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Influence of Chemical Combination on K-fluorescence Lines of Compounds of Al, Si and S

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This paper extends earlier work on the shift on the Kα-fluorescence line of sulphur, which is due to the chemical environment of the atom, and shows that similar good agreement between theory and experiment is also found for Si and Al. On the other hand the Kβ-transitions, which directly involve the electrons engaged in chemical bonding, cannot properly be described by any such monocentric model. Finally the chemical shift of the Kα line of an atom is shown to depend very strongly on the polarity of the bonds to this atom, and also on the d-character of the bonding.

Introduction

Chemical effects in the X-ray spectra of solids have been known since the early 1920's,[1,2] Recently, however, the development of electron spectroscopy has allowed the binding energies of the inner electrons in an element to be measured with very high accuracy.[3,4] We shall be concerned with elements of the third row of the periodic system (Na to A), for which the K-fluorescence lines produced after ionization of an atomic K-shell electron are of two different types. In the first type the 1s-vacancy is filled by an electron from the L shell (Kα): in the second the electron comes from the M shell (Kβ).

There is a fundamental difference between these two situations. The Kα transitions are essentially atomic, and such displacements in the energy as may occur are due to the influence of the valence-shell electrons, which is felt in the inner regions of the atom. This will therefore depend on the distributions of these valence electrons: but the effect will be small. On the other hand the Kβ transitions directly involve the valence electrons, so that the shape and energy of the emission bands will be closely related to the binding forces in the molecule or the solid: so the effect will be much larger.

It is a pity that, with our present state of computer technology, rigorous *ab initio* treatments of crystals other than pure metals and simple ionic salts are not practicable.[5] Even with the simpler situation represented by a complex ion such as the sulphate or perchlorate ion, the same difficulty occurs. Thus the recently-published molecular-orbital (MO) calculations of some of these systems, using the Wolfsberg-Helmholz approximation,[6] are still not sufficiently refined to permit an adequate correlation with experimentally observed spectra shifts. For the Kα transitions, however, because of the essentially atomic character of the inner-shell electrons involved, we can adopt a monocentric approximation, in which the central ion is considered to be in an appropriate «free-ion» situation, with a varying (usually non-integral) number of valence electrons in suitably-hybridized orbitals and spin couplings.[7,8] Such a model has proved to be very successful in reproducing both the energy shifts and the transition energies experimentally measured for sulphur and its compounds.[8] It is reassuring that some recently-published polycentric calculations[9,10] on the oxy-anions of S and Cl (obtained with an approximate, but still non-empirical, MO LCAO SCF calculation) found results very similar to [8] for the effective charges on the S atom in various compounds. Some of these values are compared in Table I.

Table I. Effective electronic charges on Sulphur atom in oxy-anions as obtained by various methods.

	SO_4^{2-}	$S_2O_3^{2-}$		SO_3^{2-}
Oxidation number	6	6	−2	4
Shared electron pairs (Lewis structure)	2	2	−1	1
C.A. Coulson and C. Zauli (1963)	2.05	1.81	−0.62	1.75
R. Manne (1967)	1.79	1.54	−0.96	0.93
C.A. Coulson and F.A. Gianturco (1968)	1.70	1.51	−0.50	1.1

The object of the present paper is two-fold: first, we propose to extend the monocentric approximation for the calculation of Kα transition energies and related chemical shifts to other elements of the third

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row, such as Al and Si; second, we shall demonstrate that, despite its occasional use in this way, the monocentric approximation is quite ill-founded and unjustifiable for Kβ transitions. These latter transitions must be related to the global structure of the solid, and cannot even qualitatively be interpreted on the basis of a local, monocentric, model.

Finally we include some comments on the influence of the electronic configurations involved in these high-energy Kα transitions.

Method of calculation. In the monocentric model[7,8] transitions occur among states ionized in one or more inner shells, and having a variable electron distribution in the valence shell. This latter distribution is related to the classical concept of a valence state,[11] in which the spins of the valence-shell electrons are supposed to be closely coupled with those of the ligand groups. Thus, for the purposes of the interaction between the valence electrons and the inner shells we may treat the spins of the valence electrons as being randomly oriented. Thus in the perfect-pairing approximation, an element such as Si, both in its valence compounds and in silicates in general, is described as having four equivalent tetrahedral hybrids in the valence shell: these hybrids are singly-occupied by electrons of random spin. More elaborate modifications of this model are possible in which we allow for the polarity of the bonds or the ionicity of the solid by permitting fractional occupation of the hybrids; or by allowing (see later) some interaction with other electronic configurations. In the case of Al and its compounds this model uses sp^2 types of hybrids.

If a single configuration is chosen to describe these atomic states, the total electronic energy can easily be written down in terms of the usual one-electron integrals I(n, l), and the two-electron exchange and Coulomb integrals, with the appropriate choice of spherical harmonics.[12,13] This leads to the definition of the Hartree-Fock non-local operator.[13] In the present calculations the eigenvalues of this operator, which are approximations to the one-electron ionization energies, were obtained by the same numerical procedures previously described by the authors.[7]

Kα fluorescence line. The X-ray emission spectrum with which we are concerned arises[14] when an electron goes into a vacant 1s hole from either the $2p_{1/2}$ or $2p_{3/2}$ levels, giving rise to the line $K\alpha_{1,2}$. Arguments have been given[15,16] to suggest that the change in the Hamiltonian as a result of the production of an inner vacancy, or hole, can be treated as a sudden perturbation. In that case the « frozen-structure » approximation in which it is supposed that the radial functions of the outer electrons do not change, allows us to use Koopmans' theorem to find how the energy of transition depends on the chemical environment of the chosen atom.[8]

Several experimental studies on silicon and numerous silicates[17,18,19] have shown that the $K\alpha_{1,2}$ doublet intensity does not change significantly along the series examined, whereas the line position suffers a measurable shift towards higher energies on going from Si to its compounds (Table II). This variation is clearly reproduced by the present calculations, reported in the second column of Table III, and by the corresponding chemical shifts shown in the fifth column.

Two features of Table III are reassuring. One is the close agreement between the calculated and measured energies of the $K\alpha_{1,2}$ lines (1756.4 and 1739.9 eV respectively): the other is agreement with some experimental work of Faessler and Kramer which used the $K\alpha_{1,2}$ shift of about 0.7 eV[17] to predict an effective charge +2 for the silicon atom in SiO_2.

Analogous conclusions can be drawn for aluminium and its compounds, where experimentalists[20,21,22] once again found no variations in intensity, but chemical shifts towards shorter wavelength, on moving from the element to compounds such as Al_2O_3 and various aluminates. Here again the results of the second column of Table IV, and the corresponding shifts in column 5, confirm the experimental results of Table II.

In close analogy with the case of sulphur[8] a parabolic fitting can be given for the energy shift as a function of the net atomic charge x. This is of the form

$$\delta E = x(x+a)/b$$

A least-squares procedure led to the values: a = 2.73, b = 14.28 for Si; a = 0.24, b = 10.0 for Al. Both of these are quite close to the previous values[8] for S(a = 3, b = 11). All three resulting curves

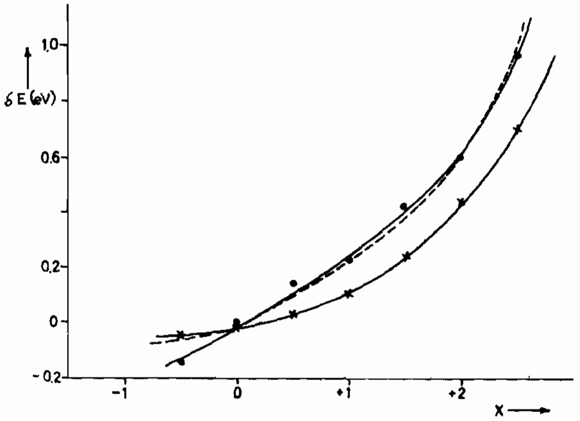

Figure 1. Energy sligts (eV) of K_α- fluorescence lines as a function of the net external charge *x*, in some third-row elements. ● silicon Kα --- sulphur Kα x aluminium Kα.

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Table II. Experimental values of some K line peaks for S, Si, Al and related compounds.

Compound	K Line*	λ(Å)⁺	E(ev)⁺	Compound	K line*	λ(Å)⁺	E(ev)⁺
[a] $S_{rhombic}$	β	5.0282	2465.61	[b] SiO_2	$\alpha_{1,2}$	7.1240	1740.0
CaS	β	5.0277	2465.82		β	6.7672	1831.6
SrS	β	5.0283	2465.52		β'	6.8185	1817.8
MnS	β	5.0285	2465.44	[d] Al	$\alpha_{1,2}$	8.3393	1486.70
K_2SO_4	β	5.0247	2467.27		β	7.9590	1557.74
	β'	5.0532	2453.41	[d] Al_2O_3	$\alpha_{1,2}$	8.3380	1486.93
$CaSO_4$	β	5.0251	2467.09		β	7.9819	1553.27
	β'	5.0519	2453.99		β'	8.0618	1537.88
[b] Si	$\alpha_{1,2}$	7.1240	1739.6				
	β	6.7514	1835.9				
[c] Si_2O	$\alpha_{1,2}$	7125.02	1740.08				
[c] Si_2O_3	$\alpha_{1,2}$	7124.58	1740.19				

[a] S element and compounds are from A. Faessler and Schmidt (29). [b] From W. L. Baun *et. al.* (18). [c] From A. Faessler and Kramer (17). [d] From A. W. Fischer *et. al.* (20). * The notation given is the one conventionally used (see [14]). ⁺ The conversion factor used between λ and E is the most recently quoted in the current literature (see [26]).

Table III. K-shell fluorescence lines in Silicon (transition energies and « chemical » shifts) (eV)

Valence shell formal charge	K_α energy (unresolved doublet)	K_β energy ([1s]→[3p]* approximation)	K_β' energy ([1s]→[3s] approximation)	Chemical shifts (ev) K_α	K_β	K_β'
−0.5	1756.27	1834.16	1824.29	−0.15	−1.31	−1.29
0	1756.42	1835.48	1835.48	(0)	(0)	(0)
+0.5	1756.57	1836.66	1827.02	+0.15	+1.19	+1.44
+1.0	1756.65	1840.09	1830.90	+0.23	+4.61	+5.32
+1.5	1756.84	1841.14	1831.93	+0.42	+5.66	+6.35
+2.0	1757.02	—	—	+0.60	—	—
+2.5	1757.39	—	—	+0.97	—	—

* The notation [1s] implies that there is a vacancy in the 1s s hell.

Table IV. K-shell fluorescence lines in Aluminium (transition energies and « chemical » shifts) (ev)

Valence shell formal charge	K_α energy (unresolved doublet)	K_β energy ([1s]→[3p] approximation)	K_β' energy ([1s]→[3s] approximation)	Chemical shifts (ev) K_α	K_β	K_β'
−0.5	1504.17	1559.03	1552.35	−0.03	−0.71	−0.70
0	1504.20	1559.74	1553.05	(0)	(0)	(0)
+0.5	1504.23	1560.77	1553.95	+0.03	+1.02	+0.90
+1.0	1504.31	1562.01	1554.91	+0.11	+2.27	+1.86
+1.5	1504.44	1563.50	1556.17	+0.24	+3.76	+3.12
+2.0	1504.63	—	—	+0.44	—	—
+2.5	1504.89	—	—	+0.70	—	—

are shown in Figure 1. The agreement with experiment seems to confirm that such a model, with the frozen-structure approximation, can give reliable interpretations for fluorescence line shifts when the transitions are essentially mono-centric.

Kβ transitions. The most important feature of the Kβ transitions for third-row atoms is that since the inner vacancy is filled by an electron from the valence shell involved in chemical bonding, the concept of a transition between two sharp states is replaced by the concept of a transition band from the continuum of levels occupied by conduction or valence electrons in the solid. The detailed shape of this spectrum will depend on the product of the density of states N(E) in the band and the square of the appropriate matrix element for the transition.[23] This matrix element may vary considerably through the band, according as the lower (*i.e.* atomic) orbital is of s or p type, and as the band wave function is more or less s-like or p-like in the interior of the atom where the first vacancy is localised. Moreover, the widths of the bands may sometimes be large compared with the expected chemical shifts. Thus for Si the orthogonalized-plane-wave calculations of Woodruff[24] sugfest 9.5 eV for the valence-band width (However similar work of Tomboulian and Bedo[25] gave the value 16.7 eV). Some experimental band widths are reported in Table V. In addition to this it is not clear whether the variation of N(E) across the band, or the variation in s, p character, is the more important. Kern,[27] in his study of the Kβ emission bands of Si, SiC and SiO_2, concluded that the variations of N(E) were predominant; but Rooke[28] in his work on

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Table V. Experimental band widths and energy shifts data for K_β lines in S, Al and Si different chemical states

Compound	K_β width at ½ max(ev)	K_β shift (ev)
Pure sulphur [a]	8.32	(0)
Na_2SO_4 [a]	5.95	+1.440
$Na_2S_2O_8$ [a]	6.70	+1.341
$Na_2S_2O_3$ [a]	7.72	+1.077
NaSCN [a]	7.51	+0.569
DL-Ethionine [a]	8.23	−0.095
CuS [a]	8.32	−0.343
Si metal [b]	~6.0	(0)
SiC [b]	~5.0	—
SiO_2 [b]	~6.0	−4.3
Al metal [c]	6.0	0
Al_2O_3 [c]	4.6	−4.2

[a] From [31]. The energy shifts are measured at ½ max relative to pure sulphur. [b] From (18). The energy shifts are from peak differences among the bands. [c] From (20). The energy shifts are again from peak differences among the bands.

Table VI. Calculated transition energies and chemical shifts for K_β lines in atomic and ionic Sulphur (ev)

Valence shell formal charge	K_β energy ([1s]→[3p] approximation		K_β' energy ([1s]→[3s] approximation		Chemical shifts (ev) K_β		K_β'	
	Present calculations	From reference (30)	Present calculations	From reference (30)	Present calculations	Ref. (30)	Present calculations	Ref. (30)
−1.0	2460.56	—	2447.74	—	−1.45	—	−1.86	—
−0.55	2462.0	2465.80	—	—	—	−1.84	—	—
0	—	2467.64	2449.60	—	(0)	(0)	(0)	(0)
+1.0	2465.40	—	2453.44	—	+3.39	—	+3.84	—
+2.0	2470.93	2474.65	2456.62	2461.99	+8.92	+7.01	+7.02	—
+3.0	2475.26	—	2462.49	—	+13.25	—	+12.89	—

aluminium concluded that the variation of the transition moment was the more important!

Despite all this attempts have been made to discuss these Kβ transitions as if they were single lines with a certain amount of broadening on either side of some maximum.[29,30,31,32] Unfortunately the physical implications of such an assumption have not always been made clear. We can illustrate the difficulty very simply by showing that the monocentric approximation is quite unable to reproduce the observed chemical effects: to do this we use the methods and approximations previously described.

Exploratory self-consistent-field calculations were therefore carried out for the upper and lower states involved in a single-line approximation to the Kβ band; these are the [1s] and [3p] states, where the symbol in brackets indicates the missing electron. The results obtained for sulphur and its oxidized and reduced states are shown in Table VI, where the present calculations are compared with others using simpler analytical forms for the orbitals.[30] The agreement between the two sets of calculations is close, and in this case it happens that the experimental trend agrees with the calculated one. However, when a similar calculation is made for Si and Al, and their related compounds, results are obtained in clear disagreement with experiment. Tables III and IV show, by comparison with Table II, that now even the sign of the calculated chemical shift is opposite to that measured, although agreement is good for the positions of the peaks of the bands in the pure elements.

A by-product of this work concerns the generally-suggested assignment of the Kβ′ line. This line appears on the low-energy side of Kβ, and has been interpreted as due to a transition [1s]→[3s], made possible by symmetry distortions due to the ligands.[30,31] Our calculations for such a transition do not agree with experiment; and in fact Mendel *et al.*[33] only found its presence in compounds containing oxygen. They also found a constant value of about 14 eV for the difference ΔE between peak values of the Kβ and Kβ′ bands of Si, Al, S and P compounds. Our calculations in Tables III IV and VI show that this would be expected to vary from 6.1 eV in Al to 9.2 eV in Si and to 13.0 eV in S. A more careful study of this band seems to be called for.

It is clear from this discussion that, unless we are prepared to embark on a difficult and extensive calculation of its band structure, we must be very careful in applying to the valence electrons in a solid the methods already found useful for isolated atoms and inner-shell electrons in solids. The mono-centric approximation, although it describes fairly well the influence of valence-electron densities on inner-shell energies, constitutes a poor approximation when dealing with electrons in valence or conduction bands, where global properties of the solid are involved.[34]

d-orbital participation. In the above description of the valence-shell electrons in Si, Al and S only 3s and 3p orbitals were considered. It has recently been pointed out, however, that spectroscopic excited states and excited valence-states of sulphur sometimes show a remarkable contraction of d orbital radii, particularly when double excitation occurs.[12,35,36] Fur-

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thermore, recent semi-empirical calculations[37] have suggested that 3d, 4s and even 4p orbitals can be involved in band formation of elements like Na, Mg, ... Cl. It therefore becomes important to investigate the extent to which such d-promotion might influence inner energy levels, and its likely importance within the free-ion approximation. With this objective we have made some explorative calculations on the sulphur atom.

Table VII. $\delta(\varepsilon_{1s}—\varepsilon_{2p})$ calculated for some excited spectroscopic states of sulphur

Configuration	Spectral term	$\lvert\varepsilon_{1s}—\varepsilon_{2p}\rvert$* (in eV)	$\delta\lvert\varepsilon_{1s}—\varepsilon_{2p}\rvert$ (in eV)
s^2p^4	^3P	2321.61	(0)
$(s^2p^3)^+$	^4S	2321.82	0.21
s^2p^3d	^5D	2321.89	0.28
sp^3d^2	^3I	2321.53	0.92
sp^3d^2	^7F	2322.55	0.94
sp^3d^2	^5H	2322.67	1.06

* The ε_i denote the single-particle energies in the HF scheme for atomic configurations.

Table VII shows the changes that occur in the HF parameters for the 1s and 2p electrons for the ground and some excited states of sulphur, when these latter involve one or more d electrons. This Table shows that the energy shift (shown in the last column) which results from promotion to a d-orbital is comparable with that obtained by ionization of the neutral atomic configuration ($s^2p^4\,{}^3P \rightarrow s^2p^3\,{}^4S$). This suggests that d-types-and perhaps also f- and g-types- of orbitals should be included for any really accurate calculation of these chemical shifts provided that we want to associate the energy shifts in molecules with excited-state orbital participation, or to Coulomb-type interaction with the ligand electrons.

Despite this conclusion we believe that the monocentric model, by fixing attention on the part played by the total electronic density in the valence shell and the role of spin-valence forces, is important; for it provides a simple physical picture, and preserves the familiar account of a chemical bond as the result of electron pairing. If we want to obtain insight into the origin of the Kα chemical shifts this monocentric model will give it. But, as we have shown, a much more elaborate analysis is needed if we are concerned with the Kβ transitions.

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