$M_{4,5}N_{4,5}X$ Auger electron spectra of free silver atoms

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The first high-resolution $M_{4,5}N_{4,5}N_{4,5}$ and $M_{4,5}N_{4,5}O_1$ Auger electron spectra from silver vapor have been measured using electron-beam excitation. The spectra reveal fine structure not observable in solid-state measurements. The spectra have been analyzed in terms of the optically known energy levels of the $4d^85s$ and $4d^9$ final-state configurations. The intensity anomaly of the high-energy components of the $M_5N_{4,5}N_{4,5}$ group found in the spectrum of solid silver does not exist in the present vapor-phase spectrum. The relative intensities of lines are found to correspond very well to the intensities of $4d^8$ parent Auger lines calculated in a mixed coupling scheme. For the binding energies of the M_4 and M_5 levels of free silver atoms 381.55 ± 0.10 and 375.55 ± 0.10 eV, respectively, have been obtained. A comparison with the published solid-state photoenergies and Auger energies shows that the free atom binding energies are 3.3 ± 0.5 eV higher and the kinetic energies of the $M_{4,5}N_{4,5}N_{4,5}$ Auger electrons 12.1 ± 0.5 eV lower than the corresponding solid-state values.

INTRODUCTION

The Auger spectrum of atomic silver is very interesting because, up until now, sodium has been the only free atom with a nonclosed electronic ground-state structure whose Auger spectrum has been presented and analyzed in detail. The optically known final-state energy levels for the $M_{4,5}N_{4,5}N_{4,5}$ and $M_{4,5}N_{4,5}O_1$ Auger transitions of atomic silver make possible an accurate location of the line components and hence a reliable determination of the intensities of lines. With the aid of the optical final-state energies and the measured Auger energies, the $3d$ binding energies can also be determined with high accuracy. A comparison with solid-state measurements further yields estimates for the extra-atomic relaxation shifts in photoelectron and Auger electron spectra on transition from atomic to solid state.

The $M_{4,5}N_{4,5}N_{4,5}$ Auger electron spectrum of solid silver has recently been investigated by several authors.[1-6] The solid-state spectrum is of special interest because the final-state holes of these Auger transitions are in the valence band and thus the spectrum could give important information on the valence-band structure. Since the photoelectron spectrum from the $4d_{3/2,5/2}$ levels shows distinct effects of the band structure,[7] one could easily expect that two holes at the same levels in the Auger transitions also produce a bandlike spectrum whose line shape is the self-convolution of the valence band.[3] In some other studies the spectrum has been expected to show an atomic character. Basset *et al.*[2] made an attempt to interpret the $M_{4,5}N_{4,5}N_{4,5}$ spectrum of solid silver using the optical data of the $4d^85s$ configuration of free silver atoms for the final-state splitting, but, due to a lack of detailed fine structure in the experimental spectrum, their interpretation is unsure. Very recently, Mariot *et al.*[4] explained that the spectrum of solid silver exhibts $4d^8$ energy splitting and can be interpreted as an atomlike spectrum with broadened linewidths. According to Sawatzky *et al.*,[8] the quasi-atomic structure is assumed to exist when the effective two-hole Coulomb interaction U_{eff} is larger than twice the bandwidth W. Parry-Jones *et al.*[6] have suggested that the lower values of U_{eff} than $2\times W$ for the ^3F components could lead to their anomalously low intensities.

EXPERIMENTAL

The spectrum was recorded on a cylindrical-mirror electron analyzer[9] with an energy resolution of $\Delta E/E \simeq 0.05\%$. A 3-keV electron beam with a beam current of ~500 μA was used to ionize the sample atoms in the oven at a temperature of ~900 °C, corresponding to a vapor pressure of ~10^{-3} Torr. The details of the instrument have been described elsewhere.[12]

The energy calibration was performed with respect to the vacuum level, using Ar and Ne Auger lines as reference lines. The energies of the Ar $L_3M_{2,3}M_{2,3}(^1D)$ line and the Ne $KL_{2,3}L_{2,3}(^1D)$ line were taken to be 203.49 (Ref. 10) and 804.557 eV,[11] respectively.

RESULTS AND DISCUSSION

The sum spectrum of several fast scans (0.1 s/ch) is presented in Fig. 1. The sharp features of the fine structure clearly indicate that the $4d^8$ two-hole representation is insufficient to describe adequately the spectrum. Furthermore, the overall shape of the $M_5N_{4,5}N_{4,5}$ group deviates considerably from that measured from solid samples.[6] The vapor spectrum has more intensity

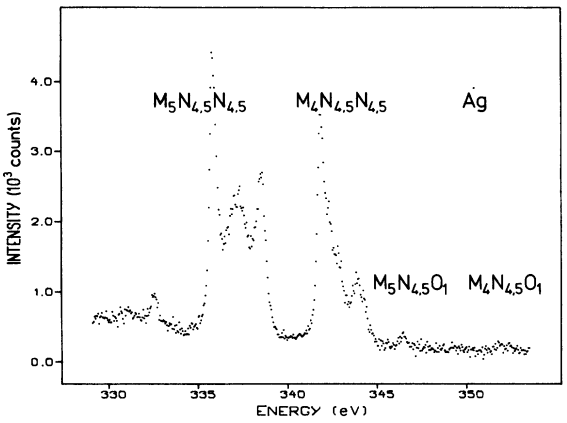

FIG. 1. $M_{4,5}N_{4,5}N_{4,5}$ and $M_{4,5}N_{4,5}O_1$ spectra of free silver atoms excited with 3-keV electrons.

on the high-energy side of the group. The $M_{4,5}N_{4,5}O_1$ transitions can be seen on the high-energy side of the M_4 group.

The rather low background in the spectrum of atomic silver is mainly caused by inelastic scattering of electrons in the target volume and can be estimated well by linear functions. The background- and dispersion-corrected spectra have been separated into different line components using as a standard-line-shape Voigt functions whose Gaussian part approximates the spectrometer contribution, and the Lorentzian part, the inherent linewidth. The relative positions of the line components are those given in the optical data for the configurations $4d^85s$ and $4d^9$ of free silver atoms.[12,13] The best fits have been obtained with 0.18 eV full width at half maximum (FWHM) for the spectrometer function and 0.21 eV for the in-

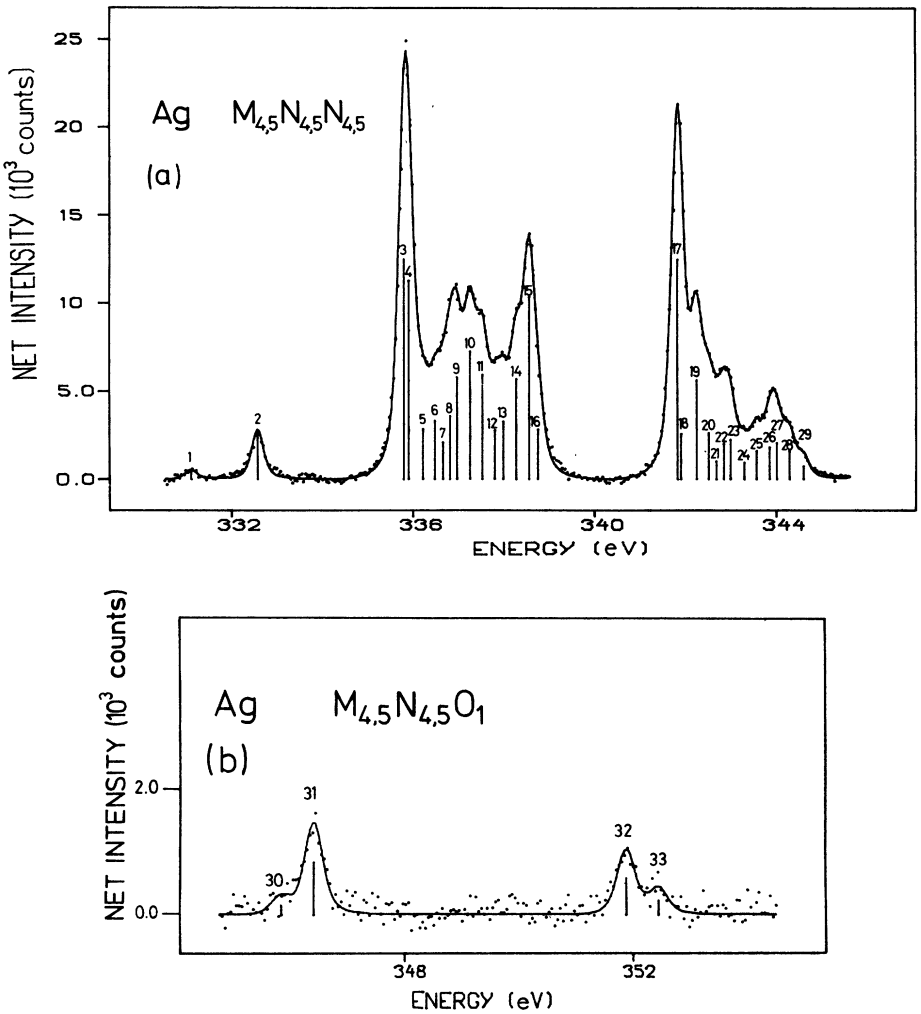

FIG. 2. Separation of (a) the $M_{4,5}N_{4,5}N_{4,5}$ spectrum and (b) the $M_{4,5}N_{4,5}O_1$ spectrum of silver into its components. The solid curve and the vertical lines represent the fit to the experimental points. Assignments of the final state for line numbers are given in Table I.

TABLE I. Experimental relative energies (in eV) and intensities (in %) of the $M_{4,5}N_{4,5}N_{4,5}$ and $M_{4,5}N_{4,5}O_1$ Auger lines of silver.

Assignment of final state	Optical energy (Ref. 12)	$M_5N_{4,5}N_{4,5}$ Line number in Fig. 2	Energy [a]	Intensity [b]	Intensity [c]	$M_4N_{4,5}N_{4,5}$ Line number in Fig. 2	Energy [a]	Intensity [b]	Intensity [c]
$(^1S)\,^2S_{1/2}$	−3.18	2	−3.22	3.2	3.2	16	−3.06	5.5	6.0
$(^1G)\,^2G_{7/2,9/2}$	0.00	3	0.00	30.0	29.6	17	0.00	38.0	37.8
	0.03								
$(^3P)\,^2P_{1/2,3/2}$	0.07	4	0.11			18	0.09		
$(^1D)\,^2D_{5/2}$	0.43	5	0.42	3.6	4.4	19	0.43	14.2	14.5
$(^1D)\,^2D_{3/2}$	0.69	6	0.68	4.2	3.5	20	0.69	6.7	5.9
$(^3P)\,^4P_{1/2}$	0.85	7	0.86	2.7	3.3	21	0.86	2.6	3.2
$(^3P)\,^4P_{3/2}$	1.03	8	1.01	4.6	4.1	22	1.02	5.1	4.8
$(^3P)\,^4P_{5/2}$	1.16	9	1.17	7.3	7.5	23	1.17	5.7	5.5
$(^3F)\,^2F_{5/2}$	1.46	10	1.47	9.1	9.5	24	1.47	2.4	2.5
$(^3F)\,^2F_{7/2}$	1.74	11	1.73	7.5	7.8	25	1.74	4.1	4.2
$(^3F)\,^4F_{3/2}$	2.03	12	2.01	3.5	3.3	26	2.03	4.6	4.4
$(^3F)\,^4F_{5/2}$	2.18	13	2.20	4.1	3.9	27	2.19	5.2	5.3
$(^3F)\,^4F_{7/2}$	2.48	14	2.48	7.2	8.2	28	2.47	4.0	4.1
$(^3F)\,^4F_{9/2}$	2.79	15	2.76	13.0	11.7	29	2.79	1.9	1.8
			$M_5N_{4,5}O_1$				$M_4N_{4,5}O_1$		
$(^1D)\,^2D_{3/2}$	10.06	30	10.22	19.4	16.0	32	10.04	70.3	71.4
$(^1D)\,^2D_{5/2}$	10.63	31	10.65	80.6	84.0	33	10.60	29.7	28.4

[a] Relative energies obtained from the fit.
[b] Relative intensities from the fit, where energies were also variable.
[c] Relative intensities obtained using the optically known energy splitting in the fit.

herent linewidth. The fits to the spectra are shown in Figs. 2(a) and 2(b) by the continuous line and the positions of the components by the vertical bars. The lines $^2G_{7/2}$ and $^2G_{9/2}$, $^2P_{1/2}$ and $^2P_{3/2}$ in the $M_{4,5}N_{4,5}N_{4,5}$ spectrum are so close to each other that they cannot be separated in the fit, whence they are represented by two lines 3 and 4 (17 and 18) in Fig. 2(a). The relative line intensities and relative energies with respect to the ^2G line are given in Table I. Because of the overlap of the ^2G and ^2P lines, only the sum of their intensities is meaningful. The fitting procedure was also applied by varying the line positions, but the values of the relative energies and intensities did not change significantly, as can be seen from Table I. The relative energies and intensities of the

TABLE II. Experimental and theoretical relative intensities (in %) of the $M_{4,5}N_{4,5}N_{4,5}$ transition of silver for $4d^8$ parent lines.

Assignment of final state	$M_5N_{4,5}N_{4,5}$ Experiment	Theory	$M_4N_{4,5}N_{4,5}$ Experiment	Theory
$(^1S)\,^2S$	3.2	3.2	6.0	5.4
$(^1G)\,^2G$	29.6	24.3	37.8	27.8
$(^3P)\,^2P$	14.9 } 44.5	22.7 } 44.0	13.5 } 51.3	19.0 } 46.8
$(^1D)\,^2D$	7.9	5.8	20.4	21.5
$(^3F)\,^2F$	44.4	44.0	22.3	26.3

TABLE III. $M_5N_{4,5}N_{4,5}$ (G) Auger and M_5 binding energies and vapor-metal energy shifts of silver (in eV).

	This work	Ref. 6 [a]	Expt	Energy shift Ref. 6	Calc [b]	Calc [c]
Auger energy	335.80 ± 0.25	347.9	12.1 ± 0.5	11.2	13.4	10.1
Binding energy	375.50 ± 0.25	372.2	3.3 ± 0.5	2.4	5.1	4.7

[a] Energies for solid silver corrected by the work function 4.0 eV.
[b] Calculated shifts according to Shirley's model (Refs. 21, 24).
[c] Calculated shifts according to William's model (Refs. 22, 24).

$M_{4,5}N_{4,5}O_1$ transitions are also given in Table I.

The energy splitting and relative intensities of lines can be roughly estimated theoretically by using a two-hole representation for the final state, i.e., according to the $4d^8$ configuration of silver. Wentzel's theory, which is based on the independent-particle frozen-core approximation and has been further improved by the mixed-coupling model, is found to be well suited to calculations of the $M_{4,5}N_{4,5}N_{4,5}$ Auger transitions for closed-shell configurations in this atomic-number region.[14] As has been pointed out in several papers,[15-17] the nonrelativistic intermediate-coupling theory gives larger calculated splitting than has been observed experimentally, but the calculated intensities usually agree better with experiment. In the mixed-coupling scheme, calculated relative intensities and the grouped experimental values are compared in Table II. It is seen that the agreement is very good, even for the $^{2,4}F$ lines, which in solid-state spectra have an anomalously low intensity. For a more detailed comparison between experiment and theory concerning the intensities of single lines, calculations using the open-shell treatment are needed. For the intensity ratio between the M_5 and M_4 groups, the value 1.52 is obtained experimentally, in good agreement with the statistical ratio of 1.5.

For the binding energies of the M_4 and M_5 levels, 381.55 ± 0.10 eV and 375.55 ± 0.10 eV with respect to the vacuum level were found from the measured absolute kinetic energies of the Auger lines with the aid of optical data, giving 6.0 eV for the $3d$ spin-orbit splitting. This value coincides very well with solid-state photoelectron results.[18,19] Vapor-phase and recent solid-state Auger and photoelectron results are compared in Table III. The energies from the solid phase are corrected by the work function of 4.0 eV.[6] Our results of 3.3 eV for the vapor-metal binding-energy shift and 12.1 eV for the vapor-metal Auger-energy shift include the uncertainty in the work function. The work function of Ag, depending on the method of determination, is in the range 4.0–4.44 eV.[20] In order to avoid such an uncertain contribution from the work function, we attempt to determine the shift from simultaneous measurements of the vapor and solid-phase spectra, analogously to the cases of Cd and Zn.[23] Barrie *et al.*[18] and Parry-Jones *et al.*[6] have obtained 2.4 eV for the Ag binding-energy shift from experimental solid-state and calculated vapor-phase values. The semiempirical and some calculated energy-shift values, which are also given in Table III, differ from our experimental values by more than by the uncertainty in the work function. In agreement with several earlier results, however, the ratio between the Auger shift and the photoelectron shift in metal is about a factor of 4.

CONCLUSIONS

High-resolution Auger electron spectra of free silver atoms have been measured for the first time, and the spectra have been found to reveal fine structure which can be interpreted using the known optical data for free atoms. Comparison with the corresponding solid-phase spectra reveals an essential difference in the $M_{4,5}N_{4,5}N_{4,5}$ spectrum; the solid-state spectrum is quasi-atomic according to the $4d^8$ configuration, not the $4d^85s$ configuration as the free-atom spectrum. Furthermore, the vapor-phase spectrum clearly shows that the anomalously low intensity of the high-energy components has no atomic origin, but is caused by solid-state effects.

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[1]S. Aksela, Z. Phys. 244, 268 (1971).
[2]P. J. Basset, T. E. Gallon, J. A. D. Matthew, and M. Prutton, Surf. Sci. 35, 63 (1973).
[3]J. M. Burkstrand and G. G. Tibbetts, Phys. Rev. B 15, 5481 (1977).
[4]J-M. Mariot and G. Dufour, J. Electron Spectrosc. Relat. Phenom. 13, 403 (1978).
[5]J. A. D. Matthew, J. Phys. C 11, L47 (1978).
[6]A. C. Parry-Jones, P. Weightman, and P. T. Andrews, J. Phys. C 12, 1587 (1979).
[7]R. A. Pollak, S. Kowalczyk, L. Ley, and D. A. Shirley, Phys. Rev. Lett. 29, 274 (1972).
[8]G. A. Sawatzky, Phys. Rev. Lett. 39, 504 (1977).
[9]J. Väyrynen and S. Aksela, J. Electron Spectrosc. Relat. Phenom. 16, 423 (1979).
[10]G. Johansson, J. Hedman, A. Berndtsson, M. Klasson, and R. Nilsson, J. Electron Spectrosc. Relat. Phenom. 2, 295 (1973).
[11]T. D. Thomas and R. W. Shaw, J. Electron Spectrosc. Relat. Phenom. 5, 1081 (1974).
[12]H. Benschop, Y. N. Joshi, and Th. A. M. van Kleef, Can. J. Phys. 53, 498 (1975).
[13]C. E. Moore, At. Energy Levels, Circ. 467, Vol. 3 (Nat. Bur. Stand., Washington, D.C.).
[14]H. Aksela and S. Aksela, J. Phys. B 7, 1262 (1974).
[15]H. Aksela, S. Aksela, J. S. Jen, and T. D. Thomas, Phys. Rev. A 15, 985 (1977).
[16]P. Weightman, J. Phys. C 9, 1117 (1976).
[17]H. Aksela, J. Electron Spectrosc. Relat. Phenom. 19, 371 (1980).
[18]A. Barrie and N. E. Christensen, Phys. Rev. B 14, 2442 (1976).
[19]V. Y. Yong, R. A. Gibbs, N. Winograd, and K. S. Kim, Chem. Phys. Lett. 54, 378 (1978).
[20]G. W. C. Kaye and T. H. Laby, *Tables of Physical and Chemical Constants* (Longman, London, 1973).
[21]S. P. Kowalczyk, L. Ley, F. R. McFeely, R. A. Pollak, and D. A. Shirley, Phys. Rev. B 9, 381 (1974).
[22]A. R. Williams and R. D. Lang, Phys. Rev. Lett. 40, 954 (1978).
[23]R. Kumpula, J. Väyrynen, T. Rantala, and S. Aksela, J. Phys. C 12, L809 (1979).
[24]M. Pessa, A. Vuoristo, M. Vulli, S. Aksela, J. Väyrynen, T. Rantala, and H. Aksela, Phys. Rev. B 20, 3115 (1979).