

Comment on the determination of charge states of ions moving through solids from the analysis of x-ray spectra

R. A. Baragiola

*Centro Atómico Bariloche and Instituto Balseiro, Comisión Nacional de Energía Atómica
and Universidad Nacional de Cuyo, 8400 S. C. de Bariloche, R. N., Argentina*

(Received 3 May 1978)

The author discusses a recent paper by Fortner and Garcia in which these workers analyze thick-target x-ray yields and spectra and derive populations of projectile inner- and outer-shell vacancies, and concludes that some effects which were not considered should be taken into account in any such analysis. These include the generation of target x rays by recoiling target atoms, vacancy sharing, collisional quenching and the effect of differences in the wave functions of outer-shell electrons, x-ray energies, and transition rates in solids as compared with gases.

In 1971, Der *et al.*¹ reported on differences in inner-shell vacancy production for Ar-C collisions in gas versus solid targets. It was observed that for energetic Ar ions colliding with CH₄ gas, inner-shell vacancies were produced essentially in the Ar *L* shell. For Ar⁺ ions incident on graphite, however, there was a high probability of producing C *K*-shell vacancies. They analyzed the data in terms of the electron-promotion model of Barat and Lichten² and argued that in solid targets, the high degree of ionization of the moving ion would cause the Ar-2*p* level to be more strongly bound than the C-1*s* level and that this interchange of level energy, called "swapping," would cause preferential excitation of the C *K*-shell electrons. They finally proposed that this type of measurement could provide a method for charge-state determination for ions moving in solids. Barat and Lichten have pointed out, however, that the degree of outer-shell ionization should have little effect in the promotion of inner-shell electrons (outer-shell ionization would have an effect in cases in which it opens closed exit channels²).

Recently, Fortner and Garcia^{3,4} (FG) presented quantitative data for Ar *L* and C *K* x-ray yields and spectra for Ar ions moving in solid carbon. Using this data and a number of assumptions they derived a distribution of outer-shell vacancies for the Ar projectiles.

The question of which is the charge composition of atomic particles moving through solids has been a long-standing problem in the field of atomic collisions. The charge of an ion moving in a solid is not a simple quantity to define, as it would be in the case of free particles. Here the outer electrons of the moving particle interact continuously with a nonuniform environment and the perturbation dies away only upon emergence of the ion from the solid. FG tried to derive these distributions of charge states from their possible

effect on x-ray spectra and yields; it is therefore of importance to discuss the assumptions made in the interpretation of these data.

The basic data reported by FG are x-ray spectra for Ar-C collisions in the energy range 30-200 keV. The spectra consists of one region below 250 eV whose shape is independent of the incident energy of the Ar ions and which can be interpreted as arising from the filling of Ar *L* holes, and a region from ~250 to ~300 eV showing a peak near 280 eV which increases in intensity (relative to features below 250 eV) with beam energy. To separate the x-ray spectra into projectile and target contributions, FG make the assumption that the spectral shape of the C *K* x rays emitted in this case is the same as that obtained under proton bombardment. This latter x-ray profile is subtracted from the data and the remaining x-ray intensity attributed to the filling of Ar *L* holes.

This procedure is of dubious validity for two reasons. First, one must know how much Ar *L* x rays contribute to the spectrum in the x-ray energy range of the C peak. Second, it is very unlikely that the C x-ray profile is the same for proton and Ar bombardment. In fact, Kamada *et al.*⁵ have shown that Mn and Co *L* x-ray profiles are much broader for Ne⁺ and O⁺ bombardment than for electron or H⁺ bombardment. Furthermore, and more related to this case, spectra of C *K* x rays from 90-180-keV sulphur ions on graphite^{3,6} are broader than for 90-keV H⁺ ions on graphite.¹

Having separated the yields of C *K* and Ar *L* x rays, FG proceed to analyze them using the method described by García.⁷ The projectile and target x-ray yields, are written in terms of the fluorescence yields of the Ar *L* and of the C *K* shells; τ , the lifetime of an Ar *L* hole; σ , the cross section for inner-shell excitation (assumed

to be equal for Ar and for C); f_1 and f_0 , the fractions of the projectiles which have one and zero inner-shell vacancies ($f_1 + f_0 = 1$) and a parameter α , defined through αf_0 which is the fraction of projectiles having no L -shell vacancy but sufficient degree of ionization to be able to excite the carbon K shell, but not the Ar L shell. In the analysis, this factor α , as well as the lifetime τ and the fluorescence yields are assumed to be independent of the velocity of the projectiles.

Before analyzing the assumptions made we would like to point out the deficiencies of this treatment. First, no account is given either of the $C K$ x rays generated between collisions of recoiling C atoms with the target, nor of the influence of energy straggling of the ion beam on the yields. Taulbjerg and Sigmund⁸ have analyzed these effects for $C K$ -shell excitation produced by Ar ions incident in graphite using the data of Der *et al.*⁹ This data was later shown to be in error.⁴ Also another set of data¹⁰ used by Taulbjerg and Sigmund to estimate the contribution from recoils to $C K$ x-ray yields, was recently shown¹¹ to be too low by a factor of 4. Making use of the corrected data it can be seen that a substantial contribution from recoils is present in the $C K$ x-ray yield, specially at low energies. In fact, the yield of $C K$ x rays at 30 keV will be mainly given by C-C collisions.

Second, the collisional filling of inner-shell vacancies in the projectile has been neglected by FG. These quenching processes could be accommodated in the model by taking the lifetime as $\tau^{-1} = \tau_0^{-1} + (N\sigma_q v)^{-1}$, where τ_0 is the lifetime in the absence of collisions, N the target-atom number density, σ_q the quenching cross section, and v the velocity of the ion. However, this will make τ velocity dependent since σ_q is a function of v , and the assumption of a constant lifetime will be inappropriate. These quenching processes should be quite important since the binding energies of C $1s$ electrons and Ar($2p^{-1}$) $2p$ electrons are very nearly the same.

Let us consider now the factor α whose use is based on the assumption that inner-shell ionization in the projectile causes a swapping in the relative order of the Ar $2p$ and C $1s$ orbitals in an energy-level diagram, i.e., that the increase in binding energy of the Ar electrons due to L -shell ionization is sufficient to make these L -shell electrons become more tightly bound than the C $1s$ electrons. This swapping would result, in the next violent collision, in excitation of $C K$ but not Ar L electrons. However the binding energy of the C $1s$ electron referenced to the vacuum level is ~ 289 eV^{12, 13} and nearly the same as the binding energy of the Ar($2p^{-1}$) $2p$ level which is about 40 eV larg-

er¹⁴ than the value of 245.2 eV for neutral Ar,¹² or about 285 eV (these values are for free Ar and we can expect a shift in the levels of a few eV when Ar is inside a solid¹⁵). Additional outer-shell ionization will cause the binding energies of the Ar electrons to increase even more. However, as stated before, at the small internuclear distances where promotion occurs (0.2–0.4 Å), both partners share the same outer-shell environment and so it makes no difference whether the projectile, or the target, brought the outer-shell vacancy to the collision initially. Therefore it is reasonable to expect that outer-shell ionization will cause a stronger binding in C $1s$ and Ar $2p$ electrons by roughly the same amount. The result is that there is no sharp swapping, the $1s$ C and $2p$ Ar electrons are now near-degenerate in energy, we can expect the probability for each of these levels to be promoted in the $3d\sigma$ molecular orbital to be nearly the same (Fig. 1).

A different interpretation of the parameter α is possible in terms of the probability of $C K$ -shell excitation by the process of vacancy sharing¹⁶ but since this mechanism is velocity dependent, α cannot be assumed to be constant.

Another questionable assumption made by FG is that the cross sections for the processes:

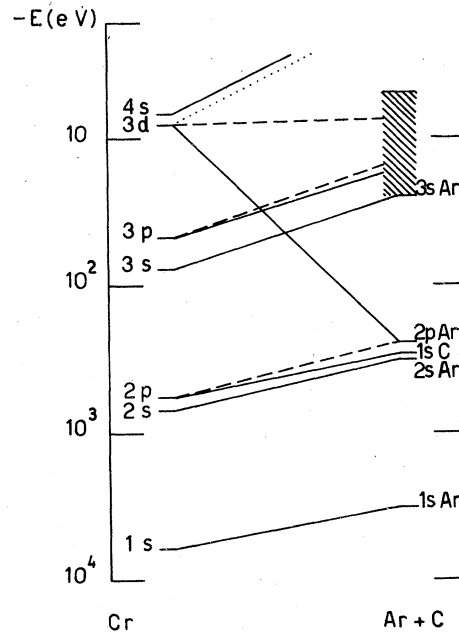


FIG. 1. Schematic argon-carbon correlation diagram. σ states, solid lines; π states, dashed lines; δ states, dotted line. The shaded region represents the unperturbed valence band of carbon. Binding energies E are referred to the vacuum level. For Ar($2p^{-1}$) $^+ C$ collisions, the binding energies of Ar $2p$ and C $1s$ electrons differ by at most a few eV.

(i) $\text{Ar} + \text{C} \rightarrow \text{Ar}(2p^{-1})$ and (ii) $\text{Ar}(2p^{-1}) + \text{C} \rightarrow \text{C}(1s^{-1})$ are equal to that for process (iii) $\text{Ar} + \text{CH}_4 \rightarrow \text{Ar}(2p^{-1})$. In fact processes (i) and (iii) should not be expected to have the same cross section since the outer-shell configuration of methane and graphite are different, and in the latter case, mechanisms such as the one proposed by Joyes¹⁷ for solid targets, may be important. In collision (ii) the situation is more basically different. Since in this case, as stated above, the Ar $2p$ and C $1s$ states are near resonant, we can expect that in the collision the vacancy originally in the Ar $2p$ shell may proceed in two ways. First, it may follow the $2p\pi(2p\sigma)$ orbital, and if the collision is violent enough, transfer by rotational coupling to the $2p\sigma(2p\pi)$ orbital and then end in any of the two partners. Second, it may follow the $3d\sigma$ molecular orbital and be filled by radial coupling with an electron from the $3s\sigma$ or $3p\sigma$ molecular orbitals or by rotational coupling with an electron from the $3p\pi$ or $3d\pi$ molecular orbital. In this case the vacancy may end up in the $2p$, $3s$, or $3p$ levels of Ar or in the valence or $1s$ levels of C. To this complicated situation we must add the possibility of the promotion and subsequent ionization of the C $1s$ electrons. We must conclude, therefore, that the *a priori* assumption that cross sections for processes (i)–(iii) are equal is probably incorrect.

Section B of FG is devoted to the analysis of the Ar x-ray spectra. These spectra have broad, unresolved features which are independent of the energy of the projectile (in the range 30–200 keV). The spectra was analyzed by unfolding it in discrete peaks using line shapes determined from gas-target spectra, centroid energies for different multiplet states from average adiabatic Hartree-Fock calculations, and fluorescence yields obtained by an averaging procedure over different atomic states. This part of the work is the one most subject to criticism. For ions moving in

solids the configuration of their outer shells will result from a competition of ionizing and electron capture events and the dynamic screening of the ions by the valence electrons of the solid.¹⁸ This screening action occurs very fast, in times of the order of $t_s = 2\pi\bar{N}/\omega_p$, where ω_p is the plasma frequency and \bar{N} the average number of oscillation before damping. For C,¹⁹ $\hbar\omega_p \approx 20$ eV, $\bar{N} \approx 1.3$ and $t_s \approx 2.5 \times 10^{-16}$ sec. The ion will then move with a cloud of screening electrons, this screening being essentially velocity independent for $v < v_F$, which is the case of FG's work, where v_F is the Fermi velocity of the electrons in the solid.¹⁸ X rays can then be emitted as the result of electronic transitions from the electron cloud of enhanced density around the ion and from normal states of the valence band. This will give rise to a broad spectrum of x-ray energies as found also in more recent work.²⁰ In summary, except for highly ionized Ar, $3p$, $3d$ and higher levels will be immersed in the C valence band and therefore broadened and the concept of atomic states will be meaningless. In this context, it is important to notice that experiments using an extremely high-resolution x-ray crystal spectrometer by Oona *et al.*, as quoted by FG, failed to show any significant structure in the spectra.

In view of the comments made above, we must regard the agreement between values obtained by analyzing the yields and the shape of the spectra as fortuitous. The fact that the values of f_1 derived by FG do not coincide with absolute experiments made using Auger electrons²¹ nor with the independence of f_1 on foil thickness in the range 100–500 Å²² supports our conclusions on the inadequacy of Fortner and Garcia's assumptions.

ACKNOWLEDGMENT

This work was supported in part by the Multinational Program in Physics of the Organization of American States.

¹R. C. Der, R. J. Fortner, T. M. Kavanagh, and J. D. Garcia, *Phys. Rev. Lett.* **27**, 1631 (1971).

²M. Barat and W. Lichten, *Phys. Rev. A* **6**, 211 (1972).

³R. J. Fortner and J. D. Garcia, in *Atomic Collisions in Solids*, edited by S. Datz, B. R. Appleton, and C. D. Moak (Plenum, New York, 1975), Vol. 1, p. 469.

⁴R. J. Fortner and J. D. Garcia, *Phys. Rev. A* **12**, 856 (1975).

⁵H. Kamada, T. Tamura, and M. Terasawa, in *Proceedings of the Sixth International Conference on X-Ray Optics and Microanalysis*, edited by G. Shinoda, K. Kohra, and T. Ichinokawa (University of Tokyo, Tokyo, 1972), p. 541.

⁶R. J. Fortner, D. L. Matthews, and J. D. Garcia, *Phys. Lett.* **53A**, 464 (1975).

⁷J. D. Garcia, *Phys. Rev. A* **11**, 87 (1975).

⁸K. Taulbjerg and P. Sigmund, *Phys. Rev. A* **5**, 1285 (1972).

⁹R. C. Der, R. J. Fortner, T. M. Kavanagh, and J. M. Khan, *Phys. Rev. A* **4**, 556 (1971).

¹⁰R. J. Fortner, B. P. Curry, R. C. Der, T. M. Kavanagh, and J. M. Khan, *Phys. Rev.* **185**, 164 (1969).

¹¹R. K. Cacak and F. W. Martin, *Phys. Rev. A* **13**, 599 (1976).

¹²J. A. Bearden and A. F. Burr, *Rev. Mod. Phys.* **31**, 49 (1967). The binding energies are referenced to the Fermi level, and need to be corrected for the work function (see Ref. 13).

¹³H. B. Michaelson, *J. Appl. Phys.* **48**, 4729 (1977).

¹⁴F. P. Larkins, *J. Phys. B* **4**, 1 (1971).

- ¹⁵P. H. Citrin and D. R. Hamann, Phys. Rev. B 10, 4948 (1974).
- ¹⁶W. E. Meyerhof, Phys. Rev. Lett. 31, 1341 (1973); N. Stolterfoht, P. Ziem, and D. Ridder, J. Phys. B 7, L409 (1974).
- ¹⁷P. Joyes, J. Phys. (Paris) 30, 243 (1969).
- ¹⁸W. Brandt, in *Atomic Collisions in Solids*, edited by S. Datz, B. R. Appleton, and C. D. Moak (Plenum, New York, 1975), Vol. I, p. 469.
- ¹⁹H. J. Hagemann, W. Gudat, and C. Kunz, DESY Report No. SR-74/7, 1974 (unpublished).
- ²⁰R. J. Fortner, D. L. Matthews, J. D. García, and H. Oona, Phys. Rev. A 14, 1020 (1976).
- ²¹R. A. Baragiola, P. Ziem, and N. Stolterfoht, J. Phys. B 9, 1447 (1976).
- ²²P. Ziem, R. A. Baragiola, and N. Stolterfoht, Proceedings of the International Conference on the Physics of X-Ray Spectra (U.S. GPO, Washington, D.C., 1976), p. 278.