

Screening effects in the KL_V Auger spectra of Na, Mg, Al, and Si

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X-ray excited KL_1V and $KL_{2,3}V$ Auger spectra of clean Na, Mg, Al, and Si are presented. The influence of core holes on the shape of the valence band is made evident by comparison with x-ray photoelectron spectroscopy and x-ray emission spectra. It is shown that such Auger spectra give experimental evidence on the local and symmetry-selected density of states around a core hole. The local density of s states is more affected by core ionization than the local density of p states.

I. INTRODUCTION

Detailed studies of Auger decay of core holes with simultaneous creation of one or more holes in the valence band have only been made possible by technical developments within the last decade. Thus it has only recently been recognized that XVV or XYV Auger spectra do not give direct information on the energy distribution of valence states¹⁻³ as was originally suggested.⁴ The chief effects leading to distortion of the spectra are the angular and radial parts of the Auger matrix elements (see, e.g., Refs. 5-8) and the Coulomb interaction between the two final-state holes (see, e.g., Refs. 9-11). This latter effect has been most extensively studied for the case of XVV transitions where the intriguing interaction between two valence electrons can be studied directly (see, e.g., Refs. 10-12). Here we consider the case of XYZ Auger spectra and extend the arguments of von Barth and Grossmann^{12,13} concerning the relationship of such spectra to the local density of states on a core-ionized atom. Our studies thus give an experimental check on the changes in the density of states (DOS) around a core-ionized atom postulated on the basis of calculations by Bryant and Mahan.¹⁴ In effect, the state we probe here is the final state of an x-ray photoelectron spectroscopy (XPS) experiment where the core hole has been screened by the valence electrons. The Auger matrix elements can be divided into radial and angular parts; the radial parts must be calculated numerically. To our knowledge the radial parts of the matrix elements for Mg, Al, and Si have not been published. For Na they have only a small effect on the calculated KL_V Auger spectra^{12,13} and we proceed on the assumption that for the KL_V transitions variations of the radial matrix elements through the valence band are not large and have similar values for KL_1V and $KL_{2,3}V$. However, it will be shown that for Na a small effect of the radial elements is probably present and we will argue that small

variations (<30%) in the intensities of the different peaks in the observed spectra must be interpreted with care. We make extensive use of the ratios of the angular parts of the Auger matrix elements for the KL_V transitions which are 1:1 and 1:3 for $KL_1s:KL_1p$ and $KL_{2,3}s:KL_{2,3}p$, respectively.^{12,13} Our results confirm the trend noted in earlier studies of Mg and its alloys³ where the $KL_{2,3}V$ line shape was found to resemble the local density of states at the neutral atom more than the KL_1V spectra. As a result of work presented here we can now interpret this trend as evidence that the density of s valence states is more sensitive to the presence of a core hole than the density of p states. In the elements Na-Si the occupation of d -like states is low (see, e.g., Ref. 15) and we neglect their influence here.

We often make reference to x-ray emission band spectra and will refer to them as KV and $L_{2,3}V$, etc., where the first symbol indicates the initial hole (here K or $L_{2,3}$) and the second symbol indicates the final hole (here the valence band). In the text double-ionization satellites are described by the symbols for the holes in the initial state and final state separated by an arrow, e.g., $L_{2,3}L_{2,3} \rightarrow L_{2,3}V$. A similar notation was previously used for Auger double-ionization satellites.¹⁶ Note that because of dipole selection rules $L_{2,3}V$ and $L_{2,3}L_{2,3} \rightarrow L_{2,3}V$, x-ray spectra reflect the valence-band density of s and d states while KV spectra reflect the density of p states.

II. EXPERIMENTAL APPARATUS AND PROCEDURES

The instrument used in this work was an x-ray photoelectron spectrometer custom built by Kratos U.K. Ltd. The x-rays used to generate the Auger spectra were produced by electron bombardment of a target separated by a thin window from the sample. For the KL_V spectra of Na and Mg, magnesium or aluminum anodes were used

as targets and a 0.005-mm aluminum window was used to preserve the vacuum at the sample. This window absorbs much of the bremsstrahlung from the anode but only approximately 40% of the Mg or Al $K\alpha$ radiation, which is then responsible for the core-hole ionization and consequent Auger emission. As the binding energies of the Al and Si $K 1s$ electrons are larger than the Mg and Al $K\alpha$ energy, Cu and Ti anodes were used with a 0.15-mm Be window. This window transmits more than 90% of the bremsstrahlung radiation above 4 keV and allowed us to achieve reasonable intensities in the KL V spectra.

Sample surfaces were prepared by evaporation of Na, Mg, or Al layers several thousand angstroms thick onto polished stainless-steel substrates, or by argon-ion bombardment of Si, and were periodically renewed to avoid buildup of contamination. Measurements were carried out at 2×10^{-10} mbar and the levels of oxygen, nitrogen, and carbon contamination were estimated using Scofield's tables of photoionization cross sections¹⁷ and the intensities of the $K 1s$ XPS peaks or the KLL Auger peaks with respect to the substrate peaks. The total contamination was less than one-half of a monolayer ($\sim 5 \times 10^{-18}$ atoms m^{-2}) for all measurements reported here. Studies of more highly contaminated samples indicated that a half-monolayer of C, N, or O contamination is insufficient to significantly affect the data reported here.

The spectra were recorded using pulse-counting methods and stored in a PDP 11 computer. Plasmons were subtracted out of the spectra, as shown in Fig. 1 for Al, in order to remove possible distortions of the KL_1V and $KL_{2,3}V$ bands which have been stressed by Steiner *et al.*¹⁸ for XPS. The procedure used will be described more fully elsewhere.¹⁹ Briefly, it involves fitting the experimental spectrum of the L_1 XPS peak plus its plasmon losses to a fold of an asymmetric Doniach-Šunjić line shape²⁰ with a Gaussian instrument function and a physically sensible plasmon loss function. The fitting procedure allows for variation of the plasmon widths and asymmetries which arise from lifetime and dispersion effects, respectively, as well as their intensity with respect to the main peak. Once the fitting procedure has produced a loss function this is then stripped from the experimental KL V data on a point-for-point basis. Note that we do *not* subtract the effects of electron-hole pair creation which give rise to the asymmetry in the Doniach-Šunjić line form and which are also present to some extent in the KL V and valence-band spectra.

Our data treatment assumes that the intensity of the plasmon losses is the same in XPS and Auger

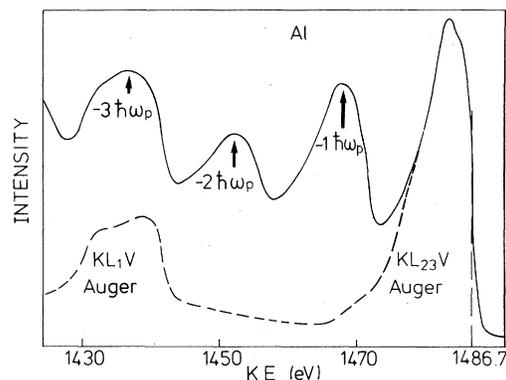


FIG. 1. The KL_1V and $KL_{2,3}V$ spectrum of Al before (—) and after (---) subtraction of the plasmon-loss features.

spectra, which is reasonable in the present context. Extrinsic losses make up at least 70% of the total plasmon losses.²¹⁻²⁵ The intensities of the extrinsic losses relative to the no-loss peak are similar in XPS and x-ray-excited Auger electron spectroscopy (XAES) because the kinetic energies of the L_1 XPS and KL V Auger peaks analyzed are in similar kinetic-energy ranges (depending on sample 1330–1420 eV for L_1 XPS and 980–1800 eV for KL V Auger). Thus differences could only occur in the intrinsic part of the losses, and as these make up less than 30% of the total, even a factor-of-2 reduction would not produce a large effect on the spectra. We tested the sensitivity of the data to errors in plasmon subtraction by subtracting 10% more or less of any particular plasmon from the data. While this gave new structure in the background, with small changes in the height of the tail on the high-binding-energy (BE) side of the Auger valence band, and made the background look less credible, it did not affect the Auger valence-band shape.

In these studies we use the KL V Auger spectra to determine the binding energy of a valence-band electron in the presence of a core hole. This is given by the energy of the KL transition (as taken from the difference of XPS binding energies or from x-ray-emission measurements) minus the KL V Auger energy. In Na, Mg, and Al we substantiated our energy scales by checking that the KL energy was equal to the KL V Auger energy at the Fermi level (E_F) (as given by the cutoff in the Auger spectra). For Si this check could not be made because there was no sharp cutoff at E_F , but we could still use the procedure based on the energies of the KL_1 and $KL_{2,3}$ transitions. The maximum error is then given by the sum of possible errors in the instrument and in K , L_1 , and $L_{2,3}$ binding energies or the $KL_{2,3}$ x-ray ener-

gy,^{26,27} and is estimated to be of the order of 0.5 eV.

III. RESULTS AND DISCUSSION

A. Sodium

The KL_V spectra of sodium are those we can best understand because von Barth and Grossmann have calculated the local densities of states for Na atoms with core holes and both the radial and angular parts of the Auger matrix elements.¹² The angular parts of the matrix elements lead to weighting of the s and p parts of the local densities of states. For $KL_1s:KL_1p$ this is 1:1; for $KL_{2,3}s:KL_{2,3}p$ it is 1:3, so that the density of p states plays a stronger role in the $KL_{2,3}V$ spectrum.¹² Figure 2 shows the KL_V Auger spectra of Na together with the densities of s and p states in the absence of a core hole and the local density of states around a core-ionized atom in an Na matrix. As previously found by Barrie and Street,²⁸ there is a strong peak at the bottom of the KL_1V band and a weak one at the bottom of the $KL_{2,3}V$ band which cannot be adequately explained by the features of the densities of states of the neutral system. As the peak is stronger in the KL_1V than in the $KL_{2,3}V$ spectrum it is reasonable to attribute it to a property of the density of s states. Calculations¹²⁻¹⁴ show a peak in the local density of s states around a core-ionized Na atom. This peak is at the bottom of the valence band and consistent with the Auger peaks as shown in Fig. 2 (which is essentially taken from¹² but with our experimental results superimposed). The calculated peak is also coincident with the peak in the $L_{2,3}L_{2,3} \rightarrow L_{2,3}V$ x-ray-emission satellite²⁹ which supports

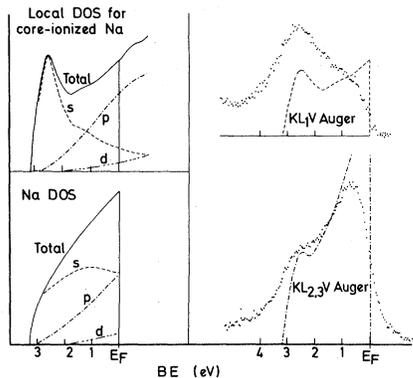


FIG. 2. Left: calculated partial and total density of states for Na and local density of states at a core-ionized Na atom in an Na matrix (Refs. 12, 13). Right: calculated (--- and ---) and experimental KL_1V Auger spectra of Na. Here, as in other figures throughout this paper, the intensity scales of the different spectra are not simply related.

its assignment. The shape of the satellite band is now thought to be related to the local density of s states around the core-ionized atom present in the final state.^{12,13} The only problem with the calculated Auger spectra of Refs. 12 and 13 is that the relative intensities of the high-BE peaks are underestimated. The reason for this is unclear. von Barth and Grossmann included radial parts of the matrix element by calculating first the s -wave density inside a sphere around the ionized atom and the free-electron wave-function density outside, and then calculating the Auger Coulomb integral for both. This treatment is approximate, but we see no concrete reason why it should fail. We remain convinced that the explanation of von Barth and Grossmann for such peaks is essentially correct and proceed in the belief that such Auger spectra give information on the position of peaks in density of states around a core-ionized atom. Clearly, interpretation of the intensity of such peaks would be premature.

B. Magnesium

Figure 3 shows the KL_1V and $KL_{2,3}V$ Auger spectra together with the $L_{2,3}V$ and KV x-ray spectra of Mg (Ref. 30) which characterize, to a good approximation, the densities of s and p states, respectively, in Mg (Refs. 30-32). Just as for sodium, the KL_1V spectrum of Mg has a peak low in the band which we attribute to s -like states because it is so much weaker in the $KL_{2,3}$ spectrum. This s -like peak again comes too low in the band to be reasonably explained by any feature in the density of states of the neutral system. The peak at approximately 1.5-2 eV in both spectra can be attributed to mainly p -like states.

In the case of Mg we can argue that the local

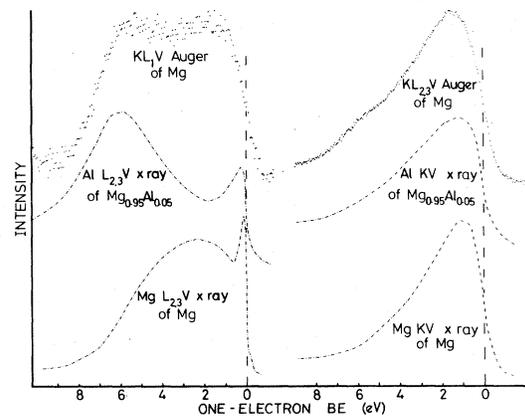


FIG. 3. Comparison of the $L_{2,3}V$ and KV x-ray-emission spectra of Mg and the $Al L_{2,3}V$ and $Al KV$ spectra of $Mg_{0.95}Al_{0.05}$ (Ref. 30) with the KL_1V and $KL_{2,3}V$ Auger spectra of Mg.

density of states around a core-ionized atom must be similar to that around an aluminum atom in a magnesium matrix. Exact equivalence is not expected because the core-ionized Mg system has a lifetime of only $\sim 10^{-15}$ s and the transition certainly takes less than 10^{-16} s. Relaxation of the nuclear coordinates of the system is thus negligible and the interatomic separations are slightly different for the core-ionized Mg and Mg with Al-impurity atoms. We have shown in Fig. 3 the Al $L_{2,3}V$ and KV x-ray-emission spectra of a dilute solution of Al in Mg as measured by Neddermeyer.³⁰ The $L_{2,3}V$ spectrum indicates a large peak in the density of Al s states about 6 eV below E_F which is clearly closely related to the s -state peak indicated by the Auger spectra from Mg metal itself. This comparison serves to illustrate the local nature of the state density investigated by x-ray-emission and KL V Auger spectra. The Mg $L_{2,3}V$ x-ray spectrum from $Mg_{0.95}Al_{0.05}$ has no peak at 6 eV BE and is similar to that from Mg metal.³⁰ If Al $L_{2,3}V$ and Mg KL V spectra did not probe predominantly the local density of states around Al and core-ionized Mg atoms, respectively, they would not have the 6-eV peak but would reflect the DOS from the majority of atoms.

Figure 4 shows a comparison of KL V Auger spectra with the Mg x-ray-emission satellite $L_{2,3}L_{2,3} \rightarrow L_{2,3}V$.²⁹ The latter is determined primarily by the density of Mg s states around a core hole although the d states,^{14,32} many-body effects,^{13,14,33,34} and the variation of x-ray cross sections through the valence band³⁵ certainly play a role near E_F . Again we see a peak low in the

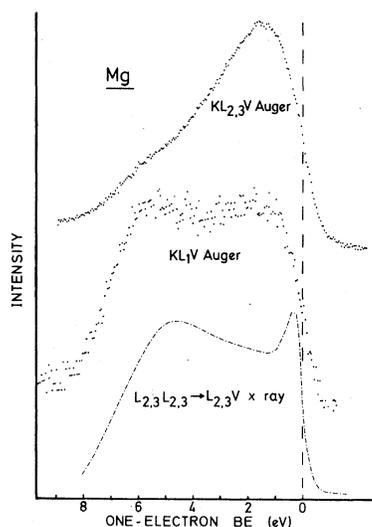


FIG. 4. Comparison of the $L_{2,3}L_{2,3} \rightarrow L_{2,3}V$ x-ray-emission satellite spectra of Mg (Ref. 29) with the KL_1V and $KL_{2,3}V$ Auger spectra of Mg.

valence band due to s states, but here its binding energy is only ~ 5 eV as opposed to 6 eV in the Al $L_{2,3}V$ spectrum of $Mg_{0.95}Al_{0.05}$ and its form is quite different. The differences in the high-BE s peak in KL_1V Auger and $L_{2,3}L_{2,3} \rightarrow L_{2,3}V$ x-ray-emission spectra of Mg or the Al $L_{2,3}V$ x-ray-emission spectrum of $Mg_{0.95}Al_{0.05}$ are due in part to different variations of matrix elements through the valence band. Unfortunately, until these are thoroughly understood it makes no sense to speculate about problems with the equivalent core approximation or the time scales of the screening processes which could both lead to changes in the position of peaks in the observed spectra.³⁶ The fact remains that all experimental evidence indicates that in Mg an increase by one in the effective nuclear charge in an atom causes the s states near that atom to be concentrated at the bottom of the band. This is exactly analogous to the peak found at approximately 6–7 eV in theoretical calculations of the local density of Mg s states¹⁴ when a core hole is present.

Comparisons of the position and shape of the peak due to p states in Mg and Al KV x-ray spectra from Mg and $Mg_{0.95}Al_{0.05}$ (Ref. 30) and in the $KL_{2,3}V$ Auger spectrum of Mg indicate that the local density of p states is far less sensitive to the presence or absence of a core hole than the local density of s states.

C. Aluminum

Figure 5 shows the KL V Auger spectra of Al together with the $L_{2,3}V$ and KV x-ray spectra of Al. There is a strong shoulder at the bottom of the KL_1V band and a much weaker one in the tail of the $KL_{2,3}V$ band which we attribute to s -like states, as in Mg and Na. Again this shoulder does not correspond to any feature in the density of s and p states in the absence of a core hole, as mirrored by the x-ray-emission spectra. But as

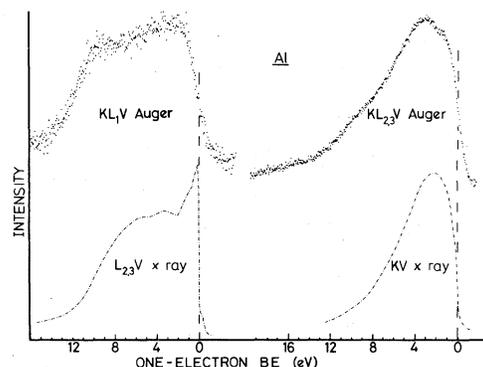


FIG. 5. Comparison of the $L_{2,3}V$ and KV x-ray-emission spectra of Al (Ref. 30) with its KL_1V and $KL_{2,3}V$ Auger spectra.

for Na and Mg, the shoulder corresponds quite well to the peak in the local density of s states around a core-ionized Al atom indicated by the $L_{2,3}L_{2,3} \rightarrow L_{2,3}V$ x-ray-emission spectrum²⁹ shown in Fig. 6. The position of the shoulders in the KL_V Auger spectra (9–10 eV) is consistent with the theoretical peak at ~ 10.5 eV in the local density of s states around a core hole in Al (Ref. 14). It must be remembered that the shoulder seen here sits on the side of the peak due primarily to p states with its maximum at 3 eV and a long tail to high BE so that the position of the shoulder cannot be determined accurately.

It is interesting that although the $L_{2,3}L_{2,3} \rightarrow L_{2,3}V$ x-ray-emission peak at high BE becomes more dominant in the series Na < Mg < Al, the corresponding peak in the KL_V Auger spectra becomes weaker in the series Na > Mg > Al. We attribute this to the increasing occupation of the p states and hence increasing weight in the KL p transitions in Na < Mg < Al. In x-ray emission, the dipole selection rules require that the $L_{2,3}$ satellite spectrum is not directly influenced by the density of p states. As the high-BE peak becomes more dominant in $L_{2,3}L_{2,3} \rightarrow L_{2,3}V$ x-ray spectra with increasing atomic number, the tendency to split off from the band also increases.

The $KL_{2,3}V$ Auger spectrum of Al has its peak about 3 eV below E_F and there is a shoulder at approximately 1.5 eV below E_F ; the spectrum does not fall smoothly from the maximum through E_F . The Al KV x-ray-emission spectrum has its maximum only approximately 2 eV below E_F and

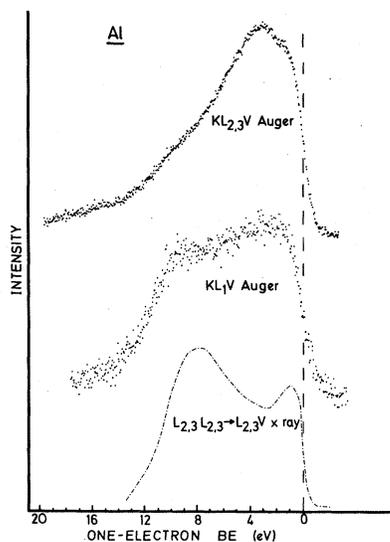


FIG. 6. Comparison of the $L_{2,3}L_{2,3} \rightarrow L_{2,3}V$ x-ray-emission satellite spectra of Al (Ref. 29) with the KL_{1V} and $KL_{2,3}V$ Auger spectra of Al.

shows a little less structure, although it must be recognized that self-absorption and many-body effects may round off the spectrum near E_F .³³ We believe the $KL_{2,3}V$ Auger spectrum is dominated by p states in this region and attribute the differences in shape of the $KL_{2,3}V$ Auger and KV x-ray spectra to screening effects rather than to the influence of the radial parts of the Auger matrix elements.

Evidence for this view comes from calculations of the variation of radial Auger matrix elements through the valence band of Si (Ref. 7) where states deep in the band have less influence on the Auger bands because they are in bonding orbitals with electrons concentrated between the atoms. Thus in Al, features lower in the band would be weakened by matrix-element effects, whereas we find an enhancement. More evidence comes from comparison of Mg and Al KV x-ray spectra from $Mg_{0.95}Al_{0.05}$ and Mg (Fig. 3, Ref. 3) which indicates the density of p states around an Al atom in Mg to be peaked at slightly higher BE than that around an Mg atom. The effect of the core hole on the density of p states in Mg could not be identified unambiguously from the $KL_{2,3}V$ Auger and KV x-ray spectra of Mg because the effect is small and confused by the poorer resolution of the Auger experiment. Here the analogous effect in Al is clearly larger and more easily identified.

D. Silicon

Figure 7 shows the KL_{1V} and $KL_{2,3}V$ Auger spectra of silicon, together with x-ray emission and XPS valence-band spectra from amorphous and crystalline Si (Ref. 37). For the KL_{1V} Auger spectra, the Fermi level has been set so that the Auger kinetic energy at E_F is equal to the K 1s binding energy minus the L_1 binding energies using data from Refs. 26 and 27. For $KL_{2,3}V$ the kinetic energy of electrons at E_F was set equal to the weighted average of the KL_2 and KL_3 x-ray energies using data from Ref. 26. The maximum possible error in placement of E_F is of the order of 0.5 eV.

We again argue that the angular parts of the Auger matrix elements cause the s states to have a larger role in the KL_{1V} spectrum and the p states to be more important in the $KL_{2,3}V$ spectrum. We then see that the peak at 13–15 eV BE with larger weight in the KL_{1V} spectrum is due to states with predominantly s characteristics. Similarly the peak at 5–6 eV with larger weight in the $KL_{2,3}V$ spectrum must be due to states with predominantly p character. As shown in Fig. 7, there is no correspondence between the peak at 13–15 eV in the Auger spectra attributed to s -like states and

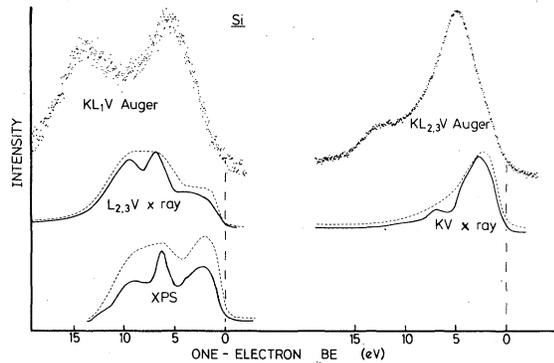


FIG. 7. Comparison of the Si KL_1V and $KL_{2,3}V$ Auger spectra of Si with the $L_{2,3}V$ and KV x-ray emission (Ref. 37) and the XPS spectra of Si (Ref. 38). The Ar^+ bombardment of Si used to clean the surface leads to some implantation and disorder at the surface used here for Auger studies. We have thus plotted out the x-ray and XPS spectra of both amorphous (---) and crystalline (—) Si to show that the difference between Auger and XPS or x-ray spectra is not due to disorder effects.

structure in the density of s -like Si states as reflected by the Si $L_{2,3}V$ x-ray emission or XPS spectra of the Si valence band. This lack of correlation can only be explained if the energy of s -like states has been shifted approximately 5 eV to higher BE by the presence of the core holes and a bound state is created below the bottom of the Si valence band. Evidence for this sort of shift can be found in the Si $L_{2,3}L_{2,3} \rightarrow L_{2,3}V$ double-ionization emission satellite spectrum investigated by Hanson and Arakawa²⁹ and illustrated in Fig. 8. In this transition there are two $L_{2,3}$ core holes in the initial state and one in the final state so that the shape of the emission reflects the energies required to remove s valence electrons in the presence of a core hole. It is not easy to locate E_F in this spectrum because the binding energy of an Si

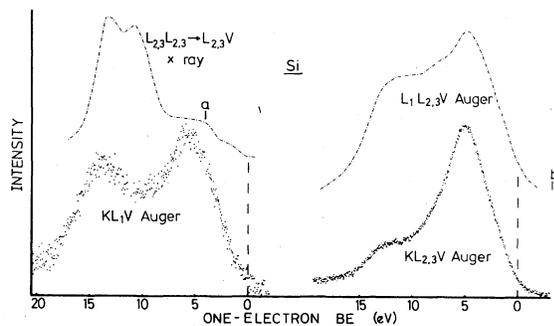


FIG. 8. Comparison of the KL_1V and $KL_{2,3}V$ Auger spectra of Si with the published $L_{2,3}L_{2,3} \rightarrow L_{2,3}V$ x-ray-emission satellite (Ref. 29) and the $L_1L_{2,3}V$ Auger spectra (Refs. 5 and 39) of Si.

$L_{2,3}$ electron in the presence of a core hole is not known and there is no clear cutoff at E_F as in the corresponding Na, Mg, and Al spectra. Hanson and Arakawa²⁹ note that the shift of the main valence-band peaks between $L_{2,3}L_{2,3} \rightarrow L_{2,3}V$ satellite emission is 16.1 eV. If the Fermi level is shifted by a similar amount it would appear at point a as shown in Fig. 8. There is too much intensity emitted above this point for this to be a sensible choice of E_F , and we have therefore set E_F at the foot of the shoulder where emission falls off as shown. One could argue that the spectrum should be shifted to the left in Fig. 8 but not to the right. It is seen that the peak in the density of s states around a core hole now indicated by the $L_{2,3}L_{2,3} \rightarrow L_{2,3}V$ satellite emission is much closer to that found by the KL_1V Auger investigations, supporting our view that screening of the core holes is responsible for the shifts.

The peaks in the Si KL_1V Auger spectra are about 5 eV broad at half-height. This is *not* due to the resolution of the experiment which is approximately 1 eV (instrumental effects plus K - and L -hole lifetime broadening) for $KL_{2,3}V$ and approximately 2 eV for KL_1V . The spectra thus indicate that the structure in the density of states around a core hole in Si is very broad. Theoretical studies of such densities of states and the role of the radial parts of the Auger matrix elements are clearly desirable here. As the s peak in the KL_1V spectrum is below the bottom of the Si valence band and apparently due to a localized bound state, it can be broadened by exchange effects due to interaction of the holes in L and bound-state levels as well as lifetime effects. The width of this peak should thus not be attributed to valence-band effects alone without further proof.

In Fig. 8 we also compare the $L_1L_{2,3}V$ Auger spectrum of Si from Ref. 39 (see also Ref. 15) with our $KL_{2,3}V$ Auger spectra. The definition of E_F in the $L_1L_{2,3}V$ spectrum was complicated by experimental difficulties with the Auger-electron-spectroscopy (AES) system used.³⁹ Here we have lined up the peaks at 5–6 eV BE in $L_1L_{2,3}V$ and $KL_{2,3}V$ spectra. The shoulders attributed to s states are then found at BE ~ 13 eV in the $L_1L_{2,3}V$ band, and its intensity relative to the p -state peak at 5–6 eV is higher than in the $KL_{2,3}V$ spectrum.

Data-handling procedures used in Refs. 39 and 40 for the $L_1L_{2,3}V$ spectra are more difficult and less unambiguous than for $KL_{2,3}V$ spectra because of the low kinetic energy (KE) of the $L_1L_{2,3}V$ electrons and the enormous number of inelastically scattered electrons in the low-KE region. However, the differences in the intensity and position of the s -state shoulder are probably real and cannot be attributed to the angular part of the

Auger matrix elements because the angular momentum quantum numbers of initial states in $KL_{2,3}V$ and $L_1L_{2,3}V$ spectra are the same. If the difference is real it must be related to either the higher surface sensitivity of the $L_1L_{2,3}V$ spectrum,⁴¹⁻⁴³ surface-damage effects in our measurements, or differences in the relative values of $XL_{2,3}s$ and $XL_{2,3}p$ radial Auger matrix elements in $KL_{2,3}V$ and $L_1L_{2,3}V$ spectra.

We wish to draw attention to the trend in shifts of the peaks in the local p -state densities as a result of the core hole in these experiments. In Na and Mg the shift is small and not shown unambiguously by our Auger experiments; in Al it is approximately 1 eV and in Si it is approximately 2.5 eV. We believe this is related to the interatomic transfer of charge to screen a core hole. In Na and Mg most of the charge is transferred to states with s -like wave functions around the ionized atom, but in Al these states are increasingly filled and screening must be done by p states. We believe this is consistent with the trends in s -wave and p -wave phase shifts in Na, Mg, and Al found theoretically and experimentally.^{14,44,45} The shift found in Si should not be discussed without reference to the covalency of the neutral system.

IV. CONCLUSIONS

We note the following.

- (1) The KL_1V and $KL_{2,3}V$ Auger spectra of Na, Mg, Al, and Si can be interpreted qualitatively using the fact that the angular parts of the Auger matrix elements give a factor 1:1 to the $KL_1s:KL_1p$ intensity ratio and 1:3 to the $KL_{2,3}s:KL_{2,3}p$ ratio.
- (2) The shapes of the KL_1V and $KL_{2,3}V$ Auger spectra of Na, Mg, Al, and Si are related to the local densities of states around atoms with core holes. This conclusion is supported by comparison with theoretical densities of s states as well as

with x-ray-satellite spectra and x-ray spectra from impurity Al atoms in an Mg matrix. Such Auger spectra thus give direct experimental evidence on the final state of the XPS process and the screening of core holes.

(3) The effect of a core hole on the local densities of s states in Na, Mg, and Al is to produce a peak near the bottom of the valence band. In Si the peak is below the bottom of the band.

(4) The effect of a core hole on the energy distribution of the p states around the ionized atom in Na, Mg, Al, and Si is smaller than the effect on the s states. With XAES the effect is barely discernible in Na and Mg. In Al and Si the effect becomes increasingly strong with a shift of the peak in the local density of p states to higher BE.

(5) Several authors have used the concept of a screening orbital to explain relaxation shifts in XPS (see, e.g., Refs. 46-48). This model incorporates the flow of charge towards an ionized atom and allows a reasonable estimate of relaxation energies. However, our results indicate that, for the elements studied here, core ionization leads to extensive changes in the local density of states throughout the whole band and not in a single screening orbital at a well-defined energy.

(6) Further theoretical studies of the radial parts of the Auger matrix elements in KL_V spectra and of the local densities of states around a core hole in these elements would be valuable.

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