PHYSICAL REVIEW B VOLUME 39, NUMBER 12 15 APRIL 1989-II

Relationship between Auger and autoionization processes

E. Sacher
Groupe des Couches Minces and Département de Génie Physique, Ecole Polytechnique de Montréal, Case Postale 6079, Succursale A, Montréal, Québec, Canada H3C 3A7

R. Brener
Solid State Institute, Technion–Israel Institute of Technology, Technion City, 32 000 Haifa, Israel

(Received 13 April 1988)

The energy difference between Auger and autoionization processes is shown to be readily calculable and to correlate with electronegativity. Furthermore, a comparison of bremsstrahlung isochromat spectra of unfilled states just above the Fermi level with high-resolution autoionization spectra for the transition-metal and lanthanide series has demonstrated a correlation between them.

INTRODUCTION

In 1971 Bonnelle and Karnatak[1] proposed that a new line in the x-ray spectra of rare-earth oxides was due to the $3f$-$4f$ resonance transition, analogous to optical resonance lines. Subsequently, Dufour and Bonnelle[2] used this to explain the $N_{4,5}$ Auger spectrum of Gd; in particular, the peak at 135 eV was assigned to a direct-recombination autoionization following a resonant transition:[3]

$$\cdots 4d^{10}4f^{7}5d^{1}6s^{2} \rightarrow \cdots 4d^{9}4f^{8}5d^{1}6s^{2} \rightarrow \cdots 4d^{9}4f^{7}5d^{1}6s^{2}+\epsilon f \ , \quad \text{(1a)}$$

where ϵf indicates electron emission into the continuum. A similar process, not involving f electrons, occurs in the first transition series:

$$\cdots 3p^{6}3d^{n} \rightarrow \cdots 3p^{5}3d^{n+1} \rightarrow \cdots 3p^{6}3d^{n-1}+\epsilon f \ . \quad \text{(1b)}$$

The concept of an autoionization process has been an important factor in the understanding of the electronic processes undergone by the transition-metal and lanthanide series.[3–23]

In a recent theoretical paper,[24] Combet Farnoux demonstrated that Auger and autoionization channels were intercoupled. That is, one could not be treated independently of the other. Thus, a relationship is expected between the two. Such a relationship has recently been demonstrated by one of the authors,[23] using the lanthanide data of Netzer and co-workers.[3] It was shown that, in every case, the easily identifiable $4d$-$4f$ autoionization process was coupled with the $N_{4,5}O_{2,3}N_{6,7}$ Coster-Kronig Auger process. Further, the difference in energy between these two processes was found to correlate with the electronegativity of the element.[23]

It is the purpose of this paper to derive this relationship and to explore its implications. Further, high-resolution Auger spectra will demonstrate that the autoionization peaks have fine structure, and this fine structure will be shown to correlate, at least in part, with the empty d-state density immediately above the Fermi level.

EXPERIMENT

Most of the Auger-autoionization data are available in the open literature.[2,3,6–10,13,15,16,18–21,25] The experimental work on pure metal foils of Sc, Ti, and Ta, to be discussed below, was carried out on a PHI model 590A Scanning Auger Microprobe. High-resolution Auger spectra were recorded in the first-derivative mode, using 3-kV, 1-μA, electron excitation and 1-eV peak-to-peak modulation. Immediately prior to analysis, the samples were cleaned by low-energy Ar-ion bombardment.

DERIVATION OF THE AUGER-AUTOIONIZATION RELATIONSHIP

The energy of an Auger electron, $E_A(XYZ)$, may be written as[26–30]

$$E_A(XYZ)=E_B(X)-E_B(Y)-E_B(Z)-E(hh)+E_A(r) \ , \quad (2)$$

where $E_B(i)$ is the binding energy of an electron in atomic level i. $E(hh)$ is the interaction energy of the two holes left in the final state, one from the XY transition and the other from the Z transition; $E_A(r)$, the relaxation term, is the sum of the energies due to the reorganization of the remaining electrons, subsequent to both the XY and Z electronic transitions. Together, $E(hh)$ and $E_A(r)$ take account of the extra-atomic polarization and relaxation effects of the solid environment. In a similar fashion, the energy of an autoionization electron, $E_{\text{auto}}(XY'Z)$, where Y' represents a previously unfilled level lying above Y, may be written as

$$E_{\text{auto}}(XY'Z)=E_B(X)-E_B(Y')-E_B(Z)+E_{\text{auto}}(r) \ , \quad (3)$$

where $E_{\text{auto}}(r)$ is the sum of reorganization energies for XY' and Z electronic transitions; note the absence of a hole-hole term in this one-hole process. Then,

$$\Delta E = E_{\text{auto}} - E_A = E_B(Y') - E_B(Y) + E(hh) + \Delta E(r) . \tag{4}$$

Since $E_B(Y') \approx E_B(Y)$,

$$\Delta E = E(hh) + \Delta E(r) . \tag{4a}$$

The $\Delta E(r)$ values can be further simplified by noting that, for the orbitals concerned, $E(r) \approx 0$ for the Z transition,[31] so that $\Delta E(r)$ represents a difference of XY- and XY'-transition reorganization energies. Unfortunately, because Y and Y' always have different symmetries, $\Delta E(r)$ cannot be set equal to zero. For the lanthanides, for example, $\Delta E(r)$ was found[23] to have the same order of magnitude as $E(hh)$; their sum, as in Eq. (4a), was able to predict ΔE values quite closely.

CORRELATION OF ΔE AND ELECTRONEGATIVITY

Electronegativity, χ, is defined as the power of an atom to attract electrons. Although often used qualitatively and semiquantitatively, a more precise definition has been elusive, until recently. With the present general acceptance of electronegativity as the chemical potential of the electrons[32] and the recent demonstration[33] that this was amenable to quantum-mechanical calculation through density-functional theory, there has been a resurgence of interest in electronegativity. This has led to a newly published book[34] describing recent advances.

As previously shown,[23] both E_A and E_{auto}, as well as their components, correlated linearly with electronegativity, albeit with different slopes. Because each component depends on the chemical potential of the surrounding electrons, such a correlation is expected; the different slopes manifest different dependences on the chemical potential of the electrons for the various components, whose understanding must await the results of theoretical calculations presently being pursued. Because these same components appear in Eq. (4a), ΔE $(= E_{\text{auto}} - E_A)$ also correlates with electronegativity. While the exact meanings of the correlation slopes for $E(hh)$ and $\Delta E(r)$ must await the results of theoretical calculations, it was previously noted[23] that $E(hh)$ is related to the energy of the outer orbital emitting the Auger electron and $\Delta E(r)$ is related to the number of orbitals across which the XY and XY' transitions occur and which, therefore, have to rearrange.

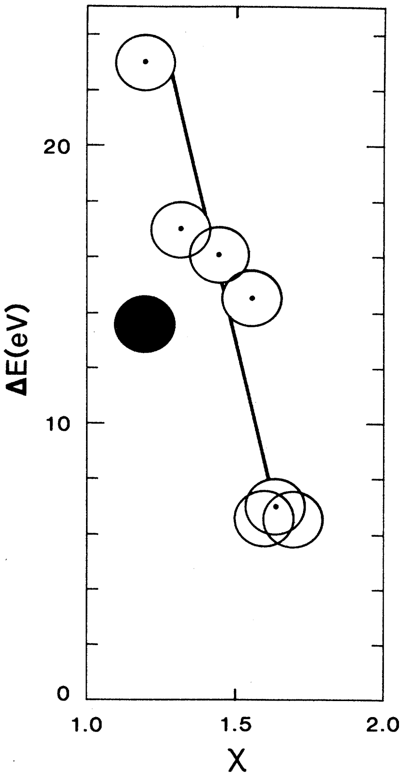

FIG. 1. Plot of ΔE vs χ for the first transition series; of the two values of $\chi = 1.20$, that at the major peak position of 34.5 eV is shaded.

Our initial attempt at correlation was made using the data of Zajac *et al.*[13] on the first transition series, from Sc to Co. These were chosen because the $M_{2,3}VV$ transition is quite simple, having one Auger peak with its associated autoionization peak. The measured peak positions are found in Table I, along with the Allred-Rochow[35,36] electronegativities, and a plot is seen in Fig. 1. Note that, except for Sc ($\Delta E = 13.5$ eV at $\chi = 1.20$), all the points fit on a straight line.

In order to clarify this, we performed a high-resolution scan on a foil of high-purity Sc, sputter cleaned prior to analysis. As seen in Fig. 2, there are two major peaks, the one at ~37 eV corresponding to the peak of Zajac *et al.*[13] at 34.5 eV. The peak at ~45 eV is not obvious in

TABLE I. $M_{2,3}VV$ Auger and autoionization-peak values for the first transition series.

Element	Auger (eV)	Autoionization (eV)	ΔE (eV)	χ
Sc	21	34.5 (44)	13.5 (23)	1.20
Ti	24	41	17	1.32
V	29	45	16	1.45
Cr	35	49.5	14.5	1.56
Mn	40	46.5	6.5	1.60
Fe	45	52	7	1.64
Co	57	63.5	6.5	1.70

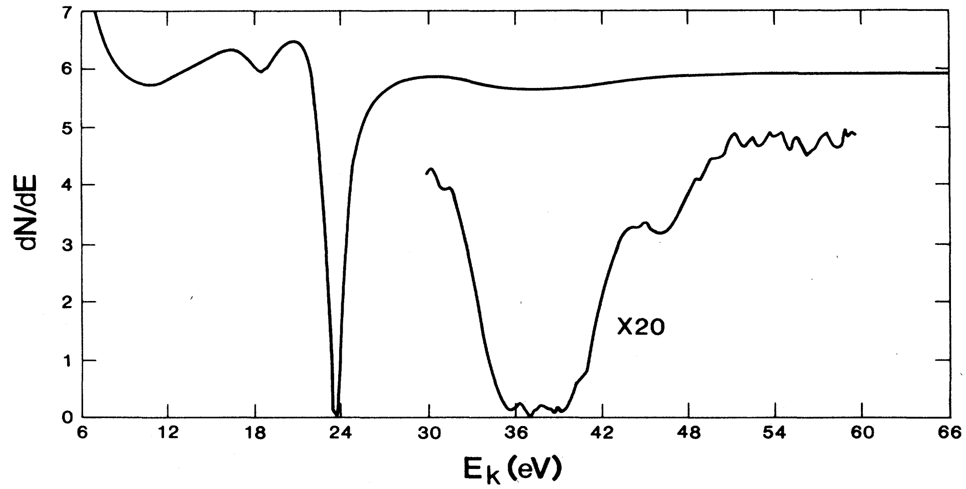

FIG. 2. $M_{2,3}VV$ Auger-autoionization spectrum of Sc.

the data reported by Zajac *et al.*, but appears to be so in the *Handbook of Auger Electron Spectroscopy.*[37] In order to maintain the same energy difference between the peaks found by us and in the *Handbook*, the data of Zajac *et al.*[13] would be expected to have an autoionization peak at 44 eV (given in parentheses in Table I). Such a peak, at a ΔE of 23 eV, is seen to fit on the straight line extending through the other points in Fig. 1.

The region of the second autoionization peak, ~45 eV, is that expected for the M_1VV Auger transition. To differentiate between these two possibilities, the sample was subjected to low-energy (i.e., Al or Mg) x-ray-

TABLE II. ΔE values found in the literature.

Element	ΔE (eV)	Reference	χ
Sc	13.5	13	1.20
	13.5	present work	
	23.0	present work	
Ti	17	13	1.32
	13	25	
	16	9	
	19.5	present work	
	24.5	present work	
V	16	13	1.45
	16	25	
	17	10	
	16.5	21	
	15	19	
Cr	14.5	13	1.56
	13	25	
	13	20	
Mn	6.5	13	1.60
Fe	7	13	1.64
	5.6	16	
	8.4	18	
	5	21	
Co	6.5	13	1.70
	4.9	18	
Ni	5.9	18	1.75
Zr	10.1	21	1.22
Nb	11.6	21	1.23
Mo	11	21	1.30
Ce	34	8	1.06
	35.5	3	
Pr	31.5	3	1.07
Nd	35.5	3	1.07
Sm	31	6	1.07
	31	7	
	33.5	3	
Eu	33	3	1.01
Gd	30	2	1.11
	30.5	3	
Tb	32	3	1.10
Dy	31.5	3	1.10
Ho	32.5	3	1.10
Er	32	7	1.11
	34.5	3	
Tm	36.5	3	1.11
Ta	9.8 (O_3VV)	21	1.33
	9.8 (O_2VV)	21	
	9.0 (O_3VV)	present work	
	9.0 (O_2VV)	present work	

induced Auger analysis because, as one of us[25] has shown, autoionization peaks are not produced. The absence of both peaks (not shown) in the presence of a strong $M_{2,3}VV$ peak clearly demonstrates that the peak near 45 eV is an autoionization peak and not the M_1VV Auger peak. The reason for two peaks will be discussed shortly.

We have collected 47 values of ΔE for 23 elements, comprising the transition and lathanide series. They are found in Table II and are plotted in Fig.3. The points fit the equation

$$\Delta E \pm 5.1\ \text{eV} = (-42.9 \pm 3.4)\chi + 76.4\ , \tag{5}$$

with a correlation coefficient of $-0.893\,90$, indicating a statistical significance of >0.9995. One must note that this straight line was obtained in spite of the approximations made in deriving Eq. (4a) (Refs. 3 and 23) and the uncertainties in peak positions.[3,7,10,21,23] Indeed, the uncertainty in ΔE, ± 5 eV, is that of determining the positions of each peak in complex spectra.[3]

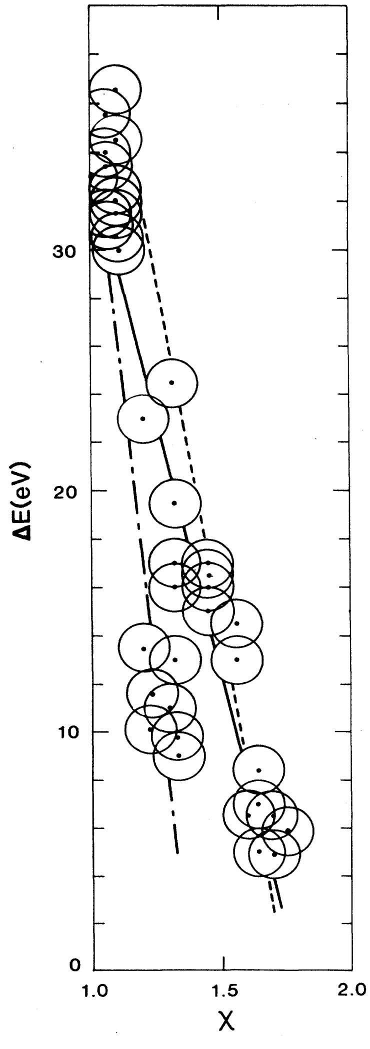

FIG. 3. Plot of ΔE vs χ: (——), correlation of all points; (— — —), correlation of points having peaks 1–2 eV above E_F; (–-–), correlation of points having peaks 3–5 eV above E_F.

AUTOIONIZATION AS A PROBE OF UNFILLED STATES

As previously noted,[38] a simplistic view of CVV Auger transitions would indicate that the total linewidth is twice the valence-band width and that the line shape is the self-convolution of the valence-band density of states (DOS). Of course, this view is insufficient on a quantitative basis, in that many-body factors, and their effects on both linewidth and line shape, must be considered. In a similar fashion, the autoionization peak should correlate with the empty states just above E_F, which are filled by the resonant transition just preceding the autoionization; this appears to have first been implied by Ramsey and Russell.[16]

A comparison between the autoionization peaks and these empty states is facilitated by recent data obtained by bremsstrahlung isochromat spectroscopy (BIS).[39] This technique, also called inverse x-ray photoelectron spectroscopy (XPS), uses a high-energy, monoenergetic electron beam. The introduction of such electrons into the empty states above E_F releases bremsstrahlung, which are measured to give the spectra, whose intensities are proportional to the DOS. BIS spectra have recently been obtained for the various transition series,[40–42] as well as the lanthanides.[41,43] Their spectra are characterized by one or two broad peaks in the range 0–5 eV above E_F; they are listed in Table III. A comparison with Fig. 3 is quite revealing.

If one were to pass a line through all the points of those elements having only one peak lying in the (1–2)-eV range (V, Cr, Mn, Fe, Co, Ni, Tm), it would also cross the higher-energy autoionization shoulder of Ti and comes near that of Sc, both found in the present study.

TABLE III. Peak energies of the unfilled DOS immediately above E_F.

	Energy above E_F (eV)					
Element	1	2	3	4	5	Reference
Sc		|		|		40
Ti	|		|			40
V		|				40
Cr	|					40
Mn	|					40
Fe		|				40
Co	|					40
Ni	|					40
Zr	|				|	40
Nb			|			40,42[a]
Mo		|				40
Ce				|		41,43
Pr		|		|		41
Nd		|		|		41
Sm	|			|		41
Eu				|		41
Gd				|		41
Tb			|		|	41
Dy		|		|		41
Ho		|				41
Er		|				41
Tm	|					41
Ta				|		41,42[a]

[a] The peaks in Ref. 42 occur about 1 eV higher in energy than those in Ref. 40.

This is seen, in Fig. 3 (— — —). Similarly, a line through all the points of those elements having only one peak lying in the (3–5)-eV range (Nb, Ce, Ta) crosses the lower-energy main peak of Sc, as well as that of Zr, Pr, Nd, Sm, Eu, Gd, Tb, and Dy. This line is also seen in Fig. 3 (-----). These two new lines, drawn as nonparallel approximations, clearly delimit the energy range of the empty states lying just above E_F. While these plots will doubtless be improved as newer high-resolution autoionization data become available, it is clear that autoionization peaks correlate with the empty states lying immediately above E_F. As with the Auger peaks,[38] the higher kinetic energy represents the lower electronic energy. We are presently pursuing theoretical calculations, in an effort to understand this correlation.

ACKNOWLEDGMENTS

One of the authors (E.S.) wishes to thank the following funding agencies for financial support; the Natural Sciences and Engineering Research Council of Canada and the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (FCAR) of Québec. Further, he wishes to thank Professor Rafi Kalish, Director of the Technion's Solid State Institute, for making his several visits there so pleasant.

---

[1] C. Bonnelle and R. C. Karnatak, J. Phys. (Paris) Colloq. **32**, C4-230 (1971).

[2] G. Dufour and C. Bonnelle, J. Phys. (Paris) Lett. **35**, L-255 (1974).

[3] J. C. Rivière, F. P. Netzer, G. Rosina, G. Strasser, and J. A. D. Matthew, J. Electron Spectrosc. Relat. Phenom. **36**, 331 (1985).

[4] R. E. Dietz, E. G. McRae, Y. Yafet, and C. W. Caldwell, Phys. Rev. Lett. **33**, 1372 (1974).

[5] L. C. Davis and L. A. Feldkamp, Solid State Commun. **19**, 413 (1976).

[6] G. Dufour, R. C. Karnatak, J.-M. Mariot, and C. Bonnelle, J. Phys. (Paris) Lett. **37**, L-119 (1976).

[7] F. P. Netzer, E. Bertel, and J. A. D. Matthew, J. Phys. C **14**, 1891 (1981).

[8] J. A. D. Matthew, J. Strasser, and F. P. Netzer, J. Phys. C **15**, L1019 (1982).

[9] E. Bertel, R. Stockbauer, and T. E. Madey, Phys. Rev. B **27**, 1939 (1983).

[10] G. Zajac, J. Zak, and S. D. Bader, Phys. Rev. B **27**, 6649 (1983).

[11] S. D. Bader, G. Zajac, and J. Zak, Phys. Rev. Lett. **50**, 1211 (1983).

[12] G. Zajac, S. D. Bader, and J. Zak, J. Vac. Sci. Technol. A **2**, 933 (1984).

[13] G. Zajac, S. D. Bader, A. J. Arko, and J. Zak, Phys. Rev. B **29**, 5491 (1984).

[14] J. A. D. Matthew, G. Strasser, and F. P. Netzer, Phys. Rev. B **30**, 4975 (1984).

[15] Y. Sakisaka, T. Miyano, and M. Onchi, Phys. Rev. B **30**, 6844 (1984).

[16] M. G. Ramsey and G. J. Russell, Phys. Rev. B **30**, 6960 (1984).

[17] Y. Sakisaka, T. Miyano, and M. Onchi, Phys. Rev. Lett. **54**, 714 (1985).

[18] M. G. Ramsey and G. J. Russell, Phys. Rev. B **32**, 3654 (1985).

[19] O. Bisi, U. del Pennino, L. Grandi, S. Valeri, and X. Yiming, Thin Solid Films **140**, 89 (1986).

[20] U. del Pennino, C. Calandra, L. Grandi, C. Mariani, and S. Valeri, Phys. Scr. **35**, 54 (1987).

[21] A. Cornaz, M. Erbudak. P. Aebi, F. Stucki, and F. Vanini, Phys. Rev. B **35**, 3062 (1987).

[22] G. Chiarello, V. Formoso, L. S. Caputi, and E. Colavita, Phys. Rev. B **35**, 5311 (1987).

[23] E. Sacher, J. Electron. Spectrosc. Relat. Phenom. **46**, 109 (1988).

[24] F. Combet Farnoux, Phys. Rev. A **25**, 287 (1982).

[25] R. Brener, J. Felsteiner, R. Tyk, and J. Zak, Phys. Rev. B **37**, 1387 (1988).

[26] D. A. Shirley, Phys. Rev. A **7**, 1520 (1973).

[27] S. P. Kowalczyk, R. A. Pollak, F. R. McFeely, L. Ley, and D. A. Shirley, Phys. Rev. B **6**, 2387 (1973).

[28] S. P. Kowalczyk, L. Ley, F. R. McFeely, R. A. Pollak, and D. A. Shirley, Phys. Rev. B **9**, 381 (1974).

[29] R. Hoogewijs, L. Fiermans, and J. Vennik, Chem. Phys. Lett. **38**, 192 (1976); **38**, 471 (1976).

[30] K. S. Kim, S. W. Gaarenstroom, and N. Winograd, Chem. Phys. Lett. **41**, 503 (1976); Phys. Rev. B **14**, 2881 (1976).

[31] U. Gelius and K. Siegbahn, Faraday Discuss. **54**, 257 (1972).

[32] R. P. Iczkowski and J. L. Margrave, J. Am. Chem. Soc. **83**, 3547 (1961).

[33] R. G. Parr, R. A. Donnelly, M. Levy, and W. E. Palke, J. Chem. Phys. **68**, 3801 (1978).

[34] *Electronegativity*, edited by K. D. Sen and C. K. Torgensen (Springer-Verlag, New York, 1987).

[35] A. L. Allred and E. G. Rochow, J. Inorg. Nucl. Chem. **5**, 264 (1958); **5**, 269 (1958).

[36] A. L. Allred, J. Inorg. Nucl. Chem. **17**, 215 (1961).

[37] L. E. Davis, N. C. MacDonald, P. W. Palmberg, G. E. Riach, and R. E. Weber, *Handbook of Auger Electron Spectroscopy*, 2nd ed. (Physical Electronics Division, Perkin-Elmer Corp., Eden Prairie, MN, 1972), p. 71.

[38] M. Thompson, M. D. Baker, A. Christie, and J. F. Tyson, *Auger Electron Spectroscopy* (Wiley-Interscience, New York, 1985), p. 242.

[39] J. K. Lang and Y. Baer, Rev. Sci. Instrum. **50**, 221 (1979).

[40] W. Speier, J. C. Fuggle, R. Zeller, B. Ackermann, K. Szot, F. V. Hillebrecht, and M. Campagna, Phys. Rev. B **30**, 6921 (1984).

[41] J. K. Lang, Y. Baer, and P. A. Cox, J. Phys. F **11**, 121 (1981).

[42] H. Merz, and K. Ulmer, Phys. Lett. **22**, 281 (1966).

[43] M. B. Chamberlain, A. F. Burr, and R. J. Liefeld, Phys. Rev. A **9**, 663 (1974).