PHYSICAL REVIEW A VOLUME 9, NUMBER 2 FEBRUARY 1974

# Titanium and copper $K$ x rays produced by collisions with fission fragments from $^{252}$Cf†

B. Budick and A. M. Rushton
*Physics Department, New York University, New York, New York 10003*
(Received 31 August 1973)

We have observed the energy shifts and intensity ratios of the $K$ x rays of titanium and copper excited by bombarding foils of these materials with fission fragments from the spontaneous fission of $^{252}$Cf. A lithium-drifted-silicon detector was employed to make the measurements. For both metals studied, larger shifts in the x-ray energies were observed than were recorded for nickel by Watson and Li in their investigation using only the light fission fragments as projectiles. In addition, the $K\beta/K\alpha$ intensity ratio for titanium, after correcting for $K$-edge absorption in the foil, was found to be very small. We interpret this last result as being due to very high stripping of the $M$ shell of the recoiling titanium atom in collisions with other titanium atoms.

## I. INTRODUCTION

In 1965, Specht measured cross sections for the production of projectile and target x rays when fission fragments collide with different materials.[1] He used the fission fragments that follow from the slow-neutron induced fission of $^{235}$U. Two magnets served as a mass separator and permitted light and heavy fragments to be studied independently. Proportional-counter detection was used.

Barat and Lichten[2] have recently extended the development of the molecular-orbital promotion model to the case of asymmetric collision partners. Rules are given for the construction of diagrams which illustrate the ordering of the levels in the separated and united atom limits, and the correlation of levels between these two limits via molecular orbitals. Electron promotion takes place from molecular orbitals which either rise steeply as a function of internuclear separation or which undergo level crossings. If levels which differ in angular momentum by $\hbar$ approach one another closely at small internuclear separation, the fast rotation of the internuclear axis induces a strong coupling between the nuclear and electronic motions, resulting in a high transition probability between the approaching levels.

This is illustrated schematically in Fig. 1(a) for a collision between a titanium atom and a lanthanum atom. Lanthanum is a typical heavy-fission fragment in $^{252}$Cf fission. The rotational coupling induces a transition from the $3d\sigma$ orbital, which correlates to the $1s$ level of Ti, to the $3d\pi$ orbital, which correlates to the $3d$ level of lanthanum. The promotion can take place if there exists a $3d$ vacancy in the lanthanum projectile as a result of a previous collision. Rotational coupling is an important mechanism for $K$-vacancy production in heavy-ion–atom collisions. In Fig. 1(b) we show the same levels for copper and lanthanum. In this case the $1s$ level of copper is tightly bound in the quasimolecule, and it is the $2p$ level of lanthanum that correlates to the $3d\sigma$ orbital. Thus heavy fission fragments are much more effective in creating $K$ vacancies in titanium than in copper. As far as the light fragments are concerned, the $K$-shell ionization cross sections for titanium and copper are within a factor of 2.5, according to Specht.

In a recent experiment, Watson and Li[3] used a Si(Li) detector to study the $K$ x rays of nickel produced by light-fission fragments from a $^{252}$Cf source. Heavy and light fragments were distinguished by pulse height in their fission-fragment detector. A standard fast-slow coincidence system was used. Watson and Li explained their data for the energy shifts of the nickel $K\alpha$ and $K\beta$ x rays in terms of multiple inner-shell plus outer-shell ionization.

Progress in the field of heavy-ion-induced x rays has been rapid. Cross sections for x-ray production with chlorine, bromine, iodine, and bismuth projectiles have been measured.[4] High-resolution studies of target and projectile x rays employing crystal-diffraction techniques have also been made.[5-7] Energy shifts in the $K\alpha$ and $K\beta$ x rays of first-row transition-metal atoms are generally interpreted in terms of multiple vacancies in the $L$ and $M$ shell at the instant of $K$ x-ray emission.

We have investigated the $K$ x rays of titanium and copper produced by fission fragments from $^{252}$Cf using a Si(Li) detector. No attempt was made to distinguish between light and heavy fragments. For both metals studied, larger shifts in the x-ray energies were observed than were recorded for nickel by Watson and Li. In addition, the $K\beta/K\alpha$ for titanium after correcting for $K$ edge absorption in the foil was found to be very small. Our results

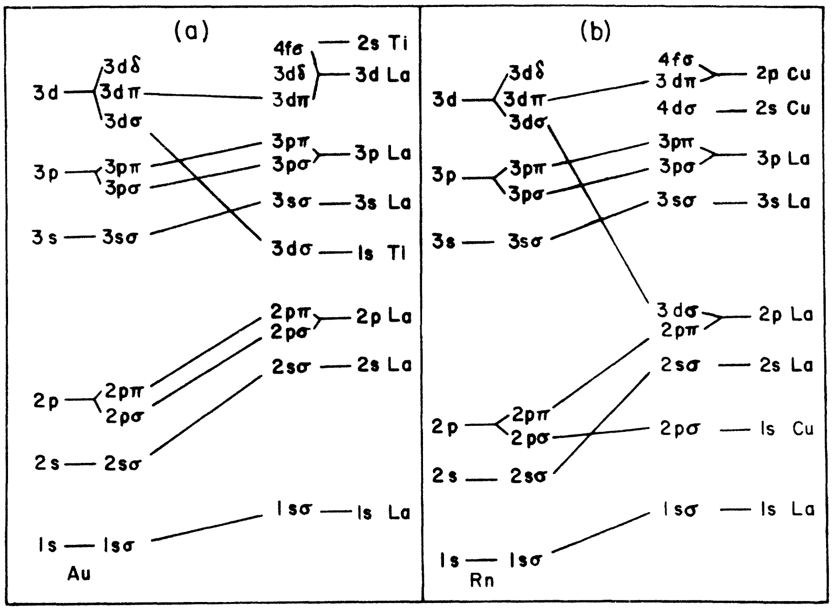


FIG. 1. (a) Correlation diagram for the inner levels of lanthanum and titanium. United atom levels are on the left-hand side. (b) Correlation diagram for lanthanum-copper.

imply that a $K$-shell vacancy, as well as some $L$- and $M$-shell vacancies, are created in the titanium ion by the fission-fragment projectile. Prior to $K$ x-ray emission the recoiling titanium ion collides with other titanium atoms, resulting in further ionization of its $M$ shell.

## II. EXPERIMENTAL TECHNIQUE

The experimental geometry is shown in Fig. 2. The Si(Li) detector had a resolution of 217 eV full width half-maximum at 4.5 keV under our operating conditions. A titanium foil (1.36 mg/cm$^2$) or a copper foil (1.13 mg/cm$^2$) was mounted such that it made an angle of approximately 55° with the front face of the Si(Li) detector. The $^{252}$Cf source had a strength of 20 $\mu$Ci. It consisted of a 1-cm diameter spot deposited on aluminum with an overcoat of 40 $\mu$g/cm$^2$ of carbon to prevent migration of the californium. As a further precaution, two pieces of Mylar, each 0.001-in. thick, were placed over the Si(Li) detector. The source was prevented from directly viewing the Si(Li) detector by lead foils. The titanium $K$ x rays could also be excited by $\alpha$ particles from a 15-$\mu$Ci $^{210}$Po source, which is essentially a pure $\alpha$ emitter. The foils were square, $\frac{3}{4}$ in. on a side, and were located approximately 1.5 cm from the source and detector.

Since $^{252}$Cf emits roughly 15 times as many $\alpha$ particles as fission fragments, it was necessary to discriminate against the $\alpha$ particles. This was accomplished by demanding a fast coincidence between the Si(Li) output and all pulses from a surface-barrier detector whose pulse heights were greater than that produced by the $\alpha$ particles. We estimate that the light fragments emerged from the foils with energies of 60 and 55 MeV and the heavy fragments with energies of 40 and 30 MeV in copper and titanium, respectively.[8] If pulses from both detectors arrived within 250 nsec of each other, a gate was generated in the multichannel analyzer for the analog output of the Si(Li) detector. The surface-barrier detector had an area of 400 mm$^2$ and was mounted 1 cm behind the foil.

Foil, detectors, and source were all contained in a single small vacuum chamber. The energy scale was calibrated at regular intervals by breaking vacuum, and using a 2-mCi $^{55}$Fe source to fluoresce the titanium foil. In the case of copper, the foil was replaced by a 1-$\mu$Ci $^{65}$Zn source which emits copper $K$ x rays.

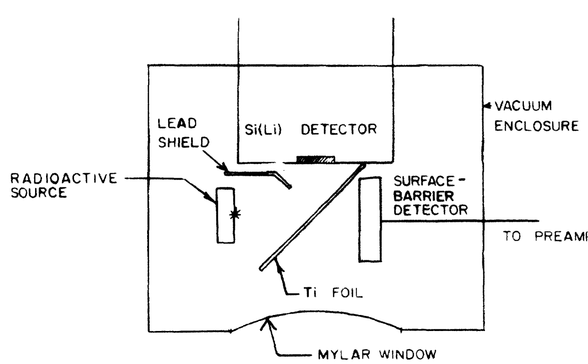


FIG. 2. Schematic diagram of the apparatus.

## III. RESULTS AND ANALYSIS

Figure 3 shows the x-ray spectra we obtained for incident $\alpha$ particles and fission fragments on titanium without background subtraction. The two arrows in Fig. 3(a) indicate the unshifted $K\alpha$ and $K\beta$ x rays and give some indication of the energy scale. Each spectrum, including the calibration spectra, was analyzed with a computerized least-squares program, which fitted the spectrum with Gaussian functions for the peaks and a quadratic function for the background. A quadratic function was chosen because, in addition to accidentals, the background contains a contribution from the $L$ x rays of heavy fission fragments produced during passage through the foil. In a separate experiment on copper, we studied the shape and position of the $L$ x rays from both light and heavy fragments. The heavy-fragment $L$ x rays show an increase between 4.1 and 4.3 keV, plateau in the range 4.4–4.9 keV, and then decrease slowly. On the basis of relative counting rates we estimate that the contribution of these projectile x rays to the total spectrum obtained from our relatively thick titanium foil is of the order of 6%. No evidence for the rise or plateau is apparent in the spectrum. Our results for the $L$ x rays are in agreement with studies of $K$ x rays and internal-conversion electrons emitted in $^{252}$Cf fission.[9,10] The most abundant elements have $Z = 53$, 55, and 57. The unshifted $L\alpha$ components of these elements occur at energies of 3.94, 4.29, and 4.65 keV. Shifts of roughly 100 eV to higher energies are expected in each of these lines. Moreover, Datz *et al.*[11] have observed that for 60-MeV iodine on copper, the $L\beta$ component is more intense than the $L\alpha$ component. With our instrumental resolution, no structure in the $L$ x rays from the heavy fragments is observable.

We have corrected our data for absorption in the Mylar covering the Si(Li) detector, and, in the case of the photon calibrations, for absorption in the air between the target and the detector. These corrections were each of the order of several percent. A much larger correction to the $K\beta/K\alpha$ ratio comes from self-absorption in the foil. This effect on the intensity ratio was treated as being equivalent to a metal layer of thickness equal to

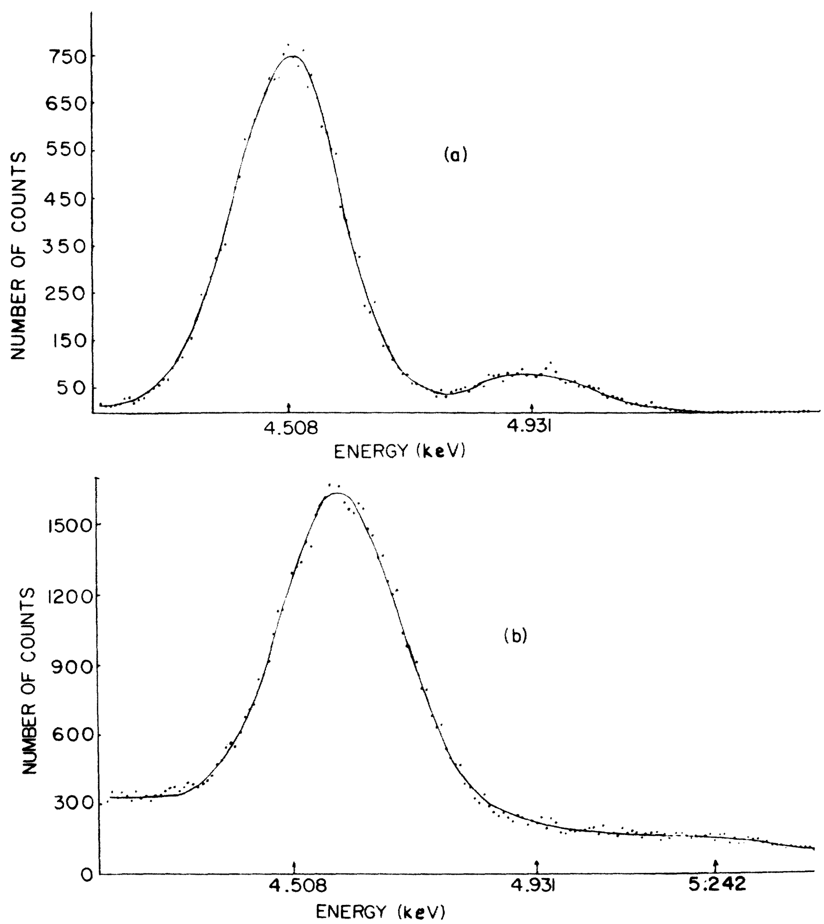


FIG. 3. (a) Ti $K$ x-ray spectrum in coincidence with $\alpha$ particles from $^{210}$Po, background included. Arrows indicate the normal energies of these x rays. (b) Ti $K$ x-ray spectrum in coincidence with fission fragments from $^{252}$Cf, background included. The arrow at 5.242 keV is at the shifted $K\beta$ energy.

the mean depth of x ray production in the foil. For the photon and $\alpha$ particle cases, this effect is only of the order of several percent. However, for fission fragments the $K\beta$ energy is shifted above the $K$ absorption edge. The observed intensity ratio must be increased by a factor of 1.73.

A summary of our results for titanium and copper as well as the light-fragment work on nickel by Watson and Li is presented in Table I. We note briefly that $\alpha$ particles produce no significant energy shifts. However, the $K\beta/K\alpha$ ratio is smaller than that obtained by photoionization for titanium in our work, and for nickel as reported by Watson and Li. The most recent values for the $K\beta/K\alpha$ ratio for photoionization are 0.1319 $\pm$0.0017 and 0.1385 $\pm$0.0011 for titanium and nickel, respectively.[12]

## IV. DISCUSSION

The energy shifts we observe for fission-fragment excitation can be interpreted in terms of $L$- and $M$-shell vacancies. House[13] has calculated that the shift produced in the $K\alpha$ transition for each additional $2p$ vacancy is 29 and 35 eV for titanium and copper, respectively. Our data on the $K\alpha$ transition are therefore consistent with between two and three $2p$ vacancies at the instant of x-ray emission. There is no need to consider $2s$ vacancies, since they are transferred to the $2p$ shell by the very fast $L_1 - L_{2,3}M$ Coster-Kronig transition before $K$ x-ray emission. The $K\beta$ transitions are much more sensitive to the number of $M$-shell vacancies. A comparison of the shifts of the $K\beta$ lines for the elements studied is the first indication of the serious depletion of the titanium $M$ shell.

We observe larger energy shifts for both titanium and copper than did Watson and Li for nickel. We attribute this result to the fact that we used both heavy and light fragments, as opposed to Watson and Li who selected only the light fragments. The effect of the heavy fragments in producing larger shifts is not necessarily through the creation of more $L$ vacancies in the initial collision. The molecular-orbital-promotion model, although not strictly applicable to $L$-shell ionization at high projectile velocities, predicts that the $2p$ level of elements with $21 < Z < 29$ correlates with the easily ionized $4f\sigma$ orbital for light-fission-fragment collisions. Rather it is the survival of the $2p$ vacancies until $K$ x-ray emission that is different for light and heavy fragments. We show below that the $M$ shell of the struck target atom has a higher probability of being ionized in *recoil collisions* for heavy fragments than for light ones. If there are many vacancies in the $M$ shell, the $L_{2,3}$-$MM$ Auger rate, which is chiefly responsible for the relaxation of $L$ vacancies in this range of $Z$, is drastically reduced.[5] The enhanced survival of $L$ vacancies in titanium and copper, and the larger shifts in the $K\alpha$ lines are further indirect evidence of the depletion of the $M$ shell which we attribute to recoil collisions.

The most direct evidence for the stripping of the $M$ shell is provided by the $K\beta/K\alpha$ ratio. For titanium this is far below the photoionization value quoted above, while for copper it is higher. The copper result is in agreement with work done with oxygen ions.[14] If the nickel result is corrected for self-absorption in the nickel foil, it too will lie above the photoionization value.

We have estimated the rates for the $K\beta$ and $K\alpha$ transitions in titanium for various combinations of vacancies in the $L_{2,3}$ and $M_{2,3}$ subshells in addition to the $1s$ vacancy. Our procedure was that suggested by Burch *et al.*[5] The transition rates for atoms having a single vacancy, given by Scofield,[15] were plotted as a function of $Z$. For defect configurations, the effective $Z$ seen by electrons in the $L$ and $M$ shells was then estimated using Slater's screening rules.[16] The transition rates

TABLE I. Comparison of energy shifts and intensity ratios of target $K$ x rays obtained in this and earlier work. The energy shifts and full width half-maximum denoted by $\Gamma$ are in units of eV. The last column lists the intensity ratio.

| Projectile | Target | $\Delta E_\alpha$ | $\Gamma_\alpha$ | $\Delta E_\beta$ | $\Gamma_\beta$ | $K\beta/K\alpha$ |
|---|---|---|---|---|---|---|
| Fission | Ti | $85 \pm 3$ | $246 \pm 2$ | $311 \pm 30$ | $277 \pm 30$ | $0.046 \pm 0.010$ |
| Fragments | Ni [a] | $69 \pm 11$ | $351 \pm 1$ | $210 \pm 16$ | $646 \pm 16$ | $0.098 \pm 0.005$ |
| | Cu | $97 \pm 7$ | $282 \pm 2$ | $246 \pm 10$ | $790 \pm 20$ | $0.22 \pm 0.020$ |
| $\alpha$ particles | Ti | $0.2 \pm 1.5$ | $216 \pm 2$ | $-2 \pm 8$ | $219 \pm 2$ | $0.094 \pm 0.002$ |
| | Ni [a] | $-6 \pm 10$ | $325 \pm 6$ | $4 \pm 11$ | $349 \pm 5$ | $0.143 \pm 0.002$ |
| Photons | Ti | ··· | $217 \pm 1$ | ··· | $220 \pm 1$ | $0.128 \pm 0.002$ |
| | Ni [a] | ··· | $316 \pm 6$ | ··· | $364 \pm 6$ | $0.153 \pm 0.002$ |
| | Cu | ··· | $251 \pm 2$ | ··· | $258 \pm 2$ | $0.131 \pm 0.003$ |

[a] See Ref. 3.

for the modified $Z$ value could then be read from the graph. For two or three vacancies in the $2p$ shell, required by the size of the shifts in the $K\alpha$ transition, we conclude that five or more vacancies must be present in the $3p$ shell at the instant of $K$ x-ray emission. These assignments are also consistent with the observed shift in the $K\beta$ transition energy. The predicted value for such defect configurations can be interpolated from the Hartree-Fock-Slater calculations of Burch and Richard[17] for calcium and vanadium.

Laubert[18] has derived an expression for the number of vacancies created by the recoiling target atom. He chooses the "power law" of Lindhard[19] to express the differential cross section for an energy transfer $T$ in the initial collision, and a form proposed by Cacak[20] for the x-ray cross section as a function of energy for the subsequent symmetric collisions between target atoms. His derivation employs the "thin-target approximation," but his formula may still serve as a guide in an analysis of our work. For Rutherford scattering of high-energy projectiles, Laubert's expression reduces to

$$Y = 5.45\times10^{-21}\, n^2 t' P \pi r_c^2 \times\left(\frac{Z_1 Z_2 (M_1+M_2)}{M_1 M_2 E_1}\right)^2 \frac{2}{5}\left(\frac{T_M}{T_m}\right)^{3/2}, \tag{1}$$

where $Y$ is the vacancy yield per incident projectile, $n$ is the target atom density in units of atoms/$\mu$g, $t'$ is the effective target thickness in units of $\mu g/cm^2$, $P$ is the probability for ionizing each promotable electron in a particular shell, $r_c$ is the radius of the shell being ionized in recoil, $M_2$ and $Z_2$ are the target mass and charge, $M_1$, $Z_1$, and $E_1$ refer to the projectile with $E_1$ in units of keV/amu, $T_M$ is the maximum energy transferred in the initial collision $= 4M_1^2 M_2 E_1/(M_1+M_2)^2$ ($E_1$ is in units of keV/amu), and $T_m$ is a lower limit to the energy transfer.

For the ionization of the $M$ shell in a collision between a 50-MeV lanthanum fission fragment and a titanium atom in our foil, these quantities have the following values: $n = 1.2\times10^{16}$ atoms/$\mu$g, $t' = 1660\ \mu g/cm^2$, $Z_1 = 22$, $Z_2 = 57$, $M_1 = 48$, $M_2 = 139$, $E_1 = 360$ keV/amu, $r_c = 9a_0/Z_2$ for the $M$ shell. Cacak[20] finds that $P$ is equal to 1 for the ionization of the electrons in the $4f\sigma$ orbital that correlates to the $L$ shell in argon ion-argon atom collisions in the range of energies possessed by our recoiling titanium ions. For the $M$ shell, $P$ may therefore be taken as 1, and the number of promotable electrons in fast-rising orbitals is 6. The lower limit on the energy transfer in our case is dictated by the fact that we want to consider those titanium atoms in which a $K$ vacancy was created in the initial collision. We estimated the energy transfer for Rutherford scattering at impact parameters equal to the radius of the $K$ shell:

$$T_m = \frac{2}{M_2}\left(\frac{Z_1^2 Z_2^2 e^4}{V^2}\right)\frac{1}{X^2}, \tag{2}$$

where $V$ is the projectile velocity and $X = a_0/Z_2$. Thus we find $T_m = 44$ keV. Substituting these values into Eq. (1) and remembering to multiply by 6 for the number of promotable electrons, we find $Y = 5$($M$ vacancies/projectile).

Specht[1] gives the $K$-shell ionization cross section for heavy fission fragments as $5\times10^4$ b. For our foil thickness, this implies that the yield of atoms with $K$ vacancies is roughly 1 for each incident projectile. Each of these recoiling atoms will then create of the order of 5 additional $M$ vacancies which are shared between the collision partners. Thus it is entirely plausible that the struck titanium atom has two or three vacancies created in its $M$ shell in the initial collision, and most or all of the remaining $M$ electrons stripped in recoil collisions.

This mechanism should be considerably less important in copper for the following reasons. From Eqs. (1) and (2), we can deduce that the $M$ vacancy yield due to recoil varies as $Z_2^{-6}$. This implies that the yield in copper is lower by a factor 5.3, or roughly 1 (vacancy/projectile). Moreover, copper starts off with many more $3d$ electrons than does titanium. Vacancies formed in the $3p$ subshell of copper are transferred to the $3d$ subshell by fast Coster-Kronig transitions of the type $M_2 - M_4 M_5$[21] before $K$ x-ray emission, leaving the $K\beta/K\alpha$ ratio unaffected. Finally, the $3p$ shell of copper is more tightly bound than that of titanium and is less easily ionized.

A $K$ vacancy in a titanium atom lacking two $L$-shell electrons has a lifetime of roughly $2.5\times10^{-15}$ sec. A titanium atom possessing the minimum recoil energy of 44 keV can make several collisions with other titanium atoms before the disappearance of the $K$ vacancy. On the other hand, a titanium atom, struck by a light fission fragment with an average energy of 85 MeV, has a recoil energy of only 10 keV, according to Eq. (2). Chances for the production of $M$ vacancies in subsequent collisions before $K$ x-ray emission are considerably reduced for recoils initiated by light fission fragments.

This provides yet another reason for the apparent absence of recoil as a mechanism for the production of additional $M$ vacancies in copper target atoms. As pointed out in Sec. I, the light fission fragments are chiefly responsible for the production of $K$ vacancies in copper. Most copper recoils with $K$ vacancies will therefore lack sufficient energy to collide with other copper atoms. Additional $M$ vacancies are less likely to be formed. This is reflected in the high $K\beta/K\alpha$ ratio observed for copper.

In view of the approximations made, and the range of masses and energies of the fission fragments, the fact that our model for stripping during recoil yields just the required number of $M$ vacancies in titanium and copper to explain our results, should be regarded as fortuitous. Nonetheless, it is clear that recoil must play an important role in determining the number of $M$ vacancies present at the instant of $K$ x-ray emission, when heavy projectiles are used to excite light target x rays.

## V. CONCLUSION

We have measured the energy shifts and intensity ratio of the $K\alpha$ and $K\beta$ x rays of both titanium and copper excited by fission fragments from a $^{252}Cf$ source. The data for copper are consistent with ion configurations having two or three $L_{2,3}$ vacancies and a comparable number of $M_{2,3}$ vacancies with additional ionization of the $M_{4,5}$ subshells at the instant of $K$ x-ray emission. For titanium we find that an explanation for the energy shifts of both x-ray transitions as well as their intensity ratio requires a much higher degree of ionization in the $M_{2,3}$ subshell at the instant of x-ray emission. We attribute this result to the creation of additional $M$ vacancies in the recoiling target atom.

## ACKNOWLEDGMENT

The authors wish to thank Dr. Roman Laubert of New York University for kindly communicating his results prior to publication.

†Work supported by the National Science Foundation under Grant No. GP-34527.

[1]H. J. Specht, Z. Phys. 185, 301 (1965).
[2]M. Barat and W. Lichten, Phys. Rev. A 6, 211 (1972).
[3]R. L. Watson and T. K. Li, Phys. Rev. A 4, 132 (1971).
[4]H. W. Schnopper, A. R. Schval, H. D. Betz, J. P. Delvaille, K. Kalata, K. W. Jones, and H. E. Wegner, in *Proceedings of the International Conference on Inner-Shell Ionization Phenomena and Future Applications*, edited by R. W. Fink, S. T. Manson, J. M. Palms, and P. V. Rao (U. S. AEC, Oak Ridge, Tenn., 1972).
[5]D. Burch, P. Richard, and R. L. Blake, Phys. Rev. Lett. 26, 1355 (1971) and earlier papers.
[6]A. R. Knudson, D. J. Nagel, P. G. Burkhalter, and K. L. Dunning, Phys. Rev. Lett. 26, 1149 (1971).
[7]The authors have performed experiments on projectile and target x rays using a graphite mosaic-crystal spectrometer and the halogen beams of the Brookhaven Tandem van de Graaff.
[8]These estimates are based on the range curves of C. B. Fulmer, Phys. Rev. 108, 1113 (1957).
[9]N. L. Shapiro, B. W. Wehring, and M. E. Wyman, Phys. Rev. C 3, 2464 (1971).
[10]F. F. Hopkins, G. W. Phillips, J. R. White, C. Fred Moore, and Patrick Richard, Phys. Rev. C 4, 1927 (1971).
[11]S. Datz, C. D. Moak, B. R. Appleton, and T. A. Carlson, Phys. Rev. Lett. 27, 363 (1971).
[12]V. W. Slivinsky and P. J. Ebert, Phys. Rev. A 5, 1581 (1972).
[13]L. L. House, Astrophys. J. Suppl. 18, 21 (1969).
[14]P. Richard, in Ref. 4.
[15]J. H. Scofield, Phys. Rev. 179, 9 (1969).
[16]J. C. Slater, *Quantum Theory of Atomic Structure*, Vol. I (McGraw-Hill, New York, 1960), p. 369.
[17]D. Burch and P. Richard, Phys. Rev. Lett. 25, 983 (1970).
[18]R. Laubert (private communication).
[19]J. Lindhard, V. Nielsen, and M. Scharff, Mat. Fys. Medd. Dan. Vid. Selsk. 36, (1968).
[20]R. K. Cacak, G. C. Kessel, and M. E. Rudd, Phys. Rev. A 2, 1327 (1970).
[21]E. J. McGuire, Phys. Rev. A 5, 1052 (1972).