[15]C. M. Lederer, J. M. Hollander, and I. Perlman, *Table of Isotopes* (Wiley, New York, 1967), 6th ed., pp. 566–569.
[16]B. Müller, J. Rafelski, and W. Greiner, to be published, and private communication.
[17]Q. C. Kessel and B. Fastrup, Case Stud. At. Phys. 3, 137 (1973).
[18]J. D. Garcia, R. J. Fortner, and T. M. Kavangh, Rev. Mod. Phys. 45, 111 (1973).
[19]C. P. Bhalla, private communication. See also C. P. Bhalla and D. L. Walters, in *Proceedings of the International Conference on Inner-Shell Ionization Phenomena and Future Applications, Atlanta, Georgia, April 1972*, edited by R. W. Fink, S. T. Manson, J. M. Palms, and P. V. Rao (U. S. Atomic Energy Commission, Oak Ridge, Tenn., 1973), p. 1572.

Nonmonotonic Target Dependence of Cl *K* X-Ray-Production Cross Sections in Single Heavy-Ion–Atom Collisions*

Loren Winters, James R. Macdonald, Matt D. Brown,
Tang Chiao, Louis D. Ellsworth, and E. W. Pettus
Department of Physics, Kansas State University, Manhattan, Kansas 66506
(Received 5 July 1973)

Chlorine *K* x-ray-production cross sections have been measured in single collisions of chlorine ions in low incident charge states with gas targets at MeV energies. The cross sections are nonmonotonic as a function of target atomic number, but they approach monotonicity with increasing projectile energy. To explain these results in terms of $2p\sigma$-$2p\pi$ transitions in nearly symmetric collisions effectively requires $2p$ vacancy production simultaneous with the promotion of Cl $1s$ electrons.

The production of Cl *K* x rays has been observed in single collisions of chlorine projectiles of low incident charge states with a variety of thin, gas targets at 0.1 to 1.5 MeV/amu. The experimental Cl *K* x-ray-production cross sections are plotted in Fig. 1 as a function of target atomic number Z_2 for projectile energies of 5 to 52 MeV. The cross sections exhibit a nonmonotonic dependence on Z_2 in contrast to the Z_2^2 dependence given by a one-electron Coulomb ionization process.[1,2] An enhancement of the cross sections observed at argon is greatest at the lowest energy and becomes less pronounced as the projectile energy increases. At the highest energy, the cross sections are monotonic as a function of Z_2. The careful monitoring of single-collision conditions and incident charge-state selection in this experiment allows one to obtain more information concerning the collision process than previous observations of nonmonotonic dependences of projectile *K* x-ray production on the atomic number of solid targets[3,4] have provided. The $2p\sigma$-$2p\pi$ transition suggested to explain the observations for solid targets is inadequate to account for the data presented in Fig. 1 for which the experimental restriction was imposed that no $2p$ vacancies be carried into the collisions that produced *K*-shell vacancies. Any promotion mechanism that attempts to account for these data by a coupling

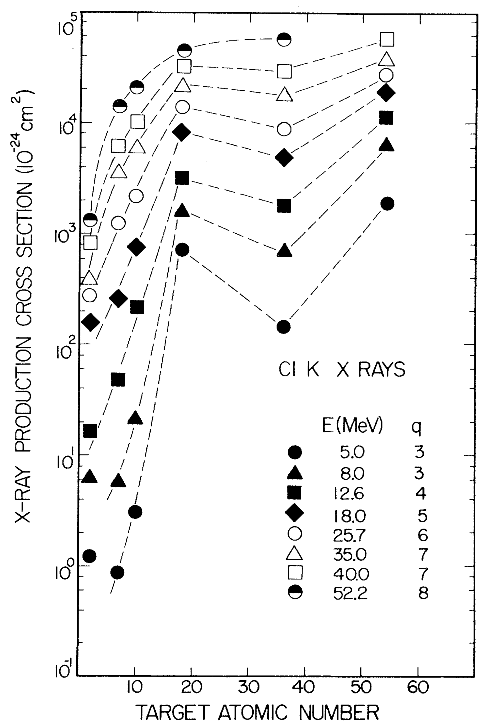

FIG. 1. Chlorine *K* x-ray-production cross section as a function of target atomic number for chlorine projectiles of incident energy *E* and charge state *q*. The dashed lines are drawn to guide the eye through the data points with constant energy.

of K electrons to projectile L-shell vacancies must provide for the removal of both K and L electrons within the time span ($\sim 10^{-17}$ sec) of a single collision.

Nonmonotonic dependences of cross sections on target and projectile atomic number were first reported[5] for K and L x-ray production induced by fission-fragment bombardment of solid targets. A number of researchers[6-8] have since observed such nonmonotonic trends for L x-ray-production cross sections measured in heavy-ion bombardment of both solid[6,7] and gaseous[8] targets at ion energies below 0.5 MeV/amu. These trends have been interpreted in terms of electron promotion resulting when the binding energy of the electron to be excited matches the binding energy of an electron of the collision partner.[9]

Recent experiments have given evidence for the occurrence of K-shell electron promotion at projectile energies greater than 0.5 MeV/amu. Kubo, Jundt, and Purser[3] report a nonmonotonic Z_2 dependence of projectile K-shell x-ray production cross sections for nickel and bromine ions incident on solid targets. These x-ray-production cross sections exhibit peaks in the region of $Z_1 \sim Z_2$, Z_1 being projectile nuclear charge. Using different techniques, Woods *et al.*[4] and Cocke *et al.*[10] have studied collisions of chlorine ions with solid targets, and have observed an enhancement in Cl K-shell x-ray production for nearly matching Z_1 and Z_2. These results suggest the occurrence of K-electron promotion in nearly symmetric collisions. The particular mechanism set forth by Kubo, Jundt, and Purser[3] and Woods *et al.*[4] is the $2p\sigma$-$2p\pi$ rotational coupling which promotes a projectile $1s$ electron to an initial $2p$ vacancy, also in the projectile. The required $2p$ vacancies are produced by stripping and excitation in the solid target.

For the experimental results presented in this paper, single-collision conditions have been demanded; moreover, the incident charge states of the chlorine ions have been selected so that a Cl $2p$ vacancy was not carried into the collision except at the highest projectile energy. The importance of the single-collision criterion lies in the ability to attribute an experimental observation to a single encounter of a projectile ion and target atom with known collision parameters (e.g., projectile velocity and charge state). Thus, the nonmonotonic behavior of the Cl K x-ray-production cross sections (see Fig. 1) cannot be explained by the proposed multiple-collision process.[3,4] For the $2p\sigma$-$2p\pi$ coupling to result in K-electron promotion requires that $2p$ vacancies be formed in the same collision in which the promotion occurs. Alternatively, one may wish to explain the data in terms of a one-step process in which a Cl K-shell electron is directly removed to a level higher than $2p$. Regardless of the particular interaction(s) invoked, however, the fact remains that a multiple-scattering mechanism is inadequate to explain the single-collision data. This has important implications for the interpretation of x-ray data which have heretofore been thought to require an explanation in terms of multiple target-projectile encounters.

Chlorine beams in charge states +2 to +8 for the experiment were accelerated by the Kansas State University tandem Van de Graaff accelerator. Low charge states were selected in order to minimize the effects of projectile electronic structure on x-ray yields[11] as well as to allow no Cl $2p$ vacancies to enter the collision. (An exception to this was the use of Cl^{+8} which was dictated by accelerator terminal voltage limitations for 52.2-MeV chlorine ions.) Of course, metastable states of chlorine ions may be produced by excitation of $2p$ electrons in the accelerator stripping canal; however, the probability that such states will not be quenched by the strong fields of the analyzing and switching magnets before reaching the gas cell is small. X rays were detected by a Si(Li) detector mounted within the differentially pumped gas cell, and the ion beams were collected in a suppressed Faraday cup located in the high-vacuum region behind the gas cell. The gas cell was operated at pressures below 20 mTorr to ensure single collisions. The low counting rates for helium targets at these pressures served to place an effective lower limit of about 3 MeV on the projectile energies that could be used. Projectile and target x rays were well resolved for all but argon targets in which case the Cl $K\beta$ x ray overlapped the Ar $K\alpha$. An estimate of the Cl $K\beta$ yield was made, however, on the basis of measurements of Cl $K\beta/K\alpha$ ratios for the other gases. The estimated values, which were never more than 9% of the Cl $K\alpha$ yield, were used to obtain the total Cl and Ar K x-ray yields. The use of this procedure cannot alter the nonmonotonic behavior of the Cl cross sections. The uncertainty in absolute x-ray-production cross sections was typically 30%, while the relative uncertainty was about 15%. Details of experimental apparatus and data analysis are described elsewhere.[12]

The x-ray-production cross sections that have been obtained are related to vacancy-production cross sections through the Cl K-shell fluorescence yield. Since vacancy production is the process of interest in discussing promotion mechanisms, a knowledge of how the fluorescence yield can be expected to affect the experimental cross sections is essential. Bhalla[13] has performed Hartree-Fock calculations of the Ar K-shell fluorescence yield as a function of the number of $2p$ and $3p$ vacancies. His results show variations of 20% at most in the fluorescence yields, and it is reasonable to expect similar variations for the chlorine K-shell fluorescence yield. Certainly, such small variations cannot appreciably influence the trends of the x-ray-production and hence vacancy-production cross sections.

An examination of the experimental results may yield information about the vacancy-production processes occurring in the collisions. From Fig. 1, one can see that from the lowest to the highest projectile energy, the Cl K x-ray-production cross sections increase by factors of 16×10^3, 6×10^3, and 4×10^2 for $Z_2=7$, 10, and 36, respectively. This decreasing trend with increasing Z_2 may be qualitatively understood in terms of the increasing importance with Z_2 of screening and binding effects[14] on the direct Coulomb ionization process. That is, the lighter targets overcome these low-velocity effects faster as a function of projectile velocity. In contrast, the increase in Cl K x-ray-production cross sections for argon ($Z_2=18$) over the energy range of the experiment is only about a factor of 60 and does not fit the trend shown for the other gases.

This weakened energy dependence of the Cl cross sections for $Z_2=18$ with respect to the other gases is an indication that processes such as electron promotion rather than direct Coulomb ionization dominate the K-vacancy production in the nearly symmetric system. Moreover, for the lower energy region of 5 to 18 MeV, the differentiation in energy dependence between argon and the other gases is considerably greater than for the region of 18 to 52.2 MeV. This result suggests the increased importance of electron promotion at the lower energies. That is, at lower energies the collision partners "see" each other as many-electron systems, and considerable rearrangement of the electrons may occur as a result of the various electronic interactions. At the highest energies, the projectile approximates a single particle and vacancy production is essentially a one-electron interaction. For such an interaction the Cl K cross section should rise monotonically[1,2] with Z_2. This situation is certainly approached with increasing projectile energy.

The argon K x-ray-production cross sections exhibit an energy dependence similar to that of the corresponding chlorine K cross sections. The ratios of Ar K to Cl K cross sections extend from 0.41 at 5 MeV to 0.64 at 52.2 MeV. These results may support the K-vacancy sharing mechanism suggested by Meyerhof.[15] On the other hand, they may indicate the occurrence of Ar K-electron promotion independent of Cl K promotion. Either explanation, however, does require the occurrence of promotion processes in single collisions for which $2p$ vacancies are not initially present.

The specific nature of the promotion processes that may be involved in a single Cl-Ar collision is not clear. One may wish to view the Cl K-vacancy formation as the result of a coupling of the $2p\sigma$ orbital to orbitals higher than $2p\pi$. Alternatively, the vacancy production may be interpreted as a multiple-promotion process in which $2p$ electrons are promoted to higher levels so that $1s$ electron promotion via the $2p\sigma$-$2p\pi$ rotational coupling is allowed. For example, Meyerhof[15] has suggested that $3p$ vacancies in the projectile are transferred to the $2p\pi$ molecular orbital via a radial coupling mechanism. Regardless of what the mechanism may be, however, the processes of $2p$ and $1s$ vacancy production in a single collision of duration $\sim10^{-17}$ sec must be considered as simultaneous. Quantitative calculations of the probability for such promotion processes are required before definitive statements regarding the mechanisms can be made. The recognition that many-electron processes are occurring in a single collision is essential in the interpretation of the heavy-ion collisions.

*Work partially supported by the U.S. Atomic Energy Commission under Contract No. AT(11-1)-2130.

[1]E. Merzbacher and H. W. Lewis, in *Handbuch der Physik*, edited by S. Flügge (Springer, Berlin, 1958), Vol. 34, p. 166.

[2]J. D. Garcia, Phys. Rev. A 1, 280, 1402 (1970).

[3]H. Kubo, F. C. Jundt, and K. H. Purser, Phys. Rev. Lett. 31, 674 (1973).

[4]C. W. Woods, F. Hopkins, R. L. Kauffman, D. O. Elliott, K. A. Jamison, and P. Richard, Phys. Rev. Lett. 31, 1 (1973).

[5]H. J. Specht, Z. Phys. 185, 301 (1965).

[6]T. 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).

[7]S. Datz, C. D. Moak, B. R. Appleton, and T. A. Carlson, Phys. Rev. Lett. 27, 363 (1971).
[8]F. W. Saris and D. J. Biermann, Phys. Lett. 35A, 199 (1971).
[9]U. Fano and W. Lichten, Phys. Rev. Lett. 14, 627 (1965); W. Lichten, Phys. Rev. 164, 131 (1967); M. Barat and W. Lichten, Phys. Rev. A 6, 211 (1972).
[10]C. L. Cocke, R. Randall, and B. Curnutte, in *Proceedings of the Eighth International Conference on the Physics of Electronic and Atomic Collisions, Belgrade, Yugoslavia, 1973,* edited by B. C. Cobic and M. V. Kurepa (Institute of Physics, Beograd, Yugoslavia, 1973), p. 714.
[11]J. R. Macdonald, L. Winters, M. D. Brown, T. Chiao, and L. D. Ellsworth, Phys. Rev. Lett. 29, 1291 (1972).
[12]L. Winters, J. R. Macdonald, M. D. Brown, T. Chiao, L. D. Ellsworth, and E. W. Pettus, Phys. Rev. A 8, 1835 (1973); L. Winters, Ph.D. thesis, Kansas State University (unpublished).
[13]C. P. Bhalla, in *Proceedings of the Eighth International Conference on the Physics of Electronic and Atomic Collisions, Belgrade, Yugoslavia, 1973,* edited by B. C. Cobic and M. V. Kurepa (Institute of Physics, Beograd, Yugoslavia, 1973), p. 739, and Phys. Rev. A (to be published).
[14]G. Basbas, W. Brandt, and R. Laubert, Phys. Rev. A 7, 983 (1973).
[15]W. Meyerhof, private communication, and in Proceedings of the Third International Seminar on Ion-Atom Collisions, Gif-sur-Yvette, France, 1973 (to be published), and Phys. Rev. Lett. 31, 1341 (1973) (preceding Letter).

EPR Evidence for Metal-Insulator Transition in the "One-Dimensional" Platinum Complex $K_2Pt(CN)_4Br_{1/3} \cdot 3H_2O$

F. Mehran and B. A. Scott
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598
(Received 12 September 1973)

Electron paramagnetic resonance has been observed in the mixed-valency platinum complex $K_2Pt(CN)_4Br_{1/3} \cdot 3H_2O$. The g factors observed are characteristic of d_{z^2}-like hole states. The variation of the observed signal intensity is not consistent with the interrupted-strand model or the disorder model but is in accord with the predictions of the Peierls-distortion model.

The mixed-valency platinum complexes (MVPC), such as $K_2Pt(CN)_4Br_{1/3} \cdot 3H_2O$ and their organic counterparts [charge-transfer complexes of tetracyanoquinodimethane (TCNQ)], have attracted considerable attention lately[1-11] as a result of their high "one-dimensional" electrical conductivities and the possibility that their base structures [$Pt(CN)_4$ or TCNQ chains] can be used as "spines"[12] for the synthesis of high-temperature superconductors. However, there are several areas of disagreement on the properties of these compounds: There ia a controversy with regard to the nature of conduction. Simple band-theory arguments,[1] optical and infrared reflectivity measurements,[4] and the observation of the giant Kohn anomaly[6] seem to indicate delocalized states and metallic conduction. On the other hand, nonmetallic dc-conductivity[8] measurements and theorems[13] on disordered one-dimensional systems favor localized states and hopping conduction. In order to reconcile these contradictions at least three models have been proposed: the "defect" or interrupted-strand model,[4,5] the "disorder" model,[9] and the "distortion" or Peierls-Kohn instability model. Recent x-ray diffuse-scattering experiments by Comes *et al.*,[6] coherent inelastic-neutron-scattering experiments by Renker *et al.*,[6] as well as the theoretical work of Rice and Strässler,[6] favor the "distortion" model. Another question is the nature of the highest occupied band in this compound. It has been surmised[1] (but not yet experimentally verified) that this band is of d_{z^2} character. In a previous paper[14] we have shown that in the "one-dimensional" semiconductor Magnus's green salt (MGS), $Pt(NH_3)_4PtCl_4$, the highest-lying band is indeed d_{z^2} like. There is also a disagreement about the sign of the carriers in MVPC.[7]

In the present paper we report on the observation of EPR in the MVPC $K_2Pt(CN)_4Br_{1/3} \cdot 3H_2O$. The results show that the observed magnetic centers are holes in d_{z^2}-like states. The temperature variation of the line intensity can be explained in terms of the "distortion model" and is in contradiction with the "defect" and the "disorder" models.

The single crystals of $K_2Pt(CN)_4Br_{1/3} \cdot 3H_2O$ used in this study were of typical size 3 mm