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Argon *KLL* Auger Spectrum: A Test of Theory*

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The relative intensities of the argon *KLL* Auger transitions, measured with an accuracy of better than 10%, are found to agree well with recent theoretical predictions based on a theory that uses intermediate coupling, configuration interaction, and good wave functions and level energies. Large widths for $KL_1L_{1,2,3}$ lines suggest high Coster-Kronig transition rates for double-hole configurations L_1L_1 and $L_1L_{2,3}$.

With the introduction of configuration interaction into the intermediate-coupling theory, Asaad[1] and Mehlhorn and Asaad[2] were able to reduce substantially the discrepancy that had existed between experiment and theory for the *KLL* Auger spectrum. Certain discrepancies, however, still remained in the range of elements $12 \lesssim Z \lesssim 35$, where correlation and relativistic effects are expected to be weak, and still persisted even when accurate wave functions and level energies were employed in the calculation.[3] This situation has been unsatisfactory both conceptually and practically because theory appeared unable to predict the branching ratios of the simplest Auger spectrum, the *KLL* spectrum. The suspicion that the source of discrepancy might lie with experiment was underlined recently when the *KLL* intensities of sodium[4] and magnesium[5] vapors were shown to differ considerably from those of solid compounds of these elements but little from the predictions based on a presumably accurate model.[3] Certainty about the validity of a model over a wide range is important since we must often depend on theoretical predictions in more complex cases, such as the Auger spectra produced in ion-atom collisions, and in applications in which Auger spectra serve to characterize chemical and solid-state systems. It is the purpose of this study to test theory at slightly higher Z using argon. Its free-atom spectrum is directly comparable with theory, and the analysis of the measured spectrum is aided by the high resolution obtainable and the possibility of interpreting and assessing extraneous structure.[6]

Argon was bombarded with electrons of 6- and 10-keV energy at a pressure of about 0.5 Pa and the Auger electrons were dispersed in a 15-cm radius, double-focusing electrostatic analyzer[6] set to a resolution of either $\Delta E/E = 0.1\%$ or 0.05%. Electrons were counted individually and spectra were recorded automatically by repetitive scanning.[7] The overall *KLL* spectrum is displayed in Fig. 1 and a detailed view of the $KL_2L_3(^1D_2)$ and $KL_3L_3(^3P_{0,2})$ lines is given in Fig. 2. Diagram lines and associated low-energy tails are indicated in both figures. Contours of the lines are convolutions of the instrumental function, which in auxiliary experiments was found to be Gaussian over more than 2 orders of magnitude, and the Lorentzian function representative of the Auger lines, whose widths were adjusted to yield the best fit to the data.

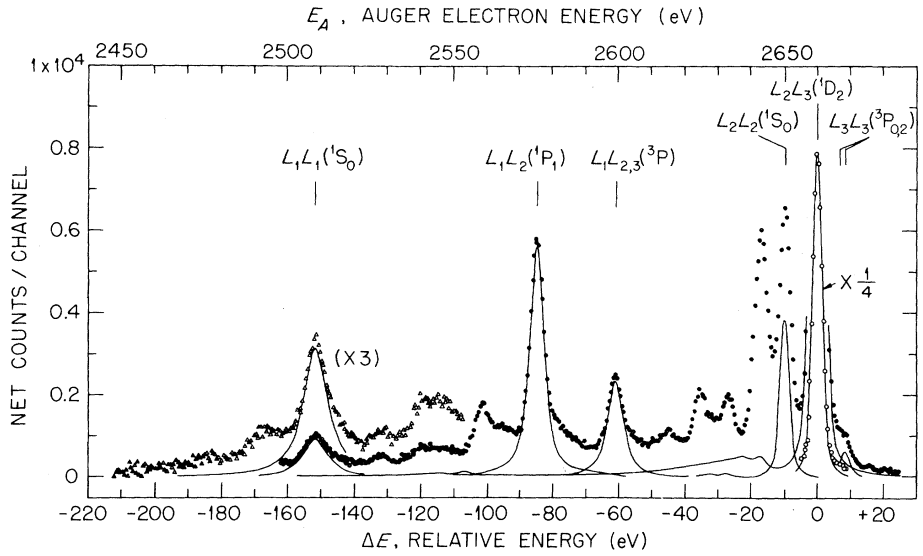

FIG. 1. Argon *KLL* Auger spectrum excited by 6-keV electrons, and recorded with $\Delta E/E = 0.1\%$. Portion designated by open triangles was recorded separately. Diagram lines are shown with their associated energy-loss spectra that were measured in auxiliary runs. A smooth background amounting to 3% of the major line was subtracted.

Table I summarizes the results averaged from four runs. Intensities are area values and fully corrected.[6] Errors quoted for the widths are estimated and errors associated with intensities reflect the possible variation of the widths and uncertainties in the corrections made for background, overlap and interference of satellites, inelastic and elastic scattering losses, continuous

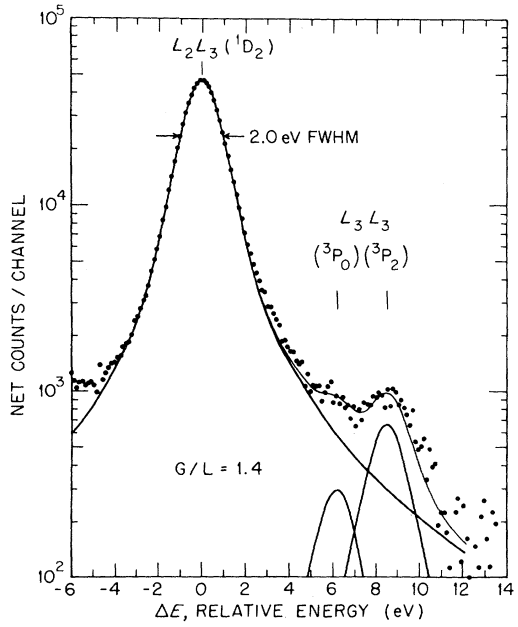

FIG. 2. Decomposition of spectrum near $\Delta E = 0$ eV into three lines. Line contours are calculated Voigt functions; thin line is the sum of all lines. Resolution $\Delta E/E = 0.052(2)\%$. G/L is the ratio of the Gaussian and Lorentzian widths. Additional intensity near $\Delta E = 3$ eV is probably due to a *K-LL* transition during which the 1*s* electron initially excited into the 3*d* or 4*p* level remains in this state (Ref. 6).

TABLE I. Linewidths Γ (full width at half-maximum) and relative intensities *I* of argon *KLL* Auger lines and groups. Intensity normalized to 100.0. CI is configuration interaction.

Line	Γ (eV)	*I*(expt) This work	*I*(theor) [a] With CI	Without CI
$KL_1L_1(^1S_0)$	7.5(9)	5.1(2)	5.6	8.0
$KL_1L_2(^1P_1)$	3.6(3)	18.4(5)	20.6	20.6
$KL_1L_{2,3}(^3P)$	3.9(4) [b]	7.7(4)	5.5	5.5
$KL_2L_2(^1S_0)$	1.0(1) [c]	7.5(7)	7.1	4.7
$KL_2L_3(^1D_2)$	1.0(1)	59.9(2)	60.0	60.0
$KL_3L_3(^3P_0)$	1.0(1) [c]	0.4(2) [d]	0.1	0.1
$KL_3L_3(^3P_2)$	1.0(1) [c]	1.0(2) [d]	1.1	1.1
2*s*2*s*	···	5.1(2)	5.6	8.0
2*s*2*p*	···	26.1(7)	26.1	26.1
2*p*2*p*	···	68.8(8)	68.2	65.9

[a] Ref. 3.
[b] Broader than ($^1P_1$) line because of multiplet.
[c] In accordance with $KL_2L_3(^1D_2)$ linewidth.
[d] The error includes a possible satellite interference.

double-Auger spectrum, and detector response. Details of the analysis, including that of the satellites, will be given elsewhere[8]; here it may suffice to state that most of the corrections were small. The $KL_2L_2(^1S_0)$ line was an exception since it needed to be separated from the strong satellite that comes from $3p \rightarrow 3d$ and $3p \rightarrow np$, $n \geq 4$, transitions concomitant with $1s \rightarrow \epsilon p$ in the initial ionization event.[6,9] The corresponding $\epsilon l, nl'$ satellite in the ArK (Ti$K\alpha$) photoelectron spectrum provided the intensity data for correction, which intensity was compatible with the intensity of the same type of satellite accompanying the $KL_1L_2(^1P_1)$ diagram line.

As Table I indicates, Chen and Crasemann's calculation[3] within the intermediate-coupling, configuration-interaction model predicts the spectral intensities satisfactorily. Similarly, Asaad's[1] original calculation gives satisfactory agreement for the line-group intensities when accurate values for the level energies are used.[2] By contrast, neglect of configuration interaction leads to poor accord with experiment (Table I, column 5) for transitions to states that can interact; and if poor choices are made for wave functions, level energies, or coupling schemes, the discrepancies increase throughout, as can be noted by consulting any of a number of reviews.[10]

The width of $KL_2L_3(^1D_2)$ corresponds to the sum of the single-hole level widths of the levels involved,[11] and shows that $\Gamma(1s) = 0.67$ eV is dominant. However, widths of lines involving the L_1 level are considerably larger than the sum of individual level widths, implying an enhanced Coster-Kronig transition rate for the double-hole states L_1L_1 and $L_1L_{2,3}$. No comparison can be made with theory since Coster-Kronig rates for double-hole states have not been calculated to date. The only calculation for any double-hole state seems to be that of Bhalla, Folland, and Hein[12] for the KK defect in neon.

As a major result of this work, we find present theory adequate to predict the spectral intensity distribution for the argon KLL spectrum except perhaps for the intensities of $KL_1L_{2,3}(^3P)$ and $KL_3L_3(^3P_0)$ which are underestimated. This conclusion should also hold for KLL spectra of other elements near $Z = 18$. For neon, in which the final states of the transitions lie in the outermost shell, Kelly[13] has shown that correlation effects other than those represented by the mixing of the $L_1L_1(^1S_0)$ and $L_2L_2(^1S_0)$ configurations to be important. For heavier elements, when relativistic effects become significant, it might be expected that the use of relativistic Hartree-Fock wave functions, with which Desclaux *et al.*[14] achieved good agreement with experiment for the *KLL energies* of uranium, may prove equally good for the calculation of *intensities*. Differences between experiment and theory near $Z = 15$, and possibly in other ranges, must be attributed to chemical and solid-state effects, as pointed out previously,[4,5] and in some cases to an analysis procedure in which satellite and the various background contributions could not be properly taken into consideration. Although separation of diagram lines from satellite lines was possible in the present work, an isolation of the diagram lines can only be accomplished by removing the satellites under selective-excitation conditions. Synchrotron radiation can provide such conditions, and the multiple-excitation satellites can be eliminated by excitation just above the K-level energy, leaving for study the diagram lines and the double-Auger structure.

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