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Initial-state screening effects in metal Auger spectra: Be

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The Auger spectrum of beryllium metal is presented and analyzed. This analysis suggests that the valence-band screening of the initial-state core hole alters the observed line shape from that predicted on the basis of band structure alone. Decomposition of the spectrum into components describing the angular momenta of the final-state holes indicates that the screening charge is largely s-like. A rigorous description of the screening-charge effect is presented together with an approximate theory which preserves the analysis in terms of band structure. The approximate theory is in qualitative agreement with the results of *ab initio* calculations on a 13 atom cluster.

I. INTRODUCTION

Valence-electron screening of a core hole in most metals has long been recognized as a local effect due to the short screening length.[1] Jennison has shown Auger spectroscopy to be a local probe of the variation of atomic (as opposed to bonding) charge across the valence bands.[2,3] Thus, if the screening charge alters the relative atomic valence configuration, it will alter the Auger line shape from that calculated from a band-theory model.[3,4] By studying the deviations from the band-theory line shape, information may be derived as to the initial-state valence configuration and thus the nature of the screening charge.

Lately, several workers have discussed the use of the so-called excited-atom model to treat the effects of the screening charge.[5-7] Owing to the small screening length in most metals, a core hole is almost completely screened at the first-nearest-neighbor distance. This fact, plus orthogonality requirements, indicates that an approximate local description of the screening charge is that it fills the excited atom's lowest unoccupied atomic orbitals. For example, in copper an atom with core-hole screening may be deemed to have the valence configuration $d^{10}s^2$ instead of the normal $d^{10}s$. However, the configuration of copper in the metal is more like $d^{9.6}sp^{1.4}$, where sp indicates an s-p band.[5] Thus, a question which has not been addressed is whether the screening charge follows a pattern in the various metal species, e.g., would it have a similar distribution of partial-wave character as the occupied portion of the valence bands or would it take on one component preferentially. While cluster or impurity model calculations can contribute here, we show below that semiempirical information may be obtained by Auger line-shape analysis.[8]

Screening-charge effects upon metal Auger line shapes were first noted in Jennison's recent analysis of the copper M_1VV spectrum.[9] This analysis showed that the correct amplitude ratio of the sd to the dd portion[10] of the spectrum could not be realized without the inclusion of the screening charge which was determined to be largely s-like. It was mentioned that a more detailed analysis was not possible without an LCAO band structure of copper, but that the inclusion of screening charge should have little effect on the previously generated Si $L_{2,3}VV$ (Refs. 2, 3) and Li KVV (Ref. 3) spectra which were in excellent agreement with experiment. While in the Si case this may be true due to the comparatively long-range nature of the screening and the preservation of the sp^3 bonding even with the core hole, in Li the agreement is now realized to be accidental and due to the great similarity in line shape and position of the sp and pp contributions whose ratios could be altered by screening (see Sec. III below). In Be, however, the sp and pp contributions differ significantly in peak position[11] and thus their detailed ratio uniquely determines the position of the peak in the Auger line. For this reason, the Be Auger line was selected as a sensitive test of the theory.

II. THEORY AND EXPERIMENT

An LCAO Be band structure was generated using Kohn-Sham exchange[12] and a potential from a superposition of Hartree-Fock atomic charge densities. The basis set used was the compact ($3s$, $3p$) Slater basis previously described for lithium[13] but scaled to the Be nearest-neighbor distance. The density of states (DOS) was generated using a Gaussian broadened histogram over 364 points in the irreducible wedge of the Brillouin zone, the points being chosen according to the prescription of Pack and Monkhorst.[14] The same method was used to generate the partial DOS (PDOS) and these, together with appropriate atomic like Auger matrix elements, were used to generate the Auger line shape as previously described.[3]

The bands and DOS were in good agreement with previous calculations,[15,16] given the differences in the exchange potentials and computational methods.[17] The PDOS were used to compute atomic (as opposed to bonding) densities of states via

$$A_l(E)=\sum_{ij}{}^{'l}F_{ij}(E)S_{ij}\,, \qquad (1)$$

where F_{ij} is a PDOS,[18] S_{ij} is the overlap matrix between basis functions i and j on the same site, and where the sum is restricted to basis functions of the lth angular momentum ($l=s$ or p). A_s and A_p are shown in Fig. 1. A_p is in excellent agreement[17] with the x-ray emission spectrum[15,19] and A_s agrees equally well[17] with the s-PDOS peak visible in the x-ray photoemission line.[20] These curves may be integrated to yield the net atomic charges. Since this set is compact (i.e., the functions are short ranged and have small interatomic overlaps), little distribution of bonding charge is needed to find, for this basis set, that Be metal has the configuration $s^{0.68}p^{1.32}$.

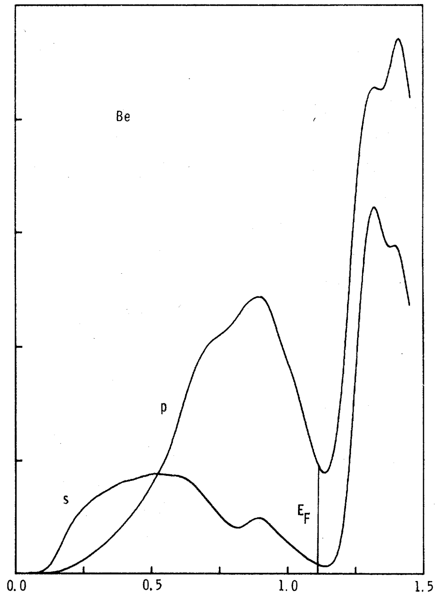

FIG. 1. Beryllium s and p atomic densities of states. The p component is in excellent agreement with the x-ray emission data (Refs. 15 and 18) and the s component with photoemission results (Ref. 20). These curves may be integrated to yield a Be configuration of $s^{0.68}p^{1.32}$.

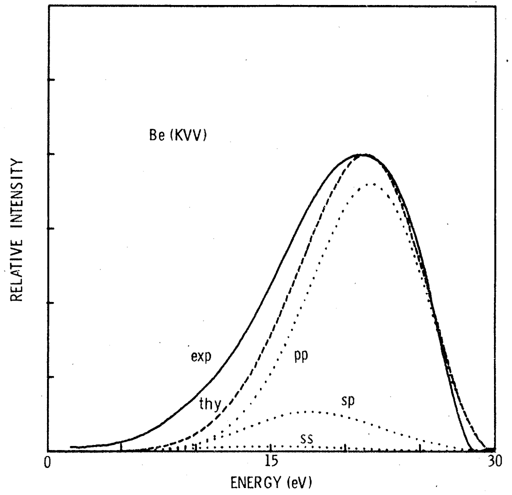

FIG. 2. Beryllium KVV experimental and theoretical Auger spectra, the latter done without screening effects, shown with the contributions from the various final-state hole angular momenta. The energy scale is relative.

The experimental data with which the calculations will be compared were taken on a polycrystalline Be sample. The surface of the sample was cleaned by argon-ion bombardment and annealing techniques. The base pressure of the experimental system was below 3×10^{-9} Pa. Auger data were taken in the dN/dE mode with a double-pass cylindrical mirror analyzer using a normally incident 2-keV, 5-μA primary-electron beam and 1-V peak-to-peak modulation. Extraction of the Be-KVV line shape from the as-measured data involved corrections for secondary-electron background and deconvolution[21] to remove signal distortions related to those Auger electrons which suffer energy losses before leaving the solid.

Owing to matrix element effects and the almost 2:1 p to s ratio, the KVV line shape without screening is dominated by the pp portion as shown in Fig. 2. However, comparison to experiment shows that there is clear disagreement,[22] strongly implying that the screening charge effect must be included in the line-shape analysis.[23]

III. ANALYSIS AND CONCLUSIONS

If we are to include the effect of the screening charge but preserve our analysis in terms of band structure and PDOS,[2-4] we may proceed by recalling that the area under the PDOS is a measure of the amount of charge available for the decay,[3] while the shape of the PDOS indicates how that charge is weighted among the possible final-state holes as a function of energy. One may note that since the screening charge does not alter the energies of the possible final states, to first order, its effect is to alter the transition probabilities by changing the areas under the PDOS and thus their relative scaling.

A rigorous description of the screening-charge effect, presented below, shows that what is actually assumed in the above approximation is that each occupied Bloch function polarizes towards the core hole and changes its local site amplitude by a relative amount which is only a function of the basis function (e.g., *s* or *p*) involved. In materials such as Be with considerably less than half-filled shells, this may be reasonable since only the lower bonding orbitals are filled. In materials with greater than half-filled levels, in which antibonding orbitals are occupied, this approximation should break down as antibonding orbitals polarize, in general, away from a core hole. Thus, for example, it is suggested that the *dd* spectrum of Co may show appreciable distortion from that predicted from the *d* PDOS even with the inclusion of spin effects.

We wish to calculate an Auger matrix element between the initial and final state,

$$M_{jk} \equiv \langle \Psi_i | \hat{H} | \Psi_f(j,k) \rangle , \tag{2}$$

where the argument indicates holes in the valence levels j and k. We write the initial and final states of the system as single Slater determinants[3] so that

$$\Psi_i = N \det | \bar{\phi}_c \phi_1' \cdots \phi_j' \phi_k' \cdots \phi_n' \bar{\phi}_a |$$

and (3)

$$\Psi_f(j,k) = N \det | \phi_c \phi_1 \cdots \bar{\phi}_j \bar{\phi}_k \cdots \phi_n \phi_a | .$$

The bars indicate holes, c and a refer to the core and continuum states, respectively, N is a normalization factor, and the primes indicate the orbitals have relaxed in response to the creation of the core hole. Since the sets $\{\phi_j\}$ and $\{\phi_j'\}$ are not the same, the above expression for the matrix element involves all permutations of the orbitals. Clarity may be gained, however, if we construct a pseudo final state of the form

$$\Psi_f'(j',k') \equiv N \det | \phi_c \phi_1' \cdots \bar{\phi}_j' \bar{\phi}_k' \cdots \phi_n' \phi_a | . \tag{4}$$

Now Ψ_f' and Ψ_i differ by just two spin orbitals and we may write a matrix element to the pseudo final state, $M_{j'k'}$, in terms of Auger Coulomb ($J_{j'k'}$) and exchange ($K_{j'k'} = J_{k'j'}$) matrix elements where

$$\begin{aligned} J_{j'k'} &\equiv (ca | j'k') \\ &\equiv \int \int d(1) d(2) \phi_c^*(1) \phi_a^*(2) \\ &\qquad \times (e^2/r_{12}) \phi_j'(1) \phi_k'(2) . \end{aligned} \tag{5}$$

Since we may express the true final states in terms of the pseudo-final-states

$$\Psi_f(j,k) = \sum_{l',m'} C_{jl'} C_{km'} \Psi_f'(l',m') , \tag{6}$$

we may write

$$M_{jk} = \sum_{l'm'}^{\text{occ}} = C_{jl'} C_{km'} M_{l'm'} , \tag{7}$$

where

$$M_{l'm'} = J_{l'm'} \pm K_{l'm'} ,$$

where the sign depends on the final-state spin,[3] and where we note $M_{l'm'}$ is zero unless l and m are occupied. Obviously, the most general theoretical method is to compute self-consistently the valence orbitals with and without a core hole and project the former upon the latter using the above equation. Screening-charge effects are thereby naturally included in finding the decay probabilities. However, to preserve the analysis in terms of the band structure and PDOS, we may proceed approximately by noting that Eq. (7) contains two parts.

While the Auger matrix element itself, $M_{l'm'}$, is linearly sensitive to the variation of the local charge due to screening, the projection of the pseudo-final-state onto the true final states is often only a weak function of l' and m' with $C_{jl} \sim \delta_{jl}$. The latter statement is not true if localized states are present, but in covalent and metallic systems for which the delocalized canonical orbitals adequately describe the valence states, the response to the core hole is localized over a very small region compared to the orbital extent; so, orthogonality quite nearly holds between the ϕ and ϕ'. We make this approximation in the case of beryllium and thus focus on the matrix elements $M_{l'm'}$. Proceeding as in Ref. 3, we use the LCAO representation to divide $M_{l'm'}$ into two parts, atomic Auger matrix elements and LCAO expansion coefficients on the core-hole site,

$$M_{l'm'} = \sum_{\mu\nu}^{c} c_{l'\mu} c_{m'\nu} (ca | \mu\nu) , \tag{8}$$

where μ and ν refer to LCAO basis functions and the sum is restricted to the core-hole site c. The $c_{l'\mu}$ (the initial-state coefficients of orbital l on site c) will differ from $c_{l\mu}$ (the final-state coefficient) by an amount which is a function of l. Since these coefficients determine the PDOS, in general PDOS from the band structure cannot be used. However, if only the lower bonding orbitals are filled, each occupied state will polarize toward the site c and the approximation $f_\mu \equiv c_{l'\mu}/c_{l\mu}$ (for all occupied l) may suffice. If this approximation is made, then the initial- and final-state PDOS on site c are related by $F_{\mu,\nu}' = f_\mu f_\nu F_{\mu\nu}$ and the effect of the screening charge is simply to scale the PDOS. Since the area under a PDOS represents the charge available for the decay,[3] this is equivalent to assigning the screening charge to a particular local angular momentum or combination thereof.

Such assignment may be made to match experiment and thus semiempirically estimate the character of the screening charge.

Best agreement with experiment, using the above approximations, was obtained (Fig. 3) when the screening charge was taken to be entirely s-like, thus producing a configuration including screening of $s^{1.68}p^{1.32}$. This configuration increases the ss and sp portions relative to the unscreened case and shifts the Auger peak towards lower energies. The fit was made by comparing the peak position to the high-energy half-maximum,[24] the latter chosen as being largely free from experimental artifacts (errors in background subtraction and deconvolution and the effect of contaminants[23]). Thus, this estimate of the partial-wave character of the screening charge indicates that, at least in Be, it does largely take on s character.

Since the above approximate analysis is based on assumptions which, though intuitively reasonable, may be tested, it is important to do so. We wish to establish whether the principal effect on the PDOS upon core-hole creation in beryllium may indeed be regarded as a change of s vs p scale (as opposed to great changes in shape) and if the screening charge significantly decreases the p to s ratio. *Ab initio* (i.e., Hartree-Fock) cluster calculations have been done on Be by Bauschlichter *et al.*[25] for the purpose of studying hydrogen chemisorption. Clusters ranging from three to ten Be atoms were studied using both minimal and large Gaussian basis sets, establishing the validity of using the minimal sets on the larger clusters. In the present work, the Hondo 76 program[26] was used with the minimal basis set of Ref. 25 and results on 10-atom clusters duplicated. Then the cluster size was increased to 13 atoms (one "bulk" Be surrounded by its 12 nearest neighbors) and convergence achieved. Bulk geometry was used. The central Be atom in the self-consistent 13-atom cluster had a p to s ratio of 3.45 which is somewhat larger than found from the band structure calculation. Using the appropriate minimal basis set for boron,[27] consistent with that used for Be, the center atom was changed to B (simulating the core hole) and the 13-atom cluster rerun to convergence. The Mulliken population analyses for the central atoms of both clusters may be seen in Fig. 4. Total populations are presented since the high overlaps of the minimal basis set make these numbers appropriate for the comparison to the band structure results of Fig. 1. As seen in Fig. 4, the overall shapes of the s and p PDOS do not distort appreciably, while the change of scale indicates a significant reduction of the p to s ratio to 1.88 with screening, compared to 3.45 without. Similar results were obtained on a *neutral* 13-atom cluster with the B impurity (the p to s ratio for this case was 2.16) and for the 10-atom cluster.

We note that even with the cluster size at 13 atoms, the center atom PDOS does not even superficially resemble that of the bulk band structure.

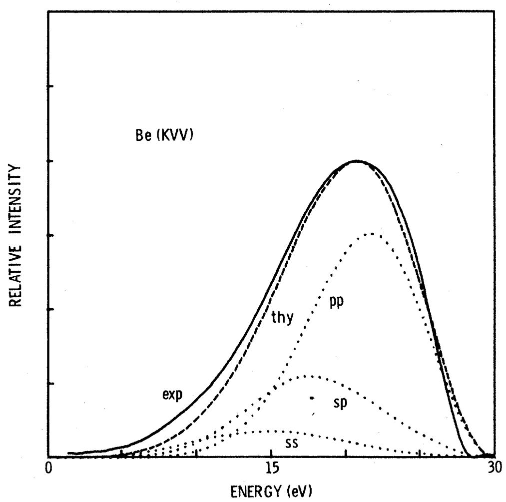

FIG. 3. Beryllium *KVV* experimental and theoretical Auger spectra, the latter done with purely s-like screening, shown with the contributions from the various final-state hole angular momenta. The energy scale is relative.

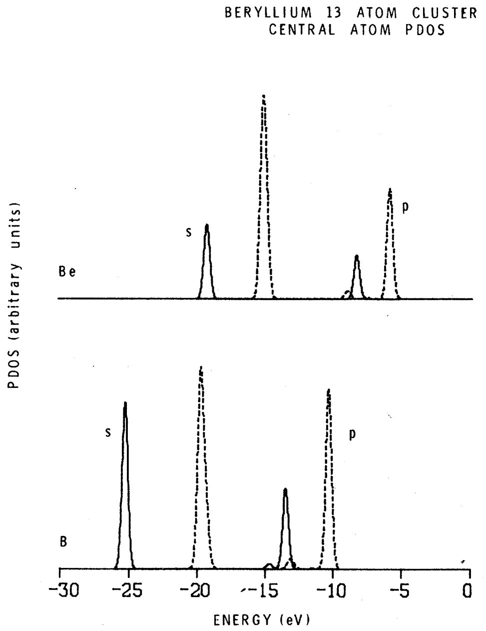

FIG. 4. Partial density-of-states results on a 13-atom beryllium cluster calculated with and without a boron impurity substituted for the central atom. The spikes have artificially been slightly broadened for clarity.

Recent work by Feibelman *et al.*[28] has shown that the surface DOS is largely influenced by the bulk DOS. Our cluster, with 12 "surface" atoms and only one "bulk" atom, may therefore be expected to be in disagreement. However, the cluster results support the approximations made above which concern the behavior of the shape of the local density of states of Be during core-hole screening. The cluster results also support the conclusion of the bulk analysis that the p to s ratio significantly decreases. The distortions in PDOS upon impurity insertion (Fig. 4) are consistent in magnitude with the residual errors seen in Fig. 3. The deviations from the bulk densities of states (seen by comparing Figs. 1 and 4) are so large that it is obvious that one has no hope of calculating the observed metal Auger line shape completely from a cluster approach unless efforts are made to embed the cluster in an appropriate potential, as recently discussed by Mednick and Lin[29] and references therein.

In summary, we have shown that one should not analyze valence Auger line shapes in terms of undistorted band structure (even if the hole-hole interaction is small enough as to make the spectra bandlike[8]) since the valence screening of the initial-state core hole appreciably affects the Auger transition probabilities. However, in some cases, as covalent solids with relatively long-range screening, or simple metals for which the above-mentioned approximations may be justified, a meaningful band structure analysis is still possible. The study of beryllium indicates that for this metal the initial-state screening is largely s-like.

Note added in proof. Recent work by Fuggle and Lässer[30] on core-core-valence lines has convincingly shown the screening charge effect.

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[17] Similar to the case of Ref. 13, the present band structure of Be has an occupied total bandwidth which is wider than that of comparable calculations (Refs. 15 and 16) by 1.4 and 0.5 eV, respectively. However, the peak position of the p PDOS (Fig. 1) agrees with the position (relative to the Fermi edge) of the x-ray emission peak (Refs. 15 and 19) within 0.1 eV while the s PDOS agrees equally well with the peak position determined by photoemission (Ref. 20). Therefore, no attempt has been made to compress our bandwidth to those of others (Refs. 15 and 16). Note that a narrower bandwidth would make the disagreement of Fig. 2 *greater* and our argument for screening effects stronger.

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[22] The disagreement is clear when compared to that achieved by band structure and matrix element calculation previously on Si (Refs. 2 and 3) and Li (Ref. 3). See also Ref. 11 on Si, Li, and Al.

[23] The magnitude of the correction of *ss*, *sp*, *pp* amplitude ratios due to screening is a factor of 7 larger than the inherent error in the present method of amplitude calculation as evidenced by the *sp* to *pp* ratio of neon [D. Chattarji, *The Theory of Auger Transitions* (Academic, New York, 1976) p. 178], and a factor of 8 for the *ss* to *pp* ratio. Surface effects are a totally *ad hoc* explanation of the disagreement as the Be surface is not reconstructed [F. Jona, J. A. Strozier, Jr., and J. Kumar, Phys. Rev. B 6, 407 (1972)] and, further, no surface effect was visible in Li (Ref. 3). Contaminants affect the low-energy side of the peak [D. M. Zehner, N. Barbulesco, and L. H. Jenkins, Surf. Sci. 34, 385 (1973)] while our comparisons are restricted to the high side. To be an explanation, surface effects would have to shift the peak backwards while Gadzuk's study [J. W. Gadzuk, Phys. Rev. B 9, 1978 (1974)] showed that the surface effect shifted the peak forwards by a quite small amount.

[24] The distance from the experimental peak to the high-energy half maximum is 4.75 eV. The corresponding theoretical distance is 4.17 eV with no screening, but 4.72 eV with *s* screening.

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