Pergamon

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ORIGIN OF ANOMALIES IN PHOTOEMISSION FROM THE CONDUCTION BAND OF POTASSIUM

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Above the threshold for K 3*p* excitation, the conduction band photoemission spectrum of metallic potassium is dominated by core excitation coupled to autoionization. This accounts for the observation of a strong response in regions where k-conserving transitions are forbidden, as well as for the angle-integrated character of data taken in an angle-resolved mode. The anomalous triangular peak at the Fermi level observed with photon energies near 25 eV is due to the selective enhancement of the 4*p* character of the conduction band by autoionization involving electrons excited into the normally empty 3*d* bands.

Keywords: A. metals, D. electronic band structure, E. photoelectron spectroscopies

Resonant photoemission has made important contributions to the analysis of valence band spectra of transition and rare earth metals and alloys. For example, it has been invaluable in the study of Ce and its compounds, where it allows the selective enhancement of the elusive 4f component[1]. Although there has been little motivation to apply this technique in simple systems like the alkali metals, we show here that the resonant process explains emission in regions of photon energy where k-conserving transitions are forbidden and provides a simple explanation for the unusual peak found in the conduction band[2,3]. The discovery of these effects led to lively exchange in which mechanisms such as a charge density wave or a modification of the surface by shear were advanced to account for the observations[4-10], but no generally accepted explanation has emerged.

We limit our study to metallic potassium, which provides a good illustration of the essential points. The data were taken with samples prepared by epitaxial growth on a Ni(100) surface at 80 K, following a procedure described in recent work on the alkali metals[11]. The K vapor was obtained from a well outgassed SAES Getters dispenser. The data were taken on the AT&T Bell Laboratories – Brookhaven 6-m toroidal grating monochromator (TGM) beam line at the National Synchrotron Light Source. The resolution varied between 80 and 200 meV, depending on the photon energy. Spectra were taken in normal emission with a 100 mm hemispherical analyzer that provides 5° angular resolution. Sample quality was assessed directly from the K 3*p* spectra.

Examples of data taken as a function of photon energy are shown in Fig. 1. The amplitude of the data is normalized to the beam flux, determined from the drain current from a fine mesh located near the TGM exit slit. Data at the two highest photon energies are amplified by the factors indicated. At photon energies below the 18.3-eV threshold for photoexciting of the K 3*p* shell, the valence band spectrum is superimposed on the broad *MVV* Auger spectrum, which extends up to to a kinetic energy of 14 eV. In the 17-eV spectrum, the Auger background has been subtracted using data taken with 19-eV photons. Below the K 3*p* threshold, the valence band signal is quite weak and the shape depends on photon energy. For photon energies just above the $3p_{3/2}$ threshold, the spectrum in the vicinity of the Fermi edge is obscured by electrons excited from the K 3*p* shell by second-order radiation. A few eV above threshold, the valence band signal emerges clearly. It is now much stronger due to the the *resonant enhancement* of the valence band emission. The total height of the the step at the Fermi level, normalized by the beam flux, is plotted vs. the photon energy in Fig. 2 and

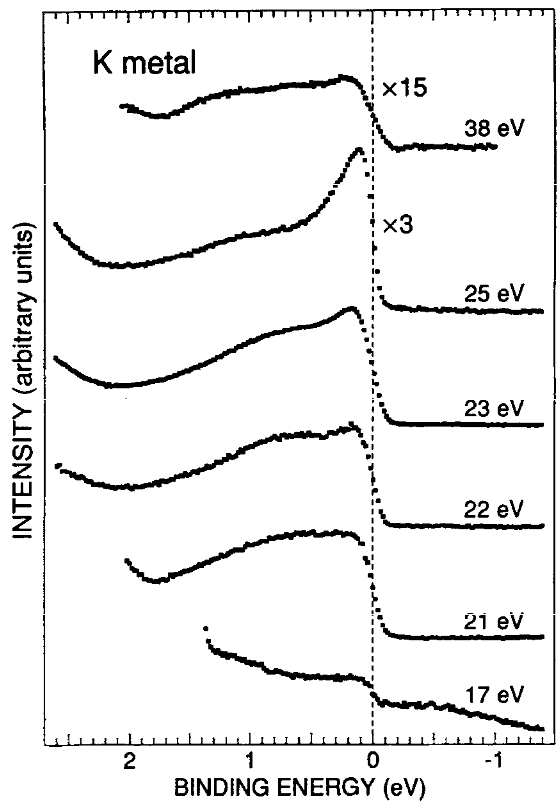

Fig. 1. Photoemission spectra from the conduction band of K taken with a range of photon energies. The spectra have been normalized by the photon flux. The instrumental resolution is 75 meV for 17, 21 and 22 eV, 110 meV for 23 and 25 eV, and 200 meV for 38 eV.

labeled "s+p". Although there is considerable scatter in the data, the essential behavior is in accord with the energy dependence of the $3p$ cross section, which drops by a factor of 40 in the first 20 eV above threshold[12]. This provides confirmation that the enhanced signal is due to the indirect process involving the $3p$ core electrons. The resonant process consists of exciting a $3p$ electron into the empty conduction band, coupled to an autoionization decay. This combination results in a final state identical to the one obtained by direct photoionization of the $4s$ conduction band. The enhancement is substantial because the atomic $3p$ cross section in much larger than the $4s$ cross section[12].

The first item of note, illustrated by the data taken with 21 eV radiation, is that above the $3p$ threshold the photoemission spectrum has a shape very similar to the density of states (DOS) obtained by soft x-ray emission spectroscopy[13]. The latter closely resembles the free-electron DOS, except near the bottom of the band where it lacks the expected sharp cut-off. This has been attributed to a binding-energy-dependent lifetime width[13], which produces sizable Lorentzian broadening at the bottom of the band. The photoemission data, even though taken with modest angular resolution in normal emission from a well-oriented surface, exhibit no vestige of angle-resolved character in this region, i. e., they appear to be fully angle-integrated. This is a clear indication that the observed signal is due mainly, or entirely, to the resonant process in which the two-electron character of the autoionization decay process averages out all angular effects.

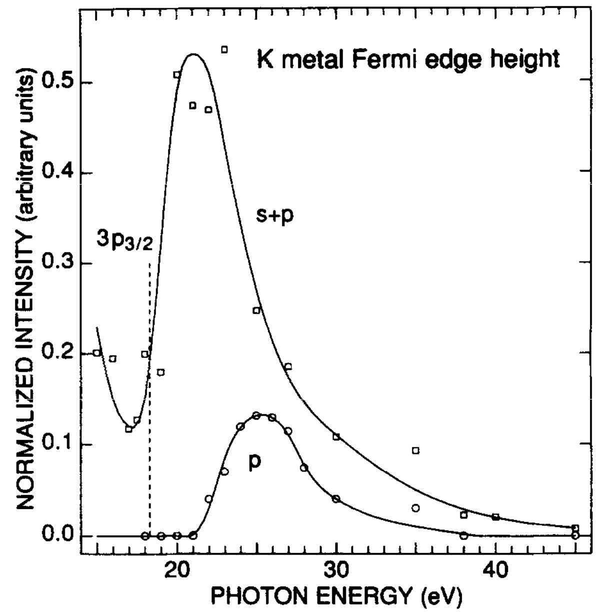

Fig. 2. Amplitude of the step at the Fermi level, normalized to the photon flux. The upper curve, labeled s+p, gives the total height of the step at the Fermi edge as shown in Fig. 1. The lower curve, labeled p, gives the contribution due to the triangular peak. The lines are drawn as a guide to the eye.

The second item of note is the undiminished signal in the region between photon energies of 20.7 and 24.5 eV, where there are no direct, k-conserving transitions according to the band structure of potassium. In this range of photon energies the entire signal must arise via an *indirect* processes involving core electron excitation coupled to autoionization. Since the $3p$ cross section is about 100 times larger than the $4s$ cross section[12], only 10% of the core excitations need result in an autoionization decay in order to overwhelm the signal from direct $4s$ photoexcitation outside the gap. The fact that the absolute magnitude of the conduction-band photoemission does not change significantly upon entering or leaving the forbidden region for direct transitions confirms that the contributions from the indirect process dominates the conduction band signal. The height of the Fermi-edge step in Fig. 2 does show a slight decrease in intensity from 20 to 21 eV photon energy, but it is within the probable error in the determination of the flux-normalized Fermi-edge step.

The third item of note is the sharp peak at the Fermi level, which first becomes noticeable in the 22-eV spectrum in Fig. 1. The contribution of this peak to the height of the step at the Fermi edge is plotted in Fig. 2 and labeled "p". This peak grows, while the free-electron-like contribution becomes weaker, until the peak dominates the spectrum in the vicinity of 25 eV. Its threshold is offset almost 4 eV from that of the 3p core-electron resonance. Finally, it weakens and disappears above 38 eV photon energy. The unusual aspect of this peak is its distinctly triangular shape. The data suggest that this shape is the result of the truncation of a broader feature by the Fermi level, i. e., it is band-like feature rather than a self-contained peak located below E_F.

The main difference between excitations near threshold, which give rise to a free-electron-like response, and those well above threshold, which yield the triangular shape is found in the character of the empty DOS. Near threshold, the DOS has mainly $4s$ character with a small admixture of $4p$ character, but a few eV above threshold there are empty $3d$ bands with DOS that greatly exceeds that of the free-electron band[14]. These empty $3d$ bands of K have been observed experimentally through their effect on the electron mean free path[15,16]. The largest reduction of the escape depth was found for electrons with kinetic energy 6.7 eV above E_F, i. e., electrons excited from the K $3p$ shell by 25 eV photon. This is very close to the photon energy where the anomalous conduction band peak reaches its maximum amplitude in Fig. 2, providing a direct confirmation that this peak is, in fact, the result of excitation into the $3d$ bands.

The autoionization process, after excitation into $4s$- or $3d$-derived states may be written $M_{2,3}N_1\,V$ or $M_{2,3}M_{4,5}\,V$, respectively, where V may be either an N_1 or $N_{2,3}$ electron from the occupied part of the conduction band. The former is analogous to an Auger process, the latter to a Coster-Kronig process. When $V = N_1$ the $4s$ part of the occupied conduction band is enhanced by the resonant process, when $V = N_{2,3}$ the $4p$ part is enhanced. Since the occupied band structure of K is dominantly of $4s$ character, a close approximation to the DOS will be obtained even if the s character is selectively enhanced. However, selective enhancement of the $4p$-character of the occupied DOS produces a spectrum with entirely different shape.

Just above threshold for $3p$ excitation only the $M_{2,3}N_1\,V$ process is active, since the $3d$ bands lie well above E_F [14]. Experimentally we find that this results in a free-electron-like conduction band DOS, see Fig. 1. Since this DOS is dominated by s-electron character in the alkali metals, it follows from the data that the rate of this autoinization process with $V = N_1$ is equal to or greater than that with $V = N_{2,3}$.

Well above threshold, where the 3d DOS is much larger than the 4s DOS, the $M_{2,3}M_{4,5}\,V$ process will dominate. Band structure calculations[14] indicate that the p character becomes appreciable about 1 eV below E_F and rises almost linearly to well above E_F. This part of the DOS, truncated by the Fermi level, is in excellent agreement with the shape of the "anomalous" peak[2,3], which is shown more clearly in Fig. 4. It therefore seems clear that excitation from $3p$ to $3d$ states strongly favors the second decay mode and strongly enhances the p part of the occupied DOS. This interpretation has the advantage over other proposed mechanisms[4-10] that it alone predicts the shape of the "anomalous" peak. A calculation of the relevant autoionization rates could serve to confirm this conclusion.

Finally, we note that quite similar behavior has been observed in photoemission from metallic sodium. Na differs from K in one important respect: there are no narrow d bands in the empty DOS, like those of potassium. Nevertheless, the free-electron-like conduction band is dominated by d character well above E_F, but with the d-like character almost an order of magnitude smaller. Band structure calculations[14] show that the d character in the Na

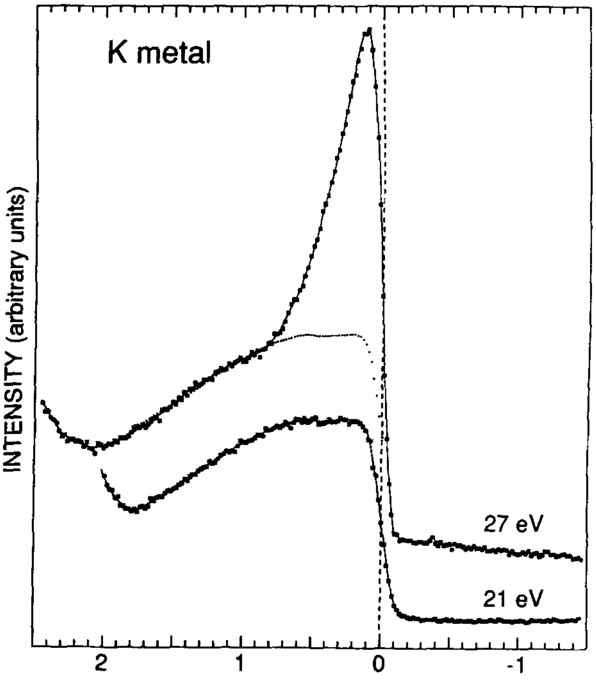

Fig. 3. Comparison of spectra taken in the resonant regime at 21 and 27 eV, below and above the onset of the d-resonance, respectively. The spectra are normalized to give the free-electron-like parts the same amplitude. The dotted line through the 27 eV data has the shape of the 21 eV data.

conduction band exceeds the *s* character for energies more than 4 eV above E_F and remains dominant at least up to 14 eV above E_F, the highest energy shown in Ref. 14. As a result, the angle-resolved signal is not entirely overwhelmed. The Na 2*p* core-excitation threshold of 30.6 eV lies just below the beginning of the gap for k-conserving transitions in the nearly-free-electron band structure, which extends from 32 to 37 eV photon energy. Accordingly, the direct transitions are seen clearly for photon energies from 18 to 29 eV, before the onset of the core resonance. Resonant effects begin just before the gap and persist well beyond it, becoming small only beyond 40 eV. Photoemission in the gap has the same explanation as in K, and the anomalous peak at the Fermi level of Na is again explained by core excitation coupled to autoionization.

In summary, we have shown that the details of the photon energy dependence of the photoemission spectra from the conduction band of K are readily understood in terms of the effects of the 3*p* core resonance and the low-lying empty 3*d* bands. They explain the free-electron band shape and the absence of angle-resolved peaks above the 3*p* threshold, the spectral intensity changes, and the origin and shape of the triangular peak which appears over a limited range of photon energies.

We should point out, however, that the above interpretation of the data raises questions regarding the role of the intermediate state in the resonant photoemission process. If this process is coherent, then the fact that the initial photoexcitation is a direct, vertical process without change in crystal momentum, would appear to place the same restriction on the autoionization process, so that identical states are created by direct and resonant excitation. That would mean that the resonant process would be forbidden for excitations from the core level to parts of the empty conduction band not accessible by direct excitation from the filled conduction band, i. e., states in the gap would remain inaccessible and the angle-resolved character would be retained, in disagreement with the experimental results. The most likely explanation is that the momentum of the core hole is not conserved in the intermediate state. The other concern is that the lifetime of the core hole would allow the electron excited from the core level to the conduction band in the intermediate state to propagate, reducing the chance for decay by autoionization. However, the observation that the lifetime width of the core hole does not appear in the final state of the resonant process suggests that it is not proper to consider temporal aspects of the intermediate state. These questions merit more detailed theoretical consideration.

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