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Applications of electron spectroscopy to the study of solids have evolved over the last decade into the most powerful set of techniques in the material scientist's arsenal. Two recent articles in this Journal have addressed the subject, emphasizing surface studies. The first\(^1\) dealt with LEED, which came into prominence in the late 1960's, while the second\(^2\) treated electron spectroscopy generally, with some emphasis on the Auger technique (AES), which has become very important since 1970. The present article will describe a third electron spectroscopic technique: ESCA\(^3\), or x-ray photoemission spectroscopy. Because ESCA employs x-rays rather than electrons as a means of excitation, it tends to sample the first 5-10 atomic layers rather than the first layer or two as in LEED and AES. ESCA has therefore been developed mainly for the study of bulk properties. The potential of ESCA for surface studies is only beginning to be fully appreciated. This article deals mainly with bulk properties, but returns briefly to surface problems at the end.
ESCA has been employed separately by chemists interested in molecules orbitals and by solid-state physicists interested in band structures. Until recently relatively little cross-fertilization has taken place, but, with increasing sophistication of the experimental techniques and particularly of the interpretive framework, it is now clear that concepts developed in molecular photoemission spectroscopy can profitably be carried over to the study of solids. A major purpose of this article is to describe several such applications.

The essential principles of ESCA are well-known and need only the briefest recapitulation here. A photon source is usually provided by characteristic x-rays, which may be monochromatized. The photons, of energy \( \sim 10^3 \text{ eV} \) (e.g., 1253.6 eV for MgK\(_\alpha\) or 1486.6 eV for AlK\(_\alpha\) x-rays), impinge on the sample, ejecting electrons via the photoelectric effect. These are energy-analyzed in a high-resolution electron spectrometer, yielding a spectrum in which electrons of kinetic energy \( K \) are ejected from orbitals of binding energy \( E_B \) according to the relation

\[
h \nu = E_B + K + \Delta \phi.
\]

Here \( h \nu \) is the photon energy and \( \Delta \phi \) is the contact potential of the sample—the amount by which \( E_B \) must be corrected if the sample's vacuum level is to be used as a reference energy. In most cases this term is neglected and the measured \( E_B \) is referred to the Fermi energy, \( E_F \).
Valence-band Densities of States

The applicability of ESCA to the measurement of electronic densities of states $\rho (E)$ in metals was appreciated early, and by 1969 the approximate forms of $\rho (E)$ for twelve 3d, 4d, and 5d transition metals had been mapped out. Earlier measurements of $\rho (E)$ were, of course, also available from x-ray emission spectroscopy (XES), but with the important qualification that XES transitions are subject to dipole selection rules, as discussed later. After 1969 progress in the ESCA measurements was slow until improved photon sources and ultra high vacuum techniques could be developed and applied. Since 1972 improved spectra have been taken on many metals throughout the Periodic Table. Two examples are shown in Figs. 1 and 2. Aluminum has a free-atom configuration $3s^2 3p$ and forms a free-electron metal. The ESCA spectrum (Fig. 1) resembles that of an electron gas, for which $\rho (E)$ varies as $(E - E_0)^{1/2}$, with a sharp drop to zero at $E_F$. The experimental spectrum is broadened, mainly by the spectrometer resolution (0.55 eV FWHM).

Figure 2 shows the ESCA spectrum of the zinc valence bands. With an atomic configuration $3d^{10} 4s^2$, zinc follows the 3d transition series, in which the d band is described in textbooks as giving a high, narrow contribution to $\rho (E)$. The itinerant 4sp bands should have a low, flat density of states. As Fig. 2 shows, these expectations are fully borne out in zinc. The d band peak is a factor of $\sim 20$ higher than the s band plateau. This structure is in turn a factor of $\sim 20$ above the background level, allowing an unambiguous determination of the location of $E_F$. A striking feature of Fig. 2 is that the intensity of the spectrum
varies over 2 decades, thereby necessitating a semilogarithmic plot.

Similar results have been obtained on many other metals and alloys. One must remember, of course, that the density of states of a metal in its ground state is not a directly measurable quantity. We can only infer the form of \( \rho (E) \) through measurements that perturb, and thereby alter, it. In most cases the ESCA spectrum provides a fairly close reproduction of \( \rho (E) \), when due allowance is made for cross-section variations. Notable exceptions include, for example, the rare earths, in which a \( 4f^n \) initial state goes on photoemission to \( 4f^{n-1} \) final configuration coupled to various levels as in the optical spectra. In general, however, the ground state form of \( \rho (E) \) can at least be readily reconstructed from the ESCA spectrum, and the latter thereby sets close limits on the valence bandwidth and band energies that future band structure calculations must reproduce if they are to be taken seriously.

**Energy Dependence of Cross Sections**

The initial state in photoemission may be regarded as an \( N \)-electron system described by a wave function of the form

\[
\Psi_1 (1, 2, \cdots N) = \mathcal{A} [ \phi_1 (1) \phi_2 (2) \cdots \phi_N (N)]
\]  

(2)

where \( \mathcal{A} \) is an antisymmetrization operator. Numbers as subscripts and in parentheses label basis functions and electrons, respectively. The basis functions \( \phi_j \) are most conveniently chosen as atomic or molecular orbitals, with more delocalized functions such as plane waves also being useful for describing valence bands in solids. The final state
may be described by a function of the form

$$\Psi_f (1, 2, \cdots N) = \mathcal{A} \left[ \phi_1^\prime (1) \phi_2^\prime (2) \cdots \phi_{N-1}^\prime (N-1) \chi_N (N) \right], \quad (3)$$

where electron N is the active (or photo-) electron, which goes into a free state \( \chi \). The N-1 passive electron stay behind in one-electron states \( \phi_j^\prime \) that are almost, but not quite, the same as the states \( \phi_j \).

Standard theoretical techniques can be used to show that the transition operator is proportional to the sum over one-electron coordinates, \( \Sigma \vec{r}_j \). The transition matrix element is therefore made up of terms having the form

$$\langle \phi_1^\prime (1) \phi_2^\prime (2) \cdots \phi_{N-1}^\prime (N-1) | \phi_1 (1) \phi_2 (2) \cdots \phi_{N-1} (N-1) \rangle \langle \chi_N (N) | \vec{r}_N | \phi_N (N) \rangle.$$ 

Here the first term—the overlap of the passive orbitals—is a number close to unity, and of little interest in this discussion. The matrix element \( \langle \chi_N | \vec{r}_N | \phi_N \rangle \) is very interesting. It can be regarded as the transformation integral of the orbital \( \phi_N \). The final-state function \( \chi_N \) is a modified plane wave, with asymptotic de Broglie wavelength \( \lambda = \hbar/\sqrt{2mK} \) where \( K \) is the photoelectron's kinetic energy, as in Eq. (1). The integral (and the photoelectric cross-section) is large when the curvature of \( \chi_N \) matches that of \( \phi_N \), and smaller otherwise. Since \( K \) and therefore \( \lambda \) can be varied at will by suitable choice of the photon energy, it is possible to determine the energy dependence of the photoemission cross section of each orbital separately. Now at x-ray energies one can predict the qualitative energy dependence of a molecular-orbital photoemission cross section by inspection of the
radial nodal structure of the constituent atomic orbitals. W. C. Price, et al. \(^8\) have shown, for example, that the \(a_1\) orbital of methane must have 2s atomic orbital character and the \(t_2\) orbital 2p character, directly from photoemission spectra. These workers compared the ultraviolet and x-ray photoemission spectra of neon, finding a 2s/2p cross-section ratio that was small at low (ultraviolet) energies but large at high (x-ray) energies. The \(a_1/t_2\) peak ratio in methane showed the same behavior, implying the orbital composition indicated above.

Similar conclusions can be drawn from ESCA measurements at two different x-ray energies. Thus M. S. Banna in our Laboratory has used the \(Y_{M_{5}}\) x-ray line (132.3 eV) to study the photoemission spectra of several small molecules. \(^9\) In Fig. 3 we have sketched the outer valence-shell spectrum of \(CF_4\) taken with the \(Y_{M_{5}}\) line and the \(MgK_{a}\) line (1253.6 eV). The molecular orbital identification is clear from the cross-section ratios. Cross-section variations with photon energy in smaller molecules compare well with those calculated by Rabalais, et al. \(^10\) Clearly this approach has a diagnostic value in molecules similar to the comparison of ultraviolet and x-ray photoemission intensities. In applications to solids it will be particularly advantageous to employ x-rays at two energies, thereby avoiding final-state effects that complicate ultraviolet photoemission spectra.

If the relative cross-sections of two atomic subshells are known, orbital-symmetry information may be obtained from an ESCA spectrum at a single x-ray energy. U. Gelius pioneered this approach and applied it to molecules. That it is also applicable to solids is evident from Fig. 4, in which the valence-shell ESCA spectra of methane and
germane are compared to those of their tetrahedrally coordinated solid-state analogues diamond and germanium. Cavell, et al., \(^{11}\) used these spectra to show that the most tightly-bound bands in diamond and germanium are mostly s-like, while the bands nearest the gap are p-like. Studies of this type should lead to elucidation of the chemical nature of bonding in simple solids.

Before leaving this topic we note that similar information about orbital symmetry is obtainable from x-ray emission spectroscopy. In XES electromagnetic selection rules are operative, and transitions proceed with appreciable intensity only if electric dipole conditions are satisfied. Thus in diamond or graphite, for example, the K x-ray emission spectrum contains contributions from \(2p \rightarrow 1s\) transitions, while \(2s \rightarrow 1s\) transitions are forbidden. These selection rules are in effect very different than those for ESCA, in which the \(2s/2p\) photo-emission ratio is quite large (\(\sim 20\)), and the two techniques play complementary roles in determining band character. An important but not widely appreciated fact that is useful in comparing XES and ESCA spectra is that the same absolute energy scale may be used if the latter are plotted vs. difference energies between valence and core photoelectron kinetic energies.

**Crystallinity and Ionicity**

At first blush ESCA would seem ill-suited for studying subtle characteristics of solids such as ionicity or crystallinity. The core-level binding energy determinations usually associated with ESCA measurements are in fact more suitable for studying atomic structure than
solid-state properties. Valence-band ESCA spectra, however, are much more sensitive to details of structure or bonding. In the Group IVB and Group VB elements, for example, a resolved doublet structure in the s-band peaks (e.g. the two small peaks in the Ge spectrum in Fig. 4) is missing in the amorphous forms of these elements. The energy separation of this doublet, which varies with interatomic distance $d$ is called the "covalent splitting", $\Delta E_{\text{cov}}$. The total observed splitting in a partially ionic material MX can be expressed as the sum of the $\Delta E_{\text{cov}}$ value appropriate for the $d$ value of MX, plus an ionic contribution,

$$\Delta E (MX, \text{obs}) = \Delta E_{\text{cov}} (MX) + \Delta E_{\text{ion}} (MX). \quad (4)$$

The fractional ionic character can then be defined as the ratio

$$\mathcal{F}^i (MX) = \frac{\Delta E_{\text{ion}} (MX)}{\Delta E (MX, \text{obs})}. \quad (5)$$

The $\mathcal{F}^i$ values derived in this way from ESCA spectra are in quite good agreement with the Phillips-Van Vechten scale based largely on optical data but appear to apply to more compounds. They also show remarkably good agreement among the alkali halides with the values that the La Trobe group derived from new optical and other data. With further refinement ESCA valence-band spectra should be quite valuable in diagnostic applications to crystallinity and ionicity questions.
Relaxation Effects on Binding Energies

In the expression for the transition matrix element given earlier, it was explicitly noted that the passive electrons' orbitals are different in the initial and final states. This shows up directly in the binding energy, $E_B(j)$, of the $j^{th}$ orbital. The orbital energy $|\epsilon_j|$, which may be calculated for simple systems by solving the Hartree-Fock equations for the initial state, is the value that the binding energy would have in the absence of passive-orbital relaxation. In fact the passive orbitals always relax, lowering the final-state energy by some amount $E_R(j)$, and

$$E_B(j) = |\epsilon_j| - E_R(j).$$

The relaxation energy $E_R(j)$ is easily estimated on a variety of simple models, because its physical meaning is straightforward: photoemission creates a positive "hole" state that attracts the passive electrons. They move toward the hole adiabatically during the photoemission process; i.e., their wave functions $\phi_i(i)$ change somewhat, to $\phi_i'(i)$, but the quantum numbers remain the same. The actual value of $E_R$ in a given chemical environment can carry considerable information about that environment.

In atomic relaxation the passive orbitals may be divided into three groups: inner-shell, intra-shell, and outer-shell, according to the relations of their principal quantum numbers to that of the active orbital. The contributions to $E_R$ are negligible for inner-shell and largest for outer-shell orbitals; this is the basis for "equivalent-core" models, in
which an atomic core with a hole state is approximated by another with equal charge. Such models yield good estimates of $E_R$. 

In molecules a large $E_R$ always accompanies photoemission from core levels. Atomic relaxation is present as before, but electronic charge is also drawn from the rest of the molecule to shield the positive hole further. The "extra-atomic relaxation" energy implied by this process yields information about the molecule's charge distribution and polarizability near the active atom. Thus $E_R$ values increase in general with molecules size, because less energy is required to attract a given shielding charge from a large reservoir than from a small one. This increase of $E_R$ saturates, however, quite rapidly, and molecules of ~10 atoms have $E_R$ values nearly as large as do much larger molecules.

Chemical bonding is also important: thus ionic molecules show smaller $E_R$ effects than do conjugated systems. For photoemission from valence-shell orbitals or orbitals intermediate between core and valence shells, $E_R$ tends to be larger for the more localized orbitals such as lone pairs. Within a homologous series of compounds RX, it is sometimes possible to isolate a core or valence orbital on functional group X and study shifts in the binding energy of that orbital as the group R is changed. This shift is closely related to the Lewis basicity of RX. Thus in alkyl alcohols the O1s binding energy shows a variation directly proportional to the proton affinity, PA. In fact to within experimental error $\Delta E_B(O1s) \approx \Delta PA$. 

Relaxation energies can be even larger in solids. This is expected if solids are regarded as the limiting case of large molecules.
This picture can even be used for calculations. Thus the binding energy of the $C_1s$ orbital in graphite has been calculated by estimating $E_R(C_1s)$ for benzene, naphthalene, etc., and extrapolating. The calculated value of 289.0(3)eV was in excellent agreement with experiment (289.2(3)eV). By estimating relaxation energies from two-electron Coulomb and exchange integrals together with atomic binding energies, it is possible to make less precise estimates of binding energies in other solids.

Auger energies also show the effects of extra-atomic relaxation. In Auger transitions the final state has two electron holes and the screening energy is thus quadrupled. Figure 5 illustrates this effect for sodium. The three peaks shown are the Na1s photoelectron, D Auger, and Na2p photoelectron peaks. For each substance—Na metal, NaF, and atomic Na—the three peaks are shown where they fall (or would fall in the case of atomic Na, for which literature values of atomic energy levels were used) on a common "binding energy" scale in an ESCA spectrum. The 2p peak energies were then aligned to give a common reference level. The 1s peak lined up very well, showing the insensitivity of core-level x-ray emission energies to chemical state. The Auger peaks for atomic Na and NaF also nearly coincide, showing little chemical shift per se. The Na metal peak is shifted to higher kinetic energy because of additional screening energy associated with the two-hole final state.

Surface studies with ESCA are underway in several laboratories. The potential of this technique for surface research seems quite
promising. Relaxation energies of adsorbed species lie between those of gases and solids, providing considerable diagnostic power. Molecular orbitals of adsorbed species yield observable peaks. Shifts of their binding energies from the gas-phase values elucidate the bonding characteristics of chemisorption. Other features of ESCA are only beginning to be used in surface studies. For example, the electron takeoff angle can be reduced to enhance surface sensitivity up to a factor of 10. This can establish definitively which peaks arise from adsorbed species. Also, variations of molecular orbital cross sections of adsorbates with photon energy should yield their atomic orbital compositions. It is still too early to be sure, but there appears to be a good chance that ESCA studies can provide a rather complete description of chemisorbed molecules.
References

6. The ESCA spectrum of Al in Fig. 1a is a smoothed version of data from our laboratory.
9. M. S. Banna and D. A. Shirley, to be published.
15. T. Koopmans, Physics 1, 104 (1934).
Figure Captions

Fig. 1. The ESCA spectrum of the valence bands of aluminum, showing the expected free-electron shape.

Fig. 2. Zinc valence-band ESCA spectrum, showing the localized d-band and itinerant s, p-band separation. Note logarithmic intensity scale.

Fig. 3. ESCA spectra of the five outer molecular orbitals of CF$_4$, taken with high energy (1253.4 eV) x-rays (top) and with low-energy (132.3 eV) x-rays (bottom) by M. S. Banna. Intensity ratios change mainly because the atomic cross-section ratios $\sigma(2s)/\sigma(2p)$ are higher at high photon energies. Thus the 4a$_1$ orbital, which has atomic s character, is emphasized at high energies. The 3t$_2$ orbital shows this effect to a lesser extent.

Fig. 4. Valence-shell ESCA spectra of tetrahedrally bonded carbon (left) and Ge (right) in the gas phase (top) and as elemental solids (bottom). Atomic s/p cross-section ratios appear in the molecular-orbital intensity ratios $a_1/t_2$ and as s-band/p-band ratios.

Fig. 5. Relative positions of the Na 1s, Na 2p, and 1D Auger peaks in ESCA spectra of the metal, NaF, and atomic sodium (arrows). The large shift in the metal's Auger line is a consequence of extra-atomic relaxation.
Fig. 1
Fig. 2

- 3d peak
- 4s, 4p bands
Fig. 3
Fig. 4
Fig. 5

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