

Vacancy configurations of argon projectile ions in solids

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(Received 10 August 1973; revised manuscript received 22 August 1974)

The use of high-resolution x-ray measurements in determining the electronic vacancy configuration of an energetic ion inside a solid has been applied to 4.0- and 5.0-MeV Ar projectiles incident on a KCl target. The Ar $K\alpha_{1,2}$ line is found to be shifted to higher energies by 6.1 ± 0.6 and 8.1 ± 0.6 eV, respectively, at these bombarding energies. These shifts correspond to five and six vacancies in the Ar $3s-3p$ subshells. The Cl $K\alpha_{1,2}$ line is used as a reference line and thin-target x-ray cross-section measurements are used to show that Cl and Ar are excited in the same manner.

I. INTRODUCTION

Numerous K x-ray spectra from target atoms excited by heavy-ion collisions have been measured with high resolution,¹ but only one high-resolution measurement has been reported for K x rays emitted by projectile ions in solid targets.² It is of interest to measure high-resolution x-ray spectra emitted by projectile ions for comparison with those emitted by target atoms in a solid under similar circumstances. Whereas the target ion generally receives all of its excitation in a single collision with the projectile ion, the projectile ion is continually interacting with target atoms. The moving ion will have a number of outer-shell vacancies and may also have inner-shell vacancies^{3,4} already present when the K -shell vacancy is produced. The electronic configuration of the ion may be further altered subsequent to production of the K -shell vacancy, but prior to decay of the K -shell hole, since a 4.0-MeV Ar ion travels more than 45 \AA in the lifetime⁵ of the K -shell vacancy. If the average charge state of the outer shells is unaffected by the K -shell hole, measurements of projectile spectra would provide, in principle, a method of determining the average charge state of the projectile inside a solid, since the energies of the x rays are determined by the electronic configuration of the emitting ion. However, the projectile may have associated with it loosely bound electrons in excited states, whose influence on the K x-ray energy is less than the uncertainty in the measured x-ray energy. It is expected that electrons in highly excited states have orbital diameters comparable to the interatomic spacing in solids, and electrons in these levels would be quickly stripped off. Further complexities are introduced by the possibility of polarization of the solid and screening of the projectile charge by the valence electrons of the solid.⁶

A method of determining vacancy configurations

of ions inside solids would be useful in resolving the question of whether the Bohr-Lindhard^{7,8} or the Betz-Grodzins^{8,9} model provides the better description of an ion inside a solid. The former model predicts that the charge state of an ion inside a solid is essentially the same as the charge state after emergence, while the latter model predicts that the charge state inside a solid is comparable to that in a gas and considerably less than the charge state after emergence from the solid.

In the present study we investigate the possibility of using high-resolution x-ray spectra to obtain information on the vacancy configuration of Ar ions in a solid target, a problem for which we know of no alternative method of investigation.

II. EXPERIMENTAL DETAILS

Ar beams from the NRL 5-MV Van de Graaff were incident on a KCl crystal which had been given a thin coating of Cu to prevent problems due to charging of the target surface. For the high-resolution measurements $K\alpha$ x rays produced by Ar ions incident on KCl were measured at 90° to the incident beam with a computer-controlled flat-crystal Bragg spectrometer with a 0.07° -divergence entrance collimator. The P-10 gas-flow proportional counter had a stretched polypropylene window about 1 \mu m thick. A (1120) quartz crystal with a $2d$ spacing of 4.916 \AA was used as the diffracting element. For the low-resolution measurements a Si(Li) detector of 165-eV resolution was used to obtain x-ray spectra produced by incident Ar ions with energies from 3.0 to 5.0 MeV. Thin targets of NaCl, KCl, and Ti were evaporated onto $20\text{-}\mu\text{g}/\text{cm}^2$ C backings. The thickness of the deposited material was determined by α -particle backscattering and in all cases was less than $20\text{-}\mu\text{g}/\text{cm}^2$, which corresponds to about a 100-keV energy loss for 3.0-MeV Ar.

III. RESULTS

A. High-resolution measurements

Ar and Cl $K\alpha$ spectra are shown in Fig. 1 as produced by a 4.0-MeV Ar beam. In each case the $K\alpha_{1,2}$ parent line appears at the left, and satellite lines, due to various numbers of L -shell vacancies, appear at higher energies. The abscissae are linear in θ , but the Ar scale has been stretched out by about a factor of 2 so that corresponding peaks in the two spectra would be directly above one another. The Cl spectrum exhibits narrower lines than the Ar spectrum when the full width at half-maximum is measured in terms of energy. The angular widths of the lines in both spectra are considerably larger than the instrumental resolution.

The width of the Ar lines results from several factors. Multiple scattering of the Ar beam will produce a velocity component transverse to the beam direction, which will result in Doppler broadening of the lines. Variations in the number of M -shell electrons present on the Ar ion will also contribute to the width, and some of the broadening may be due to spatial variations in the electron density seen by the Ar ion in the solid target. The Cl spectrum also contains a larger fraction of the total intensity in the satellite lines than does the Ar spectrum. Cl and Ar $K\alpha$ spectra measured at 5.0 MeV were almost identical in shape to the 4.0-MeV spectra, but the Ar spectrum was somewhat shifted in energy.

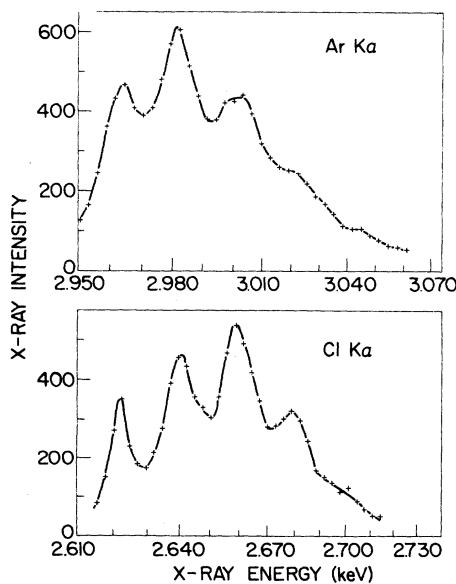


FIG. 1. Cl and Ar $K\alpha$ spectra produced by 4.0-MeV Ar ions incident on KCl. Each spectrum is the average of five sets of data.

The spectrometer energy scale was calibrated by using the Cl and K $K\alpha_{1,2}$ lines excited by protons and He^4 ions. The energy calibration was checked by exciting the Pd $L\beta_1$ line with protons. A measurement of the Pd $L\beta_1$ line, whose energy is about 30 eV higher than that of the Ar $K\alpha_{1,2}$ line, showed that its energy was within 0.2 eV of the value given by Bearden.¹⁰ The spectra obtained with 4.0- and 5.0-MeV Ar excitation were fit with a superposition of asymmetric Gaussian line shapes. The widths of the Gaussians were allowed to vary independently for each line in the spectrum. The Cl $K\alpha_{1,2}$ line showed no change in energy with heavy-ion excitation, but the Ar $K\alpha_{1,2}$ line appears higher in energy than is expected from the tables of Bearden¹⁰ by 6.1 ± 0.6 eV at 4.0 MeV and 8.1 ± 0.6 eV at 5.0 MeV. To correct for the transverse Doppler shift,¹¹ a correction of 0.3 eV has been applied at 4.0 and 5.0 MeV. Since the Cl $K\alpha_{1,2}$ line is unshifted, the very similar nature of the excitation processes for Cl and Ar, which will be established later in this paper, would tend to indicate that the shift in the energy of the Ar $K\alpha_{1,2}$ line results from its role as a projectile, rather than from the collision which produced the K -shell vacancy. We restrict our attention to the Ar $K\alpha_{1,2}$ line, since the normal energies for the Ar satellite lines are not available in the literature.

The results of Hartree-Fock-Slater¹² (HFS) calculations of the Ar $K\alpha_{1,2}$ energy for various electronic configurations are given in Table I. Part A shows that the observed shifts can be accounted for by the absence of five and six electrons, respectively, distributed between the $3s$ and $3p$ subshells. However, within the present experimental uncertainty the exact distribution of vacancies in the $3s$ and $3p$ subshells cannot be determined by

TABLE I. Calculated $K\alpha$ and $K\beta$ x-ray shifts for various M - and N -shell configurations of Ar.

Configuration $(1s)(2s)^2(2p)^6(3s)^k(3p)^m(3d)^n(4s)^p$				$\Delta E(K\alpha)$ (eV)	$\Delta E(K\beta)$ (eV)	
k	m	n	p			
A	2	2	0	0	3.9	19.7
	2	1	0	0	5.6	27.5
	1	2	0	0	5.4	27.3
	0	3	0	0	5.2	27.1
	2	0	0	0	7.7	...
B	2	1	1	0	5.9	22.6
	2	1	0	1	5.1	25.1
	2	1	1	1	5.5	20.9
	2	0	1	0	7.9	...

measurement of the K x-ray energies. Calculations by Bhalla⁵ indicate that the $K\alpha$ fluorescence yield for the Ar $K\alpha_{1,2}$ transition increases by only about 7% when all eight M electrons are removed, so various M -shell configurations should contribute to the Ar $K\alpha_{1,2}$ line approximately in proportion to their probability of occurrence. Therefore the peak of the $K\alpha_{1,2}$ line should represent the most probable electronic configuration present at the time of K x-ray emission.

Extrapolating the experimental data for Ar ions in Table V.1 of Betz⁸ would suggest average charge states of 6.0 and 3.4, respectively, for 4.0 MeV Ar ions emerging from solids and in gases. At first sight the present data appear to confirm the value for solids, especially since the x-ray spectrum includes x rays emitted by Ar ions after they have lost some energy in the KCl and changed to a lower charge state. Furthermore, some portion of the L -shell vacancies seen in the spectrum should be added on to the M -shell vacancies to obtain the average charge state of the ion. However, additional HFS calculations were performed to determine the effect on K x-ray energies of electrons excited into normally vacant bound levels. These calculations showed a rather surprising behavior for the $3d$ level, namely, that moving an electron from the $3p$ to the $3d$ level produced an even larger positive shift in the $K\alpha_{1,2}$ energy than that produced by completely removing a $3p$ electron from the atom. The positive $K\alpha$ and negative $K\beta$ energy shifts, which are shown in part B of Table I to accompany the addition of a $3d$ electron, have also been obtained in previous calculations^{13,14}; so they are not an artifact of the HFS method.

Part B of Table I indicates that the additions of one or two $3d$ or $4s$ electrons causes changes in the $K\alpha_{1,2}$ energy which are within the uncertainty in the present measurements. Although the $3s$ - $3p$ ambiguity occurs in both the $K\alpha$ and $K\beta$ portions of the spectrum, the addition of a $3d$ or $4s$ electron produces a significant change in the $K\beta$ energy. However, our efforts to measure this shift were frustrated by the low intensity of the $K\beta$ transition. Interpreting the results of such a measurement would be complicated by the fact that the $K\beta$ intensity varies strongly with the number of $3p$ electrons present.

HFS calculations of the mean radii of the electron orbits for various configurations with four to six missing electrons distributed between the K , L , and M shells yield values between 1.3 and 1.5 Å for the $4s$ orbit and between 0.6 and 0.7 Å for the $3d$ orbit. The $3d$ radius is only slightly larger than the radii of the $3s$ and $3p$ orbits. Since the inter-nuclear separation of the target atoms is about

2.3 Å, it seems unlikely that a $4s$ electron could remain attached to the Ar projectile. In summary, although the present high-resolution data permit determination of the total number of $3s$ and $3p$ vacancies, within the accuracy of our measurement of the $K\alpha_{1,2}$ energy, we cannot rule out the presence of one or two $3d$ electrons.

B. Low-resolution measurements

If the K -shell excitation of Cl and Ar occurred by two different processes, the extra M -shell vacancies seen in Ar could possibly result from the different excitation mechanisms. In order to establish that the Cl and Ar excitations occur by similar processes, cross-section measurements were performed. These measurements utilized thin targets of NaCl, KCl, and Ti and showed dramatic effects depending on the relative atomic number of the target and projectile. For example, for Ar ions on Ti, the Ar K x rays are about 200 times more intense than the Ti K x rays, although Ar and Ti differ by only 4 units in Z . As would be characteristic of a level-crossing excitation mechanism,¹⁵ the lighter of the two collision partners receives most of the excitation.

K x-ray production cross sections for Cl, Ar, and K are shown in Fig. 2. These cross sections were calculated on the assumption that all of the Ar ions entering the target chamber, which also served as a Faraday cup, are singly ionized. This assumption could be significantly in error; so these data are intended only to provide a lower limit on the value of these cross sections. The relative values of the cross sections at a given energy are good to about 10%. The cross section for

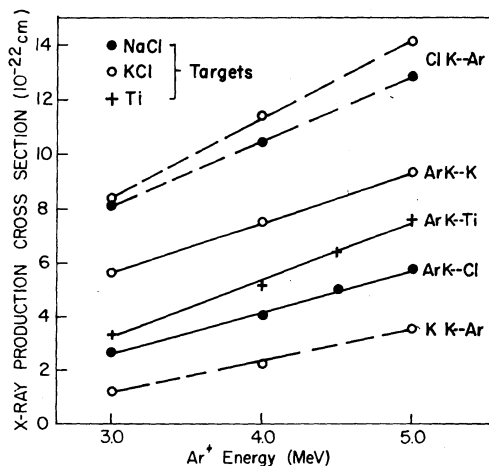


FIG. 2. K x-ray production cross section for Ar on NaCl, KCl, and Ti. Each curve is labeled by the radiation measured and the collision partner assumed to produce the required excitation.

excitation of ClK radiation is the same, within the experimental accuracy, for $NaCl$ and KCl targets. It was found that the ClK x-ray yields for excitation by 3.0-MeV Ar and 4.5-MeV protons are approximately equal. However, binary-encounter-model calculations based on Garcia's universal curve¹⁶ predict that the yield for Ar excitation should be 27 times less; so the cross sections for excitation by Ar are much larger than would be expected for direct Coulomb excitation.

The cross section for production of ClK x-rays by 5.0-MeV Cl^{3+} projectiles in an Ar gas target has been measured under single collision conditions by Winters *et al.*¹⁷ They obtain a value of $7.5 \times 10^{-22} \text{ cm}^2$, with an uncertainty of 30%. For 5.0-MeV Ar ions incident on $NaCl$ or KCl we obtain a ClK x-ray production cross section of about $13 \times 10^{-22} \text{ cm}^2$. It is expected that the cross section in a solid target would be larger because in this case the projectile may carry L -shell vacancies into the collision with subsequent transfer to the target K shell, thus providing an additional process for generating ClK -shell vacancies, which is not available in the gas target measurement.

In calculating the cross section for excitation of Ar in the composite targets, two assumptions were made. For the case of Ar in $NaCl$, it has been assumed that only the Cl is effective in exciting the Ar, since other measurements showed that Mg and Al targets are very ineffective in exciting Ar K vacancies. In calculating the x-ray cross section for Ar excited by K in KCl , it has been assumed that excitation of Ar by Cl is the same in KCl as in $NaCl$, and that component has been subtracted off to determine the excitation by K. These data for excitation of Ar by $Z-1$, $Z+1$, and $Z+4$ show a peaking of the cross section as a function of target Z in the neighborhood of $Z+2$. This peaking effect has been found to decrease as the ratio of projectile velocity to orbital velocity of the electron to be excited increases.¹⁸ This ratio is 0.14 for a 4-MeV Ar ion and an Ar K -shell electron, but peaking has been observed by Kubo *et al.*¹⁹ for ratios as large as 0.32.

IV. DISCUSSION

The low-resolution cross section measurements show that the Ar is excited predominantly by the K while the Cl is excited by the Ar in the Ar-on- KCl system. Therefore these are two similar collision systems (atomic number Z being excited by $Z+1$ in both cases), and such differences as appear in the high-resolution spectra should be due primarily to the fact that in one case the spectrum is emitted by a target atom and in the other case by a projectile ion. It was therefore somewhat unexpected that the relative satellite inten-

sity should be less in the Ar spectrum than in the Cl spectrum. However, HFS calculations indicate that the absence of five or six M electrons, which is consistent with the $ArK\alpha_{1,2}$ energy shift, increases the binding energy of the Ar L shell so that it is more tightly bound than the potassium L shell by about 50 eV. For either electron promotion or direct Coulomb processes, this increased binding would decrease the cross section for excitation of the Ar L shell. Electron capture into the L shell may also reduce the satellite intensity in the Ar spectrum.²⁰

Turning our attention next to K -shell excitation, the velocity of the Ar ion in the present experiment is about $\frac{1}{8}$ of the velocity of the $1s$ electron, and molecular-orbital (MO) effect might reasonably be expected here. The production of K -shell vacancies can be accomplished by rotational coupling between the $2p\sigma$ -MO and the $2p\pi$ -MO, as indicated in Fig. 3, where correlation diagrams are shown for Ar + Cl and Ar + K. The Ar projectile is expected to have one or more L -shell vacancies^{3,4}, which provide the $2p$ vacancies required for promotion of the Cl $1s$ electron. In the excitation of Ar by K, since the Ar L -shell is more tightly bound than the potassium L shell, electrons can be promoted from the K shell into the L shell of Ar. However, in the excitation of Ar by Ti there are no $2p$ vacancies in Ti into which the $1s$ electron may be promoted. Swapping of the Ar and Ti $2p$ levels occurs only when one $2p$ and all eight M -shell electrons have been stripped from the Ar. The small fraction of the Ar beam which would be in such a high charge state is not consistent with the fact that excitation of Ar by Ti has only a slightly smaller cross section

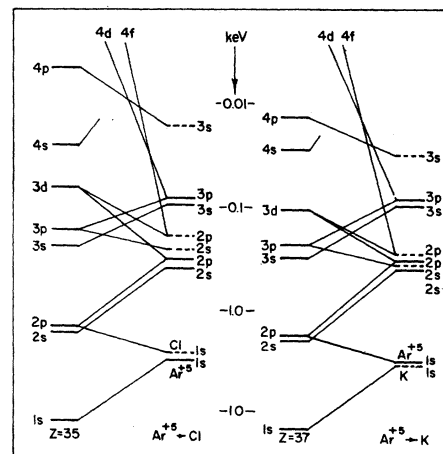


FIG. 3. Correlation diagrams are shown for the collision systems Ar + Cl and Ar + K. The Ar levels are calculated assuming five M -shell vacancies.

than excitation by K. Fastrup²¹ has pointed out that the high rotational energies occurring in these collisions may produce coupling to higher-lying MO's where vacancies exist, allowing promotion of K electrons. In fact, the production of K -shell vacancies by an MO mechanism even in the absence of L -shell vacancies has been reported by Winters *et al.*,¹⁷ but theoretical calculations are needed for rotational coupling of the $2p\sigma$ -MO to higher-lying molecular orbitals to determine whether this mechanism can account for the observed cross sections. Another possibility is that an earlier stage of the collision may provide the necessary $2p$ vacancies to allow promotion of the projectile $1s$ electron later in the same collision.

V. CONCLUSION

In conclusion, the study of projectile x-ray spectra appears promising as a tool to obtain in-

formation on the electronic configurations of energetic ions in solids. The energy shift of the $K\alpha_{1,2}$ line for 4.0- and 5.0-MeV Ar ions incident on KCl is consistent with five and six vacancies, respectively, in the Ar $3s$ - $3p$ subshells. These results are consistent with charge state measurements of Ar ions after emergence from solids. We have not been able to establish whether electrons are present in the normally vacant $3d$ and $4s$ shells, but calculations show that, where possible, measurement of the $K\beta$ energy shift allows one to identify configurations which are indistinguishable from a measurement of the $K\alpha$ energy.

ACKNOWLEDGMENT

The authors are indebted to Dr. Richard Deslattes for the loan of a quartz crystal.

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- ¹P. Richard, in *Proceedings of the International Conference on Inner Shell Ionization Phenomena, Atlanta, 1972*, Conf. 720404 (U.S. AEC, Washington, D.C., 1973), Vol. 3, p. 1641; J. D. Garcia, R. J. Fortner, and T. M. Kavanagh, *Rev. Mod. Phys.* **45**, 111 (1973).
- ²C. F. Moore, H. H. Wolter, R. L. Kauffman, J. McWherter, J. E. Bolger, and C. P. Browne, *J. Phys. B* **5**, L262 (1972).
- ³F. W. Saris, W. F. van der Weg, and H. Tawara, *Phys. Rev. Lett.* **28**, 717 (1972).
- ⁴J. Macek, J. A. Cairns, and J. S. Briggs, *Phys. Rev. Lett.* **28**, 1298 (1972).
- ⁵C. P. Bhalla, *Phys. Rev. A* **8**, 2877 (1973).
- ⁶W. Brandt, in *Proceedings of Fifth International Conference on Atomic Collisions in Solids, Gailinburg, 1973*, edited by S. Datz (Plenum, New York, 1974).
- ⁷N. Bohr and J. Lindhard, *K. Dan. Vidensk. Selsk. Mat.-Fys. Medd.* **28**, No. 7 (1954).
- ⁸H. D. Betz, *Rev. Mod. Phys.* **44**, 465 (1972).
- ⁹H. D. Betz and L. Grodzins, *Phys. Rev. Lett.* **25**, 211 (1970).
- ¹⁰J. A. Bearden, *Rev. Mod. Phys.* **38**, 78 (1967).
- ¹¹J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1963).
- ¹²F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N.J., 1963).
- ¹³K. Alder, G. Baur, and U. Raff, *Helv. Phys. Acta* **45**, 765 (1972).
- ¹⁴G. Leonhardt and A. Meisel, *J. Chem. Phys.* **52**, 6189 (1970).
- ¹⁵M. Barat and W. Lichten, *Phys. Rev. A* **6**, 211 (1972).
- ¹⁶J. D. Garcia, *Phys. Rev. A* **1**, 1402 (1970).
- ¹⁷L. Winters, J. R. Macdonald, M. D. Brown, T. Chaio, L. D. Ellsworth, and E. W. Pettus, *Phys. Rev. Lett.* **31**, 1344 (1973).
- ¹⁸T. M. Kavanagh, M. E. Cunningham, R. C. Der, R. J. Fortner, J. M. Khan, E. J. Zaharis, and J. D. Garcia, *Phys. Rev. Lett.* **25**, 1473 (1970); F. Saris and D. J. Bierman, *Phys. Lett.* **35A**, 199 (1971).
- ¹⁹H. Kubo, F. C. Jundt, and K. H. Purser, *Phys. Rev. Lett.* **31**, 674 (1973).
- ²⁰A. R. Knudson, P. G. Burkhalter, and D. J. Nagel, in *Ref. 6*.
- ²¹B. Fastrup, in *Proceedings of the International Conference on Inner Shell Ionization Phenomena, Atlanta, 1972*, Conf. 720404 (U.S. AEC, Washington, D.C., 1973), Vol. 2, p. 1188.