed separately.) Table V gives the targets used

TABLE V. Approximate excitations above threshold for targets used (eV).

Target	$\alpha_{1,2}$	$\beta_1$
Pd	13	165
Ag	155	325
Sn	620	840
Ti	1690	2110

and the approximate excess energies of their main lines above a threshold which is assumed to be given by the experimental absorption edge. The case of Pd with a Ru filter requires careful consideration which is now given.

On the basis of published wavelengths<sup>22</sup> the disposition of the L edges of Ru relative to the emission lines of Pd is shown in Fig. 4. Figure 4 also shows where the assumed threshold for K ionization of Cl<sup>-</sup> occurs. One

would therefore expect to be able to filter out  $\alpha_1$ , and leave  $\alpha_2$  with an excess energy of 10 eV above threshold. On the basis of the arguments given above, this would be expected to be insufficient to excite the KM vacancy system. Unfortunately, a study<sup>23</sup> of the beam from a Pd target excited to fluorescence and transmitted through various thicknesses of ruthenium indicated that the ratio of the Lβ intensity to the Lα increased with increasing absorber thicknesses. What this means is that there is a slight error in the tabulated wavelengths for either Pd Lα<sub>1,2</sub> or in the L<sub>III</sub> edge location for Ru. The consequence of this, for present purposes, is that there are two components in the transmitted beam, which for the thickness of Ru used, are roughly in the same ratio as without the filter. One of these, at Lα<sub>2</sub> should be capable of neither KM<sub>II,III</sub> or KM<sub>I</sub> excitations. The other, Lβ, should be capable of both. If we compare the excitation of the filtered beam with that for the unfiltered one (which is dominated by Lα<sub>1</sub>), then we must

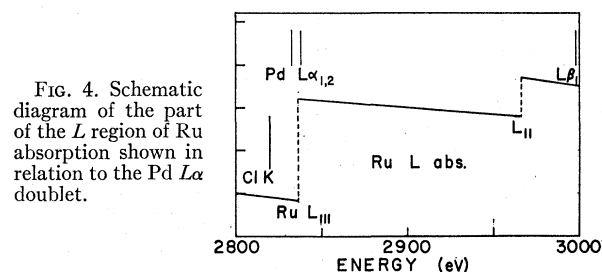


FIG. 4. Schematic diagram of the part of the L region of Ru absorption shown in relation to the Pd La doublet.

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

<sup>23</sup> This was carried out on a single-crystal instrument with helium tunnels (G.E. XRD-5).

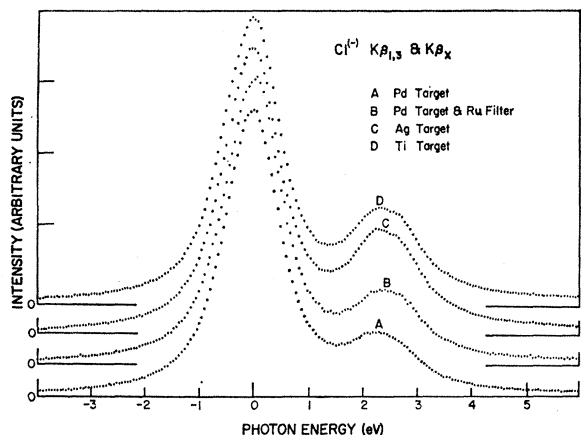


FIG. 5. Emission contours for Cl  $K\beta$  region in KCl under various conditions of excitation.

assign to the filtered beam a larger excess energy if the threshold for double-vacancy production lies above  $L\alpha_2$ . If, on the other hand, the threshold for two-vacancy production lies below  $L\alpha_2$  then we should have a lower effective excess energy with the filtered beam.

### B. Experimental Results

It is clear that the procedures employed in obtaining the data do not permit direct comparison of the spectra taken under differing excitation conditions. We must therefore adopt some normalization convention. Provisionally, it is assumed that the satellites, if any, which are degenerate with the parent line, are weak. In this case the data can be compared if peak heights of the parent are made equal. What we are then considering is the ratio of multiple vacancy to single-vacancy processes. Equivalently, this means that the study as a function of excess energy can yield the ratio of the excitation function for two-vacancy processes to that for single-vacancy processes.

Recording of these spectra required about two months. During that time, considerable care was taken to preserve the energy scale. At the time of each target change (which, incidentally, did not require that the instrument be opened), a minus position curve was recorded. This was done also, in greater detail, both before and after the complete sequence of measurements. The peak positions in these cases differed by less than 1 sec ( $\approx 0.01$  eV).

In Fig. 5 the central region of some of the observed spectra are shown; the high-energy tail region is shown on an expanded intensity scale and a compressed abscissa scale in Fig. 6. Comparison of the spectra excited by the Pd target operated at various anode potentials (not shown) revealed no significant differences in shape. This does not mean that the continuum is ineffective in either single- or multiple-vacancy production. Rather, it means that, for the spectrum under investigation, the ratio of single-to-multiple-

vacancy production is not noticeably sensitive to changes in the continuum. Again this only applies to the case of the Pd target which gave very strong excitation close to threshold. If the line spectrum has considerable excess energy, there is undoubtedly a significant amount of excitation due to the lower energy continuum.

Effects which appear in the main line indicate that the provisional normalization procedure is not satisfactory. It is not possible to infer the correct normalization from the experimental data. We may ask, however, in relation to a particular model if there is a set of reasonable normalizations which make the data consistent with the model. For instance, assume that the spectra contain a main component whose shape is independent of excess energy and some satellite emissions characterized by a single threshold. Then there should exist a set of normalizations such that difference spectra are similar and that a subtraction of a properly scaled difference spectrum from any composite one would yield the main component.

An unfortunate complication of the present situation is that the model proposed earlier suggests that there should be two thresholds of significance. These are, however, fairly close together so that we might hope for some average behavior similar to the single threshold case for excess energies large as compared to the excess of both thresholds over the single-ionization limit. Accordingly, we proceed as if there were only one threshold for the satellite emissions.

Since the correct normalizations are not known, but the trial ones are fairly good, we can proceed as follows. If  $I_1(\nu)$  is the lowest energy spectrum and  $I_2(\nu)$  is some higher one, then, with correct normalization and the assumptions above,

$$I_2(\nu) - I_1(\nu) = I_1(\nu)[R_{12}(\nu) - 1], \quad (4)$$

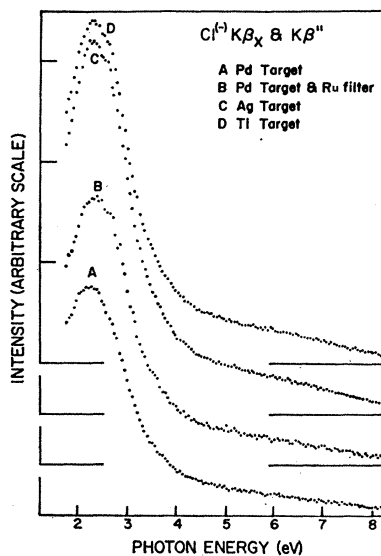


FIG. 6. The high-energy part of Fig. 5 is shown here in more detail.

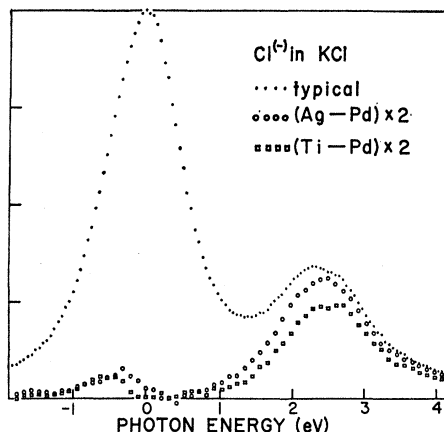


FIG. 7. Differences obtained by subtracting the Pd excited spectrum from two spectra excited at higher energies. Note that the higher energy case gives a smaller difference spectrum.

where  $R_{12}(\nu)$  is the ratio of the approximately normalized spectra. If the normalization is only slightly wrong, then the 'one' appearing in the brackets in Eq. (4) may be replaced by the minimum of  $R_{12}(\nu)$  and an estimate of the difference spectrum with correct normalization obtained.

This was carried out for two of the higher excitation conditions (Ag and Ti targets) relative to Pd as the presumed lowest excitation. The results are shown in Fig. 7 with a typical spectrum included for purposes of orientation. Such an analysis is of course not expected to yield very reasonable results in the comparison of Pd excitation with excitation by Pd filtered by Ru if two thresholds are involved. This comparison was in fact tried and no such simple picture as that in Fig. 7 could be obtained. Further analysis of the spectrum excited by filtered radiation was rendered somewhat difficult by the exceedingly low intensities and resulting poor statistics.

#### IV. DISCUSSION

Certain conclusions of this investigation are fairly clear. These are considered first and then in the last paragraphs we take up identification of  $K^+ K\beta_5$ , and the question of  $K\beta$  satellites in the nearby elements.

##### A. Satellite Positions and Thresholds

The main conclusion which can be drawn is that at least most of  $\beta_x$  in the  $Cl^-$  spectrum is a double-vacancy satellite. This is suggested by observation that it can be considerably reduced in intensity (possibly extinguished) relative to  $\beta_{1,3}$  by lowering the excess energy supplied to the system.

As to the nature of  $\beta_x$  we now have two pieces of information. First, its threshold is generally consistent with a  $KM$  initial state. Second, on the more detailed treatment given in Sec. II above, its energy displacement from the parent is reasonably well accounted for. This

treatment suggests the presence of components arising both from  $KM_{II,III}$  and  $KM_I$ . The shape changes which occur at low excess energy are not inconsistent with this two-threshold possibility.

The experimental results also indicate the presence of some satellite intensity on the lower side of the main peak. It is possible that this should be identified with the  $^1P-^1S$  transition expected from the model developed in Sec. II.

In connection with the  $Cl^-$  spectrum, it should be noted that the  $M_{II,III}$  term for  $Cl^-$  as observed in KCl will differ from that for the free  $Cl^-$  ion on account of crystal-field effects. The position of  $\beta_x$  relative to its parent will be expected to exhibit a small but significant sensitivity to environment on account of this effect. This is in accord with observation of  $\beta_x$  in the other alkali halides.<sup>24</sup> A similar state of affairs, though possibly more drastic in appearance, would be expected for the corresponding satellites in sulfur.<sup>25</sup>

We hope to extend these identifications to the other members of the isoelectronic sequence. Such an extension is, for the first high-energy satellite, variously labeled  $\beta_x$ ,  $\beta^V$ , and  $\beta''$ , based on the agreement of the calculated parent-satellite splittings with those observed. For the next high-energy satellite, which appears perhaps most clearly in the argon spectrum, there are some difficulties which are now discussed.

From the excitation characteristics which have been described for the  $Cl^-$  spectrum, we learn only that the "excess" intensity on the high-energy side of  $\beta_x$  behaves in a way which is not inconsistent with a similar excitation potential to that for  $\beta_x$ . It seems plausible to attempt to make a correspondence between the excess intensity beyond the first high-energy satellite in the  $Cl^-$  and  $K^+$  spectra and  $\beta''$  in the argon spectrum. The energy position of  $\beta''$  in argon is roughly consistent with either a singlet-triplet intercombination line from  $KM_I-M_1M_{II,III}$  or several allowed transitions between  $KM^2$  and  $M^3$ . In the latter case the sharpness of  $\beta''$  in argon is difficult to understand. In either case we are left with the problem of understanding why the transition is sharp in argon and not in the  $Cl^-$  spectrum from KCl.

The question of whether or not such a transition appears in the  $K^+$  spectrum is, if anything, more confused. There is clearly excess intensity immediately beyond the first high-energy satellite in that spectrum. It is tempting to consider that this is analogous to the situation in the  $Cl^-$  spectrum. If we ignore, for the moment, the question of why it is not sharp and identify this region with the singlet-triplet intercombination line, then we are left with the question of how  $K^+ K\beta_5$  as seen in KCl arises. On the other hand, if one chooses the possibility that the second satellite

<sup>24</sup> E. L. Jossem, dissertation, Cornell University, 1954 (unpublished).

<sup>25</sup> M. Siegbahn, *The Spectroscopy of X-Rays*, translated by G. A. Lindsay (Oxford University Press, New York, 1925), p. 99.

arises from  $KM^2-M^3$  then we expect a line where  $K^+ K\beta_5$  appears.

On this subject there is additional and relevant evidence. If the corresponding spectrum obtained from metallic potassium<sup>26</sup> is examined, the line labeled  $K\beta_5$  is not in evidence. Assuredly there is excess intensity beyond the first high-energy satellite and prior to  $\beta_{VI}$ , but at the wavelength corresponding to  $K\beta_5$  in KCl, there is certainly less than 10% of the intensity which is observed in the KCl spectrum.<sup>26</sup> The alternative possibility, suggested by Valasek,<sup>27</sup> is that  $K^+ K\beta_5$  is the "cross-transition" from the, predominantly  $Cl^- 3p$ , valence band to the potassium  $1s$  band. This appealing possibility accounts for the non-appearance of  $K\beta_5$  in metallic potassium. Insofar as this is the case, it favors the identification of the excess intensity beyond the first high-energy satellite as due to singlet-triplet intercombination transitions. This identification brings with it problems regarding the width and shape of  $K^+ K\beta_5$  in comparison with  $Cl^- K\beta_{1,3}$  as discussed extensively in the preceding paper (I).

### B. Relative Intensities

The data, although sparse, indicate some features of the cross section for two-vacancy production. If the intensity of the main line is taken as proportional to the cross section for single-vacancy production then the ratio of satellite to parent integrated intensity should give the ratio of the double-vacancy to single-vacancy production cross sections. Allowing for the well-known energy dependence of the single-vacancy production cross section, we may infer the following behavior for the double-vacancy production cross section: If the double threshold complication is neglected, then the two-vacancy cross section rises above threshold to a maximum of the order of 200 eV above threshold and slowly decreases thereafter. Near the maximum the cross section for double-vacancy production appears to be about the same as that for single-vacancy production for chlorine in KCl. The satellite to parent intensity ratio is, however, not quite as large as obtained under electron bombardment.

Good theoretical estimates for the two-vacancy cross section are not yet available. We can, however, proceed with certain simple considerations. It is assumed that either excitation or ionization of an  $M$ -shell electron is sufficient to cause subsequent  $M-K$  transitions to fall outside the main line. The primary ionization of the  $K$  shell is taken as a "sudden" perturbation for the  $M$ -shell electrons. In this approximation and using hydrogen wave function with Slater screening numbers, one obtains for the probability that an  $M$ -shell electron

is undisturbed:

$$\begin{aligned} P(3s) &= \gamma^6 [3 - 12\gamma^2 + 10\gamma^4]^2, \\ P(3p) &= \gamma^{10} [5\gamma^2 - 4]^2, \end{aligned} \quad (5)$$

where  $\gamma$  is the ratio of the geometric mean of the effective charges before and after the primary ionization to their arithmetic mean. For  $Cl^-$  these squared overlap integrals give 0.88 for an  $M_I$  electron and 0.91 for an  $M_{II,III}$  electron. If it is assumed that the probability that no electron is disturbed by the perturbation is given by  $P^2(3s)$  and  $P^6(3p)$ , respectively, then the probabilities for either an excitation or an ionization of any one or all of the outer shell electrons are 0.22 for the  $M_I$  shell and 0.43 for the  $M_{II,III}$  shell. This result would mean that in roughly 65% of the primary ionizing events, something will happen to one or more electrons in the  $M$  shell. The corresponding probabilities for argon and  $K^+$  are 50% and 40%, respectively.

There is another process which must yet be considered. It is suggested by the observation that the high-energy electron bombardment spectrum shows greater satellite intensity than is obtained with photon excitation even near the maximum yield for this process. This is contrary to our expectations since, under electron bombardment, the atom can be left with a distribution of excitation energies; this kinematic averaging should lead to an average yield lower than the maximum. Since this is not observed, we must assume another outer-vacancy production mechanism based on Coulomb interaction with the bombarding electron. But the bombarding electron and the knock-on electron are equivalent, hence in both photon and electron excitation this Coulomb interaction must be effective. The electron excitation case is favored only by the presence of two outgoing electrons.

A good calculation of such an effect is not yet available but we may proceed crudely to get some feeling for its importance. A classical picture is assumed in which, for example, a photoelectron leaves the  $K$  shell and approaches the  $M$  shell from within. The product of its flux with a typical cross section for  $M$ -shell ionization by low-energy electrons is of the order of unity. Thus, the importance of this process is clear, however, a more realistic estimate is required.

Related observations of double-excitation effects should finally be noted. Schnopper<sup>28</sup> has recently demonstrated the presence of weak structure in the  $K$ -absorption spectrum of argon below the double ionization limit estimated above. The onset of this structure is attributed to the first energetic possibility of double excitation of a  $K$ -shell electron and an  $M$ -shell electron. Other bound-bound and bound-free configurations can, of course, occur between the first threshold and the double-ionization limit which was estimated above. The

<sup>26</sup> The writer is indebted to Professor E. L. Jossem for discussion of his unpublished work on this spectrum.

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

<sup>28</sup> H. W. Schnopper, Ph.D. dissertation, Cornell University, 1962 (unpublished); Phys. Rev. **131**, 2558 (1963). See also C. Bonnelle and F. Willeumier, Compt. Rend. **256**, 5106 (1963).



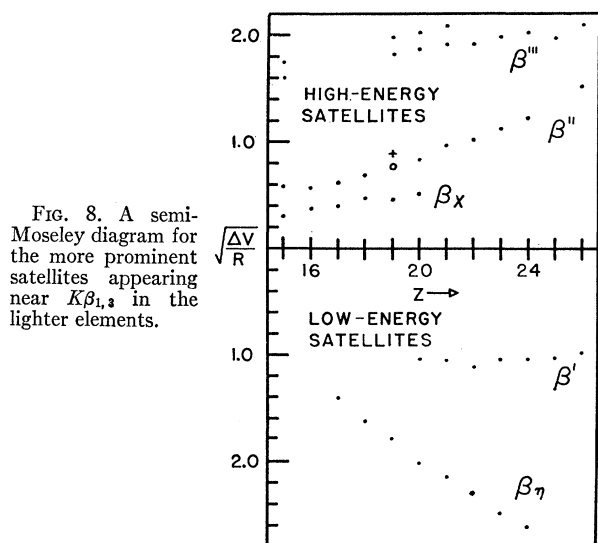


FIG. 8. A semi-Moseley diagram for the more prominent satellites appearing near  $K\beta_{1,3}$  in the lighter elements.

In Fig. 8 are collected some data on the high-energy satellites in neighboring elements mostly from the summary of Sandstrom<sup>29</sup> except that some of the results for atomic numbers 17, 18, and 19 are taken from the present work. The energy separation  $\Delta E$  of each satellite from its presumed parent ( $K\beta_{1,3}$ ) was expressed in rydberg units. As is conventional, the square root of this separation as a function of  $Z$  is shown.

For this discussion the first and second high-energy structures are arbitrarily labeled  $\beta_x$  and  $\beta''$ , respectively, even though this conflicts with historical usage. An open circle has been placed for potassium where Jossem<sup>26</sup> has located a diffuse region of surplus intensity in the spectrum of metallic potassium. The point labeled with the cross is the position of  $K^+ K\beta_5$  in KCl. The KCl data do not preclude a similar diffuse region to that for metallic potassium at the location of the open circle. Identification of  $K^+ K\beta_5$  from KCl as the cross transition is favored by the apparent absence of a likely counterpart in neighboring spectra.

fact that the absorption effects appear as quite small changes in the total cross section need not be inconsistent with the large double-vacancy yield apparently required by the present work.

### C. $K\beta$ Satellite in Neighboring Elements

It is of some interest to consider the possible extension of the model of Sec. II to the neighboring elements and to see what suggestions empirical regularities in these spectra might make regarding  $K^+ K\beta_5$ .

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<sup>29</sup> A. E. Sandstrom, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. XXX.

## Hall Effects and Magnetoresistance in Some Nickel-Copper-Iron Alloys\*†

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The ordinary and extraordinary Hall coefficients and transverse magnetoresistance of six Ni-Cu-Fe alloys have been measured in the temperature range of 20°K to room temperature. All six alloys contain nominally 70 at.% Ni, with Cu and Fe additions to provide electron concentrations from 27.7 to 28.2 electrons per atom. The ordinary Hall coefficient is found: (i) to be insensitive to electron concentration; (ii) to vary with temperature in the way predicted by the 4-band model; (iii) to have a magnitude consistent with the 4-band model if anisotropic electron scattering is assumed. The extraordinary Hall coefficient is positive for the alloys with 27.7, 27.8, 27.9, and 28.0 electrons per atom, and negative for the alloys with 28.1 and 28.2 electrons per atom. The transverse magnetoresistance shows the typical behavior of ferromagnetic alloys, except that the resistance does not vary linearly with the magnetic induction above saturation. The reduced ideal resistivity is found to be a universal function of a reduced temperature for these six alloys and Ni.

### INTRODUCTION

THE Hall electric field per unit current density  $\epsilon_H$  is given by

$$\epsilon_H = R_0 B + R_s M,$$

where  $B$  is the magnetic induction and  $M$  the magnetization in the material, and where  $R_0$  and  $R_s$  are the ordinary and extraordinary Hall coefficients, respectively.

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