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Widths of atomic 4s and 4p vacancy states, $46 \leq Z \leq 50$

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X-ray photoelectron and Auger spectra involving N_1, N_2, and N_3 vacancy states of Pd, Ag, Cd, In, and Sn were measured and compared with results of free-atom calculations. As previously observed in Cu and Zn Auger spectra that involve 3d-band electrons, we now also find free-atom characteristics, with regard to widths and structure, in the Ag and Cd M_4-$N_{4,5}N_{4,5}$ and M_5-$N_{4,5}N_{4,5}$ Auger spectra that arise from transitions of 4d-band electrons. Theoretical N_1 widths computed with calculated free-atom Auger energies agree well with measurements. Theory, however, predicts wider N_2 than N_3 vacancy states (as observed for Xe), while the measured N_2 and N_3 widths are nearly equal to each other and to the average of the calculated N_2 and N_3 widths. The calculations are made difficult by the exceedingly short lifetime of some 4p vacancies and by the extreme sensitivity of super-Coster-Kronig rates, which dominate the deexcitation to the transition energy and to the fine details of the atomic potential.

I INTRODUCTION

The lifetimes of atomic inner-shell vacancies are uniquely related, through the uncertainty principle, to widths of the corresponding atomic energy levels. In many cases, atomic level widths can be measured quite accurately by x-ray photoelectron spectroscopy,[1,2] providing an important check on calculations of transition probabilities and lending insight into deexcitation processes.[3] In particular, considerable difficulties are still encountered in theoretical estimates of Coster-Kronig rates,[4-6] which often determine the dominant partial widths of states that are characterized by vacancies in the lower L, M, and N subshells[7]; more experimental data are needed as a guide for refined calculations. Available information on atomic level widths is quite incomplete as yet, in spite of its relevance to fundamental theory and applications.[8] In the present paper, we report on measurements of N_1, N_2, and N_3 widths in Pd, Ag, Cd, In, and Sn, and compare these with new calculations.

II. EXPERIMENT

A. Measurements

The x-ray photoelectron spectrometer used in these experiments has been described previously.[1] Photoelectrons were produced by (nonmonochromatized) Mg $K\alpha_{1,2}$ x rays and retarded to ~100 eV before they entered an 11-cm-radius hemispherical electrostatic analyzer. Samples consisted of spectroscopically pure foils. Sample surfaces were sputter-cleaned with Ar ions until the 1s photoelectron lines of O and C became nondetectable or, at most, barely discernible above background. Spectra were measured at pressures of $<5\times10^{-8}$ Torr. All measurements were repeated with three different samples of each element.

Lines with favorable signal-to-background ratio were measured at a resolution characterized by 1.1 eV full width at half maximum (FWHM) of the Au N_7 photoelectron peak. Many N-shell photoelectron lines measured in this work are quite wide (>4 eV), however, and rather weak; in these cases, the spectrometer resolution was reduced to 1.5 eV FWHM for the Au N_7 line, thus enhancing the signal-to-background ratio. Even so, instrumental broadening remained negligible in comparison with the intrinsically large experimental uncertainties associated with such large widths (see Sec. II B).

B. Data analysis and results

As in our previous work on M-level widths,[1] the photoelectron spectra were smoothed with a spline-fit computer program. The background on both sides of a peak was fitted with a single fourth-degree polynomial which extends under the peak. Results were drawn with a CalComp 780 plotter. In the $46<Z<50$ region, the N_2 and N_3 photoelectron lines overlap considerably. Their background-subtracted smooth spectra were deconvoluted with a DuPont 310 curve resolver, subject

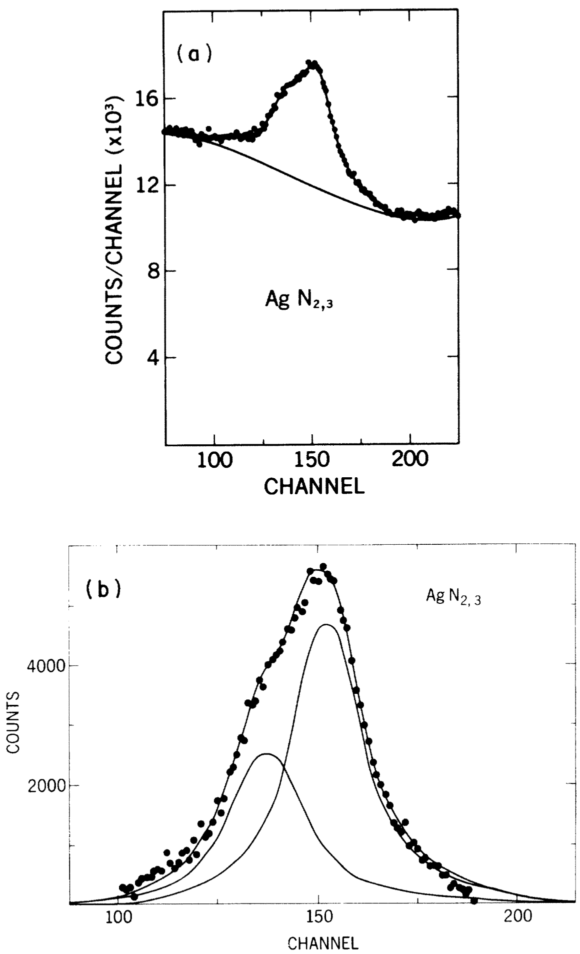

FIG. 1. Mg $K\alpha_{1,2}$ x-ray excited photoelectron spectrum of Ag. (a) Original spectrum with smoothing and computer-fitted background. (b) Deconvolution of the background-subtracted spectrum into Lorentzian shapes produced with a DuPont 310 curve resolver, subject to the criterion that the N_2/N_3 intensity ratio be $\frac{1}{2}$. Units on the abscissa are 0.4 eV/channel.

to the additional criterion that the N_2/N_3 photoelectron intensity ratio be $\frac{1}{2}$. The single-component standard in the curve-resolving process was a Lorentzian shape convoluted with the Gaussian instrumental contribution according to the procedure of Wilkinson.[9] The combined width of the vacancy state and the incident x ray is at least six times the instrumental width in all cases; hence the convoluted shape remains practically Lorentzian.

The application of these procedures to the $N_{2,3}$ photoelectron spectrum of Ag is illustrated in Fig. 1. The original data, smoothing, and computer-fitted background are shown in Fig. 1(a). It is apparent how extensively the wide N_2 and N_3 lines overlap; this makes them difficult to resolve. Moreover, the shape of the spectrum is such that background subtraction involves some degree of subjectivity. The deconvolution of the background-subtracted spectrum, based on Lorentzian line shapes [Fig. 1(b)], is more successful in this case than in some others with poorer signal-to-background ratios and broader peaks. These difficulties, due more to the nature of the photoelectron spectra than to the instrumental resolution, account for the rather large uncertainties attached to some of the measured widths.

Results of the measurements are listed in Table I, with theoretical predictions given by McGuire[10] and by our present calculations. The experimental vacancy-state widths were derived on the assumptions that the width of the Mg $K\alpha_{1,2}$ x-ray line is 0.8 eV and that the width of the photoelectron line is the Lorentzian sum (simple addition) of the incident x-ray width and the width of the vacancy state. Instrumental broadening is neglected. We believe that it is justifiable to disregard the (Gaussian) instrumental contribution, even at degraded resolution, because all uncorrected photoelectron

TABLE I. Theoretical and experimental widths $\Gamma(N_i)$ of N_i-subshell vacancy states (in eV).

	$\Gamma(N_1)$			$\Gamma(N_2)$			$\Gamma(N_3)$		
	Theory			Theory			Theory		
Element	a	b	Experiment	a	b	Experiment	a	b	Experiment
$_{46}$Pd		5.25	5.0 ± 0.5		7.79	6.5 ± 1		6.32	6.5 ± 1
$_{47}$Ag	41.9(7.0)	4.13	4.2 ± 0.5	9.69	10.55	8.5 ± 1	9.69	8.44	7.5 ± 1
$_{48}$Cd		4.07	4.0 ± 0.5		13.38	12 ± 1.5		8.65	10 ± 1.5
$_{49}$In		3.03	3.5 ± 0.5		17.59	15 ± 2		10.55	14 ± 2
$_{50}$Sn	78.2(3.1)	2.89	2.8 ± 0.5	16.2	20.81	17 ± 2	16.2	10.39	17 ± 2
$_{54}$Xe		5.87			59.48			2.38	

[a] McGuire (Ref. 10). Values in brackets are based on an alternative energy estimate for the N_1-$N_{2,3}N_{4,5}$ super-Coster-Kronig transitions. See text, Sec. III B2.

[b] Present free-atom calculations.

lines are at least 3.5 eV wide and allowance for large experimental uncertainties is made in the assigned error limits.

The question remains to what extent nonlifetime broadening[11] contributes to the line widths derived from the x-ray photoelectron spectra. In view of the metallic character of the samples and the large widths (>3.5 eV) under consideration, it is expected that such nonlifetime mechanisms as charging, thermal and phonon broadening, and many-electron (conduction-electron) excitations[12-14] do not contribute significantly. Plasma frequencies in the elements studied here correspond to energies[15] of $\geqslant 12$ eV and their excitation intensities are generally much lower than those of the main photoelectron peaks, so that broadening due to this cause should be minimal. We have chosen to study only elements with filled d shells so as to avoid significant broadening due to multiplet splitting and other related final-state effects arising from localized unpaired electrons. Although the precise nature of pronounced shakeup satellites in solids (~5–12 eV) is still somewhat ambiguous, it is an experimental fact that such satellites are observed only in metal compounds and not in the metals themselves.[16-25] Broadening contributions from shakeup or shakeoff satellites should therefore be insignificant in the pure metallic samples used in the present work.

III. DISCUSSION

A. Quasiatomic Auger spectra

In a previous paper we discussed the quasiatomic character of the Auger spectra from solid Cu and Zn.[1] In particular, we showed that the L_3-$M_{4,5}M_{4,5}$ Auger transition, which involves *two* electrons from the $M_{4,5}$ ($3d$) band of solid Cu and Zn, does not exhibit band structure, but instead contains fine structure similar to that in spectra of free atoms. In width and shape, these Auger spectra thus differ sharply from the x-ray photoelectron (XPS) spectra of the $3d$ band itself. The same fine structure has recently been observed in Auger spectra of Zn vapor which contains only free Zn atoms,[26] as well as in solid germanium[27] and in gaseous GeH_4,[28] where the $3d$ electrons are more corelike.

Two reasons exist for this quasiatomic behavior of Auger spectra in contrast to the solid-state character of soft-x-ray emission spectra. On one hand, in the presence of an inner-shell photohole, the more localized valence electrons are likely to be preferentially selected by the Coulomb operator to participate in the Auger process, while the x-ray emission dipole operator has relatively long-range character. On the other hand, the doubly ionized final state of Auger transitions is more free-atom-like than the singly ionized final state of radiative transitions.[29,30] Our original suggestion[1] concerning a lifetime difference between radiative and radiationless processes is in error, as pointed out by Mehlhorn.[30]

The important physical implications of the quasiatomic characteristics of Auger spectra from solids are as follows:

(i) Because Coster-Kronig and Auger transitions are caused by the same Coulomb operator and both lead to doubly ionized final states, the quasiatomic behavior of Auger transitions in solids implies similar behavior of Coster-Kronig transitions.

(ii) In the outer shells, such as the M or N shells of medium-Z elements, the width of a vacancy state is almost entirely governed by Auger and Coster-Kronig transition rates. If these transitions are quasiatomic in solids, then the vacancy-state widths as deduced from XPS of solid samples should reflect the quasiatomic transition rates, provided that other nonlifetime contribu-

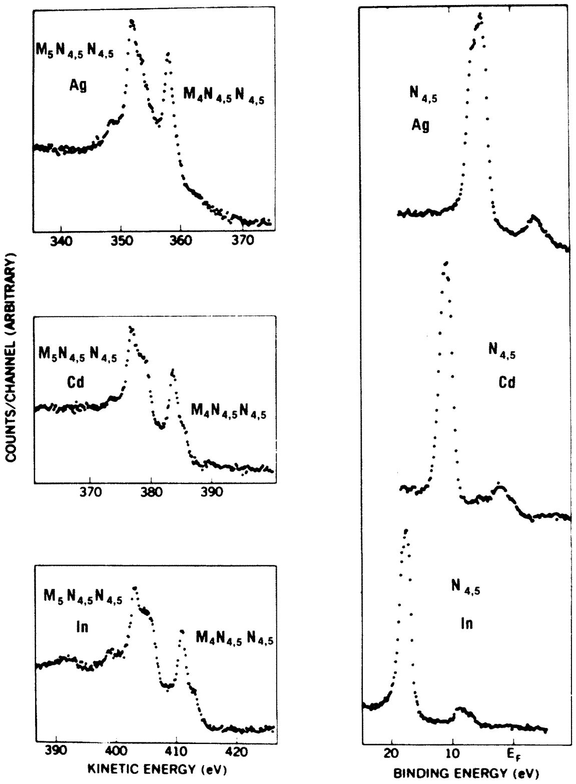

FIG. 2. M_4-$N_{4,5}N_{4,5}$ and M_5-$N_{4,5}N_{4,5}$ Auger spectra (left-hand side) and Mg $K\alpha$ x-ray excited $N_{4,5}$ photoelectron spectra (right-hand side) of Ag, Cd, and In. The small peak in the $N_{4,5}$ photoelectron spectra is caused by the Mg $K\alpha_{3,4}$ satellite radiation from the x-ray source.

tions to the XPS widths are negligible.

(iii) Whereas the fine structure of Auger spectra and the width of photoelectron lines in solids may be quasiatomic in character, their kinetic energies, and hence the measured binding energies of electrons in various shells, are definitely not free-atom-like, but are influenced by solid-state effects such as extra-atomic relaxation.[31,32]

These points are borne out by the fact that the large discrepancies between theoretically predicted M-vacancy widths[33] and experimentally measured values could be resolved by recalculating the widths using free-atom Auger and Coster-Kronig energies and neutral-atom potentials.[1] We now inquire whether similar free-atom behavior of N Auger spectra exists in metals such as Ag and Cd. Figure 2 shows the M_5-$N_{4,5}N_{4,5}$ and M_4-$N_{4,5}N_{4,5}$ Auger spectra of Ag and Cd and the respective photoelectron spectra of the $N_{4,5}$ ($4d$) band. The spectra of In are included for comparison because the In $N_{4,5}$ level is more corelike. As in the case of Cu and Zn, we note a similarity among the Auger features of Ag and Cd, even though the width and shape of the photoelectron spectra are quite different. The fine structure of these Auger spectra is not well resolved. However, the fine structure is definitely similar to that in the free-atom inner-shell $M_{4,5}$-$N_{4,5}N_{4,5}$ Auger spectra of gaseous Xe.[34,35] This similarity was already noted by Aksela[36] under coarse resolution. More recently, Powell conducted a high-resolution study of Ag and specifically emphasized the lack of band structure, and hence the quasiatomic character of these Auger transitions.[29] Additional evidence for the quasiatomic characteristics is provided by the recently obtained Auger spectrum of Cd vapor,[37] which exhibits features similar to those of Cd metal, although much better resolved. We can thus anticipate that in the $46 < Z < 50$ range the N-shell widths should be essentially free-atom-like. Hence we compare the measured widths with free-atom calculations.

B. Comparison with theory

1. *Calculation of N-subshell widths for quasifree atoms*

Free-atom Auger energies, which differ by the extra-atomic relaxation energy from energies measured on solid samples,[32] were calculated from first principles.[1] Relativistic Hartree-Fock-Slater wave functions were used with Slater's $X\alpha$ approximation to the exchange correlation term in the expression for the statistical total energy.[38-40] The parameter α was chosen to be 0.7 throughout. The calculated Coster-Kronig energies are listed in Table II.

Auger and Coster-Kronig transition rates were computed with Herman-Skillman[41] nonrelativistic Hartree-Slater wave functions. The Latter tail correction[42] was included, and $X\alpha$ exchange was used. Radiationless transition rates were calculated in j-j coupling in the standard manner.[5,6] The rates with which we are here concerned are exceedingly sensitive to the atomic potential. This

TABLE II. Theoretical N Coster-Kronig and super-Coster-Kronig transition energies from free-atom calculations (in eV).

Element	N_1-N_2N_{45}	N_1-N_3N_{45}	N_1-N_2O_1	N_1-N_2O_{23}	N_1-N_3O_1	N_1-N_3O_{23}	N_1-$N_{45}N_{45}$	N_2-$N_{45}N_{45}$	N_3-$N_{45}N_{45}$
$_{46}$Pd	11.45	15.74					63.17	30.53	26.24
$_{47}$Ag	7.82	11.57	18.20		21.95		64.27	29.74	25.99
$_{48}$Cd	4.60	10.60	18.21		24.21		66.16	29.38	23.38
$_{49}$In		5.02	16.77	24.48	23.70	31.41	65.91	27.64	20.71
$_{50}$Sn			15.01	23.48	22.84	31.31	63.10	24.27	16.47
$_{54}$Xe			21.10	32.52	34.66	46.08	61.23	6.23	

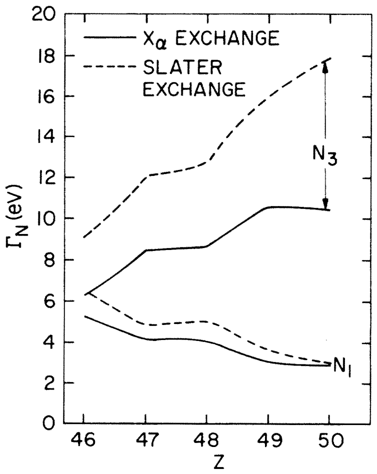

FIG. 3. Dependence of the N_1- and N_3-level widths on the choice of exchange used in the calculation, illustrating extreme sensitivity of the dominant radiationless transition rates to the atomic potential.

fact is illustrated by the dependence of N-level widths on the choice of exchange potential, as plotted in Fig. 3. Radiative transitions were disregarded, the radiative partial width of N-shell vacancy states being negligible compared with the radiationless width.[10] Total widths computed in this manner are included in Table I.

2. N_1-level widths

Figure 4 shows that the measured N_1 widths in the $46 < Z < 50$ region agree exceedingly well with the free-atom calculations. These widths are chiefly determined by the N_1-$N_{2,3}N_{4,5}$ super-Coster-Kronig rates. Coster-Kronig transition rates are extremely energy sensitive, particularly near threshold.[1] This fact is well illustrated by the difference between two sets of results for the N_1 widths obtained by McGuire,[10] who estimated the continuum-electron energy in two different ways; these results differ by a factor of ~6 at $Z = 47$ and by ~25 at $Z = 50$. The higher values (not included in Fig. 4), which increase rather than decrease with Z, were found by estimating the super-Coster-Kronig electron energy ϵ through the formula

$$\epsilon = E_{n_1 l_1}(Z) - \tfrac{1}{2}\left[E_{n_3 l_3}(Z) + E_{n_3 l_3}(Z+1) + E_{n_4 l_4}(Z) + E_{n_4 l_4}(Z+1)\right], \qquad (1)$$

where $E_{nl}(Z)$, the binding energy for the nl subshell of the neutral atom with nuclear charge Ze, was taken from the ESCA table of binding energies.[43] The subscript 1 refers to the hole in the initial atom, while 3 and 4 refer to the final holes. The lower set of widths found by McGuire,[10] on the other hand, which agrees well with ours (Fig. 4), was calculated with super-Coster-Kronig energies estimated according to the prescription of Asaad and Burhop[44] with a work-function correction to the ESCA binding energies.[43] Clearly, the latter method of arriving at Coster-Kronig energies is far more realistic.

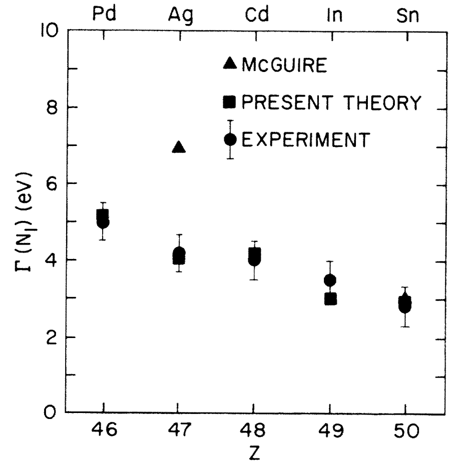

FIG. 4. Comparison of theoretical and experimental widths of N_1 vacancy states. Experimental data and free-atom calculations are from the present work; triangles represent the lower of two sets of results obtained by McGuire (Ref. 10) under different energy assumptions (see text, Sec. IIIB2).

3. $N_{2,3}$-level widths

Except for $_{47}$Ag, the $4p_{1/2}$-$4p_{3/2}$ spin-orbit splitting had not heretofore been resolved in the

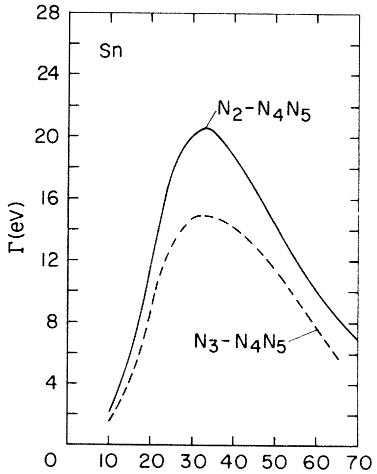

FIG. 5. N_2-N_4N_5 and N_3-N_4N_5 partial widths of Sn as functions of Auger electron energy, illustrating steep energy dependence of these super-Coster-Kronig transition rates.

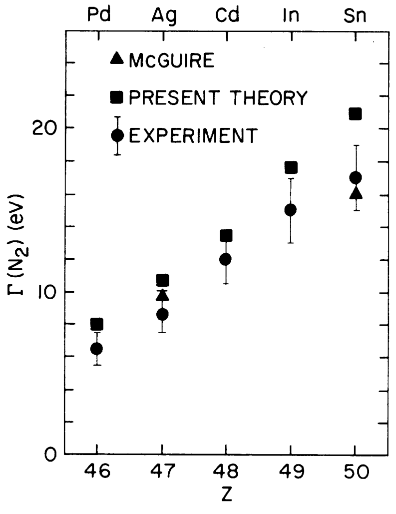

FIG. 6. Comparison of measured N_2-level widths with theoretical results from the present work and of McGuire (Ref. 10).

$46 < Z < 50$ region. Even though the experimentally resolved N_2 and N_3 peaks are separated by 8–15 eV, their widths are comparable with their separation, causing substantial overlap (Fig. 1). Taking experimental uncertainties into account, however, we find that the measured N_2 and N_3 vacancy-state widths are nearly equal, for each element. Equal N_2 and N_3 widths are also obtained theoretically through McGuire's calculation,[10] in which the N_2 and N_3 levels are assigned the same (average) energy, i.e., spin-orbit energy splitting is neglected. In our own, free-atom calculations, on the other hand, we take account of the difference between N_2 and N_3 binding energies. The widths of the N_2 and N_3 levels in this region are primarily governed by the super-Coster-Kronig transitions N_2-$N_{4,5}N_{4,5}$ and N_3-$N_{4,5}N_{4,5}$, which are very energy sensitive (Fig. 5). Different binding energies for N_2 and N_3 electrons therefore lead to different N_2 and N_3 vacancy-state widths. Somewhat surprisingly, McGuire's calculation,[10] which includes a kind of averaging by treating the N_2 and N_3 levels as degenerate, agrees well with our measurements (Figs. 6 and 7, Table I). Our calculation, on the other hand, leads to N_2 widths that are too large and to N_3 widths that are too small, in general, compared with experiment. The average of our theoretical N_2 and N_3 widths does, however, agree with the (nearly equal) measured N_2 and N_3 widths. In view of the good agreement of our calculated N_1 widths with measurement, the discrepancy in the N_2 and N_3 widths is puzzling. We note that the large (59.5 eV) N_2 width that we calculate for Xe (Table I) is not contrary to observation; in ESCA measurements, it was found that the N_2 level of Xe is far too broad for positive identification.[34]

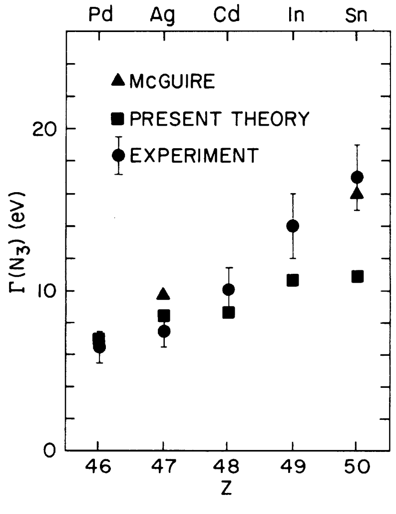

FIG. 7. Comparison of measured N_3-level widths with theoretical results from this work and of McGuire (Ref. 10).

4. $N_{4,5}$-*level widths*

The $N_{4,5}$ levels form the 4*d* band of Ag and Cd and are not split in In or Sn (Fig. 2). No effort was therefore made to measure the individual widths of these levels for comparison with atomic calculations.

5. *Concluding remarks*

The following difficulties are encountered in the calculation of theoretical N-level widths:

(i) The super-Coster-Kronig transition rates which largely govern the widths are exceedingly energy sensitive.

(ii) These radiationless transition rates are extraordinarily sensitive to the fine details of the atomic potential.

(iii) The very short lifetime of the $N_{2,3}$ hole states casts some doubt upon the basic validity of perturbation theory to calculate the decay of these states.

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