New Correlation Effects Observed for Inner-Shell Excitations in Titanium and Vanadium

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An interpretation of energy-calibrated appearance-potential spectra for Ti and V reveals new correlation effects. A proposed initial-state, final-state rule is utilized to understand these and other many-body effects which arise in the x-ray, Auger-electron, and appearance-potential spectra for these metals.

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A quantitative interpretation of new energy-calibrated L_3 appearance-potential spectra (APS) for Ti and V reveals large and positive (5 to 7 eV) core-hole, valence-electron interaction energies (U) in the final state. This result is in sharp contrast to a recent interpretation[1] of x-ray-absorption spectra (XAS), which indicates negative U values (-2 to -3 eV).

Both APS and XAS probe the unfilled electronic states, and the above apparent contradiction is only one of several hard-to-explain results reported for the filled and unfilled states of the early $3d$ transition metals. For example, while the L_{23} and M_{23} XAS line shapes appear atomiclike (i.e., are very similar to gas-phase atomic Ti and V line shapes), the x-ray-emission spectra (XES) generally reflect the filled one-electron density of states (DOS) of the metal.[1-3]. Another example, the $L_{23}VV$ Auger-electron spectra (AES), which probe the filled states, reveal negative hole-hole repulsion energies for these metals.[4]

All of the above results are consistently explained in this work on the basis of two newly proposed many-body interaction effects. The first of these indicates that the monopole term in the core-hole, valence-electron interaction energy is driven by the higher-multipole terms, and further experiences large screening effects. The second indicates that for the early transition metals, initial-state electron coupling is more appropriate than final-state hole coupling. These two correlation effects are discussed in the context of a proposed initial-state, final-state rule for interpretation of spectroscopic line shapes.

APS data have been recorded with several different techniques,[5] but a particularly simple method to realize is Auger-electron APS (AEAPS) in which electrons of variable energy bombard the target material and a measurement is made of the target current, I, as a function of electron energy, eV, in the vicinity of expected core-level binding energies. When core levels are ionized, they can initiate an Auger-electron cascade that leads to a change in the secondary emission coefficient. Since this change is small, it is convenient experimentally to apply a small modulation voltage to the gun cathode and detect the target current at the modulation frequency; that is, dI/dV is measured as a function of V.

APS data have frequently been interpreted in terms of a simple one-electron model in which both the excited core electron and the incident electron have final states near the Fermi level of the target. According to this model, a self-convolution is made of the empty DOS and this is convolved with a Lorentzian function to represent core-hole lifetime broadening. A derivative is then taken for comparison with experiment. While this model has long been known to be oversimplified,[5] it has been employed successfully for a number of materials including some $3d$ metals.[6]

Our AEAPS measurements were made with polycrystalline Ti and V foils that were cleaned by prolonged Ar^+ sputtering. The measured AEAPS data (Figs. 1 and 2) were obtained with a modulation of 0.35 V peak to peak and are similar to those reported previously.[7]

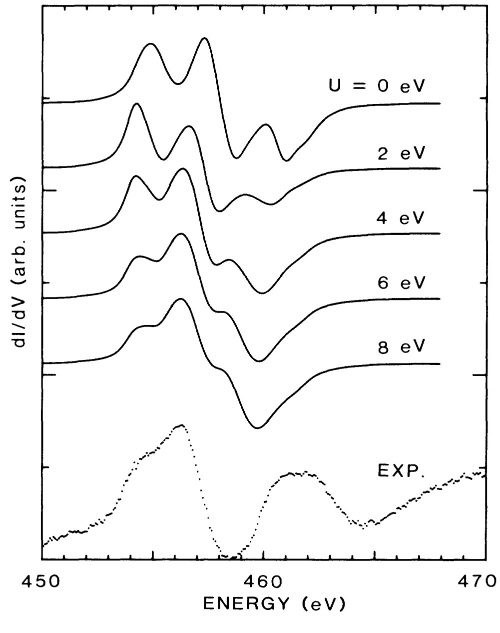

FIG. 1. Comparison of measured (bottom) and calculated appearance potential spectra for Ti. The top curve ($U=0$) was calculated with $N(E)$ and the other curves with $N_{\mathrm{mod}}(E)$ for the indicated values of U. The calculated spectra were plotted with an XPS L_3-shell binding energy of 454.1 eV.

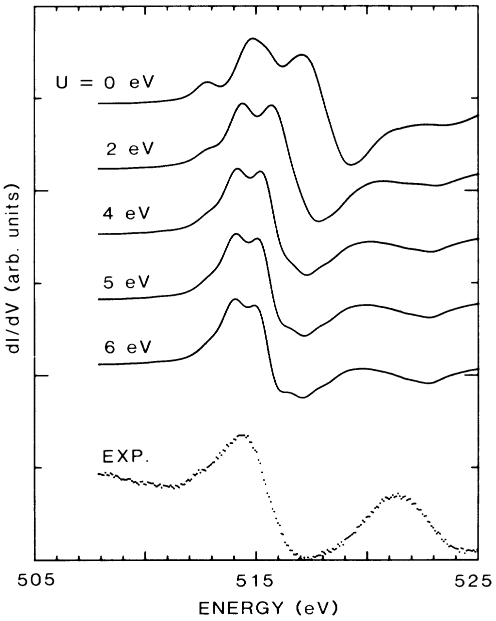

FIG. 2. Comparison of measured and calculated appearance potential spectra for V (see Fig. 1 caption). The calculated spectra were plotted with an XPS L_3-shell binding energy of 512.6 eV.

The top curve in each figure has been calculated by use of the one-electron model for each metal and the empty DOS computed by Jepsen[8] for Ti and by Boyer *et al.*[9] for V. We used the bulk DOS since, for our electron energies, the APS signal due to bulk atoms is expected to predominate over that due to surface atoms; use of a surface DOS is not expected to change materially the present results. In each calculation, a Lorentzian full width at half maximum of 1 eV was assumed to represent both the core-hole lifetime broadening[10] and the energy spread of electrons from the thermionic source.

The energy scales in Figs. 1 and 2 were based on the sum of the voltages applied to the gun cathode and 4.95 eV to represent together the thermionic work function of the tungsten cathode and the mean thermal energy of the electrons.[11] The zero of energy in the XPS convolution calculation corresponds to two electrons having final states at the Fermi level. We chose to plot the calculated spectra by making this energy zero correspond to the L_3-shell binding energy determined by x-ray photoelectron spectroscopy (XPS) with the same target materials.

Close agreement in the shapes and positions of the measured and calculated APS would indicate: (1) reliable calculations of the empty DOS; (2) validity of the one-electron model; and (3) correspondence of the core-level binding energies measured by XPS and APS. It is clear that the top curves in Figs. 1 and 2 do not agree at all with the corresponding measured spectra. We note that our comparison is directed to the main features shown to the left in Figs. 1 and 2. We have not attempted to include spin-orbit effects in the calculated spectra (i.e., the L_2 component shown to the right in the experimental data) or the effects of inelastic electron scattering (which would smear out much of the structure on the right side of the calculated curves). Similar calculations using DOS reported by other authors did not materially affect the resulting APS data.

We interpret the inconsistency between the calculated and measured spectra in terms of an initial-state, final-state (IS-FS) rule. A final-state rule was first proposed for the XES and XAS one-electron process by Mahan, von Barth, and Grossman.[12] It was extended to the AES two-electron process by Ramaker,[13] and is here extended to the APS process. The IS-FS rule arises from a dynamical calculation based on the independent-fermion model due to Mahan, Nozières, and De Dominicis (MND).[14] In this model the system is represented by an effective one-electron Hamiltonian H^* in the initial state, and a different one-electron Hamiltonian H in the final state, the difference being that one state has a core hole and the other does not (e.g., AES and XES have an initial core hole, XAS and APS a final core hole). The transition probability is then given by the appropriate many-electron matrix element, M_{kvv}, involving these two states. It has been shown that for both one- and two-electron processes,[13,15] M_{kvv} reduces to the product of a one- or two-electron matrix element and a many-electron overlap (the latter introduces the edge effects) plus small higher-order terms. This approximation is known as the final-state (FS) rule because the line shapes far from threshold reflect the one-electron DOS in the final state; however, the relative intensities of the components (e.g., the *ss*, *sp*, and *pp* contributions in AES or AEAPS) reflect the initial state.[13,15] The FS rule is derived by use of the hole picture, i.e., it enumerates the final- and initial-state holes. By instead enumerating the electrons, we could similarly derive an initial-state (IS) rule. It turns out that both the IS and FS rules indicate that the intensity is determined by the initial state, and the line shape far from threshold by the DOS appropriate to the final state.[16]

In spite of the similarity between the IS and FS rules indicated above, they do not give similar results with regard to the particle coupling and multiplet structure. The reduction of the many-electron matrix element to the well-known one- or two-electron matrix elements implies the validity of a two-particle coupling scheme. This is most fortunate since many-particle coupling is very complex, and introduces a large number of multiplets.[17] Clearly a two-electron coupling scheme is more appropriate when the band is nearly empty, and a two-hole coupling scheme more appropriate when the band is nearly filled. Thus we conclude that the IS rule, with electron coupling, is more appropriate for less than or equal to half-filled bands, and the FS rule, with hole coupling, more appropriate for more than half-filled bands.

The IS-FS rule can be summarized as follows: (a) The spectral intensities should reflect the initial state, (b) the spectral line shapes should reflect the final one-electron DOS, (c) the multiplets should reflect *electron* coupling for the lighter elements of the transition series, and *hole* coupling for the heavier elements.

Application of the above to APS is not straightforward because the final state has three particles, the core hole and the two participating electrons. However, the interaction of two electrons added to the relatively broad $3d$ bands in Ti and V is not expected to be significant.[1] We shall ignore the valence-electron, valence-electron interaction, but include the core-hole, valence-electron interaction for both excited electrons. Points (b) and (c) of the IS-FS rule then indicate that the APS should reflect a fold of the one-electron DOS appropriate to the final state (i.e., in the presence of the core hole) and p^5d *electron* coupling. We can determine the DOS in the presence of a core hole by use of the central-cell tight-binding approximation (TBA) and Green's-function techniques, which give[18]

$$N_{\text{mod}}(E)=\frac{N(E)}{[1-UI(E)]^2+[U\pi N(E)]^2}, \tag{1}$$

where $N(E)$ and $N_{\text{mod}}(E)$ are the calculated and modified DOS, respectively, $I(E)$ is the Hilbert transform of the DOS, and U is the effective core-hole valence-electron attractive energy.

Figures 1 and 2 show calculated APS curves for the values of U indicated. As U is increased the calculated curves become closer in agreement with the experimental spectra. For Ti, the calculated curves for $U=6$ and 8 eV provide the best agreement with the experimental spectrum: The small peak in the calculated spectrum at 458 eV is not seen experimentally. For V, the computed curves for $U=5$ and 6 eV are the most similar in shape to the experimental APS. Although the measured spectrum does not show two clear peaks, there is a weak shoulder at 515 eV. Better agreement could be obtained by addition of more broadening in the calculated spectra. Such broadening could be ascribed to the lifetime of the excited two-electron state.

The U values of 7 and 5 eV obtained here for Ti and V, respectively, are in sharp contrast to those obtained recently from a similar interpretation of the L_{23} XAS.[1] To understand this we need to express the U's in terms of the Coulomb, F^k, and exchange, G^k, Slater integrals. U is equal to the difference between the total interaction energies of the p^5d final state and the p^6 ground state. For simplicity, we will work here in the LS coupling scheme, although a mixed coupling scheme is more appropriate (i.e., jj coupling for the core hole and LS for the $3d$ electron).[1,17] The dipole selection rule of the XAS process dictates that of the six terms, ^3F, ^1F, ^3D, ^1D, ^3P, ^1P, only the ^1P term is populated, which has $U=F^0+(\frac{7}{35})F^2-(\frac{20}{15})G^1$.[1,17] The Slater integrals have the values $F^0=0.4$, $F^2=4.84$, and $G^1=3.37$ eV for Ti as determined by our assuming a 20% reduction of F^2 and G^1 from the tabulated atomic values, and empirically determining F^0 from the XAS.[1] The large reduction by screening of the more symmetric monopole F^0 integral, but only slight reduction of the nonsymmetric multipole F^2 and exchange G^1 and G^3 integrals has been generally found for the $3d$-$3d$ and $3p$-$3p$ interactions in the transitions metals, as exhibited by the multiplet structure seen in many of the Auger line shapes.[1] The APS process populates all of the six terms; however, the simple degeneracy of the terms dictates that the ^3F term dominates. This interpretation is supported by large changes found in the L_3 electron-energy-loss spectra (EELS) as the incident electron is reduced from 1500 eV, where the dipole selection rule dictates population of the ^1P state, to about 80 eV above the L_3-shell binding energies, when the dipole selection rule breaks down.[19] For the ^3F term, $U=F^0+(\frac{2}{35})F^2$.[17] If the APS spectra are reflecting primarily the ^3F state, then a U of 7 eV indicates F^0 must now be 6.7 eV for Ti, much larger than the 0.4 eV reflected in the XAS, but still significantly reduced from the free-atomic value of 24.2 eV.[20] Similar results are obtained for V, where F^0 increases from 1.1 eV for the XAS[1] to 4.7 eV for the APS, compared with 26.5 eV in the free atom.[20] We assumed above that F^2 and G^1 remain constant (i.e., reduced 20% from the atomic values), but that the spherical monopole term varies as a result of screening, consistent with the assumption of Ref. 1.

The large differences found for F^0 in the ^3F (AEAPS) and ^1P (XAS) final states indicates that substantially different screening occurs in the two states. The large negative exchange contribution in the U expression for the ^1P term causes U to be negative. Utilization of Eq. (1) above on the calculated $N(E)$ for Ti shows that $N_{\text{mod}}(E)$ with a $U=-3$ eV (i.e., that exhibited by the XAS) exhibits large unoccupied intensity at the top of the $3d$ band. This means that the $3d$ orbital on the atom with the core hole is primarily unoccupied in the ^1P state, and therefore F^0 is small. On the other hand, the ^3F term has a positive F^2 contribution, which when added to F^0, causes U to be large and positive (i.e., 7 eV as exhibited by the AEAPS). N_{mod} then exhibits a nearly localized state at the bottom of the $3d$ band in the ^3F state, and the core-hole, localized-$3d$-electron interaction is large. We see then that the higher-multipole terms not only may dominate F^0 in metals, as found in Ref. 1, but actually dictate the magnitude of the screening process which determines the value of F^0. Consequently, the effect of the band structure is to spread the terms over a larger energy range compared with the free atom.

The IS-FS rule, in particular point (b) as summarized above, also explains several other characteristics of the transition-metal spectra. The change in the L_{23} EELS and XAS[1,19] as one progresses up the series (the elements on the left exhibit peaks 2 to 3 eV above the Fermi level while those on the right exhibit peaks immediately above the Fermi level) can be explained by the p^5d-*electron* coupling on the left, which causes the ^1P term to have the highest energy, while on the right *pd-hole* coupling causes the ^1P term to have the lowest energy. Similarly, the changes in the AEAPS spectra (elements on the left exhibit large final-state core-hole effects while those on the right exhibit negligible core-hole effects[21]) can be explained by the same p^5d-*electron* coupling on the left and *pd-hole* coupling on the right and its effect on the ^3F term.

The changes in the $L_{23}VV$ Auger spectra (elements on the left exhibit negative values of U while those on the right exhibit positive values[4]) can also be explained by the IS-FS rule, since initial-state $3d$-*electron* coupling on the left makes U negative, and final-state $3d$-*hole* coupling on the right makes U positive. U is effectively negative for initial-state *electron* coupling because a large repulsion interaction in the initial state increases the Auger-electron kinetic energy. The $^1G_4$ and $^1S_0$ terms of the d^2 configuration together dominate the Auger intensity, and both terms have large repulsive F^2 contributions in either electron or hole coupling,[22] so that this helps to increase the magnitude of U, even though U has different signs on the left and right. Thus we believe the negative U values in the early transition metals arise directly from initial-state "two-body" correlation effects, rather than from "many-body" bipolaron relaxation[4] or initial-state–final-state orthogonality[23] effects as previously proposed. Initial-state–final-state orthogonality effects should also be present in XES spectra, but they reflect the normal one-electron DOS[3] (the final state has no core hole and only a single valence hole) suggesting that such effects are small. Further, the IS-FS rule can explain similar trends in both the $L_{22}VV$ and $L_{23}M_{23}V$ AES data, but initial-state–final-state orthogonality effects should not be present in the $L_{23}M_{23}V$ line shapes, since both the initial and final states in this case have a core hole.[4]

In summary, a comparison of our interpretation of L_3 APS for Ti and V with previously published XAS reveal large differences in the magnitudes for F^0, which are attributed to the different higher-multipole terms that drive the many-body screening effects in the metal. The utilization of a proposed initial-state, final-state rule helps to explain several apparent contradictions in the spectroscopic line shapes found for the transition metals.

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[1] J. Fink *et al.*, Phys. Rev. B **32**, 4899 (1985); J. Zaanen *et al.*, Phys. Rev. B **32**, 4905 (1985).

[2] J. P. Connerade, M. W. D. Mansfield, and M. A. P. Martin, Proc. Roy Soc. London, Ser. A **350**, 405 (1976); B. Sonntag and R. Haensel, Solid State Commun. **7**, 597 (1969).

[3] D. W. Fischer, J. Appl. Phys. **41**, 3561 (1970).

[4] D. K. G. de Boer, C. Haas, and G. A. Sawatzky, J. Phys. F **14**, 2769 (1984).

[5] R. L. Park, Surf. Sci. **48**, 80 (1975); J. Kirschner, Scanning Electron Microsc. **1983**, 1665 (1983); R. L. Park, J. E. Houston, and G. E. Laramore, Jpn. J. Appl. Phys. Suppl. **2**, 757 (1974).

[6] V. Dose, Th. Fauster, and H. Scheidt, J. Phys. F **11**, 1801 (1981); S. W. Schulz, K. -Th. Schleicher, D. M. Ruck, and H. -U. Chun, J. Vac. Sci. Technol. A **2**, 822 (1984).

[7] Y. Fukuda, W. T. Elam, and R. L. Park, Phys. Rev. B **16**, 3322 (1977); B. T. Jonker, J. F. Morar, and R. L. Park, Phys. Rev. B **24**, 2951 (1981).

[8] O. Jepsen, Phys. Rev. B **12**, 2988 (1975).

[9] L. L. Boyer, D. A. Constantopoulos, and B. M. Klein, Phys. Rev. B **15**, 3685 (1977). The DOS with $\alpha = \frac{2}{3}$ exchange approximation was used.

[10] J. C. Fuggle and S. F. Alvarado, Phys. Rev. A **22**, 1615 (1980); R. Nyholm, N. Martensson, A. Lebugle, and U. Axelsson, J. Phys. F **11**, 1727 (1981).

[11] C. J. Powell, N. E. Erickson, and T. Jach, J. Vac. Sci. Technol. **20**, 625 (1982).

[12] U. von Barth and G. Grossman, Solid State Commun. **32**, 645 (1979), and Phys. Rev. B **25**, 5150 (1982), and Phys. Scr. **28**, 107 (1983); G. D. Mahan, Phys. Rev. B **21**, 1421 (1980).

[13] D. E. Ramaker, Phys. Rev. B **25**, 7341 (1982).

[14] G. D. Mahan, Phys. Rev. **163**, 612 (1967); P. Nozières and C. T. De Dominicis, Phys. Rev. **178**, 1097 (1969).

[15] L. C. Davis and L. A. Feldkamp, Phys. Rev. B **23**, 4269 (1981).

[16] It has been indicated [E. A. Stern and J. J. Rehr, Phys. Rev. B **27**, 3351 (1983)] that for nearly empty bands the spectroscopic line shape reflects the initial state DOS, but this is true only for very empty bands, when the width of the occupied band is so narrow that no structure would be evident in XES or AES.

[17] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge Univ. Press, Cambridge, 1967).

[18] E. N. Economou, in *Green's Functions in Quantum Physics*, Springer Series in Solid-State Sciences Vol. 7, edited by M. Cardona, P. Fulde, H. J. Queisser, K. von Klitzing (Springer, Berlin, 1983), 2nd ed., Chap. 6.

[19] N. E. Erickson and C. J. Powell, J. Vac. Sci. Technol. A **1**, 1165 (1983), and Phys. Rev. Lett. **51**, 61 (1983); F. P. Netzer, G. Strasser, and J. A. D. Matthew, Phys. Rev. Lett. **51**, 211 (1983).

[20] J. B. Mann, Los Alamos Scientific Laboratory Report No. LASL-3690, 1967 (unpublished).

[21] N. E. Erickson, C. J. Powell, and D. E. Ramaker, to be published.

[22] M. H. Chen, Phys. Rev. A **31**, 177 (1985).

[23] D. R. Jennison, F. U. Hillebrecht, and J. C. Fuggle, J. Van. Sci. Technol. A **2**, 1049 (1984); P. Hedegard and F. U. Hillebrecht, Phys. Rev. B **34**, 3045 (1986).