

Readjustment of the Neon Atom Ionized in the *K* Shell by X Rays*

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The distribution of neon ions that result from ionization by x rays has been measured with a coincidence time-of-flight mass spectrometer. Radiation from an aluminum target, filtered through a beryllium foil, was used so that in more than 95% of the events a *K* electron was removed. The observed charges, including *L* ionization, are distributed as follows: $\text{Ne}^{1+}=3\%$; $\text{Ne}^{2+}=66\%$; $\text{Ne}^{3+}=24\%$; $\text{Ne}^{4+}=6\%$; $\text{Ne}^{5+}=0.8\%$. On the average 2.4 electrons are removed per interaction. The charge spectrum has also been computed using calculated *K-L-L* Auger transition rates and electron shake-off probabilities as given by the β^- decay of Ne^{20} . The assumptions of the models used as well as the applicability to the present study have been examined. Comparison of the calculations with the experimental data indicates the presence of other modes of ionization.

TWO processes compete in the transfer of a vacancy from an inner shell of an atom to the outermost shell: (a) the radiative transition with the emission of a quantum and (b) the radiationless transition, commonly known as the Auger effect, with the ejection of an electron. Either process may occur in one single step or, more likely, in several consecutive steps. Each Auger transition increases the charge of the ion by +1, while radiative transitions leave the charge state unaltered.

The observation of the final charge state following the completion of the readjustment ($\sim 10^{-14}$ sec) would then give the number of Auger transitions involved and, together with intensity measurements, yield data related to the transition rates for the processes. This simple correlation, however, holds true only in a first approximation. Self-ionization, following the creation of an inner shell vacancy, is not only produced by Auger processes but also by Coulombic electron shake-off¹ and possibly, by the ejected electrons themselves.

Evidence for more extensive ionization than that to be expected from cascading Auger transitions has been found by Snell and Pleasonton² in 1955, by Fiquet-Fayard³ in 1961, and more recently, by one of the authors.⁴

In the present work we have investigated the readjustment process of the neon atom as a consequence of a vacancy in the *K* shell. The vacancies were produced by x rays from an aluminum target, which provided radiation of wavelengths shorter than the *K*-absorption edge of neon. The charge states and intensities of the ions formed were determined with a special mass spec-

trometer.^{5,6} Because of its simple electronic configuration, neon was chosen. This facilitated comparison with the calculated charge distribution. In particular, we hoped to gain more detailed information on the various processes occurring in the reorganization without being hampered by an undue number of parameters.

APPARATUS AND METHOD

The experimental apparatus is shown in Fig. 1. A detailed description of its operation is given elsewhere.⁶ The following is a brief outline describing the features essential to this study. The x-ray beam from the aluminum anode enters the ionization chamber through a 0.0025-cm-thick beryllium window and is shaped by the slit in plate X-1 of the collimator system. The additional plates X-2 to X-4 suppress "ricochet" x rays and secondary electrons from metal surfaces along the path of the x rays. Plate X-5 repels electrons emerging from the x-ray trap. The effective region of ionization constitutes a thin disk, which is common to the x-ray sheet beam and the paraxial pencils through the aperture of plate G-3. The ions and electrons produced in this space

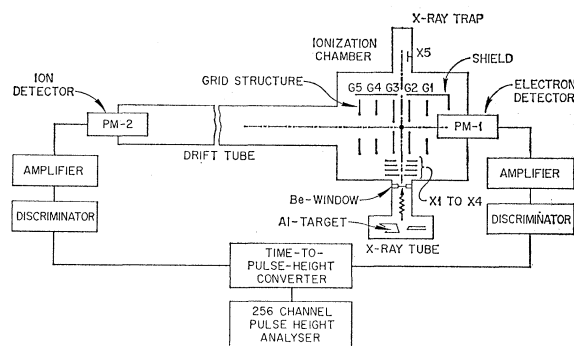


FIG. 1. Schematic diagram of the apparatus.

* The experimental portion of this study was performed under the auspices of the U. S. Air Force, Wright Patterson Air Force Base, at Wm. H. Johnston Laboratories Inc., Baltimore, Maryland.

¹ See, for example: A. Migdal, *J. Phys. (U.S.S.R.)* 4, 449 (1941); E. L. Feinberg, *J. Phys. (U.S.S.R.)* 5, 423 (1941); H. M. Schwartz, *J. Chem. Phys.* 21, 45 (1953); M. Wolfsberg and M. L. Perlman, *Phys. Rev.* 99, 1833 (1955).

² A. H. Snell and F. Pleasonton, *Phys. Rev.* 100, 1396 (1955).

³ F. Fiquet-Fayard, *J. Chem. Phys.* 59, 439 (1962); 131, 1050 (1962).

⁴ M. O. Krause (unpublished).

⁵ H. M. Rosenstock, U. S. Patent No. 2,999,157.

⁶ M. Vestal, M. O. Krause, A. L. Wahrhaftig, and Wm. H. Johnston (unpublished); see also, American Society for Testing Materials Meeting, eleventh Annual Conference, San Francisco, 1963 (unpublished).

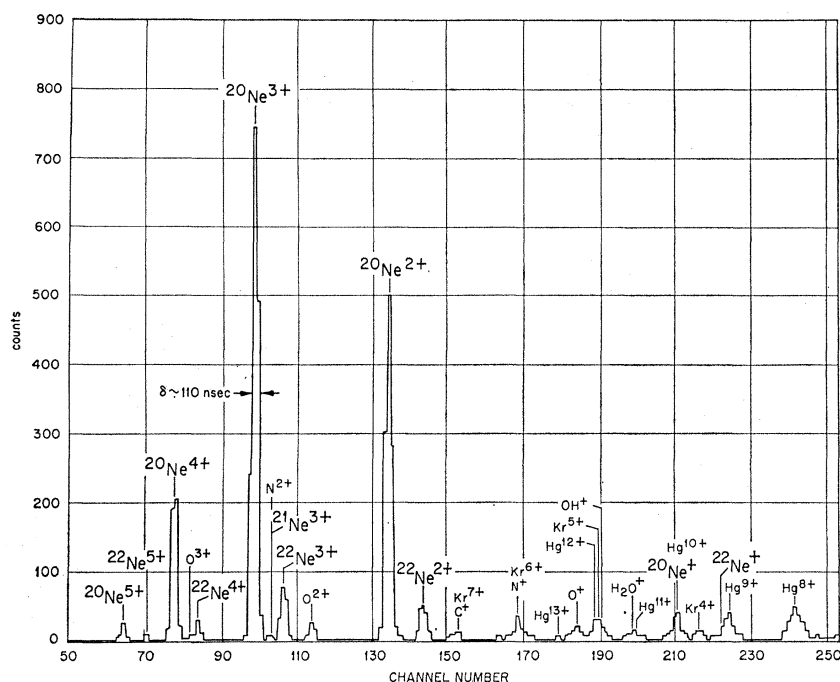


FIG. 2. Charge spectrum of neon resulting from inner shell ionization by x rays. Reproduction from chart record of pulse-height analyzer.

are extracted by an electrical field between G-2 and G-3. The ions are accelerated up to plate G-5 and drift with the acquired velocity through the 3-m-long drift tube. Shortly before striking the first dynode of a multi-stage dynode structure PM-2 the ions are further accelerated. The electrons are detected by another dynode structure PM-1.

The arrival of the electron determines the zero time of the ionization event within 10 nsec. The ion and electron(s) of a single event are placed in delayed coincidence with the aid of a gated time-to-pulse-height converter. The converter, in conjunction with a pulse-height analyzer, also samples the ions according to their transit times, which are related to the mass-to-charge ratio by the equation: $\tau = f(m/q)^{1/2}$. The constant f is determined by the geometry and operating voltages of the apparatus.

The detection of the ion in coincidence with the corresponding electron allows the use of a continuous source of radiation and procures a good signal-to-noise ratio even for rates of ionization of much less than 0.1 event per second. At the same time, however, the probability of detecting an ion becomes dependent upon the probability of detecting the corresponding electron. For the ion of charge n it is given by

$$P_n = 1 - \prod_{i=1}^n (1 - P_i), \quad (1)$$

where P_i is the collection probability of the i th electron.⁷ P_i is a function of the electron expeller field and the electron energy.

⁷ The time spread of the secondary electrons upon arrival at the first dynode of PM-1 is less than the resolution of the detector electronics; therefore, they are not separated.

In simple cases, when P_i is known, P_n can be calculated and be used to find the true abundances of the charge- n ion by dividing the observed figures by P_n .

EXPERIMENTAL PROCEDURE

The x rays from the aluminum target consisted of the Al K_α line at 1.5 keV and the superimposed bremsstrahlung with high-frequency cutoff at 5.2 keV. Since the intensity of the continuous radiation decreases toward the longer wavelengths, while the absorption of the beryllium window increases, nearly the entire radiation entering the ionization chamber lies above 1 keV and thus above the K -absorption edge of neon at 0.87 keV. A weak tail extends to about 0.8 keV, at which point the transmission⁸ of the 0.0025-cm-thick Be foil is less than 1%. The flux⁹ through the effective ionization region is about 10^8 photons/sec. The neon sample was introduced by a capillary leak into the ionization chamber at pressures from 4 to 10×10^{-6} Torr for various runs. In this range the charge distribution of the ions was not noticeably affected by pressure effects, as was tested by increasing the pressure up to 2×10^{-5} Torr. The reported pressures are ionization gauge readings and should be multiplied by a factor of 4.5 to arrive at the actual pressures.¹⁰

It is noteworthy that the contribution of the residual gas to the total spectrum was very small, although the background pressure amounted to about 25% of the sample pressure in some runs. This discrimination

⁸ Calculated with the mass absorption coefficient given by J. Taylor and W. Parrish, Rev. Sci. Instr. **26**, 4 (1955).

⁹ J. A. Bearden (private communication).

¹⁰ F. W. Lampe, J. L. Franklin, and F. M. Field, J. Am. Chem. Soc. **79**, 6129 (1957).

TABLE I. Charge distribution of neon ions produced by soft x rays (percent abundance).

Charge of Ion	Experiment I		Experiment II
	Observed	Corrected	Observed
1	0.9±0.6	3.3±0.6	2.7±0.5
2	35.5±1	66 ±5	65.6±2.5
3	48.5±1	26 ±4	22.7±1.5
4	13.8±0.7	4.8±1.5	7.7±0.9
5	1.2±0.2	0.3±0.2	1.3±0.4
Mean charge	2.8	2.4	2.4

against the light molecules of the residual gas, consisting largely of water vapor and nitrogen, is mainly due to poor collection of the fragments produced by a violent rupture of the bonds after inner shell ionization.¹¹ On the other hand, heavier monoatomic gases at very low partial pressures were detected, viz., mercury from the Dubrovin gauge on the sample reservoir.

The entire charge spectrum of neon was obtained by collecting at one time all ions in the mass range from 2 to 26 amu. This eliminated errors due to fluctuations and drifts of the x-ray flux, pressure and noise levels of various origins during the time of operation which lasted up to 15 h in some instances.

Two sets of experiments were performed. In the first experiment, the charge spectrum was measured by collecting with greatest possible efficiency all electrons transmitted through the aperture G-2. In the second experiment the charge spectrum was measured by collecting only those ions that were in coincidence with electrons of energies greater than 120±40 eV. For this purpose two mesh grids were introduced between G-1 and G-2, providing a simple device for retarding electrons. The meaning and correlation of the two experiments are discussed in the following section.

EXPERIMENTAL RESULTS

In Fig. 2 a typical run of the charge spectrum is reproduced from the chart record of the pulse-height analyzer. Both the neon ions and the contaminants are identified. The relative abundances of the charge of Ne²⁰, averaged from two runs, are listed in the second column of Table I. The errors quoted account for statistical and background fluctuations. The intensity of Ne¹⁺ is corrected for the contribution of the obscuring charge-10 mercury isotopes with the aid of Hg⁹⁺ and Hg⁸⁺ and the uncertainty for this adjustment is included in the given error. The required figures were obtained in a separate run on mercury, which yielded the relative intensities of Hg⁸⁺, Hg⁹⁺, Hg¹⁰⁺ as 14.4%, 11.1%, 7%, respectively.

This spectrum was obtained by collecting all electrons passing through G-2, experiment I. Since the electrons associated with the ions vary in number and energy, the observed spectrum needs to be corrected for

the variations in the electron collection efficiency by using Eq. (1). The necessary probabilities are obtained from the measured mean collection efficiency for all electrons, $\bar{P}_n=0.22$, and from the collection efficiency for slow electrons with energies of less than 50 eV, $P_s=0.21$, as obtained from electron ionization. The corrected values are listed in column 3 of Table I; the given errors are deduced from the uncertainty of \bar{P}_n and P_s .

It was assumed that the ejected electrons may be divided into two groups each of nearly equal collection efficiency. One group comprises the photoelectron and the *KLL* Auger electron with energies of about 700 eV and above. The other group contains slow electrons, whose energy is predominantly below 50 eV. They arise from one or more of three possible processes: shake-off, Auger transitions filling 2s vacancies, and direct ionization of *L* electrons by the photo- and *KLL* Auger electrons.

The slow electrons can be assigned to charges 3 and 5, while the photoelectron is common to all charges, and the *KLL* Auger electron is associated with all charges except charge one. This offers a possibility of measuring directly the "true" abundances by retarding the slow electrons. The results of this type of experiment, experiment II, using a retarding potential of 120±40 V are given in column 4 of Table I. The reported spectrum is the average of four runs and the quoted errors account for statistical and background fluctuations. The corrected spectrum of the first experiment and the spectrum of the second experiment agree satisfactorily. In the following, reference is made to the average values of the two spectra.

No additional corrections were applied to the charge spectra. An evaluation of the various systematic errors shows that the deviations are generally well within the above cited limits. This applies to the discrimination between the differently charged ions due to variations in electron multiplier response, lens defects of the acceleration system, recoil from the ejected electrons, and ionizations from other sources than by x rays. The contribution of ionization by spurious secondary electrons, which would primarily produce ions of charge 1, was carefully checked by measuring pressure dependence curves and by referring to the charge spectra of krypton and xenon⁴; Kr¹⁺ and Xe¹⁺ constitute a very sensitive test, because of the low probability of a purely radiative adjustment to an initial *L* or *M* vacancy. The results show that the percentage of charge 1 due to electron ionization is less than 0.4% of the total number of ions observed.

In the second experiment charge 1 was detected slightly less efficiently than the other charges because of the absence of the second (Auger) electron. The correction would be relatively small (about 0.3% added to charge 1) due to the fact that the photoelectron is preferentially ejected perpendicular to the x-ray beam and is thus detected with an enhanced probability over the isotropically distributed Auger electron.

¹¹ S. Wexler and G. R. Anderson, J. Chem. Phys. **33**, 850 (1960); T. A. Carlson and R. M. White, J. Chem. Phys. **36**, 2883 (1962).

In order to reduce the data to the spectrum resulting from a K vacancy alone, primary ionization in the L shell by x rays should be taken into account. For radiation near the K -absorption edge the ratio of L/K ionization¹² would be roughly $E_{L_1}/E_K \approx 5.5\%$. Since most of the existing radiation is somewhat above the K -absorption edge, namely, $E_{ph} \gtrsim 2E_K$, the above value is likely to be upper limit for L ionization. The partial ionization in the L_I level is 2 to 5 times greater than in the $L_{2,3}$ levels.¹³ Since no precise numbers are available, a correction is omitted and it may only be stated that the contribution to the charge spectrum from direct L ionization is small, i.e., within the given error, except for charge 1.

CALCULATION OF THE CHARGE SPECTRUM

We consider first the transfer of a $1s$ vacancy to the outermost shell and the consequences in regard to the charge state of the atom. There are four possible paths available for filling a $1s$ hole in neon. For the first path, a $2p$ electron fills the vacancy and an x ray is emitted. According to the selection rules for dipole transitions this is the only allowed transition. No extra electron is removed, so that this transition, path 1, will result in a singly charged ion. A purely radiative adjustment will occur in 0.7% of the cases as given by the fluorescence yield.¹⁴ In the remaining 99.3% of the cases, the $1s$ vacancy is filled by one of three possible Auger processes, designated as paths 2, 3, and 4. They involve the following pairs of electrons: ($2p, 2p$); ($2s, 2p$); and ($2s, 2s$). Whether or not these three alternative paths are equivalent in respect to the final charge state depends upon the fate of the $2s$ vacancies. If the $2s$ hole is filled exclusively by a radiative transition, no further electron will be removed and paths 2 to 4 result in Ne^{2+} . If, however, a mechanism can be found to allow an Auger process to occur for each $2s$ vacancy produced, paths 2, 3, and 4 can result in Ne^{2+} , Ne^{3+} , and Ne^{4+} , respectively. The abundances of these charge states are then determined by the relative transition probabilities of the Auger processes ($1s; 2p, 2p$), ($1s; 2s, 2p$), and ($1s; 2s, 2s$). Since neither experimental data nor theoretical calculations of the K - LL transition probabilities exist for neon we have undertaken to calculate these probabilities by assuming pure LS coupling.

The number of radiationless transitions occurring in time dt is given¹⁵ by first-order perturbation theory as:

$$b_n dt = \frac{2\pi}{\hbar} \left| \int \int \chi_f^*(\mathbf{r}_1) \psi_f^*(\mathbf{r}_2) \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|} \chi_i(\mathbf{r}_1) \psi_i(\mathbf{r}_2) \times d\mathbf{r}_1 d\mathbf{r}_2 \right|^2 dt. \quad (2)$$

¹² E. Jönsson, thesis, Uppsala, 1928 (unpublished).

¹³ G. Wentzel, Z. Physik 40, 574 (1927); M. Stobbe, Ann. Physik 7, 661 (1930).

¹⁴ A. H. Wapstra, G. J. Nijgh, and P. Van Lieshout, *Nuclear Spectroscopy Tables* (North-Holland Publishing Company, Amsterdam, 1959), p. 82.

¹⁵ E. H. S. Burhop, *The Auger Effect* (Cambridge University Press, New York, 1952), p. 11.

TABLE II. Auger transition probabilities for filling a $1s$ vacancy in neon.

Final vacancies	l_a^a	Transition rate ^b	Relative transition probability
$2s\ 2s$	0	0.577	0.04
$2s\ 2p$	1	2.11	0.14
$2p\ 2p$	0	1.07	0.82
$2p\ 2p$	2	11.13	

^a l_a is the angular momentum of the Auger electron in the continuum.
^b The transition rates are expressed in atomic units $\times 10^{-3}$.

The wave functions for the initial states, $\chi_i(\mathbf{r}_1)$ and $\psi_i(\mathbf{r}_2)$ are taken from the Hartree-Fock solutions¹⁶ for the $2s$ and $2p$ states of Na^+ . The final-state wave functions, $\chi_f(\mathbf{r}_1)$ and $\psi_f(\mathbf{r}_2)$, are taken from the Hartree-Fock solution¹⁷ for the $1s$ state of Ne^0 and the free wave solution¹⁸ in a Hartree-Fock field for Na^+ . We have attempted in our choice of wave functions to use those which correspond to electrons that see nearly the same effective charge seen by the electrons in the actual case. The calculations were carried out on a 7090 IBM computer. In general, we have followed procedures as given in detail by Rubenstein.¹⁹ The results of the calculations are given in Table II. From the ratio of these results we obtain the relative transition probabilities for paths 2, 3, and 4. They are, respectively, 0.82, 0.14, and 0.04. To find the relative abundance of Ne^{2+} , Ne^{3+} , and Ne^{4+} we have only to multiply these ratios by 99.3%.

There are other sources of ionization available from the production of a vacancy in the K shell. For example, there is the contribution of Coulombic shaking as the result of changes in the effective charge due to the initial loss of the K electron. According to Slater's rules²⁰ removal of the K electron will create a change of 0.85 units in the effective charge seen by the $2s$ and $2p$ electrons. If the velocity of the ejected photoelectron is large compared to the orbital velocities of the $2s$ and $2p$ electrons, the outer shell will suffer a sudden perturbation similar to that found with beta decay, in which the orbital electrons see a sudden change in nuclear charge of one unit.^{1,21} We have estimated²² from calcu-

¹⁶ D. R. Hartree and G. Hartree, Proc. Roy. Soc. (London) A193, 299 (1948).

¹⁷ B. H. Worsley, Can. J. Phys. 36, 289 (1958).

¹⁸ W. R. Garrett and R. A. Mann (private communication).

¹⁹ R. A. Rubenstein, thesis, University of Illinois, 1955 (unpublished).

²⁰ J. C. Slater, Phys. Rev. 36, 57 (1930).

²¹ J. S. Levinger, Phys. Rev. 90, 11 (1953).

²² The probability of vacating the ground state of an atom, following a sudden change in the effective charge is given by:

$$1 - \left| \int \psi_{z+2}^* \psi_z d\tau \right|^2.$$

We have examined the probability as a function of the change in effective charge, by using hydrogenic wave functions which are expressed as a function of Z : e.g., L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1935), p. 135.

TABLE III. Charge distribution of neon ions resulting from a 1s vacancy (percent abundance).^a

Charge of ion	Experiment	Theory A ^b	Theory B ^c
1	3	0.6	0.6
2	66	84	69
3	24	15	24
4	6	1	6
5	1	0.04	0.8

^a Note added in proof. The experimental distribution contains a small percentage of initial *L* ionization.

^b 2s vacancies filled by radiative processes.

^c 2s vacancies filled by Auger processes.

lations with screened hydrogenic wave functions that the probability for single electron shake-off in our study is $\frac{3}{4}$ of that observed²³ in the β^- decay of Ne²³. From the extent of single electron shake-off, one can also estimate²³ the amount of double and triple electron shake-off. With the assistance of the data available from the β^- decay of Ne²³ we have thus calculated the probabilities for single, double, and triple electron shake-off following removal of the *K* electron to be, respectively, 14.6%, 1.0%, and 0.04%. The final charge spectrum is obtained by superimposing the probabilities for electron removal, both from shaking and Auger processes. The results are given in Table III for the two extreme cases of filling a 2s vacancy exclusively by a radiative transition or exclusively by a radiationless process with the ejection of another electron.

DISCUSSION

The low abundance of Ne¹⁺ due to initial ionization in the *K* shell is in agreement with known values of the fluorescence yield. Correspondingly, the large abundance of Ne²⁺ appears reasonable. The magnitude of the abundances of Ne³⁺, Ne⁴⁺, and Ne⁵⁺, however, resists a straightforward interpretation in terms of Auger processes involving two electrons and the sudden perturbation theory of electron shake-off.

In the previous section we made use of calculated *K*-*LL* Auger transition rates and adjusted shake-off probabilities from the β^- decay of Ne²³. Two spectra were calculated to show the effects of having a 2s vacancy filled by transitions with or without the ejection of a further electron. Though the filling of a 2s hole by an Auger process leads to a satisfactory agreement of the observed with the calculated charge spectrum, it is difficult to defend such an assumption. The energy balance for the Auger process from the initial configuration (1s²2s2p⁵) to the final configuration (1s²2s²2p³) is endothermic by about 40 eV according to

$$E(1s^2 2s 2p^5 - 1s^2 2s^2 2p^3) \\ = E_{L_1}(\text{NeII}) - E_{L_{2,3}}(\text{NeII}) - E_{L_{2,3}}(\text{NeIII}),$$

²³ T. A. Carlson, Phys. Rev. **130**, 2361 (1963).

where $E_{L_1}(\text{NeII}) = 68 \text{ eV}^{24}$; $E_{L_{2,3}}(\text{NeII}) = 41 \text{ eV}^{25}$ and $E_{L_{2,3}}(\text{NeIII}) = 64 \text{ eV}^{25}$. Likewise the reactions (1s²2s⁰2p⁶) to (1s²2s¹2p⁴) and (1s²2s¹2p⁴) to (1s²2s²2p²) are endothermic. Consequently, these processes are not permitted. The filling of a 2s vacancy by an Auger process would, therefore, require that at least one electron would have been previously promoted to an excited state. It seems to be improbable, however, that in every case when a 2s hole is formed, one or more electrons would be found in the optical levels.²³

On the other hand, suppose Auger processes do not occur to any appreciable extent, following the production of a 2s vacancy. Then sources of further ionization beyond charge 2 are electron shake-off, and collision of photoelectron and *KLL* Auger electrons with orbital electrons. In the calculation we have transferred the data on the β^- decay of Ne²³ to the present case and by doing so, implied that the photoelectron is fast enough to justify electron excitation due to a *sudden* change in effective charge. Hence collision of the photoelectron with *L* electrons would be negligible.¹ This constitutes an idealized approximation, since the velocity of the photoelectron is not much greater (3 to 8 times) than the velocity of the *L* electrons in their orbits. Consequently, the amount of shake-off, as given in the preceding section, represents an upper limit for this source of ionization. At the same time, with the decrease of the shakeoff probability, the probability of direct ionization by the photoelectron increases. If we assume an ionization of shape similar to that known from electron bombardment,²⁶ the energy of the photoelectron is approaching the "resonance" energy. The *KLL* Auger electron also has a certain probability of ionizing another *L* electron, which process could also be considered as an Auger process of a three-electron interaction. This latter suggestion is not in contradiction with existing measurements of Auger lines and intensities, because such a process would, as a small effect, be buried in the background of the measurements.

As to the magnitude of ionization by slow electrons on their passage through the electron cloud no direct data are available in literature. Feinberg¹ estimates that the excitation by direct collision amounts to about 1% of that by shake-off in the special case of raising a *K* electron to the *L* level by an electron of energy comparable to the *K* binding energy. A definitive estimate for the ionization under our conditions is, however, still lacking.

In conclusion, Auger and shake-off processes do not seem to account for all the ionization observed in neon. More work, both theoretical and experimental, is indi-

²⁴ Interpolated from values given by R. H. Garstang, Proc. Cambridge Phil. Soc. **47**, 243 (1951).

²⁵ *Landolt-Börnstein Tables*, edited by A. M. Hellwege (Springer-Verlag, Berlin, 1950), Vol. I/1, pp. 148, 165.

²⁶ H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, England, 1956), p. 175; R. D. Richtmyer, Phys. Rev. **49**, 1 (1936).

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.

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$K\beta$ 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.^{1,2} The extent to which difficulties associated therewith have affected interpretations of x-ray spectra in general may be seen in recent review articles.^{3,4} 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 Howland⁵ 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.⁶ 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 β_x . Most discussions of this spectrum have considered $\beta_{1,3}$ as the valence emission band which was sought, and β_x as a satellite or satellite complex.⁷

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

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

³ L. G. Parratt, *Rev. Mod. Phys.* **31**, 616 (1959).

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

⁵ L. P. Howland, *Phys. Rev.* **109**, 1927 (1958).

⁶ J. O. Porteus, *J. Appl. Phys.* **33**, 700 (1962).

⁷ 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.