$L_{2,3}$ and $M_{2,3}$ level widths and fluorescence yields of copper

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Subshell-resolved M and L level widths and fluorescence yields are derived from high-resolution $K\alpha_{1,2}$ and $K\beta_{1,3}$ x-ray emission spectra of copper. As the contribution of spectator hole satellites was removed from the spectra by computer fits based on an *ab initio* calculated transition array, the widths and yields obtained pertain to pure one-hole states and single-electron diagram transitions. A considerable improvement in the agreement with theoretical widths and yields is observed for all levels studied. A significant contribution of Coster-Kronig transitions to the L_2 level width is confirmed. Individual M_2 and M_3 widths and yields are derived from x-ray spectra. They are in good agreement with recent theoretical Dirac-Hartree-Slater calculations, but the widths are consistently larger than those measured for the same subshells by photoelectron spectroscopy. $3d$ spectator holes are found to broaden the widths of the corresponding x-ray emission lines by up to a few tenths of an eV.

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I. INTRODUCTION

Although important for both basic science and applications, reliable values of fluorescence yields ω_i, where i denotes an atomic shell or subshell, are scarce [1]. Most of the experimentally derived yields have been obtained by measuring the intensities of the relevant emission lines. These measurements are usually done using low-resolution solid state detectors, which provide only yields averaged over all subshells of a given shell, $\overline{\omega_i}$. Measurements of individual subshell yields such as ω_{L_2} or ω_{L_3} require the use of high-resolution crystal monochromator techniques. As all absolute intensity determinations, these become increasingly difficult and inaccurate for outer atomic levels where the fluorescence yields are extremely low. Furthermore, lifetime and nonlifetime broadening of closely spaced transitions results in strong overlap of the lines, which severely limits the ability to determine the individual subshell contributions. For the iron group transition elements the scarcity of data is further compounded by the deviations of the yields from the general trends in the Periodic Table, making semiempirical extrapolations from higher- and lower-Z elements even more inaccurate [2,3].

An alternative to intensity measurements is the derivation of the yields from the level widths, which, in turn, are obtained from either the measured natural widths of the x-ray emission lines (XES) or x-ray induced photoelectron spectroscopy (XPS). XES, the method used here, requires precision line-shape measurements and an accurate knowledge of, and correction for, the finite instrumental resolution. Moreover, the Cu$K\alpha$ and Cu$K\beta$ spectra studied here include strongly overlapping emission lines as well as contributions from multielectronic, spectator-hole transitions [4]. Thus, a careful line-shape analysis is required to separate out the individual widths of each of the several transitions contributing to the spectra.

We have recently completed a detailed study [4] of the Cu$K\alpha$ and Cu$K\beta$ line shapes, in which the same well characterized and optimized double crystal spectrometer [5] was employed to measure both spectra. Using atomic *ab initio* Dirac-Fock calculations, we were able to separate out the contributions due to the diagram $1s \rightarrow np$ (where $n=2,3$ for $K\alpha$ and $K\beta$, respectively) and the $\overline{3d}$ spectator hole $1s\overline{3d} \rightarrow np\overline{3d}$ transitions, the only ones contributing significantly to the line shape (an underline denotes a vacancy state in this paper). These measurements are used here to derive experimental values for the total widths Γ_i and the fluorescence yields ω_i of the individual L_2, L_3, M_2, and M_3 subshells. The elimination of the contribution of the spectator-hole transitions results in a considerable improvement in the agreement of the present L level widths and yields with theory, as compared with the few existing previous measurements. These are, to the best of our knowledge, the only x-ray determined diagram-transition-only level widths and yields for all levels studied.

The experimental methods employed are described in the next two sections, with the third detailing and discussing the results obtained for the various subshells. Conclusions and suggestions for future work are presented in the last section.

II. METHOD

The creation of a vacancy in an inner atomic shell leaves the atom with an excess energy. The deexcitation that follows is not immediate, as the vacancy has a finite lifetime τ_i, where i indicates the initial state. This corresponds, through the uncertainty principle, to a finite width Γ_i of the energy level of the excited atom. The deexcitation can proceed either by a radiative (R) process (the emission of an x-ray photon) or nonradiative (NR) Auger or Coster-Kronig processes (denote A and CK, respectively, in the following). Assuming these decay modes to be independent , the total level width will be given by $\Gamma_i = \Gamma^R + \Gamma^A + \Gamma^{CK}$, where Γ^R, Γ^A, and Γ^{CK} denote the partial widths due to the three processes mentioned. The fluorescence yield of the level is

then defined as $\omega_i=\Gamma^R/\Gamma_i$ and the two nonradiative yields are defined similarly [1,6]. The deexcitation processes leave the atom in a final state having a vacancy in a higher shell. This has its own lifetime τ_f and width Γ_f. The width of an x-ray emission line will be the sum of these two widths $\Gamma_x=\Gamma_i+\Gamma_f$. All the diagram transitions studied here have an initial state with a single vacancy in the K shell, and a final state with a single vacancy in one of either the L or the M subshells. Since the total width of the K level, Γ_K, is known to a rather high accuracy ($\lesssim 3\%$) (see below), the measured emission linewidths can be used to obtain the total widths of the final state levels. Specifically,

$$\Gamma_{L_3}=\Gamma_{K\alpha_1}-\Gamma_K, \quad \Gamma_{L_2}=\Gamma_{K\alpha_2}-\Gamma_K \tag{1}$$

and

$$\Gamma_{M_3}=\Gamma_{K\beta_1}-\Gamma_K, \quad \Gamma_{M_2}=\Gamma_{K\beta_3}-\Gamma_K. \tag{2}$$

Using published radiative widths, Γ_f^R, it is now possible to obtain the corresponding fluorescence yields as

$$\omega_{L_3}=\Gamma^R_{L_3}/\Gamma_{L_3}, \quad \omega_{L_2}=\Gamma^R_{L_2}/\Gamma_{L_2} \tag{3}$$

and

$$\omega_{M_3}=\Gamma^R_{M_3}/\Gamma_{M_3}, \quad \omega_{M_2}=\Gamma^R_{M_2}/\Gamma_{M_2}. \tag{4}$$

This approach has several advantages. As shown by Härtwig *et al.* [5], a well characterized spectrometer can be optimized so that the distortions in the line shape due to the finite resolution are virtually eliminated. Consequently the widths and eventual yields derived from the measurements are more accurate. Also, for strongly overlapping emission lines, such as the $K\beta$ spectrum, it is virtually impossible to separate out the contributions from individual transitions by intensity measurements only. Using the present method, however, a detailed line-shape analysis based on *ab initio* transition array calculations is possible, yielding the widths due to the individual transitions [4]. Thus, an accurate determination of the widths and yields due to pure diagram transitions is possible.

III. EXPERIMENT

The measurements and the data analysis were discussed in detail in Refs. [5] and [4], and hence only a brief description will be given here.

A double crystal spectrometer was employed in the measurements, based on a commercial DTS two-circle goniometer [7]. The radiation source was a commercial sealed-tube generator, operated at 40 kV and 45 mA. The diffractometer employed symmetric silicon (333) reflections in both crystals for all spectra. The (444) reflection was out of the range of the spectrometer. The tube was mounted nearly perpendicular to the diffraction plane, with an input side collimator of length 560 mm. Two pairs of slits of widths of 1.0 mm (focus side) and 10 mm (sample side) and equal heights of 0.4 mm (for the Cu$K\alpha$ radiation) or 0.8 mm (for the Cu$K\beta$ radiation) were used to define the beams' divergence. The optimization study [5] showed that in this configuration the transmission function of the spectrometer was so narrow that no correction of the measured spectra for window function effects was necessary.

To account for the line shape in detail, we have carried out *ab initio* relativistic Dirac-Fock (DF) atomic structure calculations [8] for transitions involving up to two-vacancy states, of the forms $1s\rightarrow np$ and $1s3l\rightarrow np3l$, where $n=2,3$ for $K\alpha$ and $K\beta$, respectively, and $l=s$, p, or d. The first of these are the diagram transitions and the second are the same transitions in the presence of a single l-level spectator hole. The transition energies were calculated assuming full atomic relaxation, which was found to be important in several previous studies [9]. The resultant multiplets were then fitted to the line shape in different combinations with the diagram lines. Each line was represented in the fits by a Lorentzian line shape, and physical insight and plausible assumptions were employed to restrict the number of fit variables to a value supportable by the structure observed in the measured spectrum. Further details of the experiment, calculations, and fits are given in Ref. [4].

The results show unambiguously that in addition to the diagram lines only the $3d$-spectator transitions contribute significantly to the line shape. The fit yielded the linewidths Γ_x of the various diagram and $3d$-spectator transitions, which are used here in Eqs. (1)–(4) to obtain the widths and fluorescence yields of the various levels.

IV. RESULTS AND DISCUSSION

A. *K*-level widths

Since the results derived from the x-ray linewidths measured here depend sensitively on the values adopted for the K-level width in Eqs. (1)–(4) above, we first discuss the reliability and accuracy of the Γ_K values available in the literature.

Several factors conspire to make the determination of the K level width and fluorescence yield more accurate than that of higher levels [1,6,10]. First, the j splitting of the x-ray emission lines is much larger than the linewidth. Thus, the lines are well separated and individual widths can easily be determined. Second, CK transitions are not possible, so that the only NR process that needs to be considered is the Auger process. Third, the fluorescence yield is almost equal to the Auger yield. By contrast, the fluorescence yields for the next level, L, are two orders of magnitude smaller. Recent measurements of the K yield [11,12] agree to within their experimental errors and have an average error of only [1] 1.6%: $\omega_K^{\text{meas}}=0.442\pm 0.007$. Slightly worse agreement is obtained for theoretical [13–15] and semiempirical [6] yields which range from 0.4678 for the nonrelativistic Hartree-Slater calculations of Walters and Bhalla [13] to the widely used semiempirical 0.440 of Krause [6].

Unfortunately, no direct measurement of the K level width by x-ray photoemission spectroscopy (XPS) is available in the literature. The widths obtained in the theoretical and semiempirical studies mentioned above, which range from [14] $\Gamma_K=1.437$ eV to [6] $\Gamma_K=1.55$ eV, still agree to within $\pm 3\%$. The Γ_K level widths employed here and listed in Table I were obtained from the extensive relativistic Dirac-Hartree-Slater (RDHS) calculations of Chen and

TABLE I. $L_{2,3}$ level widths (in eV) in copper. The measured $K\alpha_{1,2}$ widths $\Gamma^{meas}_{K\alpha_{1,2}}$ were taken from Ref. [4].

				Theory			Experiment				
Level	Present $\Gamma^{meas}_{K\alpha_{1,2}}$	Γ_K	Present Γ_{L_i}	CS [a]	CCM [b]	YACC [c]	KO [d]	CEMAUK [e]	YACC [c]	NMLA [f]	FA [g]
						Raw					
L_3 $(K\alpha_1)$	2.29(2)	1.437 [a]	0.853	0.614	0.625	0.551	0.56	0.73(3)	0.54(3)	0.41	0.73
		1.48 [h]	0.810								
		1.55 [d]	0.740								
L_2 $(K\alpha_2)$	3.34(6)	1.437	1.903	0.599	0.631	0.520 [i]	0.62	1.36(3)	0.98(4)	1.09	1.17
		1.48	1.860			0.838 [j]					
		1.55	1.790			1.442 [k]					
						DF					
L_3 $(K\alpha_1)$	2.09	1.437	0.653	0.614	0.625	0.551	0.56	0.73(3)	0.54(3)	0.41	0.73
		1.48	0.610								
		1.55	0.54								
L_2 $(K\alpha_2)$	2.69	1.437	1.253	0.599	0.631	0.520 [i]	0.62	1.36(3)	0.98(4)	1.09	1.17
		1.48	1.210			0.838 [j]					
		1.55	1.140			1.442 [k]					

[a]Reference [14].
[b]Reference [19].
[c]Reference [25].
[d]Reference [16].
[e]Reference [22].
[f]Reference [23].
[g]Reference [21].
[h]Reference [13].
[i]Assuming that Coster-Kronig L_2-L_3M_4,L_2-L_3M_5 are both not possible.
[j]Assuming that Coster-Kronig L_2-L_3M_4 is the only one possible.
[k]Assuming that both L_2 Coster-Kronig are possible.

Scofield [14], the nonrelativistic Hartree-Slater (HS) calculations of Walters and Bhalla [13], and the widely used semiempirical (SE) tabulation of Krause and Oliver [6,16]. While it is difficult to estimate the accuracy of the theoretical *ab initio* calculations, the accuracy claimed for the SE widths is $\sim 5\%$, which is consistent with, but slightly larger than, the $\sim 3\%$ difference between the two theoretical values, both of which are lower by a few percent than the semiempirical value. Based on a careful Cu$K\alpha_1$ linewidth study and using the XPS-measured Cu $2p_{3/2}$ width [17], Heinonen *et al.* [18] concluded that Γ_K cannot be higher than 1.5 eV, i.e., lower than the SE value. Trehan and co-workers [2,3] also find the SE Γ_K values slightly too high for the iron group and neighboring elements, and the RDHS values of Chen, Crasemann, and Mark [19] to give the best agreeement with their fluorescence yield measurements. The nonrelativistic HS calculations were found [20,12] to neglect the K-LM Auger transitions, causing a slight increase in the calculated K-shell fluorescence yield. All issues considered, the RDHS Γ_K value (taken here from the extensive tabulation of Chen and Scofield [14]) is probably the most realistic. The same conclusion concerning the L widths was also obtained in the XPS study of Fuggle and Alvarado [21]. As we show below, the RDHS values are found here to yield an excellent agreement with our L and M width results.

B. $L_{2,3}$ levels

1. Level widths

Table I presents the results obtained for the L_2 and L_3 level widths for various values of the K-level width along with results obtained from theory and previous measurements. The values denoted "raw" were derived directly from the as-measured emission lines. They are taken from Table I in Ref. [4], and shown there to be in good agreement with previous measurements. However, these lines were shown [4] to include $\sim 25\%$ contributions from $3d$-spectator transitions. The values denoted by "DF," taken from Table III in Ref. [4], are the widths of the Lorentzians representing the pure diagram transitions in the fit which takes the contribution of the $3d$-specator transitions explicitly into account, based on our DF calculated spectra. Since the widths listed under DF are those of the pure diagram transitions, with the contribution of the multielectronic transitions separated out, they are expected to be in better agreement with the theoretical values which also take into account the one-electron diagram transition only.

Note first that the DF x-ray linewidths $\Gamma^{meas}_{K\alpha_{1,2}}$ are systematically smaller than those of the raw data. This is because the contribution of the spectator transitions is spread out over a region larger than the width of each line [4], and thus

provides a wide "pedestal" on top of which the narrow Lorentzian contributions of the diagram transitions are added. This, in turn, shifts the half-height points lower on the Lorentzians, with a consequent increase in the apparent width. Comparing the resultant raw Γ_{L_3} values in the fourth column of Table I with the theoretical results indeed shows it to be consistently too high. On removing the influence of the spectator transition the agreement is considerably improved as seen in the DF Γ_{L_3} values in the table. The improved agreement with the theoretical values is particularly significant, since as far as we know this is the only study where the calculations, which consider only the one-electron diagram transition, can be compared with equivalent, measured diagram-transition-only widths.

The spread in the experimental values for Γ_{L_3} in the table is larger than that of the theoretical ones. The low $\Gamma_{L_3}=0.56$ eV width of Krause and Oliver [16] results from subtracting a too large Γ_K from the measured x-ray widths, as discussed above. Indeed, the XPS measurements of Fuggle and Alvarado [21] as well as those of Citrin *et al.* [22] yield a somewhat higher value. Additional discrepancies between our and other values may result in part from the difficulty in properly deconvolving the resolution function of the experimental setup from the measured XPS spectrum, as discussed by Fuggle and Alvarado [21]. The exceptionally low value of Nyholm *et al.* [23] was recently commented on by Pease [24], who concluded that these measurements are less accurate than those of Fuggle and Alvarado.

The agreement among published values of Γ_{L_2} is much less satisfactory. While the removal of the spectator transitions improves the agreement considerably, our value is still a factor of 2 larger than the RDHS value of Chen and Scofield (CS). However, as Yin *et al.* [25] pointed out, all calculations assume that the L_2-$L_3M_{4,5}$ Coster-Kronig transitions, which are not possible energetically in free atoms, remain so in the solid as well. This assumption they find incorrect. Indeed, allowing one, or both, transitions considerably enhances the width and, as can be seen in the table, if we assume that both are allowed a rather reasonable $\sim 15\%$ agreement with our DF value ensues. Again, a particularly good agreement is obtained with the measurements of Fuggle and Alvarado and Citrin *et al.*, where the discrepancies are $7-8$ % only. Note that the removal of the spectator transition contribution is still necessary; using the raw Γ_{L_2} width increases the discrepancy to $\geqslant 30\%$.

The different widths of the L_2 and L_3 levels result from CK transitions which are possible from L_2, but not from the L_3 level. Our widths yield, therefore, $\Gamma_{L_2}^{\mathrm{CK}}=\Gamma_{L_2}-\Gamma_{L_3}=0.6$ and 1.05 eV for the DF and raw results, respectively. The first of these is in excellent agreement with the measured 0.68, 0.63, and 0.56 eV of Nyholm *et al.*, Citrin *et al.*, and Antonides *et al.*, [26] respectively, but less so with the 0.44 eV measured by Fuggle and Alvarado and Yin *et al.* It is midway between the calculated $\Gamma_{L_2}^{\mathrm{CK}}=0.318$ and 0.922 eV of Yin *et al.*, assuming that only L_2-L_3M_4 CK transition, or both L_2-$L_3M_{4,5}$, are possible, respectively. This points towards at least the first of these being allowed. The raw value is, again, unreasonably large, and is in some agreement only with the last-mentioned theoretical value of Yin *et al.*

The results presented above lead, then, to several conclusions. The contribution of the spectator transitions to the line shape is considerable, and it is necessary to remove it before a reasonable agreement with diagram-transition-only calculations can be achieved. Once this is done, and the extra CK broadening is taken care of where necessary, an excellent agreement with the RDHS calculations ensues. This suggests that the extra broadening previously assigned to exchange interaction [21] may in fact be due to the spectator transitions and the exchange interaction contribution is small. Finally, our results support the conclusion of Yin *et al.* that at least the first of the L_2-$L_3M_{4,5}$ Coster-Kronig transitions is possible in solid copper. If indeed only the first of these is allowed energetically, as concluded recently by Pease [24] on the basis of L-level soft x-ray spectroscopy measurements, our measured width difference shows that an extra broadening of ~ 0.4 eV in the L_2 level still remains to be accounted for. Further work to elucidate this point is clearly indicated.

2. *Fluorescence yields*

The fluorescence yields obtained from the widths discussed above are listed in Table II. As the RDHS K-level widths are considered to be the most accurate [2,3,10], we have selected from Table I the Γ_{L_i} widths calculated using the RDHS Γ_K value of Chen and Scofield [14]. The radiative widths required to calculate the yields were taken from several sources; the relativistic DHS calculations of Chen and Scofield, the nonrelativistic Hartree-Slater results of Manson and Kennedy [27] and McGuire [28], and the interpolation by Campbell and Wang [29] of the "two-potential" relativistic Dirac-Fock (DF) calculations of Scofield [30]. These values have a spread of $\sim 25\%$. However, the RDHS and DF values, which are probably the most accurate, as discussed above, differ by only $\sim 10\%$.

When the spectator transition contributions are ignored (the raw data) the theoretical yields overestimate the measured values. The agreement improves considerably once the contribution of the spectator-hole transitions is eliminated (the DF data) and, for ω_{L_2}, the L_2-$L_3M_{4,5}$ Coster-Kronig transitions are taken into account, as discussed above. The value derived here for ω_{L_2} supports, again, the conclusion that at least the lowest of these transitions is allowed in solid copper. We have no explanation for the large deviation of the Chen, Crasemann, and Kostroun [31] results from both our results and those of the other theoretical and experimental values listed.

Of the experimental values listed, the values of Krause [6] are an extrapolation of a semiempirical formula fitted to high-Z elements. The error estimated by the author in this region is at least 25%. To the best of our knowledge, the only direct subshell-resolved, measured L fluorescence yields to date are those of Auerhammer, Genz, and Richter [32]. These are based on soft x-ray spectroscopic measurements of the L x-ray emission spectrum and a subsequent resolution of the resultant lines into diagram and satellite lines. As can be seen in the table, while the L_3 yield is reasonably, though not very, close to our result, the L_2 yield

TABLE II. $L_{2,3}$ fluorescence yields of copper. The total level widths Γ_{L_i} (in eV) are taken from Table I. As discussed in the text, the preferred yield values, where the contribution of nondiagram transitions was eliminated, are those listed under DF.

				Theory					Experiment	
Level	Present Γ_{L_i}	$10^3\Gamma_{L_i}^{rad}$	Present $10^3\omega_{L_i}$	CS [a]	CCK [b]	CCM [c]	McG [d]	YACC [e]	AGR [f]	K [g]
					Raw					
L_3	0.853	5.39 [a]	6.32	8.78	3.83	9.87	9.41	9.78	12(2)	11
		5.17 [h]	6.06							
		6.06 [i]	7.10							
		6.71 [d]	7.89							
L_2	1.903	5.50 [a]	2.89	9.18	3.57	9.9		10.6 [j]	14(3)	10
		5.17 [h]	2.72					6.56 [k]		
		6.09 [i]	3.20					3.81 [l]		
		7.16 [d]	3.76							
					DF					
L_3	0.653	5.39	8.25	8.78	3.83	9.87	9.41	9.78	12(2)	11
		5.17	7.92							
		6.06	9.28							
		6.71	9.45							
L_2	1.253	5.50	4.39	9.18	3.57	9.9		10.6 [j]	14(3)	10
		5.17	4.13					6.56 [k]		
		6.09	4.86					3.81 [l]		
		7.16	5.71							

[a]Reference [14].
[b]Reference [31].
[c]Reference [19].
[d]Reference [28].
[e]Reference [25].
[f]Reference [32].
[g]Reference [6].
[h]Reference [27].
[i]Reference [29].
[j]Assuming that Coster-Kronig L_2-L_3M_4, L_2-L_3M_5 are both not possible.
[k]Assuming that Coster-Kronig L_2-L_3M_5 is the only one possible.
[l]Assuming that both L_2 Coster-Kronig are possible.

is much higher. No reason can be given at present for this discrepancy, and further measurements are clearly called for.

C. $M_{2,3}$ levels

1. Level widths

The experimental situation for the M levels is considerably worse than that of the L levels. The strong overlap of the XPS signals from the M_2 and M_3 subshells makes the determination of individual widths highly uncertain. Usually only Γ_{M_3} can be determined from the relatively overlap-free high energy side of the line, and Γ_{M_2} is then assumed to be equal to Γ_{M_3} [21]. The x-ray $K\beta_{1,3}$ emission spectrum exhibits a similar overlap [33,4]. The strong multielectronic contributions further complicate the accurate extraction of the M widths from the measured spectrum. Finally, the soft x-ray $L\alpha$ spectrum can also be used in principle to determine the M-level widths in a way analogous to that used here to derive the L-level widths from the $K\alpha$ spectrum. However, while the Γ_K value required for the L levels is known to a few percent accuracy, the Γ_{L_i} values required for the soft x-ray spectrum are much less accurate, as discussed above. This greatly inhibits the use of the $L\alpha$ spectrum for M-level widths determination.

Our results are presented in Table III along with (the very few) previous theoretical and experimental results. As can be seen in Figs. 8–10 of Ref. [4], the strong overlap of the two diagram transitions does not allow us to determine the individual widths of these transitions from the raw data, as done in Table I above. Thus, only the DF resolved data appear in the table. These widths were taken from Table VII in Ref. [4]. They are free from the $3d$-spectator transition contributions and pertain to the pure diagram transitions only. Using again the same Γ_K widths employed above, we obtain the Γ_{M_i} listed in the table. These values exhibit the same trend and about the same broadening as those of the L levels upon going from subshell $i=3$ to $i=2$. As can be seen, a reasonable agreement is obtained with the relativistic DHS values

TABLE III. $M_{2,3}$ level widths (in eV) in copper; only the DF resolved data are listed. The measured $K\beta_{1,3}$ widths $\Gamma^{\text{meas}}_{K\beta_{1,3}}$ were taken from Ref. 4.

				Theory			Experiment			
Level	Present $\Gamma^{\text{meas}}_{K\beta_{1,3}}$	Γ_K	Present Γ_{M_i}	CS [a]	McG [b]	YATCRC [c]	LaV [d]	YATCRC [c]	FA [e]	NMLA [f]
$M_3(K\beta_1)$	4.08	1.437 [a]	2.643	3.458	5.22	1.98	1.68 [i]	1.6(3)	1.7(4)	1.78
		1.48 [g]	2.6				3.17 [j]			
		1.55 [h]	2.53							
$M_2(K\beta_3)$	4.60	1.437	3.163	3.562	5.22	1.98	1.68 [i]	2.0(3)	1.7(4)	1.78
		1.48	3.12				3.17 [j]			
		1.55	3.05							

[a]Reference [14].
[b]Reference [34].
[c]Reference [35].
[d]Reference [33].
[e]Reference [21].
[f]Reference [23].
[g]Reference [13].
[h]Reference [16].
[i]Assuming Lorentzian resolution function.
[j]Assuming Gaussian resolution function.

of Chen and Scofield [14]. The nonrelativistic HS calculations of McGuire [34] overestimate the widths considerably as already noticed by Yin *et al.* [35]. The theoretical values of Yin *et al.* were calculated assuming neutral free-atom Auger energetics, based on their observation of free-atom-like L_3-$M_{4,5}M_{4,5}$ Auger spectra in Cu and Zn. They also show that assuming an initial state with a $3p$ vacancy for the Auger process increases Γ_{M_2} to 3 eV for Zn. Since Zn and Cu have equal $\Gamma_{M_{2,3}}$ in their neutral atom calculations, a similar increase can be expected in Cu. The $3p$ vacancy in our case is the final state of the $1s \rightarrow 3p$ transition, and may be sufficiently long lived to survive the emission of the Auger electron. This effect, if present, could bring the calculated $\Gamma_{M_{2,3}}$ of Yin *et al.* to ~ 3 eV, which is in very good agreement with our measurements.

With the exception of LaVilla's [33], all measured values listed in the table were obtained from XPS measurements. LaVilla obtained the width of the diagram transitions by fitting two Lorentzians to his measured x-ray $K\beta_{1,3}$ spectrum. Subtracting the measured resolution width of 1.84 eV and $\Gamma_K = 1.48$ eV from the ~ 5 eV fitted linewidths, the $\Gamma_{M_{2,3}} = 1.68$ eV, listed in the table, was obtained. However, this method of correction for the resolution width is appropriate only when both the resolution and the true line shape are Lorentzians. For Gaussian functions subtraction in quadrature is more appropriate. This gives a width of $\sqrt{5^2 - 1.84^2} = 4.65$ eV for the diagram transitions, and a $\Gamma_{M_i} \approx 3.2$ eV, both very close to our values. This demonstrates how sensitive is the derived width to the proper correction for, or elimination of, the finite resolution of the spectrometer. Note that LaVilla assumed equal widths for the M_2 and M_3 Lorentzians and did not include the spectator spectrum in the fit of his spectrum. Hence the contributions to the line shape from spectator transitions are only partially accounted for by his procedure.

The XPS-measured Γ_{M_i} values are consistently lower than our results and the calculations of Chen and Scofield. The equal widths cited in the last two columns of the table for M_2 and M_3 reflect the difficulty in separating the overlapping lines and thus in both studies cited equal widths were assumed, rather than obtained independently. Note also that in the only XPS measurement providing separate values for the two subshells, they differ by 0.4 eV , in good agreement with the 0.5 eV difference obtained from our results. The difference between XPS and x-ray derived Γ_{M_i} may reflect subtle differences in the initial and/or final states of the atom in the two cases. A similar explanation was invoked to account for the different linewdths observed in the $M_{4,5}$ XPS and the L_3-$M_{4,5}M_{4,5}$ Auger spectra of Cu and Zn [35,36]. It was shown there that the ionization of L_3 in the Auger process changes the screening of the $M_{4,5}$ electrons, causing a tighter binding and partial withdrawal from the valence band. The increased localization results in narrower, more free-atom-like level width. Although a specific explanation cannot be offered at this point, a similar mechanism, involving interaction with the valence band, may account for the observed level width differences in the two methods.

2. Fluorescence yields

The fluorescence yields derived from the widths in Table III are given in Table IV. As before, the total level widths are those derived using the Γ_K of Chen and Scofield. The radiative widths were taken from two sources: the nonrelativistic HS calculations of Manson and Kennedy [27], using the Herman and Skillman [37] wave functions, and the RDHS calculations of Chen and Scofield [14]. The resultant fluorescence yields are in good agreement with the DHS calculated yields of Chen and Scofield, in particular for the M_2 level. The nonrelativistic Hartree-Slater calculations of McGuire [34], which contain several severe approximations, underes-

TABLE IV. $M_{2,3}$ fluorescence yields; only the DF resolved data are listed. The total level widths Γ_{M_i} (in eV) are taken from Table III.

Level	Present Γ_{M_i}	$10^5\ \Gamma^{\rm rad}_{M_i}$	Present $10^5\ \omega_{M_i}$	Theory CS [a]	Theory McG [b]
M_3	2.643	8.429 [a]	3.19	2.438	1.6
		8.088 [c]	3.06		
M_2	3.163	9.097 [a]	2.88	2.55	1.6
		8.088 [c]	2.56		

[a]Reference [14].
[b]Reference [34].
[c]Reference [27].

timate our results, and those of Chen and Scofield, considerably. To the best of our knowledge, no other experimentally derived, subshell-resolved fluorescence yields are available in the literature for the M shell of copper.

D. Spectator-hole transitions

The presence of a spectator hole during the emission process introduces additional splitting in the initial and final energy levels and consequently increases considerably the number of distinct transition lines. As shown in Ref. [4], it is possible to separate out the contribution of these transitions from those of the diagram ones by fitting the measured line shape by an *ab initio* calculated transition array. However, to obtain a meaningful fit it is imperative to keep the number of fit variables as low as possible, and limit their range of variation by using physical insight and previous knowledge. In our case it was found necessary to assign a single width to all lines of a given spectator multiplet. Thus all $3d$-spectator transitions of the $K\alpha_{1,2}$ spectrum, the only spectator transition contributing significantly to the spectrum, have a common width. This was found in the fit to be $(\Gamma^{\rm meas}_{K\alpha_{1,2}})_{3d}=2.75$ eV, i.e., ~ 0.1 and ~ 0.6 eV broader than the diagram $K\alpha_2$ and $K\alpha_1$ lines, respectively. For the $3d$-spectator transitions of the $K\beta_{1,3}$ spectrum we obtain $(\Gamma^{\rm meas}_{K\beta_{1,3}})_{3d}=4.88$ eV, a broadening of ~ 0.3 and ~ 0.8 eV over the diagram $K\beta_3$ and $K\beta_1$ lines, respectively. Since very little is known on the influence of additional holes on level widths in atoms [38], and since no theoretical or experimental results are available in the literature for copper, it is difficult to assess the significance and causes of these differences. Kawai *et al.* [39] measured a smaller broadening of ~ 0.1 eV of the $K\alpha_1$ line of CuO over metallic copper. However, although the valence shell configuration of CuO, $3d^9$, is the same as that of metallic copper with a $3d$ spectator, and hence an equal broadening may be argued for, the molecular bonding electrons may partially mask the $3d$ hole and reduce the extra broadening it generates.

V. CONCLUSIONS

The study presented here has several advantages. It employed a double crystal spectrometer, the resolution function of which was studied in detail and optimized to eliminate resolution broadening and distortions of the measured spectra. The same spectrometer was used to measure both the $K\alpha_{1,2}$ and the $K\beta_{1,3}$ spectra, allowing determination of the M and L level widths under practically identical conditions. Most importantly, the data analysis, based on computer fits of the measured spectra by an *ab initio* calculated transition array, allowed us to separate out the contribution of spectator transitions and obtain widths and yields for the pure one-electron diagram transitions only.

The main conclusions of this study are as follows.

(i) The removal of spectator contribution results in a general improvement in the agreement with theory, and in particular with the recent relativistic DHS results of Chen and Scofield [14]. The agreement corroborates several previous conclusions [2,3] on the superiority of the DHS calculations in this Z range.

(ii) The opening of at least the L_2-L_3M_4 Coster-Kronig channel in solid copper is confirmed. As the L_2 level width shows additional broadening beyond that due to this transition, it is possible that the L_2-L_3M_5 Coster-Kronig transition is also allowed in solid copper. Both of these transitions are not possible energetically in the free copper atom.

(iii) The x-ray derived M-level widths are systematically higher than those derived from XPS measurements. This may be related to the valence shell rearrangement effects proposed by Yin *et al.* [36] to account for differences between the Auger and XPS derived $3d$-level widths in copper and zinc.

(iv) We provide experimentally derived, subshell-resolved values for the M-level fluorescence yields of copper. To the best of our knowledge, no similar values are available in the literature. These values are found to be in very good agreement with the DHS calculations of Chen and Scofield.

(v) The level widths addressed here are broadened by the presence of an additional $3d$ spectator hole in the atom by as much as a few tenths of an eV . The physical reason for this broadening is, however, not clear.

The study indicates the need for further experimental and theoretical work. More detailed DHS calculations including contributions from Coster-Kronig transitions are required, as well as calculations of the various level widths in the presence of additional holes in the same atom. On the experimental side, measured individual M-subshell widths are still very scarce for all iron group elements. Further studies, similar to that presented here, which include precision measurements of x-ray emission line shapes and their fits by calculated transition arrays for neighboring transition elements, may yield Z-dependent trends in the widths and shed light on the physics and relative importance of the various contributing processes. Such measurements are currently in progress in our laboratory.

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