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Interpretation of the silver L x-ray spectrum*

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A new analysis of the Ag L-series x-ray spectrum has been performed, based on relaxed-orbital relativistic transition-energy calculations. Satellite energies were computed in intermediate coupling. It is found that satellites arising from LN double-hole states generally fall within the natural width of the parent diagram lines. Contrary to previous assumption, the observed high-energy satellites are due to LM double-hole states produced by L_1-$L_3M_{4,5}$ Coster-Kronig transitions and by shakeoff. The observed peak structure in the satellite spectrum is due to multiplet splitting of the initial and final double-hole states. Theoretical L_1-$L_3M_{4,5}$ transition rates based on the new Coster-Kronig energies are closer to experiment than previous results, but still are too large by a factor of $\sim$2, indicating an as yet undetected flaw in the theory.

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I. INTRODUCTION

The Ag L x-ray spectrum has recently been analyzed by McGuire,[1] on the basis of Parratt's measurements.[2] McGuire used calculated radiative, Coster-Kronig, and Auger transition rates and a hypothesis on the origin of L-series x-ray satellite lines to compute the Ag L x-ray spectrum. In order to obtain reasonable agreement between theory and experiment, McGuire proposed that L_1-$L_3M_{4,5}$ Coster-Kronig transitions are energetically impossible in Ag and that the L satellites arise from LN doubly ionized states.

A systematic *ab initio* computation of L Coster-Kronig transition energies has now been carried out by Chen *et al.*,[3] who used an improved relativistic Hartree-Fock-Slater potential model.[4] These calculations show that, while L_1-$L_2M_{4,5}$ transitions are energetically forbidden in Ag, this is not the case for L_1-$L_3M_{4,5}$ transitions, contrary to McGuire's[1] assumption: the L_1-L_3M_4 transition energy is found to be 31 eV, and the L_1-L_3M_5 energy, 39 eV.

In the light of these new Coster-Kronig energy calculations, we proceed to re-analyze the Ag L x-ray spectrum and to re-examine the origin of the satellites. In Sec. II, we compare theoretical and experimental x-ray energies. In Sec. III, we describe a calculation of the x-ray spectrum and compare the results with experiment.

II. L X-RAY ENERGIES

Silver L x-ray energies were calculated using theoretical binding energies from relaxed-orbital relativistic Hartree-Fock-Slater calculations.[4] Theoretical x-ray energies are compared in Table I with experimental results.[2,5] Agreement between calculated and measured energies is reasonably good, within

7 eV, showing that the theoretical transition-energy calculations are good to within an uncertainty of a few eV.

The same relativistic Hartree-Fock-Slater model has been used to calculate the x-ray energy shift between diagram and satellite lines (Table II). It is found that an N_i spectator hole causes the $L\alpha_{1,2}$ and $L\beta_1$ x rays to shift by $\lesssim 0.5$ eV. The measured $L\alpha_{1,2}$ and $L\beta_1$ x-ray widths[2] are ~ 2.3 eV, hence the satellites of these lines arising from LN_i double ionization will be indistinguishable from the diagram lines. Similarly, satellites arising from N-shell spectator vacancies will also coalesce with other L-M transition diagram lines, because these lines are much wider than $L\alpha_{1,2}$ and $L\beta_1$.[2] Even $L\beta_2$ (L_3-N_5) satellites produced by an extra N-shell vacancy will disappear within the natural diagram-line width: the N_i hole shifts the $L\beta_2$ transition energy by $\lesssim 5$ eV (Table II), which falls within the observed[2] x-ray width.

The $L\alpha_{1,2}$ satellites observed by Parratt[2] are shifted from 10 to 27 eV with respect to the diagram line, whence they cannot be due to LN doubly ionized atoms. An additional M_1 hole, on the other hand, shifts $L\alpha_{1,2}$ and $L\beta_1$ transitions by ~ 10 eV and $L\beta_2$ transitions by ~ 33 eV, which is of the same order of magnitude as the observed satellite shifts. We conclude that Parratt's[2] Ag L satellites arise from LM doubly ionized atoms, and not from LN atoms.

We have calculated the energies of the $L\alpha_{1,2}$ satellites that arise from $L_3M_{4,5}$-$M_{4,5}M_{4,5}$ transitions, using intermediate coupling[6] and the relativistic Hartree-Fock-Slater model.[3,4] The relativistic LS multiplet energies were obtained by following Larkins' approach.[7] Results are listed in Table III. The terms indicated in the first column of Table III are the dominant components in the wave-function expansion. The eight initial states included in

Table III are the states that can be reached by L_1-$L_3M_{4,5}$ Coster-Kronig transitions in Ag. For comparison, the observed broad satellite peaks are also included in Table III. These peaks can be interpreted as resulting from many closely bunched lines. The gross structure of the observed peaks agrees quite well with the calculation.

III. RELATIVE INTENSITIES

A. Theoretical model

In treating the relative intensities, we have followed the model of Krause *et al.*[8] We take into account (a) the initial L-hole population N_1, N_2, N_3 and shakeoff probabilities P_1, P_2, P_3; (b) shifting of the L-shell holes by Coster-Kronig transitions, with yields f_{12}, f_{13}, f_{23}; (c) distinction between satellite lines that arise from LM and LN double-hole states.

In order to separate the LM and LN double-hole states, we express the shakeoff probabilities and Coster-Kronig yields as

$$P_i = P_{iM} + P_{iN} \tag{1}$$

and

$$f_{ij} = f_{ijM} + f_{ijN},$$

where P_{iX} is the X-shell shakeoff probability during i-shell ionization, and f_{ijX} is the Coster-Kronig yield leading to the jX double-hole final state.

The number of single-hole states left after Coster-Kronig transitions have taken place is

$$\begin{aligned} n_1(L_1) &= (1-P_1)(1-f_{12}-f_{13})N_1 \\ n_2(L_2) &= (1-P_2)(1-f_{23})N_2 \\ n_3(L_3) &= (1-P_3)N_3. \end{aligned} \tag{3}$$

The number of double-hole states is

$$
\begin{aligned}
n_1(L_1M) &= P_{1M}N_1(1-f_{12}-f_{13}) \\
n_1(L_1N) &= P_{1N}N_1(1-f_{12}-f_{13}) \\
n_2(L_2M) &= P_{2M}N_2(1-f_{23}) \\
n_2(L_2N) &= P_{2N}N_2(1-f_{23}) + f_{12}(1-P_1)N_1 \\
n_3(L_3M) &= P_{3M}N_3 + f_{13M}(1-P_1)N_1 \\
n_3(L_3N) &= P_{3N}N_3 + f_{23}(1-P_2)N_2 + f_{13N}(1-P_1)N_1 .
\end{aligned}
\tag{4}
$$

Here, we have used the fact that $f_{12}=f_{12N}$ and $f_{23}=f_{23N}$.

We neglect the contribution due to triple-hole states.

In Sec. II we concluded that the satellites arising from LN double-hole states are not resolved from diagram lines, and that the observed satellite structure is due to LM doubly ionized atoms. The number of hole states producing x rays observed as diagram lines therefore is

$$n_i' = n_i(L_i) + n_i(L_iN) \tag{5}$$

and the apparent diagram-line intensity is

$$I(L_iX) = n_i'[R(L_iX)/T_i'], \tag{6}$$

where $R(L_iX)$ is the radiative transition rate filling L_i holes with X-shell electrons, and T_i' is the total transition rate, excluding Coster-Kronig transitions. Similar expressions can be written for the satellite intensities.

B. Numerical calculations

The Ag L_1 Auger and Coster-Kronig transitions were recalculated using Herman-Skillman[9,10] wave functions. The L_1-$L_3M_{4,5}$ Coster-Kronig transitions were calculated in intermediate coupling with the newly available transition energies.[3,10] In Table IV we list the Coster-Kronig yields and L_1 widths for two cases: (i) the full L_1-$L_3M_{4,5}$ transition rate is included, (ii) the calculated L_1-$L_3M_{4,5}$ transition rate is reduced by a factor of 1/2.5. The Coster-Kronig yield f_{23} is taken to be 0.143.[11]

The experimental L_1 level width is found to be 3.95 eV by subtracting the measured $M_{2,3}$ level width[12] of 2.3 eV from the measured $L\beta_{3,4}$ (L_1-$M_{2,3}$) x-ray width[2] of 6.25 eV. It is seen in Table IV that the "case (ii)" L_1-level width agrees well with experiment, while the "case (i)" width that includes the full calculated L_1-$L_3M_{4,5}$ transition rate is too large, even though it represents an improvement over previous theoretical calculations.[13,14]

The initial L-shell hole distribution is taken to be[1] N_1:N_2:N_3 = 1.00:1.48:2.83 assuming an incident Kramers spectrum. We follow the procedure of Krause et al.[8] to find the Ag shakeoff probabilities P_i=0.18, P_{iM}=0.02, and P_{iN}=0.16, with i=1,2,3. The final hole distributions after Coster-Kronig transitions, calculated with the above parameters and results, are listed in Table V. The relative intensities (normalized to the apparent L_3-M_5 diagram line) are obtained by combining the final hole populations (Table V) and the normalized radiative transition rates $R(L_iX)/T_i'$ given by McGuire.[1] Results are listed in Table VI. For comparison, the experimental relative intensities[2] are also included in Table VI. Case (i) leads to an underestimate of the L_1 x-ray intensity and an overestimate of the strong $S(L_3M_{4,5})$ satellite intensity by a factor of 2. Case (ii) leads to very good overall agreement with experiment, except for underestimating the weak satellite lines $S(L_2M_4)$ and $S(L_2N_4)$ by a factor of 2. This is probably due to an error in the shakeoff probability P_{2M}, since these satellites are produced by that shakeoff process. If P_{2M} is taken to be 3% instead of 2% as used in the present calculation, then the $S(L_2M_4)$ and $S(L_2N_4)$ satellite intensities are increased by a factor of 1.5, bringing the result into much better agreement with observation.

IV. CONCLUSION

This analysis of the Ag L-series x-ray spectrum leads to several significant conclusions.

Satellites arising from LN double-hole states are not, in general, resolvable from the parent diagram lines. The observed high-energy satellite lines are due to LM doubly ionized states created by L_1-$L_3M_{4,5}$ Coster-Kronig transitions and by shakeoff. The observed peak structure in the satellite spectrum is due to the multiplet splitting of the initial and final double-hole states.

The L_1-$L_3M_{4,5}$ Coster-Kronig transitions are energetically possible in Ag. A L_1-$L_3M_{4,5}$ transition-rate calculation using newly available Coster-Kronig energies has reduced the discrepancy between theory and experiment, but the theoretical result still is too large by a factor of $\sim$2. It appears that a reexamination of the theory of L_1 Coster-Kronig transitions is indicated.

References

[1] E. J. McGuire, Phys. Rev. 5, 2313 (1972).

[2] L. G. Parratt, Phys. Rev. 54, 99 (1938).

[3] M. H. Chen, B. Crasemann, K.-N. Huang, M. Aoyagi, [illegible] H. Mark, At. Data Nucl. Data Tables 19, 0000 (1977).

[4] K.-N. Huang, M. Aoyagi, M. H. Chen, B. Crasemann, and H. Mark, At. Data Nucl. Data Tables 18, 243 (1976).

[5] J. A. Bearden, Rev. Mod. Phys. 39, 78 (1967).

[6] E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra (Cambridge U.P., Cambridge, England, 1953).

[7] F. P. Larkins, J. Phys. B: Atom. Molec. Phys. 9, 37 (1976).

[8] M. O. Krause, F. Wuilleumier, and C. W. Nestor, Jr., Phys. Rev. A 6, 871 (1972).

[9] F. Herman and S. Skillman, Atomic Structure Calculations (Prentice-Hall, Englewood Cliffs, N.J., 1963).

[10] M. H. Chen, B. Crasemann, K.-N. Huang, M. Aoyagi, and H. Mark, (unpublished).

[11] M. H. Chen and B. Crasemann, in Proceedings of the International Conference on Inner-Shell Ionization Phenomena and Future Applications, ed. by R. W. Fink, S. T. Manson, J. M. Palms, and P. Venugopala Rao. U.S. Atomic Energy Commission Report No. CONF-720404 (unpublished), p. 43.

[12] L. I Yin, I. Adler, T. Tsang, M. H. Chen, D. A. Ringers, and B. Crasemann, Phys. Rev. A 9, 1070 (1974).

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

[14] B. Crasemann, M. H. Chen, and V. O. Kostroun, Phys. Rev. A 4, 2161 (1971).

TABLE I. Silver L x-ray energies (in eV).

Transition	Energy: Experiment, Parratt[a]	Energy: Experiment, Bearden[b]	Energy: Theory
L_1-N_3	3749.7	3749.8	3752.2
L_1-N_2	3743.1	3743.2	3747.2
L_2-N_4	3519.5		3521.0
L_1-M_5	3440.3	3439.2	3445.9
L_1-M_4	3432.2	3432.9	3439.9
L_2-N_1	3428.6	3428.3	3421.4
L_3-N_5	3348.0		3348.8
L_3-N_1	3256.0	3256.0	3248.6
L_1-M_3	3234.7	3234.5	3238.2
L_1-M_2	3203.6	3203.5	3207.0
L_2-M_4	3151.0	3150.9	3151.7
L_3-M_5	2984.4	2984.3	2985.0
L_3-M_4	2978.3	2978.2	2978.9
L_2-M_1	2805.5	2806.1	2803.4
L_3-M_1	2633.8	2633.7	2630.6

[a] Ref. 2.

[b] Ref. 5.

TABLE II. Energy shifts (in eV) of x-ray transitions to the Ag L shell, caused by the presence of an additional vacancy in the M or N shell. Results from relativistic Hartree-Fock-Slater calculations.

Diagram line	State of spectator vacancy									
	M_1	M_2	M_3	M_4	M_5	N_1	N_2	N_3	N_4	N_5
L_2-M_4	-	-	-	-	10.7	0.5	0.4	0.7	0.4	0.2
L_3-M_4	-	-	-	-	9.0	0.5	-	0.5	-	0.2
L_3-M_5	10.2	11.4	11.7	11.1	9.6	0.5	0.7	0.5	0.2	0.3
L_3-N_5	30.2	33.0	30.0	34.5	32.8	5.2	4.6	5.0	2.1	1.9

TABLE III. Energies (in eV) of $L_3M_{4,5}$-$M_{4,5}M_{4,5}$ $L\alpha_{1,2}$ satellites, calculated in intermediate coupling.

Transition	Energy: Theory	Energy: Experiment[a]
$^3P_1 \rightarrow {}^1S_0$	2977	Mixed with L_3-M_4 diagram line at 2978.3 eV
$^1P_1 \rightarrow {}^1S_0$	2979	
$^1D_2 \rightarrow {}^1D_2$	2981	
$^1D_2 \rightarrow {}^3P_1$	2984	Mixed with L_3-M_5 diagram line at 2984.4 eV
$^3D_3 \rightarrow {}^1D_2$	2985	
$^3D_3 \rightarrow {}^1G_4$	2986	
$^3F_4 \rightarrow {}^3F_3$	2989	2992
$^3D_2 \rightarrow {}^1D_2$	2990	
$^3D_3 \rightarrow {}^3P_2$	2991	
$^3P_1 \rightarrow {}^1D_2$	2991	
$^1D_2 \rightarrow {}^3F_3$	2991	
$^1D_2 \rightarrow {}^3F_2$	2991	
$^3D_2 \rightarrow {}^3P_1$	2992	

TABLE III continued

Transition	Energy	
	Theory	Experiment
${}^3F_4 \rightarrow {}^3F_4$	2994	2995
${}^1P_1 \rightarrow {}^1D_2$	2994	
${}^3P_1 \rightarrow {}^3P_1$	2994	
${}^1F_3 \rightarrow {}^1D_2$	2995	
${}^3D_3 \rightarrow {}^3F_2$	2995	
${}^3D_3 \rightarrow {}^3F_3$	2995	
${}^3D_2 \rightarrow {}^3P_2$	2995	
${}^3P_1 \rightarrow {}^3P_0$	2995	
${}^3P_0 \rightarrow {}^3P_1$	2996	
${}^1F_3 \rightarrow {}^1G_4$	2996	
${}^1P_1 \rightarrow {}^3P_1$	2997	2999
${}^3P_1 \rightarrow {}^3P_2$	2997	
${}^1P_1 \rightarrow {}^3P_0$	2998	
${}^3D_2 \rightarrow {}^3F_3$	2999	
${}^3D_3 \rightarrow {}^3F_4$	3000	
${}^3D_2 \rightarrow {}^3F_2$	3000	
${}^1P_1 \rightarrow {}^3P_2$	3000	
${}^1F_3 \rightarrow {}^3P_2$	3001	

TABLE III continued

Transition	Energy	
	Theory	Experiment
$^3P_1 \rightarrow {}^3F_2$	3002	
$^1P_1 \rightarrow {}^3F_2$	3005	3003
$^1F_3 \rightarrow {}^3F_3$	3005	
$^1F_3 \rightarrow {}^3F_2$	3006	3009
$^1F_3 \rightarrow {}^3F_4$	3010	

[a]Ref. 2.

TABLE IV. Silver L_1-level width $\Gamma(L_1)$ and Coster-Kronig yields.

Case	f_{12}	f_{13M}	f_{13N}	f_{13}	$\Gamma(L_1)$ (ev)
(i)	0.067	0.617	0.113	0.730	6.17
(ii)	0.107	0.392	0.179	0.571	3.89

TABLE V. Final hole populations after Coster-Kronig transitions. Case (i): using full $L_1-L_3M_{4,5}$ transition rate $\Gamma(L_1-L_3M_{4,5})$. Case (ii): using $\Gamma(L_1-L_3M_{4,5})/2.5$.

n	Case (i)	Case (ii)
$n_1(L_1)$	0.166	0.264
$n_2(L_2)$	1.040	1.040
$n_3(L_3)$	2.321	2.321
$n_1(L_1M)$	0.006	0.006
$n_1(L_1N)$	0.052	0.052
$n_2(L_2M)$	0.0255	0.0255
$n_2(L_2N)$	0.259	0.291
$n_3(L_3M)$	0.563	0.378
$n_3(L_3N)$	0.719	0.773

TABLE VI. Relative intensities of Ag L-series x-ray lines.

Transition	Calculated relative intensity		Experiment[a]
	Case (i)	Case (ii)	
L_1-M_2	2.62	3.73	3.9
M_3	4.33	6.17	7.2
M_4	0.03	0.04	0.04
M_5	0.04	0.06	0.07
N_2	0.49	0.69	0.66
N_3	0.81	1.15	1.04
L_2-M_1	1.42	1.43	2.0
M_4	48.6	49.0	49.1
N_1	0.28	0.28	0.28
N_4	5.02	5.05	4.36
$S(L_2M_4)$	0.96	0.94	2.06
$S(L_2N_4)$	0.10	0.10	0.16
L_3-M_1	4.14	4.14	4.4
M_4	11.3	11.3	8.61
M_5	100	100	100
N_1	0.80	0.80	0.56
N_5	10.1	10.1	11.9
$S(L_3M_{4,5})$	20.6	13.6	11.7
$S(L_3N_5)$	1.87	1.36	1.78

[a]Ref. 2.