Aust. J. Phys., 1974, **27**, 177–80

Identification of $K\alpha$ X-ray Satellite Lines Induced by MeV Heavy-ion Bombardment of Elemental Targets

F. P. Larkins

Department of Chemistry, Monash University, Clayton, Vic. 3168.

Abstract

It is shown that multiply ionized atoms with one or two holes in the 2s subshell in addition to holes in the 2p subshell may contribute directly to the observed $K\alpha$ satellite and hypersatellite spectra reported for targets bombarded with highly energetic heavy ions. The direct participation of such defect configurations results because the normally rapid $L_1 - L_{23}M$ Coster–Kronig transition processes are energetically forbidden for most excited atomic species that are multiply ionized in the L shell. Adiabatic nonrelativistic Hartree–Fock calculations are presented to support this conclusion. A detailed calculation for the $K\alpha$ satellite and hypersatellite spectra of the silicon system is given.

Introduction

Recent studies with high resolution crystal spectrometers have shown that rich $K\alpha$ X-ray satellite spectra are induced by the bombardment of elemental targets of low and medium atomic numbers with heavy ions having MeV energies. Detailed experimental investigations of the sodium (Moore *et al.* 1972*a*), magnesium (McCrary and Richard 1972), aluminium (Knudson *et al.* 1971), silicon (McCrary and Richard 1972), chlorine (Moore *et al.* 1972*b*), titanium (Moore *et al.* 1972*c*) and iron (Burch *et al.* 1971) systems have led to the conclusion that the excited species is initially singly ionized in the K shell and multiply ionized in the L shell. In addition, for calcium, Richard *et al.* (1972) have observed $K\alpha$ hypersatellite lines corresponding to excited atomic configurations initially doubly ionized in the K shell and multiply ionized in the L shell.

It has been consistently argued that $L_1 - L_{23}M$ Coster–Kronig (hereinafter designated CK) transition probabilities are large for these elements, so that any holes initially induced into the 2s subshell should be rapidly transferred via nonradiative processes to the 2p subshell *before* the $K\alpha$-type radiative de-excitation. Hence, where assignment was possible, observed $K\alpha$ satellite lines were considered to originate from $[1s\,2p^n]$, $0 < n \leqslant 5$, initial hole configurations. Adiabatic Hartree–Fock–Slater (hereinafter designated HFS) calculations were used to support this conclusion. The validity of this assignment relies upon two basic assumptions: (1) $L_1 - L_{23}M$ CK processes are energetically favourable for atoms that are multiply ionized in the L shell; (2) $L_1 - L_{23}M$ transition probabilities which are calculated to be large for neutral atoms (McGuire 1971) will also be large in the multiply ionized species. The fact that K and L shell fluorescence yields, and hence X-ray and Auger rates, may vary significantly with the degree of multiple ionization of the atom (Larkins 1971*a*; Burch *et al.* 1972) provides indirect evidence that assumption (2) should be re-examined.

However, in the present paper, attention is focused on the more fundamental assumption (1) concerning the energetics of the CK transition.

A detailed study of the dependence of $L_1 - L_{23} M$ CK transition energies on atomic configuration using an adiabatic nonrelativistic Hartree–Fock (hereinafter designated HF) procedure has recently been conducted (Larkins 1974). Contrary to assumption (1), $L_1 - L_{23} M$ CK processes for all elements rapidly become energetically unfavourable when atoms are multiply ionized in the L shell. The consequences of this general finding for the interpretation of the relevant $K\alpha$ satellite spectra form the subject of this paper. A detailed study of the silicon system is reported, followed by a discussion of the CK results for other systems.

Results

The transition energies for the $L_1 - L_{23} M_1$ and $L_1 - L_{23} M_{23}$ CK processes corresponding to various initial hole configurations of the silicon atom are shown in Table 1. These values were determined using the average atomic configuration concept and the adiabatic procedure as in Larkins (1971*b*).

Table 1. $L_1 - L_{23} M$ Coster–Kronig energies for various initial hole configurations of the silicon atom

Process	Energy (eV) for indicated initial hole configuration							
	[2s]	[1s 2s]	[1s 2s 2p]	[1s $2s^2$]	[1s $2s^2$ 2p]	[$1s^2$ 2s]	[$2s^2$]	[$2s^2$ 2p]
$L_1 - L_{23} M_1$	26·2	6·2	−16·3	−6·6	−31·1	−17·9	15·8	−5·4
$L_1 - L_{23} M_{23}$	34·5	15·2	−6·7	2·4	−22·0	−8·6	24·6	3·9

Experimental values for the CK energies in the parent atom ($Z = 14$) are not available. However, for argon ($Z = 18$), the calculated HF values and the experimental findings are in good agreement whereas HFS results deviate significantly from experiment (Larkins 1974). Table 1 clearly shows that the presence of additional inner-shell holes reduces the CK energies. Of special relevance to this study is the finding that, for the initial hole configurations [1s 2s 2p], [1s $2s^2$ 2p] and [$1s^2$ 2s], all $L_1 - L_{23} M$ CK processes are energetically forbidden. Since inner-shell orbitals are primarily involved in these transitions the findings should not be significantly modified by solid state effects. Furthermore, the experimental results for the argon system (Mehlhorn 1968) suggest that the individual multiplet transitions should be within ± 5 eV of the transition energy determined for the average configuration. Hence it would seem reasonable to apply the findings for the isolated atoms to interpret the experimental results deduced from an investigation of solid targets. The calculations lead to the conclusion that, in the $K\alpha$ X-ray satellite spectrum of silicon, a series of lines resulting from the de-excitation of [1s 2s $2p^n$] and [1s $2s^2$ $2p^n$], $0 < n \leqslant 5$, initial hole configurations should be possible in addition to the [1s $2p^n$], $0 \leqslant n \leqslant 5$, $K\alpha$ satellite series. The intensities of these lines would be related to the population of the hole state and to the various transition rates. Of course, intra-shell $L_{23} \rightarrow L_1$ radiative processes are always present. In the parent atom, rates for such processes are several orders of magnitude less than the inter-shell Auger rates. This situation is unlikely to change significantly in multiply-ionized atoms, even when the processes are forbidden.

The calculated energies $E_{av} - E_{K\alpha_{12}}$ of the satellite lines relative to the $K\alpha_{12}$ line for the three series of defect configurations are shown in columns 2–4 of Table 2.

Column 5 contains the experimental shifts reported by McCrary and Richard (1972), who measured the energies to an accuracy of 0·5 eV with a crystal spectrometer resolution of 2·5 eV (FWHM). The calculated HF energy for the $K\alpha_{12}$ line is within 3 eV of the value reported by Bearden (1967).

Table 2. Shift in silicon $K\alpha$ X-ray satellite energies from the $K\alpha_{12}$ line for various initial hole configurations

(1)	(2)	(3)	(4)	(5)
	$E_{av}-E_{K\alpha_{12}}$ (eV) for indicated configuration			
n	$[1s\,2p^n]$	$[1s\,2s\,2p^{n-1}]$	$[1s\,2s^2\,2p^{n-2}]$	Experiment[A]
0	0·0[B]			0·0[C]
1	10·8	10·4		11·0 13·3[D]
2	23·0	22·2	22·0	22·8 26·6[D]
3	36·2	35·5	34·8	35·5 39·0[D]
4	51·1	49·6	49·0	54·4
5	68·2	65·5	64·2	69·9
6		83·5	81·0	
(7)			99·9	

[A] Experimental results of McCrary and Richard (1972).
[B] Calculated $K\alpha_{12}$ value 1737·1 eV.
[C] Experimental $K\alpha_{12}$ value 1739·8 eV (Bearden 1967).
[D] Multiplet splitting.

Columns 2, 3 and 4 of Table 2 show that the energy shifts associated with hole configurations having the same number of L shell vacancies are very similar and close to the observed shifts, the calculated differences being less than the energy resolution of the spectrometer. Hence, when the CK process is forbidden, it is probable that the observed satellite lines possess components corresponding to the de-excitation of atomic configurations that contain one or two holes in the 2s subshell. The doublet splitting of some of the experimental lines has been tentatively assigned by McCrary and Richard (1972) to multiplet structure. The closeness of the transition energies for various subshell distributions of the L shell holes suggests that the observed splittings do not primarily originate from different atomic configurations. Furthermore, if spin–orbit corrections are applied to the satellite lines via first-order perturbation theory, the maximum doublet splitting ($\frac{3}{2}\zeta_{2p}$) for any transition is determined to be 1·2 eV on the basis of calculations with HFS wavefunctions for the final hole configurations. These findings suggest that spin–orbit splitting is not the major contributing factor to the splitting. Indeed, multiplet transitions resulting from LS coupling in the initial and final hole states appears to be the explanation. Table 2 also reveals that satellite lines corresponding to configurations with six or seven L-shell holes are in principle possible. With the experimental conditions used in the heavy-ion studies so far reported, these lines have not been observed.

Calculations for the $K\alpha$ hypersatellite series in silicon using an adiabatic HF procedure are reported in Table 3. It can be seen from Table 1 that $L_1-L_{23}\,M$ CK transitions are unfavourable for all atomic configurations which include a doubly-ionized K shell. The author is not aware of any reported $K\alpha$ hypersatellite spectra induced by heavy ions apart from the calcium work of Richard *et al.* (1972). The results in Tables 1 and 3 suggest that, when the hypersatellite spectrum of silicon is observed, multiply ionized L-shell configurations with 2s holes will contribute to the

spectral lines. Higher energy resolution than is at present employed by experimenters will be required to resolve the various atomic configuration series contributing to these lines.

Adiabatic HF calculations for the elements sodium ($Z = 11$) to calcium ($Z = 20$) predict that the $L_1 - L_{23}M$ CK transitions are energetically forbidden for the $[1s\,2s\,2p^n]$, $[1s\,2s^2\,2p^n]$ and $[1s^2\,2s\,2p^{n-1}]$, $n \geqslant 1$, initial hole configurations. For the transition metals ($Z = 21$–30) all $L_1 - L_{23}M$ CK transition processes are forbidden for $n \geqslant 2$ in the defect configuration series cited above. It is therefore predicted that the $K\alpha$ satellite and hypersatellite spectra associated with these elements will include contributions from defect configurations with one or two holes in the 2s subshell.

Table 3. Shift in silicon $K\alpha$ X-ray hypersatellite energies from the $K'\alpha_{12}$ line for various initial hole configurations

n	$E_{av} - E_{K'\alpha_{12}}$ (eV) for indicated configuration $[1s^2\,2p^n]$	$[1s^2\,2s\,2p^{n-1}]$	$[1s^2\,2s^2\,2p^{n-2}]$
0	0·0[A]		
1	12·2	11·5	
2	25·9	24·8	23·7
3	40·5	39·4	37·9
4	56·8	55·0	53·5
5	75·1	72·2	70·0
6		91·4	88·2
(7)			108·3

[A] Calculated $K'\alpha_{12}$ value 1875·6 eV.

Acknowledgment

Financial assistance from the Universities Grants Commission to perform these computer calculations is gratefully acknowledged.

References

Bearden, J. A. (1967). *Rev. mod. Phys.* **39**, 78.
Burch, D., Ingalls, W. B., Risley, J. S., and Heffner, R. (1972). *Phys. Rev. Lett.* **29**, 1719.
Burch, D., Richard, P., and Blake, R. L. (1971). *Phys. Rev. Lett.* **26**, 1355.
Knudson, A. R., Nagel, D. J., Burkhalter, P. G., and Dunning, K. L. (1971). *Phys. Rev. Lett.* **26**, 1149.
Larkins, F. P. (1971*a*). *J. Phys.* B **4**, L29.
Larkins, F. P. (1971*b*). *J. Phys.* B **4**, 1.
Larkins, F. P. (1974). *J. Phys.* B **7**, 37.
McCrary, D. G., and Richard, P. (1972). *Phys. Rev.* A **5**, 1249.
McGuire, E. J. (1971). *Phys. Rev.* A **4**, 587.
Mehlhorn, W. (1968). *Z. Phys.* **208**, 1.
Moore, C. F., Olsen, D. K., Hodge, W., and Richard, P. (1972*a*). *Z. Phys.* **257**, 288.
Moore, C. F., Wolter, H. H., Kauffman, R. L., McWherter, J., Bolger, J. E., and Browne, C. P. (1972*b*). *J. Phys.* B **5**, L262.
Moore, C. F., Senglaub, M., Johnson, B., and Richard, P. (1972*c*). *Phys. Lett.* A **40**, 107.
Richard, P., Hodge, W., and Moore, C. F. (1972). *Phys. Rev. Lett.* **29**, 393.

Manuscript received 5 September 1973