Comparison of Binding Energies Determined by Appearance-Potential Spectroscopy and X-Ray Photoemission Spectroscopy

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We show core-electron energy spectra determined by means of (soft) x-ray photoelectron spectroscopy and appearance potential spectroscopy to be closely related for $2p$ electrons in iron and nickel. An earlier comparison for the first transition-series elements had indicated a systematic difference between appearance-potential-spectroscopy data and tabulated values based on x-ray emission and hard-x-ray-excited x-ray photoelectron-spectroscopy data.

Various spectroscopic techniques are being increasingly employed in both chemical and physical investigations in order to measure the electronic binding energies of core electrons in solids. X-ray photoelectron spectroscopy (XPS), in which a pseudomonochromatic x-ray beam excites photoelectrons whose energy spectrum is then measured, is perhaps the commonest technique. The usual definition of "binding energy" in this case is the separation between the peak in the core-level density of states and the Fermi level. The inverse process, in which monoenergetic incident electrons excite soft-x-ray emission, has given rise to the technique of appearance potential spectroscopy (APS). Essentially one would expect that binding energies measured in either case would be identical. Park and Houston[1] in comparing their APS data with tabulated binding energies[2] observed a systematic difference in the two cases. They attribute this to a higher degree of surface sensitivity in the case of APS, and suggest[3] that the reduced coordination of the surface atoms would lead to a relaxation in their energy states and accordingly to lower binding energies being observed by APS. Although the tabulated values were not directly determined by XPS (but by x-ray-wavelength data) they were set on an absolute scale using mainly XPS-measured K-shell binding energies. Since Mo $K\alpha$ radiation was used the kinetic energies of the emergent photoelectrons would be in the range 13–7 keV for scandium to nickel. (In fact it appears from the tables that in the case of iron the L_1 value obtained by XPS was used as the reference but since Cu $K\alpha$ radiation was used in this case the kinetic energy of the emergent electrons would still be about 7 keV.) Since in XPS the sampling depth is governed mainly by the kinetic energy of the photoelectrons, such high energies would imply that mainly bulk atoms were sampled, as assumed by Park and Houston. It is clearly of interest to make a direct comparison between APS and XPS binding energies using soft x radiation for the XPS experiment so that similar proportions of surface atoms contribute in both cases. This Letter reports such a comparison for samples of iron and nickel.

The specimens were in the form of foils, ion bombarded and annealed at 800–1000°K. The operating pressure was about 5×10^{-10} Torr for the Ni XPS spectrum and 10^{-8} Torr for the Fe; the latter spectrum did not differ significantly from other spectra recorded at 5×10^{-10} Torr, but the present data are reproduced as they were recorded in digital form which facilitates on-line differentiation (as in Fig. 3). XPS data were obtained using a hemispherical analyzer system —Vacuum Generators Ltd., ESCA 3. APS spectra were recorded at about 10^{-7} Torr, though in the latter case the partial pressure of argon was at least an order of magnitude greater than that of the other residual gases.

In APS the surface is bombarded with electrons whose energy may be linearly varied, and the total intensity of x rays emitted is detected as a function of the incident electron energy. When the latter is in excess of the binding energy, core electrons may be excited to vacant electronic states above the Fermi level. Small increases therefore occur in the intensity of soft-x-ray emission as a result of the de-excitation of surface atoms. Although these increases are small compared with the bremsstrahlung background, their sharpness leads to a greatly enhanced structure if the derivative of the total x-ray intensity is measured with respect to the incident electron energy, using the potential-modulation technique, as suggested by Park, Houston, and Schreiner.[4]

The additional x-ray intensity that occurs at the threshold is then directly proportional to the rate of production of core holes. Both the incident and core electrons have final states above the Fermi

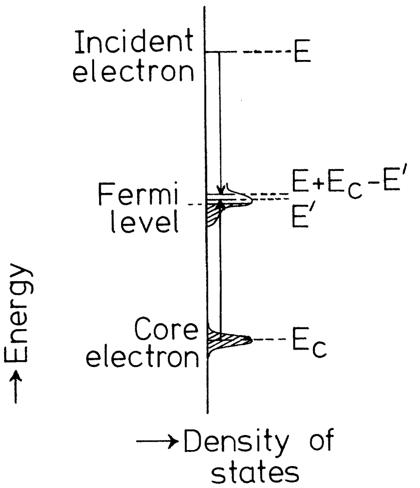

FIG. 1. The excitation process in APS where both the incident and core electrons have final states just above the Fermi level at the threshold energy.

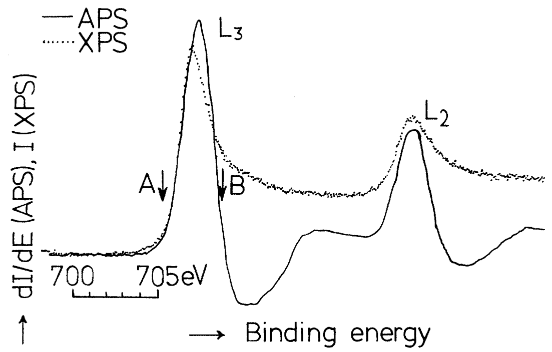

FIG. 2. APS and XPS spectra for L_2 and L_3 levels in iron. Two extreme interpretations of the APS threshold lead to the binding energy being associated with different characteristic points of the threshold indicated A,B. The APS spectrum has been corrected in energy to allow for the work function of the tungsten emitter. I is the total x-ray intensity (APS) or number of electrons per unit energy range (XPS).

level, as shown in Fig. 1. Then for monoenergetic incident electrons, the rate of production of core holes (R_c), taking account of final states consistent with conservation of energy, is proportional to a self-convolution of the density of states above the Fermi level convolved with the function representing the core-level density of states, i.e.,

$$R_c \propto \int_{E_c=-E}^{0}\int_{E'=0}^{E+E_c} C(E_c)N(E') \times N(E+E_c-E')\,dE'\,dE_c.$$

Here E is the energy of the incident electron, $C(E_c)$ is the core-level density-of-states function, $N(E')$ is the density of electronic states above the Fermi level, and the zero of energy is taken to lie at the Fermi level. The expression assumes that transition probabilities vary sufficiently slowly over the effective region of the integration.

A simple interpretation of the shape of the APS threshold, given by dR_c/dE, may be made on the basis of two extreme approximations. In the first (A), it is assumed that the core level is sufficiently narrow to be represented by a δ function, in which case the threshold shape is related to the self-convolution of the conduction-band density of states. Alternatively (B), since in transition elements there may be a large density of unfilled d states at the Fermi level, $N(E')$ can be a δ function and in this case the APS threshold shape is simply the derivative of the core-level function. Clearly, the true interpretation must be somewhere between these two extremes but both predict similar shapes for transition elements, i.e., a positive-going pulse followed by a negative dip. This is indeed observed as shown in Fig. 2, where the APS and XPS spectra for the L_3 and L_2 levels in iron are superimposed. [The usual correction[5] for the work function of the tungsten filament (4.5 eV) has been made to the APS spectrum.] The L shell of Fe (and Ni) should permit a direct comparison between APS and XPS since the kinetic energies of the electrons involved in both processes are almost identical. (Al $K\alpha$ radiation was used for the XPS measurements.)

The XPS binding energy as noted previously is taken to correspond to the peak. However, the two extreme interpretations for the APS threshold lead to the binding energy being identified with either the low- or high-energy sides of the peak, indicated in Fig. 1. As would be expected the XPS peak is intermediate between these points, but since the APS threshold shape may be related in some way to the *derivative* of the core-level function a more direct comparison between the two techniques may be obtained by on-line differentiation of the XPS spectrum. This is shown in Fig. 3, where the derivative XPS and APS spectra are compared for the L shell of both Fe and Ni. In both cases there is close agreement over the low-energy rise in the spectra, being well within the error involved in superimposing the curves (~0.5 eV).

Both techniques are subject to instrumental broadening effects. In XPS this is due mainly to

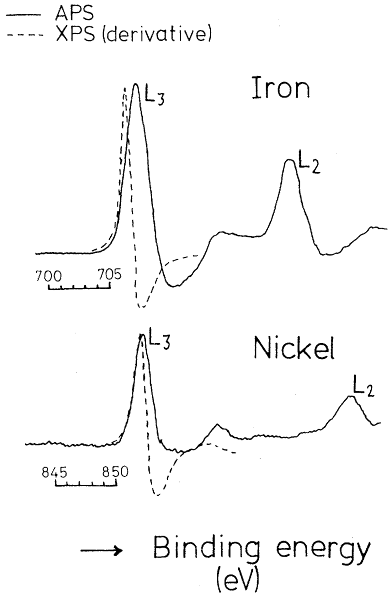

FIG. 3. The APS and derivative XPS spectrum for L_2 and L_3 levels in iron and nickel. Agreement is expected in the region of the low-energy edges. At higher energies the significance of final-state effects in APS leads to deviations.

the finite width of the x-ray line. The resolution of the instrument was determined from the extent of the broadening of the Fermi level and gave a value of 1.1 eV for the full width at half-maximum. The APS spectrum is broadened to a smaller extent as a result of the finite amplitude of the potential modulation and the energy spread of the incident electrons. The shift of the low-energy edges because of such broadening is, however, small (≤ 0.5 eV) and in the same direction for both APS and XPS.

The close agreement therefore strongly suggests the following interpretation. Because of the sharpness of the Fermi level (~ 0.025 eV at room temperature), effects due to the core-level width (~ 0.5 eV) may be expected to dominate the low-energy part of the APS threshold as, of course, in the case of the XPS spectrum. The spectra differ markedly at high energies when final-state effects become the more significant in APS, in agreement with the observations in Fig. 3.

Binding energies determined from the peak in the XPS spectrum are listed in Table I. These values are some 2 eV higher than the Park and Houston APS values, but still lower than Bearden and Burr's tabulated values. If binding energies are determined from the present APS spectra using the Park and Houston method then there is fair agreement with their results. However, in view of the close agreement seen in Fig. 3 between APS and XPS there would seem to be little justification in the neglect of the core-level width in order to determine the true core-level binding energies from APS spectra. A straightforward estimate of the "binding energy" in APS consistent with the peak in the XPS core level (the first zero in the derivative) is therefore difficult.

TABLE I. Comparison of binding energies for the L_3 shells of Fe and Ni as given by Park and Houston (PH, Ref. 1), Bearden and Burr (BB, Ref. 2), and Webb and Williams (WW). It should be noted that allowance for the core-level width will effectively increase the APS binding energy relative to the PH value, giving closer agreement between XPS and APS.

	PH (APS)	WW (APS using PH method)	WW (XPS)	BB (tables)
Fe	706.3 ± 0.5	705.8 ± 0.5	707.1 ± 0.5	708.1 ± 0.9
Ni	850.9 ± 0.5	850.8 ± 0.5	852.8 ± 0.5	854.7 ± 0.4

The effect of the core-level width seen above is greater than would be expected on the basis of theoretical predictions (~0.4 eV for Fe and Ni) by McGuire.[6] These values, however, might be better regarded as the minimum observable under experimental conditions. Such effects as a "surface shift" would give rise to a broadening of the observed core-level width if a sufficient proportion of surface atoms contribute. If, for example, it is assumed that the inelastic mean free path of the electrons is 10 Å then this would imply about 20% contribution from surface atoms. A "surface shift" would not then significantly displace the XPS peak but would broaden the observed core level. A similar effect would displace the onset of the APS threshold to lower binding energies, and this suggests that greater caution should be exercised in interpreting APS threshold shapes in terms of band structure. However, if the XPS peak does indeed give binding energies characteristic of the bulk, these values would be expected to correspond to those tabulated by Bearden and Burr, contrary to observation. It would clearly be of interest to make direct XPS determinations of binding energies for the same shell using both soft- and hard-x-radiation to see if this difference is genuine.

The present measurements, then, show close agreement for iron and nickel between the derivative of the XPS spectrum and the low-energy region of the APS threshold over which effects due to the core-level width are expected to dominate. This close agreement strongly suggests that identical initial (core) energy states are involved for both XPS and APS in this case. However, as a result of the increasing predominance of final-state effects on the high-energy side of the APS threshold, there is no obvious correspondence between features in APS and the peak in the XPS core-level density of states from which the "binding energy" is usually determined.

[1] R. L. Park and J. E. Houston, Phys. Rev. B 6, 1073 (1972).

[2] J. A. Bearden and A. F. Burr, Rev. Mod. Phys. 39, 125 (1967).

[3] See Ref. 1 and also J. E. Houston, R. L. Park, and G. E. Laramore, Phys. Rev. Lett. 30, 846 (1973).

[4] R. L. Park, J. E. Houston, and D. G. Schreiner, Rev. Sci. Instrum. 41, 1810 (1970).

[5] J. E. Houston and R. L. Park, J. Chem. Phys. 55, 4601 (1971).

[6] E. J. McGuire, Phys. Rev. A 3, 587 (1971).

Quantum States of Confined Carriers in Very Thin $Al_xGa_{1-x}As$-GaAs-$Al_xGa_{1-x}As$ Heterostructures

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Quantum levels associated with the confinement of carriers in very thin, molecular-beam–grown $Al_xGa_{1-x}As$-GaAs-$Al_xGa_{1-x}As$ heterostructures result in pronounced structure in the GaAs optical absorption spectrum. Up to eight resolved exciton transitions, associated with different bound-electron and bound-hole states, have been observed. The heterostructure behaves as a simple rectangular potential well with a depth of $\approx 0.88\Delta E_g$ for confining electrons and $\approx 0.12\Delta E_g$ for confining holes, where ΔE_g is the difference in the semiconductor energy gaps.

One of the most elementary problems in quantum mechanics is that of a particle confined to a one-dimensional rectangular potential well.[1] In this Letter, we report the direct observation of numerous bound-electron and bound-hole states of rectangular potential wells, formed by a thin layer of GaAs sandwiched between $Al_xGa_{1-x}As$ slabs. The levels are observed by measuring the optical absorption of the central GaAs layer of the structure. The presence of the bound states introduces a series of resolved exciton transitions in the above-band-gap absorption spectrum of GaAs layers less than 500 Å thick. A range of heterostructures, with central GaAs layers as thin as 70 Å, has been studied. The heterostructures produce two attractive potential wells of different depths, one for electrons and one for holes. Analysis of the spectra shows that the wells are extremely rectangular and that the electron and hole well depths are approximately 88 and 12% of ΔE_g, respectively.

The investigation was made possible by two recent developments. The first is the emergence of molecular-beam epitaxy[2,3] (MBE) as a technique for the growth of layers of III-V semiconductors. Our observations demonstrate the great precision of MBE in fabricating thin and uniform layers. The second is the development of selective chemical etches[4] for the removal of the GaAs substrate without damaging the thin epitaxial layers of the heterostructure.

During the last decade there has been intense activity in the study of electrons confined to thin layers. These studies were primarily experiments on metals, superconductors, and metal-oxide-semiconductor devices.[5] Recently, Chang, Esaki, and Tsu[6] reported observing two levels in tunneling experiments involving GaAs-$Al_xGa_{1-x}As$ heterostructures, grown by MBE, with GaAs thicknesses of 40–50 Å. This confining layer is thinner than any we have studied and in their experiment the applied electric field distorts the rectangular well into a trapezoidal shape. Nevertheless, the energies they quote are consistent with our more detailed observations.

With the use of MBE, the precision growth of multilayer GaAs-$Al_xGa_{1-x}As$ heterostructures has been possible. The usual growth conditions are as follows: vacuum before growth, $\leq 1\times10^{-9}$ mm; vacuum during growth, $\sim 1\times10^{-7}$ mm (ar-