Atomic structure calculations for the analysis of Auger parameters of elements K to Kr

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Abstract. The values of atomic parameters, k and dk/dN, used in the analysis of Auger parameter shifts have been determined from the results of atomic structure calculations for the elements K to Kr. The values of the parameters for free atoms have been corrected for the effect of valence electron compression in solids. Calculations for Ni and Ge shows that the values obtained for the atomic parameters are independent of the configuration of passive valence electrons and of the character of the inner shell core hole.

1. Introduction

The determination of the charge transfer between atoms in molecules and solids is one of the most important problems in physics and chemistry. However, the concept of charge transfer is difficult to define, since even if we were able to map the variation of the electron density of a material in space it would be unclear which particular regions of valence charge should be associated with which particular atom. Any attempt to use the results of electronic structure calculations to define charge transfer between atoms encounters this problem since the results are very dependent on the assumed values of atomic radii.

One way out of this dilemma is to concentrate on the variation of the potential in the core of an atom arising from charge transfer since there are experimental probes, such as measurements of core level binding energies by x-ray photoelectron spectroscopy (XPS), which are sensitive to the atomic potential. The observations [1,2] that for deep core levels XPS shifts between chemical environments are independent of core level, and that the energies of x-ray transitions between deep core levels are almost independent of chemical environment [3], indicate that changes in valence charge produce uniform changes in the average potentials experienced by core electrons. However, the analysis of XPS shifts alone in terms of potential models leads to difficulties in accurately referencing the experimental spectra and in treating relaxation of the atom in the final state [4,5]. These problems can be resolved by considering changes in the Auger parameter, α, defined by

$$\alpha = I + K \tag{1}$$

where I is the ionization energy of a core level and K is the kinetic energy of a core–core–core (CCC) Auger line is an accurate measurement of relative charges in the kinetic energies of XPS and Auger transitions.

The Auger parameter was introduced by Wagner [6] as a way of combining data from both XPS and Auger studies. The analysis of Auger parameter shifts has been discussed by

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a number of authors [7, 8]. A recent approach by Thomas and Weightman [4] offers a way of resolving the charge transfer problem in alloys and has been extended to yield insight into the local electronic structure of semiconductors [9] and interfaces [10]. This approach relies upon the evaluation of potential parameters, from atomic structure calculations and in this work we present results for these potential parameters for the elements K to Kr.

2. Theory

Following the approach of Thomas [5] we write the potential in the core of the atom in the form

$$V = C + kq + U \tag{2}$$

where C represents contributions from the nucleus and core electrons, which will cancel in a comparison between different atomic environments, q is the valence charge and U represents contributions to the atomic potential from the atomic environment. The quantity k is the change in core potential resulting from the removal of a valence electron. The parameters k, q and U are functions of N, the number of core electrons, but are assumed not to depend upon which core electrons are removed.

Expanding the total energy of the atom in a Taylor series [11, 12] in terms of core occupancy Thomas and Weightman [4] showed that the Auger parameter could be written to first order as

$$\Delta\alpha = \Delta[q\,dk/dN + (k - 2\,dk/dN)\,dq/dN + dU/dN. \tag{3}$$

In the derivation of (3) it is assumed [4, 5] that k and q vary linearly with N. The derivatives are with respect to the number of core electrons. The first term represents the relaxation contribution from the shrinkage of the valence orbitals when the atom is core ionized, the second represents the contribution from transfer of screening charge from the surroundings to the core ionized atom and the third gives the change in external potential due to the effect of polarization of the surroundings by the core hole.

Generally more than one valence orbital may be involved in the bonding and (3) should be expanded into a sum over partially occupied valence orbitals, i:

$$\Delta\alpha = \Delta\sum_i \left[q_i \left(\frac{dk_i}{dN} \right) + \left(k_i - 2\frac{dk_i}{dN} \right) \left(\frac{dq_i}{dN} \right) \right] + \Delta\frac{dU}{dN}. \tag{4}$$

3. The parameters

Clearly the analysis of Auger parameter shifts in terms of (4) requires values for the parameters k and dk/dN and we now derive these from the results of atomic structure calculations.

Thomas and Weightman [4] have discussed various ways in which k and dk/dN can be derived from atomic structure calculations and we follow their procedures, making use of the Dirac–Fock code of Desclaux [13, 14]. We equate k with the difference between the Koopmans energy of the relevant core orbital in the neutral and valence ionized atoms.

The results of atomic structure calculations show that the value of k depends on the orbital character of the valence electron that is removed. It is this dependence which gives

the method the potential to determine environmental changes in atomic configurations. We denote the orbital character of the valence level by subscripts: k_s, k_p and k_d and the values of these parameters given by our calculations are shown in table 1 and figures 1, 2 and 3. Values of dk/dN were determined in two different ways using the expressions [4]

$$dk/dN = 2(k - \Delta I) \tag{5}$$

$$dk/dN = k_{atom} - k_{core\text{-}ionized\ atom} \tag{6}$$

where

$$\Delta I = I_{ion} - I_{atom}. \tag{7}$$

I_{atom} is the core-ionization energy determined from a difference in the total energy of the atom in its ground state and core-ionized state and I_{ion} is the corresponding value for an atom that has lost a valence electron.
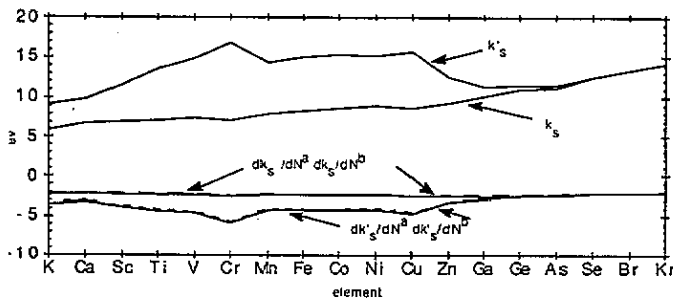

Figure 1. Variation of k and dk/dN calculated using a 4s valence hole configuration across the fourth period. Renormalization (denoted by k' and dk'/dN) alters the calculated values greatly and can be directly related to moving from values calculated for single atoms to values calculated for a solid. a, Difference between k for neutral atom and k for core-ionized atom. b, Calculated from $dk/dN = 2(k - \Delta I)$ where ΔI is the difference in core-ionization energy obtained from total energy calculations between a neutral atom and a valence-ionized atom.
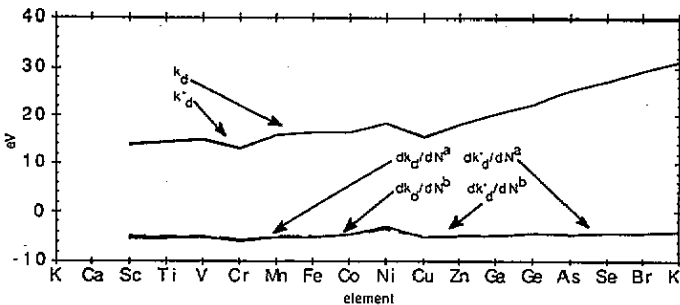

Figure 2. Variation of k and dk/dN calculated using a 3d valence hole configuration across the fourth period. In this case renormalization (denoted by k' and dk'/dN) does not alter the values to any great extent, see figure 4. a–b, as for figure 1.

The values of dk/dN for valence orbitals of s, p and d character given by the two approaches are shown together in table 1 and graphically in figures 1, 2 and 3.

The values of k and dk/dN shown in table 1 are the results of free atom calculations. For atoms in a solid state environment we expect the values of these parameters to be modified by the compression of the valence wavefunctions. We allow for this compression using

Table 1. k and dk/dN (in eV). Primes denote renormalized values.

Element	k_s	k_s'	dk_s/dN^a	dk_s'/dN^a	dk_s/dN^b	dk_s'/dN^b
K	5.98	9.12	−2.17	−3.31	−2.29	−3.49
Ca	6.69	9.75	−2.09	−3.05	−2.18	−3.18
Sc	6.87	11.43	−2.17	−3.61	−2.27	−3.78
Ti	7.14	13.42	−2.18	−4.10	−2.28	−4.28
V	7.43	14.75	−2.19	−4.35	−2.28	−4.53
Cr	7.11	16.84	−2.39	−5.64	−2.50	−5.92
Mn	7.99	14.32	−2.22	−3.98	−2.30	−4.12
Fe	8.26	15.00	−2.24	−4.07	−2.33	−4.23
Co	8.53	15.38	−2.27	−4.09	−2.35	−4.24
Ni	8.88	15.08	−2.30	−3.94	−2.38	−4.08
Cu	8.55	15.68	−2.44	−4.47	−2.55	−4.68
Zn	9.32	12.50	−2.36	−3.16	−2.40	−3.22
Ga	10.02	11.33	−2.37	−2.68	−2.48	−2.80
Ge	10.87	11.41	−2.32	−2.44	−2.42	−2.54
As	11.09	11.48	−2.23	−2.31	−2.31	−2.39
Se	12.46	12.51	−2.17	−2.18	−2.16	−2.17
Br	13.28	13.32	−2.13	−2.14	−2.20	−2.21
Kr	14.09	14.09	−2.06	−2.06	−2.10	−2.10

Element	k_d	k_d'	dk_d/dN^a	dk_d'/dN^a	dk_d/dN^b	dk_d'/dN^b
Sc	13.97	14.12	−4.94	−5.02	−5.25	−5.34
Ti	14.44	14.70	−4.94	−5.03	−5.20	−5.30
V	14.96	15.20	−4.91	−4.99	−5.16	−5.24
Cr	13.03	13.39	−5.49	−5.64	−5.79	−5.95
Mn	16.04	16.17	−4.87	−4.91	−5.07	−5.11
Fe	16.59	16.71	−4.86	−4.89	−5.05	−5.09
Co	16.48	16.58	−4.57	−4.60	−4.69	−4.72
Ni	18.34	18.43	−3.47	−3.49	−3.04	−3.06
Cu	15.56	15.65	−4.99	−5.02	−5.16	−5.20
Zn	18.16	18.18	−4.62	−4.63	−4.75	−4.75
Ga	20.44	20.44	−4.60	−4.60	−4.74	−4.74
Ge	22.30	22.30	−4.33	−4.33	−4.38	−4.38
As	25.19	25.19	−4.46	−4.46	−4.58	−4.58
Se	27.21	27.21	−4.33	−4.33	−4.43	−4.43
Br	29.34	29.34	−4.20	−4.20	−4.27	−4.27
Kr	31.30	31.30	−4.11	−4.11	−4.16	−4.16

Element	k_p	k_p'	dk_p/dN^a	dk_p'/dN^a	dk_p/dN^b	dk_p'/dN^b
Ga	8.31	12.42	−2.63	−3.93	−2.75	−4.11
Ge	8.86	10.72	−2.54	−3.07	−2.63	−3.18
As	9.80	11.17	−2.44	−2.78	−2.52	−2.87
Se	10.48	10.77	−2.38	−2.42	−2.49	−2.56
Br	11.55	11.75	−2.31	−2.35	−2.35	−2.39
Kr	12.23	12.23	−2.27	−2.27	−2.29	−2.29

[a] Difference between k for neutral atom and k for core-ionized atom.
[b] Calculated from $dk/dN = 2(k - \Delta I)$ where ΔI is the difference in core-ionization energy obtained from total energy calculations between a neutral atom and a valence-ionized atom.

the renormalization procedure introduced by Watson [15] and co-workers and discussed in terms of its influence on the values of k and dk/dN by Thomas and Weightman [4]. That is

$$k' = k(\langle 1/r\rangle_m/\langle 1/r\rangle_{atom}) \tag{8}$$
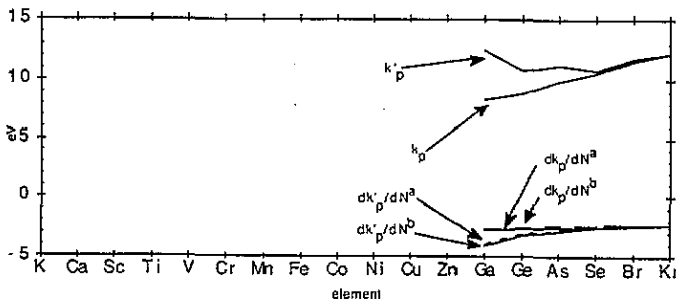
$$dk'/dN = (k'/k)(dk/dN) \tag{9}$$

Figure 3. Variation of k and dk/dN calculated using a 4p valence hole configuration across the fourth period. Renormalization (denoted by k' and dk'/dN) does alter the calculated values in this case. a–b, as for figure 1.

where $\langle 1/r \rangle_{\text{atom}}$ and $\langle 1/r \rangle_{\text{m}}$ are the expectation values of $1/r$ for the atomic and renormalized valence electron wavefunctions, respectively and a prime is used to denote renormalized k and dk/dN. The evaluation of $\langle 1/r \rangle_{\text{m}}$ requires a value for the Wigner–Seitz radius which is the upper limit of integration. The values used for the elements K to Kr are shown in table 2. The renormalized values of the parameters are shown in table 1 and figures 1–3.

4. Discussion

The renormalization procedure is the largest factor affecting the values of the parameters, (table 1 and figures 1–3) and it is the uncertainty in how to treat the valence wavefunction compression which introduces the largest error into the analysis of Auger parameter shifts. Thomas and Weightman [4] have discussed this problem and conclude that the 'true' value of the atomic parameters lies between the atomic values and the results from the renormalization procedure followed here.

Renormalization 'compresses' all the valence charge inside the Wigner–Seitz radius. The values of k_s and k_p are most affected by this procedure as the 4s and 4p wavefunctions for a free atom extend much further outside the Wigner–Seitz radius than the 3d valence wavefunction (figure 4). The values of the parameter for the more localized 3d wavefunctions are hardly changed by the renormalization procedure (figure 2).
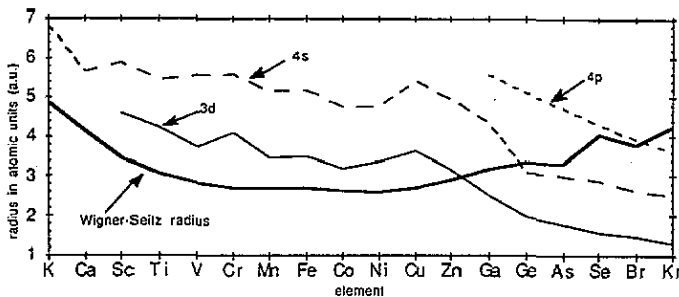

Figure 4. A comparison of the Wigner–Seitz radius with the radial extent of valence wavefunctions as determined from tables of density of states given by atomic structure calculations within the Dirac–Fock scheme.

The results for k_s and k'_s (figure 1) show the importance of the renormalization procedure for the extended 4s wavefunctions of the 3d transition elements. All the k parameters show a general increase with atomic number as the valence wavefunction becomes more localized. The renormalization process introduces reductions in the value of k'_s from Cr to Mn and Cu to Zn which are not present in the free atom results for k_s and which arise from changes in Wigner–Seitz radius (table 2) associated with changes in the bonding in the solid state. Such changes are probably related to the change in 3d and 4s occupancy at these atomic

Table 2. Wigner–Seitz radii for elements of the 4th period [17].

Element	Z	Crystal Phase	Atoms/unit cell	Wigner-Seitz Radius(au)
K	19	BCC	2	4.87
Ca	20	FCC	4	4.12
Sc	21	HCP	6	3.43
Ti	22	HCP	6	3.05
V	23	BCC	2	2.81
Cr	24	BCC	2	2.68
Mn	25	BCC	58	2.70
Fe	26	BCC	2	2.67
Co	27	HCP	6	2.61
Ni	28	FCC	4	2.60
Cu	29	FCC	4	2.67
Zn	30	HCP	6	2.90
Ga	31	ORC	8	3.15
Ge	32	DIA	8	3.31
As	33	RHL	2	3.28
Se	34	HCP	6	4.02
Br	35	ORC (123K)	8	3.75
Kr	36	FCC(20.5K)	4	4.23

FCC-Face Centred Cubic	BCC-Body Centred Cubic	HCP-Hexagonal
DIA-Diamond	ORC-Orthorhombic	RHL-Rhombohedral

Crystal Phase	Cell Volume	Wigner-Seitz Radius
Cubic	a^3	$\sqrt[3]{\dfrac{3}{4\pi N}}a$
for Simple: N=1,BCC, N=2, FCC, N=4, Diamond N=8		
Hexagonal	$\dfrac{2\sqrt{3}}{2}a^2c$	$\sqrt[3]{\dfrac{3V}{4\pi N}}$
usually N=6		
Orthorhombic	abc	$\sqrt[3]{\dfrac{3abc}{4\pi N}}$
usually N=8		
Rhombohedral	$a^3\sqrt{1-3\cos^2\alpha+2\cos^3\alpha}$	$\sqrt[3]{\dfrac{3V}{4\pi N}}$
usually N=2		

(1 au=0.529Å)

numbers which can be seen to have a direct influence on the values of k for the more localized d electrons (figure 2).

dk/dN represents the shrinkage of the valence orbitals caused by the removal of a core electron; its sign is always negative. The results of Siegbahn and Goscinski [16] indicate [5] that $dk/dN = -2$ eV per atomic charge unit for second row elements and is borne out by the results of our calculations. We find the values of dk/dN to be less influenced by renormalization than the value of the k parameters.

The observation that the values obtained for the k and dk/dN parameters depend, via the renormalization process, on the local atomic configuration suggests that we should consider the influence of the atomic configuration on the results of the atomic calculations. It is important here to make a distinction between the difference in the values of k_l and dk_l/dN resulting from a difference in the valence level to be ionized, l, such a difference being essential if (4) is to be used to probe the environmental dependence of the valence configuration, and the difference arising from a different choice of the configuration of 'passive' valence electrons by which we mean those unchanged by the valence ionization

of level l and appropriate to k_l. While the former differences are important and have been evaluated, the latter differences are in fact negligibly small as can be seen from the results of calculations for the Ni atom (table 3). The Ni atom can adopt a number of configurations of its eight 3d electrons yet these various configurations have a negligible influence on the values of k_s and dk_s/dN obtained from the results of atomic structure calculations (table 3).

Table 3. k_s and dk_s/dN as a function of valence configuration for Ni (eV).

	Valence configurations		
	$3d_{3/2}^4 3d_{5/2}^4 4s^2$	$3d_{3/2}^3 3d_{5/2}^5 4s^2$	$3d_{3/2}^2 3d_{5/2}^6 4s^2$
k^a	8.80	8.80	8.80
dk/dN^b	2.30	2.30	2.29
dk/dN^c	2.39	2.38	2.38
k^d	8.80	8.80	8.80
dk/dN^e	2.30	2.30	2.30
dk/dN^f	2.38	2.38	2.39

[a] Difference in Koopmans energy between neutral atom and valence-ionized atom using $2p_{1/2}$ core hole and a 4s valence hole.
[b, c] Difference between k for neutral atom and k for core-ionized atom.
[d] Difference in Koopmans energy between neutral atom and valence-ionized atom using $2p_{3/2}$ core hole and a 4s valence hole.
[e, f] Calculated from $dk/dN = 2(k - \Delta I)$ where ΔI is the difference in core-ionization energy obtained from total energy calculations between a neutral atom and a valence-ionized atom.

The data in table 3 also show that the values obtained for k_s and dk_s/dN from atomic calculations for Ni are also independent of whether the core hole is created in a $2p_{1/2}$ or $2p_{3/2}$. This latter result is in accordance with our basic assumption that all core levels experience similar changes in core potential as a result of changes in valence state. We examined this basic assumption in more detail for Ge and table 4 shows the results k and dk/dN obtained from atomic structure calculations for all the core levels in the first and second shells of Ge. We find the results for k constant to 1% at (8.95 ± 0.09) eV and those for dk/dN, evaluated by either method, constant to 4% at (2.65 ± 0.11) eV. The results for Ni and Ge support the basic assumption of this approach to the evaluation of charge transfer.

Table 4. Core hole dependence of k_p and dk_p/dN for Ge (eV).

Core hole	k (eV)^a	dk/dN^b	dk/dN^c
1s	9.02	−2.85	−2.77
2s	8.95	−2.67	−2.60
$2p_{3/2}$	8.97	−2.54	−2.62
$2p_{1/2}^d$	8.86	−2.54	−2.63

[a] Difference in Koopmans energy between neutral atom and valence-ionized atom.
[b] Difference between k for neutral atom and k for core-ionized atom.
[c] Calculated from $dk/dN = 2(k - \Delta I)$ where ΔI is the difference in core-ionization energy obtained from total energy calculations between a neutral atom and a valence-ionized atom.
[d] The results shown here for the 1s, 2s and $2p_{3/2}$ core hole states are derived from atomic structure calculations involving a $4p_{1/2}$ valence hole $(4s^2 4p_{1/2}^1)$. Since the Desclaux code does not converge for configurations involving more than one unfilled shell with the same j value the results for the $2p_{1/2}$ core hole state were derived using configurations involving a $4p_{3/2}$ valence hole $(4s^2 4p_{3/2}^1)$.

5. Conclusion

We have determined from the results of atomic structure calculations the values of the atomic parameters k and dk/dN for the elements K to Kr which are needed in Thomas and Weightman's [4] method of analysing Auger parameter shifts.

The values of the parameters obtained for free atoms have been corrected for the compression of the valence electrons in solids by renormalizing the valence charge to the Wigner–Seitz sphere. The renormalization has a large effect on the values of the parameters for s and p valence levels but is a negligible correction for the more localized 3d wavefunctions.

Studies of Ni show that the atomic configuration of passive valence electrons has a negligible effect on the results of the atomic structure calculations. For Ge it is shown that the values of the atomic parameters are independent of the orbital character of the inner core levels in accordance with the basic assumption of this approach to the analysis of Auger parameter shifts.

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