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Onset of *d* screening in alkali and alkaline earths

R.J. Cole, N.J. Brooks, and P. Weightman
Department of Physics and Surface Science Research Centre, University of Liverpool, Liverpool L69 3BX, United Kingdom

J.A.D. Matthew
Department of Physics, University of York, Heslington, York Y01 5DD, United Kingdom

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A modified excited atom model incorporating a polynomial expansion of the core potential is used to predict relaxation and Auger parameter shifts between free atoms and elemental solids for alkali and alkaline earths systems. Na and Mg are well described by *sp* screening; the other alkaline earth metals exhibit *d* screening in both single and double hole states, while the other alkalis require *d* screening in the final state of the Auger process. These results for simple metals are used to aid interpretation of electron spectroscopic shifts in more complex alloy systems.

I. INTRODUCTION

Environmental shifts in photoelectron and Auger spectroscopy contain information both about the initial state potential experienced by localized core electrons and relaxation effects associated with the screening of core holes by the other electrons in the system. The relaxation energy contribution can be effectively separated by combining an experimental core binding energy E_b with a corresponding core-core-core Auger transition energy E_k to form the Auger parameter ξ.[1,2] ΔE_b, the shift in binding energy, is of the form

$$\Delta E_b = \Delta V + \Delta\phi - \Delta R, \qquad (1)$$

where V is the ground state core potential, ϕ is a reference potential, and R is the final state relaxation energy. Assuming linear screening

$$\Delta E_k = -\Delta V - \Delta\phi + 3\Delta R\ , \qquad (2)$$

reflecting the quadratic dependence of the relaxation energy on the number of core holes. Then $\Delta\xi = \Delta E_b + \Delta E_k \approx 2\Delta R$, while, if consistent energy referencing is achieved, an initial state parameter shift $\Delta\beta = \Delta E_k + 3\Delta E_b \approx 2\Delta V$ may be constructed to emphasize the initial state. Although this simple analysis requires some modification to take account of higher-order relaxation effects,[3] it can be effectively exploited to give insight into bonding and charge transfer at surfaces and interfaces.[4,5] How reliable is such an approach? One test of this is to see how effectively one can account for the shifts $\Delta\xi$ between free atoms and elemental solids where there is unambiguous charge neutrality in both states.

This problem has been tackled by a wide range of techniques.[6–19,3] The original cavity model of Wagner and Biloen[7] gives immediate insight into the rough magnitude of $\Delta\xi$ and ΔR but has no clear rational for determining cavity radius. The polarizable atom model of Moretti,[17] and Moretti and Porta[16] in the limit $\alpha \rightarrow \infty$ emphasizes the role of local geometric structure, while linear dielectric response theories[10] relate relaxation energies to free electron densities with no information about the number or distance of neighboring atoms. The suggested insensitivity to the details of the local environment is enshrined in the excited atom model,[6,11] which simulates "perfect" extra-atomic screening by considering the properties of a neutral core excited atomic system. Such ideas were then developed by Thomas,[20] and Thomas and Weightman[21] to give measures of charge transfer in alloys. Full self-consistency is embodied in electron gas studies,[10] and the ultimate self-consistent approach involves total energy calculations for large unit cells in which a single atom contains a core hole, as has been attempted for Au by Weinert *et al.*[15] It is, however, important to blend the insights from relatively simple models with the specific results of high-level computation.

One important distinction becomes clear. In some systems, e.g., free electron metals, screening of a core hole is by electrons of *sp* character, while in the transition metals *d* screening becomes very important.[11,6,14] The crucial difference is that the *d* screening electron is able to collapse into a highly localized orbital leading to an enhanced "super-screening."

This paper extends the excited atom model of Williams and Lang (WL)[11] through application of a potential model treatment of chemical shifts in which dependence of the core potential on the atom charge is no longer linear,[22] and which explicitly takes account of nonlinear screening. $\Delta\xi$ and ΔR are calculated for a series of paired elements (Na,Mg), (K,Ca), (Rb,Sr), and (Cs,Ba) and compared with existing x-ray photoelectron spectroscopy (XPS) and Auger data. The objective is to highlight differences in the screening pattern between (Na,Mg), where localized *d* screening is not to be expected, with the other systems where *d* localization may follow core excitation. Single core holes in Ca, Sr, and Ba might be expected to screen by this route, and the final two hole state of core-core-core Auger processes in K, Rb, and Cs may involve *d* screening. The possibility of *f* screening in Cs and Ba is also investigated. The quality of comparison between theory and experiment in these simple intrinsically neutral systems then gives insight into the level of information that can be reasonably inferred from the electron spectroscopy of more complex systems.

II. POTENTIAL MODEL

Assuming the contributions to V the potential in the atomic core arising from the nucleus and core electrons is chemically invariant, ground state shifts may be written

$$\Delta V = \Delta V^{v} + \Delta V^{\text{ea}}, \tag{3}$$

where V^v is the contribution due to the valence charge density ρ, and V^{ea} is the extra-atomic term. According to classical electrostatics, V^v is given by

$$V^{v} = \int \frac{\rho(r)}{r} dr = kq, \tag{4}$$

where k, the contribution to the core potential per valence electron, is of the order of the reciprocal valence radius $1/r_v$, and q is the total valence charge in units of e. Assuming point charges, ΔV^{ea} is the Madelung potential $M\Delta q$. Using the potential model approach in its most simplistic form, final state contributions to photoelectron shifts are neglected and the expression

$$\Delta E_b \approx \Delta q(k - M) \tag{5}$$

is used to deduce charge transfer.

More rigorously, k may be defined as the derivative of the core potential with respect to valence charge, and can be evaluated from the results of atomic structure calculations.[21–23] Noting that the scaling "constant" k in Eq. (4) varies with q, we have recently shown[22] that V^v is well described by

$$V^{v}(n_c, q) = \int_0^q k(n_c, q')dq', \tag{6}$$

with

$$k(n_c, q) = a + bn_c + cn_c^2 + (d + en_c)q, \tag{7}$$

where n_c is core level occupancy. To be more precise $n_c = -H$, where H is the number of core holes. At the ground state (i.e., $n_c = 0, q = q_0$), $k = a + dq_0$ is found to be of order $\langle 1/r_v \rangle \sim 10$ eV. b and d have magnitude ~ 2 eV, with b negative representing the contraction of the valence shell on core ionization, and d positive corresponding to the expansion/contraction of the valence shell with gain/loss of valence charge. Coefficients of the next-order terms c and e are an order of magnitude smaller than b and d. k for a given element generally decreases with the principal quantum number of the core level due to the increased overlap of the core level wave function with the valence levels. This leads also to slightly smaller XPS chemical shifts for more shallow core levels[24] and the phase dependence of x-ray energies.

Values of parameters a to e obtained by parametrizing atomic Dirac-Fock[25] core level eigenvalues $\epsilon(n_c, q)$ are given in Table I for core levels of a number of elements. In some cases, insufficient eigenvalues could be obtained for the higher-order coefficients c and e to be determined.

III. METAL-ATOM SHIFTS

A. The Williams-Lang model

Williams and Lang have shown[11] how chemical shifts in core level binding energies can be expressed in terms of the derivatives of core level eigenvalues with respect to occupancy n_c:

$$\Delta E_b(\delta) = -\delta \Delta\epsilon_c + \frac{\delta^2}{2!}\Delta\left(\frac{d\epsilon_c}{dn_c}\right)_{n_c=0} - \frac{\delta^3}{3!}\Delta\left(\frac{d^2\epsilon_c}{dn_c^2}\right)_{n_c=0} + \cdots. \tag{8}$$

The $n_c = 0$ subscripts indicate evaluation of the deriva-

TABLE I. Atomic potential parameters *a* to *e* in eV for core level *j* and valence charge with angular momentum character *v*.

Z_j^v	a	b	c	d	e
Na_{2p}^{s}	8.49	-2.87	-0.17	2.00	0.12
Na_{2p}^{p}	7.62	-3.03	-0.14	2.42	0.16
Na_{2p}^{sp}	8.81	-2.91	-0.17	2.35	0.03
Mg_{2p}^{s}	12.17	-2.17	-0.11	2.24	0.30
Mg_{2p}^{p}	11.29	-2.69	-0.12	2.44	0.18
Mg_{2p}^{sp}	13.01	-2.24	-0.01	2.91	0.19
K_{3p}^{s}	6.63	-1.67	-0.12	1.37	0.14
K_{3p}^{p}	5.85	-2.35	-0.18	2.04	0.19
K_{3p}^{d}	11.53	-2.22		2.32	
Ca_{2p}^{s}	9.06	-1.81	-0.12	1.57	0.20
$\text{Ca}_{3p_{3/2}}^{s}$	8.77	-1.37	-0.12	1.44	0.24
Ca_{2p}^{p}	8.92	-2.05	-0.16	2.01	0.23
$\text{Ca}_{3p_{3/2}}^{p}$	8.42	-1.68	-0.18	1.77	0.23
Ca_{2p}^{d}	20.30	-4.80	-0.36	4.46	0.37
$\text{Ca}_{3p_{3/2}}^{d}$	17.46	-2.45	-0.29	3.45	0.37
$\text{Rb}_{3p_{3/2}}^{s}$	6.29	-1.93	-0.22	1.54	0.23
$\text{Rb}_{3p_{3/2}}^{p}$	5.30	-1.65		1.21	
$\text{Rb}_{3p_{3/2}}^{d}$	9.72	-2.74		2.15	
Sr_{3p}^{s}	8.11	-1.46	-0.14	1.34	0.24
Sr_{3p}^{p}	7.54	-1.71	-0.14	1.56	0.16
Sr_{3p}^{d}	13.38	-2.99	-0.28	2.81	0.28
Cs_{3d}^{s}	5.57	-1.45	-0.08	1.14	0.11
Cs_{3d}^{p}	4.65	-1.36		0.98	
Cs_{3d}^{d}	8.20	-2.08		1.60	
Cs_{3d}^{f}	18.50	-3.73		3.19	
Ba_{3d}^{s}	7.11	-1.24	-0.09	1.12	0.16
Ba_{3d}^{p}	6.21	-1.43		1.04	
Ba_{3d}^{d}	10.29	-2.11		1.63	
Ba_{3d}^{f}	21.74	-3.95		3.33	

tives at the ground state. Likewise $\delta = 1$ and $\delta = 2$ correspond to singly and doubly core ionized states, respectively. On the right-hand side of Eq. (8), the first term corresponds to the ground state shift, while the remaining terms constitute the final state contribution, i.e., the change in core hole relaxation energy. Using this expression, we may write the Auger parameter shift $\Delta\xi$ defined[2] by $\Delta\xi(c) \equiv 2\Delta E_b(c) - \Delta E_b(c') + \Delta E_k(c'cc)$ [i.e., $2\Delta E_b(c) - \Delta E_b(cc)$], as

$$\Delta\xi = \Delta\left\{\left(\frac{d\epsilon_c}{dn_c}\right)_{n_c=0} - \left(\frac{d^2\epsilon_c}{dn_c^2}\right)_{n_c=0} + \frac{1}{12}\left(\frac{d^3\epsilon_c}{dn_c^3}\right)_{n_c=0} - \cdots\right\}. \tag{9}$$

In solids, a core hole potential pulls a conduction band state below the Fermi level. The "excited atom" model (EAM), which replaces the final state of a core ionized site in an extended solid with a core ionized atom with a self-consistently added screening charge, can be used to model this extra-atomic screening process. Although the derivatives in Eqs. (8) and (9) cannot be evaluated for the true solid, application of the EAM at the level of the eigenvalue derivative replaces these terms with expressions for the "excited atom":

$$\left(\frac{d\epsilon_c}{dn_c}\right)^{\text{solid}} = \left(\frac{\partial\epsilon_c}{\partial n_c}\right)^{\text{atom}} + \left(\frac{\partial\epsilon_c}{\partial n_v}\right)^{\text{atom}} \frac{dn_v}{dn_c}, \tag{10}$$

where n_v is valence occupancy and there are $-dn_v/dn_c$ $(= dq/dn_c)$ screening electrons per core hole. The application of the EAM at this stage distinguishes the WL model from the earlier work of Watson *et al.*[9] and Hoogewijs *et al.*[8] where the EAM is used at the ΔSCF (self-consistent-field) level.

B. Application of the potential model

The potential parametrization procedure gives a good description of the core potential of isolated atoms and the WL model enables extra-atomic screening to be treated, but care is required for extending the potential model to the solid state. It is well known that the compression of the valence charge density within the Wigner-Seitz cell of a solid increases $\langle 1/r_v\rangle$, and hence $k_{\text{solid}} = \gamma k$ with $\gamma > 1$.[26,21] An upper bound for γ may be established[21] by comparing $\langle 1/r_v\rangle$ for the atomic wave function with its value for a renormalized valence wave function truncated at the Wigner-Seitz radius, as suggested by Watson *et al.*[26] Following this method, Gregory *et al.*[27] found that γ is typically ~ 1.3 for simple metals, suggesting contributions to the ground state metal-atom shifts of ~ 4 eV. Band calculations confirm this estimate of the compression effect.[9] However, it is not possible to directly calculate the full ground state metal-atom shift using the potential model (or any purely atomic approach) since the surface dipole of a finite solid introduces an unknown referencing level shift into Eq. (1). Band calculations[9,11] suggest that the effects of compression and surface dipoles in metals are approximately equal and opposite to an accuracy of $\sim$1 eV. On this basis, evaluation of the metal-atom relaxation shift $\Delta R(m-a)$ is expected to provide a reasonable estimate of the metal-atom photoelectron binding energy shift $\Delta E_b(m-a)$, provided there are not important valence electron configuration changes, which would tend to give rise to a further initial state shift.

The extra-atomic screening charge density of a core ionized impurity in a metal has recently been investigated by Nieminen and Puska.[28] These studies have shown that the extra-atomic screening charge is well represented by the excited atom model and "perfect" screening (i.e., $dq/dn_c = 1$) without need for renormalization procedures. Indeed the maxima in extra-atomic charge density were found[28] to be beyond the Wigner-Seitz radii, so that the ground state compression does not directly affect the extra-atomic relaxation. Consequently efforts to determine γ empirically from $\Delta\xi$, a purely final state quantity, have led[22] to the conclusion $\gamma \sim 1$. The present study is only concerned with final state quantities ΔR and $\Delta\xi$ and so we have assumed $\gamma = 1$ and $dq/dn_c = 1$ for the metallic state throughout.

Neglecting terms with coefficients c and e, the metal-atom shifts ΔR and $\Delta\xi$ in the WL model are

$$\Delta R = \frac{1}{2}(a + dq_0) - \frac{1}{6}(2b + d) \tag{11}$$

and

$$\Delta\xi = (a + dq_0) - (2b + d), \tag{12}$$

where q_0 is the ground state valence charge per atom, e.g., $q_0(\text{Mg}) = -2$. As can be seen from Eqs. (1) and (2), departure of the ratio $\Delta\xi/\Delta R$ from 2 is a direct measure of the relative importance of nonlinear screening.[18,3] Clearly, nonlinear screening is implicit in a model potential of the form in Eqs. (6) and (7).

k is sensitive to the angular momentum character of the valence charge and more generally Eqs. (6), (11), and (12) should involve a summation over the different valence subshells with a separate k for s, p, and d charges. In general the valence term is then

$$V^v(N, q_1, q_2\cdots) = \int_0^{q_1} k_1(N, q')dq' + \int_{q_1}^{q_1+q_2} k_2(N, q')dq' + \cdots. \tag{13}$$

For Na metal, for example, the valence configurations corresponding to $n_c = 0, n_c = -1$, and $n_c = -2$ are approximately s^1, s^2, and s^2p, respectively. Since there is a discontinuity in the first derivative of V^v, the two hole binding energy $E_b(2) = E[-2] - E[0]$ for Na metal cannot be obtained by expanding about the ground state. Rather we write $E_b(2) = \{E[-2] - E[-1]\} + \{E[-1] - E[0]\}$ and expand the first total energy difference about $n_c = -2$ and the second about $n_c = 0$.

Calculations for $\Delta R(m-a)$ and $\Delta\xi(m-a)$ for the group IA and IIA elements are presented in the following section, including higher-order terms with coefficients c and e. The WL formalism has been used with the potential model as described above, taking the required model parameters from Table I. Although it was not necessary, for simplicity we have assumed that the ground state valence configurations in the metals are those of the corresponding atoms. While configuration changes can produce core level eigenvalue shifts of several eV, the shifts in total energy are much smaller.

IV. RESULTS

Experimental metal-atom photoelectron and Auger shifts for the group IA and group IIA elements are shown in Table II. All values have been taken from reviews in the literature,[13,29–32] together with more recent free atom data,[33–36] where necessary referenced to the vacuum level using tabulated work functions.[31,37] The scatter in experimental metal-atom shifts quoted in the literature is of the order of 0.5 eV. (A comprehensive discussion of the problems in deducing metal-atom shifts from data in the literature can be found in Ref. 14.) Using the assumption that all core levels undergo equal chemical shifts, Auger parameter shifts $\Delta\xi(m-a)$ have been constructed. While this approximation is usually accurate to a few tenths of an eV, the Ca $2p$ and $3p$ shifts are found to be significantly different. This has been accounted for in constructing $\Delta\xi^{\mathrm{Ca}}$.

Calculated relaxation shifts and Auger parameter shifts are shown in Table III for various screening assumptions. For Na assuming s screening of the first core hole and p screening of the second hole gives $\Delta\xi(m-a)$ in good agreement with experiment and $\Delta R(m-a)$ is seen to account quite well for the metal-atom binding energy shift. A similar level of agreement is found for Mg, where both holes are assumed to be p screened. It is interesting to note that for Na and Mg ignoring the distinction between s and p screening and using a single function $k(n_c, q_{sp})$ yields very similar results. For both Na and Mg, we find $\Delta\xi/\Delta R \sim 2.5$, showing that the extra-atomic relaxation energy scales with n_c faster than quadratically.

For K, Rb, and Cs we find that s screening of a single core hole gives ΔR in reasonable agreement with the experimental binding energy shifts. However, for K and Cs, p screening of the second core hole yields $\Delta\xi = 6.7$ eV and 5.9 eV, respectively, in rather poor agreement with the experimental values of 9.1 eV and 7.2 eV. On the other hand, assuming d screening of the second hole gives $\Delta\xi = 9.0$ eV and 7.5 eV for K and Cs, respectively, in excellent agreement with experiment. For Cs there is still another possibility, namely f screening of the second core hole. With this assumption we calculated $\Delta\xi = 12.2$ eV.

The situation for Ca is somewhat more complicated as the experimental metal-atom photoelectron binding energy shifts for the $2p$ and $3p_{3/2}$ levels are significantly different, prompting the use of a separate k for each core level. Table I shows that parameterizing the $2p$ and $3p_{3/2}$ atomic eigenvalues yields significantly different potential parameters. Ley *et al.*[38] also noted a dramatic increase in spin-orbit splitting from 0.4 eV in the free atom to 1.4 eV in the metallic phase. The same effect was observed to a lesser extent in Sr and Ba. Ley *et al.*[38] attributed this to the strength of collective excitations in the metals. Performing ΔSCF Dirac-Fock calculations for the $3p$ binding energies of atomic Ca, we obtain a spin-orbit splitting of 0.38 eV. If a p screening electron is added in the final state this splitting is 0.34 eV, while for d screening electron the splitting is 1.37 eV, in excellent agreement with experiment. The solid state increase in the Ba $4p$ spin-orbit splitting is also reproduced by the ΔSCF calculations with a d screening electron in the final state. It would appear that, rather than being related to the specific solid state environment as such, the enhanced splitting is a signature of d screening through the interaction of the $3p$ hole with the d electron. Comparison of the experimental data for Ca, Sr, and Ba with potential model calculations is also strongly suggestive of d screening in these metals for both single and double core holes. It should be noted that for Ca, Sr, and Ba metals, one may imagine a component of d charge in the ground state and hence a significant metal-atom eigenvalue shift. However, since the s^2 and say $s^{1.5}d^{0.5}$ configurations have similar *total energy*, consideration of ground state configuration effects would simply reapportion part of the role of $3d$ electrons in Ca metal from ΔR to ΔV and would not affect the main thrust of the conclusions in the present work.

TABLE II. Experimental metal-atom shifts in photoelectron binding energy ΔE_b, Auger kinetic energy ΔE_k, and the Auger parameter $\Delta\xi$. All measurements are in eV with E_b and E_k relative to the vacuum level.

Element	ΔE_b	ΔE_k	$\Delta\xi$
Na (Ref. 13)	-4.6 ($2p$)	14.3 (KLL)	9.7
Mg (Ref. 13)	-4.8 ($2p$)	15.0 (KLL)	10.2
K (Ref. 29)	-3.75 ($3p$)	12.85 (LMM)	9.1
Ca (Refs. 30–34)	-7.0 ($2p$) -6.1 ($3p_{3/2}$)	19.3 (LMM)	14.1
Rb (Ref. 30)	-3.4 ($3p$)		
Sr (Ref. 30)	-5.7 ($3d$)		
Cs (Refs. 35, 36, 29, and 31)	-3.0 ($3d$)	10.2 (MNN)	7.2
Ba (Refs. 31–33)	-5.0 ($3d$)		

TABLE III. Calculated metal-atom relaxation and Auger parameter shifts in eV are shown in columns three and four, respectively. The angular momentum character of the assumed screening charges for a single core hole and a second core hole are given in columns one and two, respectively. Also given for comparison are experimental Auger parameter shifts (column 6) and calculated one hole relaxation and Auger parameter shifts (columns 5 and 7, respectively) obtained by Castellani and Leroy (Ref. 18).

	One hole screening charge	Second hole screening charge	ΔR (calc)	$\Delta\xi$ (calc)	ΔR (CL)	$\Delta\xi$ (exp)	$\Delta\xi$ (CL)
Na	*s*	*p*	3.9	9.4	3.6	9.7	9.4
Na	*sp*	*sp*	3.8	9.4			
Mg	*p*	*p*	3.8	10.0	3.6	10.2	10.0
Mg	*sp*	*sp*	4.0	9.8			
K	*s*	*p*	3.0	6.7	3.1	9.1	9.0
K	*s*	*d*	3.0	9.0			
Ca	*p*	*p*	2.9	7.2	4.7	14.1	12.8
Ca	*d*	*d*	6.7	13.1			
Rb	*s*	*p*	2.8	6.7			
Rb	*s*	*d*	2.8	8.7			
Sr	*p*	*p*	2.6	6.7			
Sr	*d*	*d*	4.6	11.6			
Cs	*s*	*p*	2.5	5.9		7.2	
Cs	*s*	*d*	2.5	7.5			
Cs	*s*	*f*	2.5	12.2			
Ba	*p*	*p*	2.4	6.0			
Ba	*d*	*d*	4.0	9.6			
Ba	*f*	*f*	8.3	19.6			

V. DISCUSSION

The objectives of the present work are twofold: (i) to analyze how well simple excited atom models account for the extra-atomic screening in elemental solids with particular reference to the interplay between *sp* and *d* screening, (ii) to use the results obtained for these intrinsically neutral elemental solid systems to give insights into the interpretation of electron spectroscopic shifts in binary alloys and compounds, where substantial charge redistribution between sites may occur.

Auger parameters and relaxation energies calculated by Castellani and Leroy[18] (CL) are also shown in Table III. Theoretical results obtained in the present work agree well with those of CL on systems studied in common: the essential physics included in the two models is very similar with the polynomial expansion of the core potential [Eqs. (6) and (7) in this study] being replaced by a numerical specification of the core eigenvalue by CL. In both cases, the screening charge distribution strays beyond the confines of the Wigner-Seitz cell for *sp* screening, but the screening process appears then to be well approximated by $dq/dn_c = 1$.

Of course the fine details of the extra-atomic relaxation involve Friedel oscillations in the screening density, but, when these contribute in integral form to the potential at a core hole site, their effects largely average out. That would certainly appear to be the message indicated by the very close agreement between the observed Auger parameter shifts $\Delta\xi$ with experiment for both Na and Mg, where *sp* screening will dominate. Furthermore, the fact that the ratio of the Auger shifts to the binding energy shifts are close to -3 suggests that the binding energy shifts are due mainly to relaxation effects with only small contributions from initial state potential shifts.

The elemental pair (K, Ca) paints a distinctly different picture. Empirically the marked difference between the binding energy and Auger parameter shifts of the two elements suggests that different kinds of screening processes are operating in these systems. The binding energy differences (assumed mainly due to final state effects) are consistent with *p* extra atomic screening for K, but *d* screening for Ca, while the Auger parameters are best accounted for by *d* screening of the second hole in K and of both holes in Ca. However, the agreement with experiment is less precise than for (Na, Mg) indicating that integral attribution of excited atom screening electron quantum numbers may be oversimplified, even if the trends are clear. We note that CL assumed a ground state configuration of $s^{1.5}d^{0.5}$ for Ca metal. This assumption is expected to give rise to a one hole relaxation energy shift in between values obtained for pure *s* screening and pure *d* screening, and a reduction of the Auger parameter shift of the order of half an eV. Comparison of our results for Ca with *d* screening and those of CL confirms both these expectations.

Auger data are not available for (Rb, Sr), but the marked difference in binding energy shifts indicates behavior very similar to that of (K, Ca). For Cs there is again evidence of *d* screening for the second hole; *f* screening for the second hole leads to far too large an Auger parameter consistent with the absence of $4f$ electrons in the La ground state, the equivalent $Z+2$ system. For Ba only single hole shifts are available, but, even allowing for referencing uncertainties, the binding results strongly suggest that *d* screening is dominant. For the first hole (La-like), *f* screening is highly unlikely, and would lead to far too high a relaxation shift, but the final two hole state (Ce-like) might be influenced by partial *f* screening; an experimental test of the Auger parameter shift would be particularly interesting here.

Overall, we find that *sp* screening calculations within the potential model approach gives a good account of the one hole and two hole excitation energies for the simple metals Na and Mg. For K, Rb, and Cs *s* screening of a single hole and *d* screening of a second hole is suggested by the model. Calculations for Ca, Sr, and Ba indicate *d* screening even for a single core hole. Further discussion of the nature of extra-atomic screening can be found in the paper of Martensson, Hedegard, and Johansson,[14] where particular regard is taken of the solid state modification of the screening orbitals. Although the thermochemical model does not directly distinguish initial state potential shifts (ΔV) from relaxation shifts (ΔR), Martensson *et al.* used this approach to calculate metal-atom Auger parameter shifts, effectively isolating extra-atomic relaxation. Their results also suggest that Ba core holes are *d* screened but not *f* screened. Estimates of extra-atomic relaxation for the alkali and alkaline earth elements within the thermochemical model (Ref. 14) and the potential model (this work) are consistent, and both approaches imply the same pattern of core hole screening.

Finally we must consider how the insights gained from this analysis influence interpretation of Auger parameter shifts in binary alloys or compounds. Generalizing Eq. (12), we obtain the Auger parameter shift of an atom between alloy and elemental solid as

$$\Delta\xi = \Delta\left\{bq + \left(a + dq - 2b - d\frac{dq}{dn_c}\right)\frac{dq}{dn_c} + \frac{dV^{\mathrm{ea}}}{dn_c}\right\} , \tag{14}$$

where V^{ea} is a long-range screening contribution, and q is the effective valence charge on the atom. In metal alloys $dq/dn_c = 1$ and $dV^{\mathrm{ea}}/dn_c = 0$ should be good approximations leading to

$$\Delta\xi \approx (b + d)(q_A - q_0) , \tag{15}$$

where q_A is the valence charge in the alloy, provided that the nature of the screening is the same in metal and alloy. This generalizes the original expression of Thomas and Weightman[21] through the addition of the term involving *d*. It suggests a very direct relationship between the Auger parameter shift and the deviation of local charge from neutrality, due to changes in the intra-atomic screening at the site. However, inspection of Table I reveals that *b* and *d* are similar in magnitude but opposite in sign, leading to a rather small contribution to $\Delta\xi$; typically $q - q_0 \sim 0.2$ leads to $\Delta\xi_A \sim 0.1$ eV, and even the sign of the effect is in doubt in some cases. Setting $dq/dn_c = 1$ for both elemental metal and alloy has the implication that the charge transfer screening contribution to the relaxation energy is identical in the two systems. This should be approximately true if *sp* screening dominates in metal and alloy, e.g., for alloys involving Na, Mg, and Al with noble metals, but is unlikely to be sufficiently precise for Eq. (15) to be valid. Given that the extra-atomic screening in the elemental solid gives a contribution of 6–10 eV to $\Delta\xi$ (Table II), small changes in charge transfer screening between metal and alloy are likely to lead to significant additional contributions to Eq. (15), casting some doubt on simple initial state interpretations of Auger parameter shifts. In spite of this, binary metal alloys do typically exhibit $\Delta\xi$ values of opposite sign for the two atomic species,[21,39] qualitatively in agreement with Eq. (15). If there is the possibility of *d* screening for a core hole on one or both sites, any change in the balance of *sp* screening and *d* screening will lead to substantial contributions to $\Delta\xi_A$, and will complicate charge transfer arguments. However, the sign of $\Delta\xi$ for atoms with filled *d* shells, e.g., Au, Ag, and Cu alloyed to transition metals may well indicate the direction of charge transfer.

VI. SUMMARY

Comparison of binding energy and Auger parameter shift calculations between free atoms and elemental solids with experiment provides a stern test of our understanding of extra-atomic screening in solids and gives insight into the interpretation of the environmental dependence of Auger parameter shifts. Simple excited atom models give an excellent account of electronic relaxation in systems where the screening is exclusively by *sp*-like electrons, e.g., in Na and Mg, but it has been shown that *d* screening is of importance for single- and double-hole relaxation in Ca, Sr, and Ba, and appears to be of some significance for two hole states of K, Rb, and Cs. The precision with which we can account for the extra-atomic screening in intrinsically charge neutral elemental solids puts into perspective the ability of electron spectroscopy to describe charge transfer in binary metal alloy systems.

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