Contrasting Valence-Band Auger-Electron Spectra for Silver and Aluminum*

C. J. Powell
National Bureau of Standards, Washington, D. C. 20234

(Received 27 December 1972)

Measurements of the $L_{2,3}VV$ (V=valence) Auger spectrum of aluminum and the $M_{4,5}VV$ Auger spectrum of silver cannot be simply related to the valence-band density of states. The data for Al indicate a strong energy variation of the transition probability. For silver, the position and shape of the Auger spectrum are associated with multiplet splitting of localized double-d-hole final states.

Lander[1] suggested in 1953 that valence-band density-of-states information could be derived from Auger-electron energy distributions (excited by electron impact), but it is only recently that attempts have been made to analyze experimental Auger spectra with this objective.[2] Implicit in Lander's suggestion is the assumption, common to all forms of valence-band spectroscopy involving removal of valence electrons, that localized hole states do not cause appreciable perturbations in the observed spectral distributions.[3] In addition, it is usually[4] assumed that the relevant transition probabilities are not a strong function of energy across the band.

We report here measurements (with ≈ 0.2 eV resolution) of the $L_{2,3}VV$ Auger spectrum of aluminum and the $M_{4,5}VV$ Auger spectrum of silver (V=valence). Analyses of the spectra show a significant energy dependence of the transition probability for Al and the formation of atomic-like double-d-hole final states in the valence band for Ag. The existence of such localized hole states that could perturb x-ray spectra[5] or uv photoemission energy distributions[6] has been postulated,[7] but this is believed to be the first direct experimental evidence for the presence of such states.[8]

In the absence of perturbations caused by initial- or final-state effects,[3] the Auger-electron intensity distribution for an XVV transition would be given by[1,2]

$$I(E_X-2\zeta)=\int_0^{\zeta} g(\zeta+\Delta)g(\zeta-\Delta)\,d\Delta,\quad 0\le\zeta\le\tfrac{1}{2}\zeta_1,$$
$$I(E_X-2\zeta)=\int_0^{\zeta_1-\zeta} g(\zeta+\Delta)g(\zeta-\Delta)\,d\Delta,\quad \tfrac{1}{2}\zeta_1\le\zeta\le\zeta_1. \qquad (1)$$

In this equation, ζ represents electron energy in the valence band ($\zeta=0$ at the Fermi level, $\zeta=\zeta_1$ at the bottom of the band), 2Δ is the energy difference of the two valence electrons involved in the Auger transition, and $g(\zeta)$ is proportional to the density of states times the square root of the spatially integrated square of the transition matrix element. The Auger-electron energy distribution would thus be expected to have a width of $2\zeta_1$, and to be superimposed on the continuous secondary-electron energy distribution with maximum energy equal to the binding energy E_X of an electron in the inner shell X.[9]

Initial ionizations in the evaporated samples were created by 1.1-keV electrons, and electron energy analysis was performed with a Kuyatt-Simpson analyzer system.[10] Figure 1(a) shows the measured energy distribution for the $L_{2,3}VV$ Auger transition of Al; in this case, the maximum energy of the Auger structure is close[11] to the L_2-electron binding energy.[12,13] The Auger structure is superimposed on a smooth secondary-electron background, represented approximately by the dashed line in Fig. 1(a). The difference between the experimental data and this arbitrary background is compared in Fig. 1(c) with a self-convolution of the Al density of states, $N(E)*N(E)$, as represented by Eq. (1). We have here used the density of states calculated by Koyama and Smith,[14] shown in Fig. 1(b), which is in close agreement with the results of other calculations.[4,15] The low-energy peak in the experimental curve of Fig. 1(c) is believed due to plasmon excitations by the emerging Auger electrons,[10] and an approximate correction for such scattering is indicated by the long-dashed line. It is clear that the experimental Auger distribution has approximately the same width as $N(E)*N(E)$, but the peak in the experimental curve is at a much higher energy [regardless of the mode of background estimation in Fig. 1(a)] than that in the $N(E)*N(E)$ curve. This difference can be ascribed to a strong energy dependence of the Auger-transition matrix

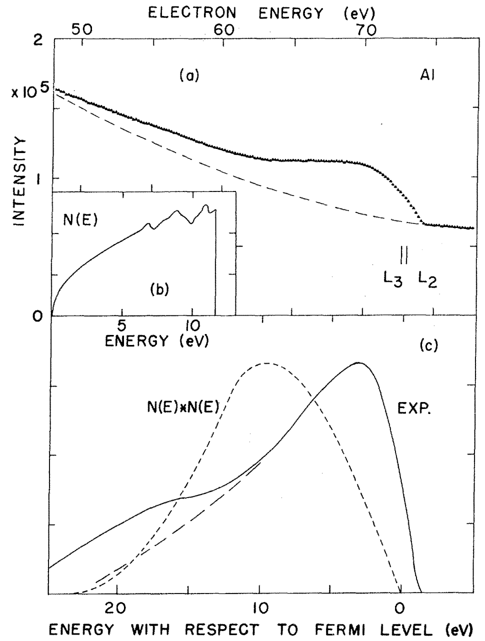

FIG. 1. (a) $L_{2,3}VV$ Auger spectrum of aluminum. Dashed line, assumed smooth background of secondary electrons. Vertical bars, L_2- and L_3-subshell binding energies. Ordinate scale, recorded number of counts per channel in a multichannel analyzer. (b) Al density of states $N(E)$ calculated by Koyama and Smith (Ref. 14). (c) Comparison of a self-convolution of the theoretical density of states, $N(E) * N(E)$ (short-dashed line), with the difference between the experimental data and the assumed background of (a) (solid line). Long-dashed line, approximate correction of the experimental curve for inelastic scattering.

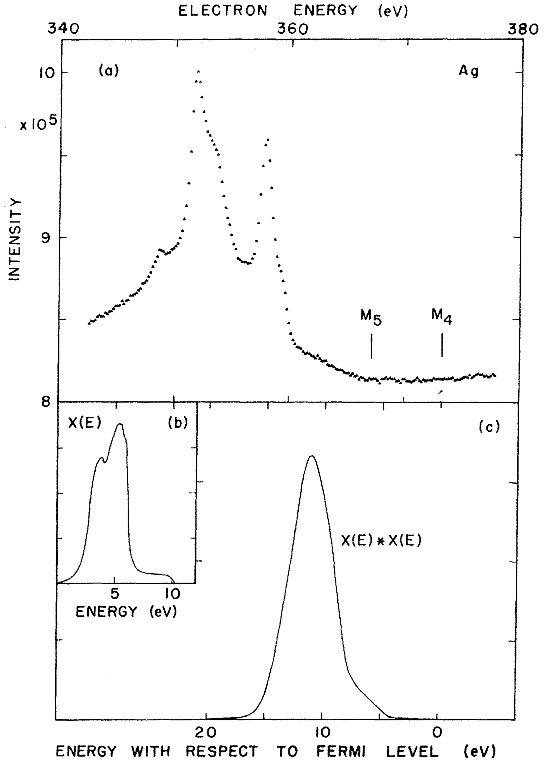

FIG. 2. (a) $M_{4,5}VV$ Auger spectrum of silver. Vertical bars, M_4- and M_5-subshell binding energies. (b) X-ray photoelectron spectrum $X(E)$ of valence-band electrons of silver measured by Hüfner *et al.* (Ref. 20). (c) Self-convolution of the Ag x-ray photoelectron spectrum shown in (b), $X(E) * X(E)$, plotted as a function of energy with respect to the Fermi level. The curve has been aligned so that the zero of the energy scale corresponds with the M_4-subshell binding energy in (a).

elements[4]; in essence, transitions involving p-like states near the top of the band are strongly enhanced compared to the s-like states at the bottom of the band.

The $M_{4,5}VV$ Auger spectrum of silver is shown in Fig. 2(a) from which the following observations can be made. The main structure is displaced substantially from the M_4-subshell binding energy[12] of 373.2 ± 0.5 eV.[11] The separation of the major peaks (at 351.7 and 357.7 eV) and the subsidiary structure (on the low-energy side of the main peaks at 348.7 and ≈ 354.5 eV, and on the high-energy side of the main peaks at ≈ 353.5 and ≈ 359.5 eV, respectively) corresponds closely to the M_4-M_5 binding-energy difference of 6.1 eV.[12] Separate energy-loss experiments showed that neither the weak peak at 348.7 eV nor the shape of the distribution between 340 and 350 eV could be attributed to inelastic scattering. The spectrum thus consists, in large part, of two regions associated with M_4- or M_5-subshell ionizations, each containing one strong and two weaker components of sharp structure superimposed on a weak background extending to about 365 eV and a background decreasing with electron energy below 350 eV. Finally, the shape of the $M_{4,5}VV$ Auger spectrum for Ag is very similar to the shape of the $M_{4,5}N_{4,5}N_{4,5}$ Auger spectra for solid Cd, In, Sb, and Te, as noted by Aksela,[16] even though the 4d electrons (in their ground state) are evolving from band states in Ag to atomiclike core states for $Z \geqslant 49$ (In).[17]

The average width of the 4d band in Ag is believed theoretically[18,19] and experimentally[20] to be about 3 eV, with the top of the 4d band located about 4 eV below the Fermi level. Hüfner *et al.*[20] found that their x-ray photoelectron spectrum for Ag was in reasonable agreement with a density-of-states curve derived from Snow's calculation[19]; the experimental spectrum $X(E)$ is shown in Fig. 2(b). A self-convolution of the photoelectron spectrum, $X(E)*X(E)$, is shown in Fig. 2(c) aligned with respect to the M_4-subshell binding energy, according to Eq. (1). The peak in $X(E)*X(E)$ is located at an energy 4.3 eV higher than the most intense component of the experimental spectrum associated with M_4-subshell ionization; in addition, the full width at half-maximum (FWHM) of the peak in $X(E)*X(E)$ is about 4.4 eV, whereas the FWHM of the experimental peak at 357.7 eV is about 1.5 eV. These differences might be considered as being due to errors in the M_4- and M_5-subshell binding energies and to energy-dependent transition probabilities. These explanations are inadequate, as the binding energies are believed known[12,11] to within 0.5 eV, and as matrix-element variations could not then be responsible for the more intense structure or the intensity on the low-energy side of the main peaks [e.g., between 340 and 350 eV in Fig. 2(a)]. We therefore conclude that the $M_{4,5}VV$ Auger spectrum of Ag is inconsistent with the description on which Eq. (1) is based.

We consider now the effects of the initial- or final-state holes on the observed Ag spectrum. Additional measurements of analogous Auger transitions for Cu and Au and a comparison with x-ray emission spectra indicate that there does not appear to be any significant relaxation of the valence band during the lifetime of the initial core hole.[21] The shape and position of the Ag $M_{4,5}VV$ Auger spectrum can, however, be interpreted on a quasiatomic model, with double d holes localized on the emitting Ag atoms. The position of the Ag $M_{4,5}VV$ Auger structure is consistent with the increased binding energy of a $4d$ electron in Ag$^+$ (estimated to be ≈ 11 eV from x-ray photoelectron spectra for Cd).[17] The prominent structure in Fig. 2(a) appears to be due to multiplet splitting of the $4d^8 5s$ configuration,[22] while the quasicontinuous intensity at lower intensities (e.g., between 340 and 350 eV) is believed due to excited final states (e.g., having the $4d^8 5p$ configuration).[23] The present results for Ag thus appear to be direct evidence for the atomiclike final states postulated by Friedel[7] and discussed by Parratt[5] and Spicer, Phillips, and Doniach[6] in relation to x-ray and photoelectron spectra. It should be noted that if final-state holes were significant for Al, the peak in the $N(E)*N(E)$ curve of Fig. 1(c) would be shifted to lower energies, creating a greater discrepancy with the experimental curve.

The present results have a number of implications which will be discussed in more detail elsewhere.[21]

(1) Auger spectra of the type measured here are not necessarily simply related to the density of states. Even for a nearly free-electron metal such as Al, an energy-dependent transition probability dominated $N(E)$ in the observed Auger spectrum; comparisons of data for a material obtained with different probes may not suffice to determine $N(E)$.[4] The XVV Auger spectrum for a d-band metal, such as Ag, appears to reflect a density of final states more than the ground-state density of states. In general, it would be expected that valence-band holes would be more localized in d-band metals such as Ag than in free-electron metals such as Al.[7]

(2) Auger-electron spectra of surface atoms and complexes measured with slow-ion excitation[23] may be expected to show similar effects to those observed here.

(3) Single-hole final-state effects may be observable in soft-x-ray emission and photoemission experiments in d-band metals.[8,24] The anomalously narrow x-ray photoelectron spectrum obtained by Hüfner *et al.*[20] for Ni may be evidence for such an effect, although there are other possible explanations for this result.

(4) "Chemical shifts" in Auger spectroscopy can be much larger than in, for example, x-ray photoelectron spectroscopy. The peak in the Al $L_{2,3}VV$ transition for Al_2O_3 occurs at 55 eV [compared to 70 eV in Fig. 1(a)],[25] even though the binding energy of the Al $L_{2,3}$ electrons increases with oxidation.[13] Smaller chemical shifts, similar to those found in x-ray photoelectron spectroscopy, would be expected for elements like Ag which have quasiatomic Auger spectra that would be expected to be relatively insensitive to chemical environment.

(5) The more intense Auger transitions of interest for surface analysis are often of the XVV type. Simple formulas for the calculation of Auger-electron energies and tabulations based on such formulas cannot be expected routinely to give reliable results (say, to better than 15 eV).

The author wishes to thank his colleagues, particularly Dr. E. W. Plummer and Dr. J. W. Gadzuk, Professor W. E. Spicer, and Dr. J. C.

Tracy for stimulating discussions.

---

*Work carried out at the U. S. National Bureau of Standards under the sponsorship of the U. S. Atomic Energy Commission, Division of Biomedical and Environmental Research.

[1] J. J. Lander, Phys. Rev. 91, 1382 (1953).

[2] G. F. Amelio and E. J. Scheibner, Surface Sci. 11, 242 (1968); G. F. Amelio, Surface Sci. 22, 301 (1970); R. G. Musket and R. J. Fortner, Phys. Rev. Lett. 26, 80 (1971); H. G. Maguire and P. D. Augustus, J. Phys. C: Proc. Phys. Soc., London 4, L174 (1971); E. J. LeJeune and R. D. Dixon, J. Appl. Phys. 43, 1998 (1972); C. J. Powell and A. Mandl, Phys. Rev. Lett. 29, 1153 (1972); J. Tejeda, N. J. Shevchik, D. W. Langer, and M. Cardona, *ibid*. 30, 370 (1973).

[3] H. Ehrenreich, J. Res. Nat. Bur. Stand., Sect. A 74, 293 (1970); L. Hedin, B. Lundqvist, and S. Lundqvist, *ibid*. 74, 417 (1970).

[4] G. A. Rooke, J. Phys. C: Proc. Phys. Soc., London 1, 767 (1968).

[5] L. G. Parratt, Rev. Mod. Phys. 31, 616 (1959).

[6] W. E. Spicer, Phys. Rev. 154, 385 (1967); J. C. Phillips, *ibid*. 140, A1254 (1965); S. Doniach, Phys. Rev. B 2, 3898 (1970).

[7] J. Friedel, Proc. Phys. Soc., London, Sect. B 65, 769 (1952).

[8] Similar conclusions have been reported by M. Prutton and D. A. Shirley, in Proceedings of the Thirty-third Physical Electronics Conference, Berkeley, California, 26–28 March 1973 (to be published).

[9] Binding energies of electrons and Auger-electron energies are measured with respect to the Fermi level [J. A. Bearden and A. F. Burr, Rev. Mod. Phys. 39, 125 (1967); R. E. Watson, J. E. Hudis, and M. L. Perlman, Phys. Rev. B 4, 4139 (1971); C. J. Powell and A. Mandl, Phys. Rev. B 6, 4418 (1972)].

[10] Powell and Mandl, Ref. 9.

[11] The maximum Auger-electron energy in Fig. 1(a) is slightly greater (by 1 eV) than the L_2-shell binding energy. Further work has shown no such discrepency, and it is believed that the difference in Fig. 1(a) is due to a systematic error in the calibration of the electron energy scale; for example, the work function of the effective emitting area of the tungsten-filament cathode could have been greater than the thermionic work function of 4.5 eV assumed here (Ref. 10). The variation in the absolute position of Auger features for other materials measured with the present instrument has been otherwise less than 0.2 eV.

[12] Bearden and Burr, Ref. 9; Watson, Hudis, and Perlman, Ref. 9.

[13] V. A. Fomichev, Fiz. Tverd. Tela 8, 2892 (1966) [Sov. Phys. Solid State 8, 2312 (1967)].

[14] R. Y. Koyama and N. V. Smith, Phys. Rev. B 2, 3049 (1970).

[15] N. W. Ashcroft quoted by F. Wooten, T. Huen, and R. Stuart, in *Proceedings of the International Colloquium on Optical Properties and Electronic Structure of Metals, Paris, 1965,* edited by F. Abelès (North-Holland, Amsterdam, 1966), p. 333.

[16] S. Aksela, Z. Phys. 244, 268 (1971).

[17] R. A. Pollak, S. Kowalczyk, L. Ley, and D. A. Shirley, Phys. Rev. Lett. 29, 274 (1972).

[18] N. E. Christensen, Phys. Status Solidi (b) 54, 551 (1972), and references to earlier work cited therein.

[19] E. C. Snow, Phys. Rev. 172, 708 (1968).

[20] For example, S. Hüfner, G. K. Wertheim, N. V. Smith, and M. M. Traum, Solid State Commun. 11, 323 (1972).

[21] C. J. Powell, to be published.

[22] C. E. Moore, *Atomic Energy Levels as Derived from Analyses of Optical Spectra,* National Bureau of Standards Circular No. 467 (U. S. GPO, Washington, D. C., 1958), Vol. III.

[23] H. D. Hagstrum, J. Res. Nat. Bur. Stand., Sect. A 74, 433 (1970).

[24] N. F. Mott, in Ref. 15, p. 314.

[25] D. T. Quinto and W. D. Robertson, Surface Sci. 27, 645 (1971); M. Suleman and E. B. Pattinson, J. Phys. F: Metal Phys. 1, L21 (1971); C. J. Powell, unpublished.