

Solid-state effects in $M_{4,5}N_{4,5}N_{4,5}$ Auger spectra of elements from $_{49}\text{In}$ to $_{52}\text{Te}$

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The $M_{4,5}N_{4,5}N_{4,5}$ Auger electron spectra have been measured for the elements from $_{49}\text{In}$ to $_{52}\text{Te}$ in solid phases and compared with the same transitions in vapor phases. The linewidths are found to be broadened in the solids by the amount of 0.5–0.9 eV compared to the estimated widths of the atomic 3d levels. The lines are shifted toward higher kinetic energies by 7–12 eV while the relative energies and intensities of the component lines remain essentially the same for vapor and solid phases of the same element. The experimental extra-atomic relaxation energies are determined from the observed line shifts and compared with theoretical relaxation energies calculated within the framework of a simplified model where screening electrons are assumed to occupy the first unfilled atomic orbitals. All the main features in the spectra can be interpreted as due to multiplet splitting of the two-hole final-state configuration. Therefore, quasiatomic rather than bandlike descriptions of the final states seem to be correct for these transitions.

I. INTRODUCTION

During the past few years solid-state effects in Auger-electron and photoelectron emission processes have been studied intensively. It has become apparent that Auger electrons from vapors and gases exhibit kinetic energies which are usually 10–15 eV lower than those observed for metals.^{1–9} This large vapor-metal kinetic-energy shift is associated with extra-atomic relaxation of conduction electrons in metals. The vapor-metal shifts of Auger lines are found to be three to four times larger than the corresponding shifts of photoelectron lines. This can be expected because the polarization energy should be, in a first approximation, proportional to the square of the charge of the ion to be screened by the conduction electrons,⁵ and in the final state of the Auger process two holes are created instead of the single hole of photoemission.

To obtain reliable information about extra-atomic relaxation and the line broadening (another characteristic of the solid-state effect), precision measurements from solid and vapor phases of the same elements are needed. Also of interest are the Auger spectra that involve valence-band electrons because it is not entirely clear under what conditions Auger spectra should be interpreted predominantly in terms of quasiatomic transitions and under what bandlike transitions are of main importance.^{10–18}

As a part of our studies on extra-atomic relaxation, line-broadening phenomena, and quasiatomic versus bandlike behavior of Auger transitions, we wish to put forward here measurements on $M_{4,5}N_{4,5}N_{4,5}$ Auger spectra and the 3d

and 4d photoelectron spectra of pure metals from indium through tellurium. These solid-phase studies are warranted because the vapor-phase MNN Auger spectra of InCl_3 , SnCl_2 , Sb_4 , and Te_2 molecules have been recently measured.¹⁹ Since these molecules have closed electron configurations, in a good approximation, comparisons between the Auger spectra of the molecules and the metals can be made.

II. EXPERIMENTAL

Indium, tin, antimony, and tellurium films were grown from pure metals onto a copper-plate substrate by *in situ* vacuum evaporation. The specimen preparation chamber of an electron spectrometer²⁰ used in these measurements was maintained at a base pressure of about 8×10^{-9} Pa. Freshly prepared samples were transferred through an isolation valve into the analysis chamber where base pressure was below 5×10^{-9} Pa.

A compositional analysis of the samples was performed using a peak-to-peak heights of modulated Auger spectra obtained in the first-derivative mode. These spectra taken at an estimated instrumental sensitivity limit of a few thousand parts per million did not reveal any impurities in the surfaces. Carbon and oxygen impurities did not accumulate above the detection limit within 10 h, thereby indicating that the surface of the film remained reasonably clean and stable during the $M_{4,5}N_{4,5}N_{4,5}$ Auger-electron measurements.

The primary radiation used to excite Auger emission was provided by a Mg $K\alpha$ x-ray tube operated at 12 kV and 20 mA. The spectra were recorded in a standard pulse counting mode using a

multichannel pulse analyzer.

The electron analyzer was operated at the pass energy of 10 eV for the Auger spectra of In and Sn, and at 20 eV for Sb and Te, corresponding to energy resolution of the analyzer of 0.2 and 0.4 eV, respectively. Emission was collimated by the analyzer acceptance cone of about 2° full opening and was measured in the direction of 20° relative to the normal of the surface of the sample. The $3d$ and $4d$ photoelectrons were measured at the resolution of 0.2 eV. At 0.2 eV resolution the instrumental contribution to the observed linewidths was about 0.07 eV, and at 0.4 eV it was about 0.19 eV. The analyzer was calibrated against the binding energy of $3d_{5/2}$ photoelectrons of a vacuum-deposited silver film. The binding energy of these electrons was taken to be 368.20 eV relative to the Fermi level.

III. RESULTS

A. Auger spectra

One of the main difficulties encountered in data handling of the solid-state Auger spectra is estimating the slope and shape of the background under the line groups. A high background in the present spectra, typically 70% the intensity of the strongest Auger peak, was subtracted applying the common approach that the background increases proportionally to the integrated intensity as the kinetic energy of electrons decreases.⁹

The $M_{4,5}N_{4,5}N_{4,5}$ Auger spectra corrected for the background are displayed in Figs. 1–4. Each Auger group was decomposed into six component lines by using a least-squares fitting procedure.²¹ This decomposition corresponds precisely to the analysis of the vapor-phase Auger spectra of the

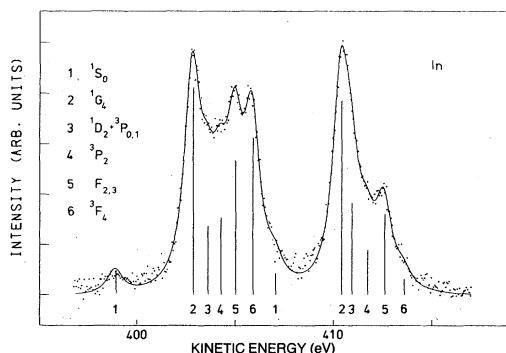


FIG. 1. $M_{4,5}N_{4,5}N_{4,5}$ Auger spectrum of indium metal excited by Mg $K\alpha$ x-rays after background subtraction. The solid curve represents a least-squares fit to the experimental points. Assignment of the final state is indicated. The energy locations and intensities of the component lines are shown by vertical bars.

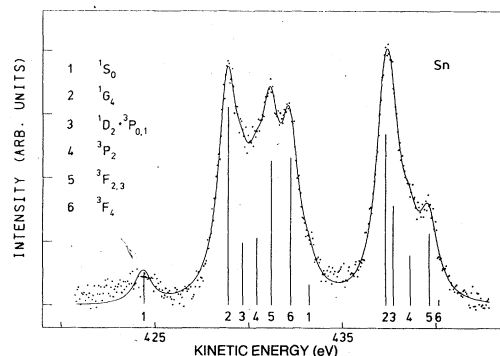


FIG. 2. $M_{4,5}N_{4,5}N_{4,5}$ Auger spectrum of tin metal; see caption of Fig. 1.

same elements studied by Aksela *et al.*⁹ The number of components was obtained from that predicted in intermediate-coupling theory of $4d^8$ double-hole final states²² when unresolved lines in the experiment were treated as single lines.

The standard shape for each component of the spectrum was a Voigt profile having the full width at half maximum (FWHM) value of Γ_V which was computed by convoluting a Gaussian function (width Γ_G), representative of the analyzer response function, with a Lorentzian function (width Γ_L) which is characteristic of the total inherent width of the one-hole initial state and the two-hole final state. The energies, intensities, and half-widths of the standard lines were varied until the best fit to the experimental data was obtained. These fits are represented by the solid curves in Figs. 1–4. The energy-level schemes are indicated by vertical bars. The relative kinetic energies and intensities of the Auger lines are compiled in Tables I and II together with the corresponding quantities for the vapors.

The absolute kinetic energies of the $M_{4,5}N_{4,5}N_{4,5}$ ($1G_4$) electrons are presented in Table III. For the metals, the energies are given relative to the

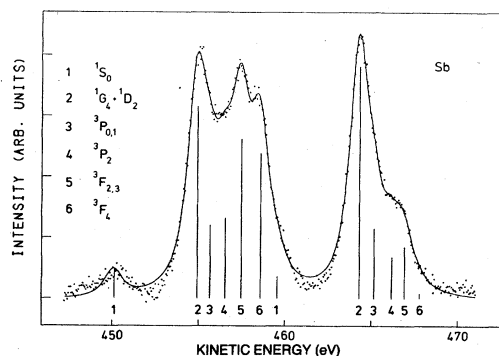


FIG. 3. $M_{4,5}N_{4,5}N_{4,5}$ Auger spectrum of antimony metal; see caption of Fig. 1.

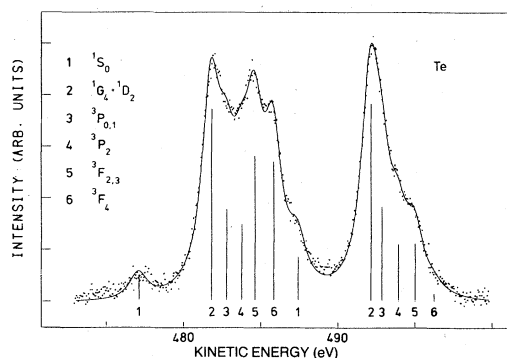


FIG. 4. $M_{4,5}N_{4,5}N_{4,5}$ Auger spectrum of tellurium metal; see caption of Fig. 1.

Fermi level, for the vapors in reference to the vacuum level. To calculate the vapor-metal Auger line shifts, the solid-state values should be corrected for the work function $e\phi$. We have taken $e\phi$ to be 4.12, 4.42, 4.55, and 4.95 eV for In through Te, respectively.²³

B. Photoelectron spectra

The binding energies of 3d and 4d photoelectrons are listed in Table III. Also given are binding energies from the works of Bahl and Watson,⁸ Pollack *et al.*,²⁴ Shevchik *et al.*,²⁵ and Wagner.²⁶ The natural linewidths $\Gamma(3d)$ and $\Gamma(4d)$ of 3d and 4d photoemission, as determined from least-squares fits similar to those used in the analysis of the Auger

spectra, are listed in Table IV, (columns 2 and 3), and are compared with theoretical $\Gamma(3d)$ and $\Gamma(4d)$ reported by Keski-Rahkonen and Krause²⁷ (columns 4 and 5). When determining experimental $\Gamma(d)$ we assumed that the FWHM of Mg $K\alpha$ radiation was 0.68 eV and Lorentzian in shape.

IV. DISCUSSION AND CONCLUSIONS

A. Comparison of experimental Auger spectra of metals and vapors

A survey of Tables I and II indicates that there exists a good overall agreement between the relative energies of the Auger components for the two different phases of the same element. For instance, the strong $1G_4$ component can be located precisely in both Auger groups. This observation is further substantiated when the measured spin-orbit splittings Δ_{3d} of the 3d states in metals and vapors are compared, see Table III. It is also gratifying to compare these Δ_{3d} 's with those obtained directly from the photoelectron measurements; all three independent measurements are in accordance within ± 0.09 eV. For other Auger terms the energy location is less accurate and in a few cases relative shifts of ± 0.2 eV are indicated. The energy splitting between different terms should be the same in M_4 and M_5 groups. The variations in the relative line positions inside the groups are felt to reflect an inaccuracy in the decomposition procedure rather than any physical effect. It should

TABLE I. Relative kinetic energies (eV) of the $M_{4,5}N_{4,5}N_{4,5}$ Auger lines for In to Te from solid metals and vapor molecules.

	In		Sn		Sb		Te	
Transition	Solid	InCl ₃ vapor	Solid	SnCl ₂ vapor	Solid	Sb ₄ vapor	Solid	Te ₂ vapor
$M_5N_{4,5}N_{4,5}$								
$1S_0$	-3.94	-3.86	-4.48	-4.29	-4.81	-4.56	-4.71	-4.44
$1G_4$	0.00	0.00	0.00	0.00				
$1D_2$	} 0.76	} 0.69	} 0.77	} 0.72	} 0.00	} 0.00	} 0.00	} 0.00
$3P_0$								
$3P_1$	} 1.41	} 1.28	} 1.53	} 1.40	} 1.61	} 1.50	} 1.96	} 1.60
$3P_2$								
$3F_2$	} 2.16	} 2.06	} 2.30	} 2.16	} 2.54	} 2.54	} 2.82	} 2.82
$3F_3$								
$3F_4$	3.05	3.20	3.34	3.36	3.66	3.75	4.04	4.13
$M_4N_{4,5}N_{4,5}$								
$1S_0$	-3.36	-3.47	-4.08	-4.26	-4.76	-4.69	-4.72	-4.68
$1G_4$	0.00	0.00	0.00	0.00				
$1D_2$	} 0.53	} 0.70	} 0.41	} 0.60	} 0.00	} 0.00	} 0.00	} 0.00
$3P_0$								
$3P_1$	} 1.32	} 1.32	} 1.31	} 1.35	} 1.88	} 1.48	} 1.80	} 1.56
$3P_2$								
$3F_2$	} 2.19	} 2.08	} 2.34	} 1.99	} 2.62	} 2.51	} 2.88	} 2.71
$3F_3$								
$3F_4$	3.19	3.72	2.84	3.34	3.50	3.78	4.11	4.10

TABLE II. Relative intensities (%) of the $M_{4,5}N_{4,5}N_{4,5}$ Auger lines for In to Te from solid metals and vapor molecules.

Transition	In		Sn		Sb		Te	
	Solid	InCl ₃ vapor	Solid	SnCl ₂ vapor	Solid	Sb ₄ vapor	Solid	Te ₂ vapor
$M_5N_{4,5}N_{4,5}$								
$^1S_0$	3.6	3.9	5.0	2.6	4.1	3.5	3.9	4.5
$^1G_4$	31.0	20.3	30.3	24.7	28.3	24.8	28.6	23.3
$^1D_2$	} 10.3 41.3	} 10.8 31.1	} 9.6 39.9	} 10.9 35.6	} 10.8 39.1	} 10.6 35.4	} 13.7 42.3	} 12.2 35.5
$^3P_0$								
$^3P_1$								
$^3P_2$	11.4	13.5	10.3	11.9	11.8	12.1	11.4	11.7
$^3F_2$	} 20.2	} 19.1	} 22.1	} 13.9	} 23.5	} 24.8	} 21.6	} 26.0
$^3F_3$								
$^3F_4$	23.5	21.8	22.7	23.4	21.4	24.2	20.8	22.3
$M_4N_{4,5}N_{4,5}$								
$^1S_0$	4.8	13.0	5.0	11.5	5.2	9.5	9.7	12.7
$^1G_4$	43.1	31.4	40.8	34.0	54.9	44.3	43.0	40.3
$^1D_2$	} 20.7 63.8	} 15.6 47.0	} 23.8 64.6	} 18.5 52.5	} 16.6 71.5	} 16.2 60.5	} 20.5 63.5	} 16.1 56.4
$^3P_0$								
$^3P_1$								
$^3P_2$	10.0	11.7	11.9	13.4	9.8	11.5	12.4	13.4
$^3F_2$	} 18.1	} 15.7 23.9	} 17.2	} 3.4 18.0	} 12.3	} 16.7	} 12.5	} 15.2
$^3F_3$								
$^3F_4$	3.5	4.5	1.3	4.5	1.1	1.8	1.7	2.3

be noted that the resolving of the overlapping lines by any kind of fitting program is never unambiguous. This holds true especially for the lines which are separated by less than the half-width of the standard line. This is exactly the case in the present spectra for the components $^1G_4$, $^1D_2$, $^3P_0$, and $^3P_1$ which all appear inside of the half-width range of the standard line. The same is also true for $^3F_2$ and $^3F_3$. Therefore, caution should be exercised so as not to take too literally the relative splittings and intensities of the above-mentioned components, when only the total intensities of these lines are well reproducible.

Some general remarks can be made on the relative intensities presented in Table II. In both groups the sum intensities of the $^1G_4$, $^1D_2$, $^3P_{0,1}$ lines are higher for the solid-state spectra, whereas the intensities of weaker lines are almost always higher for the vapor-phase spectra. This phenomenon arises probably from the way the background has been subtracted. It is often observed that the "continuous background," where the background intensity increases proportionally to the net intensity in each channel with exponential attenuation on going from higher to lower kinetic energies, represents fairly well the background for solids. In the case of molecular vapors, the background level on the low-energy side is rather high, much higher than for atomic vapors, and is not well represented by such a continuous-background model. Therefore, in addition to the continuous-background subtraction, we have also

made an attempt to fit the spectra of the molecular vapors by using a "linear background" under the line groups in question and adjusting the levels properly on both sides of the groups. The values given on Table II for the vapors are the mean values for both these fits. Characteristic of the continuous background is that it decreases the intensities of stronger lines and increases those of weaker lines in comparison with the intensities obtained by the linear-background subtraction. It is probable that the linear background is more valid for the spectra of molecular vapors and gives rise to the intensity trend indicated in Table II. Another noticeable feature is that the intensities of the weak $^1S_0$ lines in the M_4 group are considerably higher for vapors than for the solids. This effect is attributable to the differences in the backgrounds of the two spectra and may not be regarded as evidence of differences in the Auger transitions themselves. It should be added that the $^1S_0$ lines fall into the high-energy shoulder of the M_5 groups so that their energy locations and intensities are very sensitive to the estimate of the background level. The overlapping of the $M_{4,5}N_{4,5}N_{4,5}$ ($^1S_0$) line with the $M_5N_{4,5}N_{4,5}$ ($^3F_4$) line is largest for In, for which the most remarkable differences in intensities occur between the vapor and solid-state spectra.

Keeping in the mind the possible sources of errors of the relative intensities presented in Table II we suggest that the relative intensities of the Auger lines exhibit an appreciable constancy when

TABLE IV. Natural linewidths $\Gamma(M_{4,5}N_{4,5}N_{4,5})$, $\Gamma(3d)$, and $\Gamma(4d)$ of the $M_{4,5}N_{4,5}N_{4,5}$ Auger transitions, and of the $3d$ and $4d$ photoemission as obtained in experiment and theory.^a Experimental and theoretical two-hole final-state widths $\Gamma(4d4d)$ are also indicated. Units in eV.

Element	Experiment		$\Gamma(4d)$	Theory		Experiment	Theory ^b	Theory ^c
	$\Gamma(M_{4,5}N_{4,5}N_{4,5})$	$\Gamma(3d)$		$\Gamma(3d)$	$\Gamma(4d)$	$\Gamma(4d4d)$ $= \Gamma(M_{4,5}N_{4,5}N_{4,5}) - \Gamma(3d)$		
In metal	0.93(10)	0.32(15)	<0.09	0.50	~0.1	0.61	0.43	~0.2
InCl ₃ vapor	0.85							
Sn metal	1.10(10)	0.19(10)	0.15(8)	0.52	~0.1	0.91	0.62	~0.3
SnCl ₂ vapor	0.65							
Sb metal	1.15(10)	0.29(10)	0.19(8)	0.56	~0.1	0.86	0.66	~0.4
Sb ₄ vapor	0.95							
Te metal	1.36(10)	0.25(10)	0.13(8)	0.60	~0.1	1.11	0.75	~0.3
Te ₂ vapor	0.85							

^aReference 27.

^bReference 28.

^cCalculated from the equation $\Gamma(4d4d) = 2\Gamma(4d)$ using experimental $\Gamma(4d)$.

measured from the metals and vapors. This finding lends full support to earlier observations made for Cd *MNN* Auger spectra.⁶ On the basis of great similarities of the Auger spectra of the two phases we are tempted to suggest that there exists no essential difference either in the relative energies or intensities of the $M_{4,5}N_{4,5}N_{4,5}$ Auger components for Cd to Te between the vapor and metal phases which have approximately the same outer shell configuration.

B. Quasiatomic versus bandlike emission

All the main features of the solid-state Auger spectra can be interpreted as being due to multiplet splitting of atomiclike two-hole final states. It should be noted that similarities between the profiles of the Auger groups throughout the range from Ag (Ref. 18) to Te suggest that there are no observable spectral features which could be said to be directly related to the $4d$ band structures of these metals. It has been established by Mariot *et al.*¹⁸ for silver and Aksela *et al.*⁶ for cadmium that the solid-state $M_{4,5}N_{4,5}N_{4,5}$ Auger spectra can be interpreted satisfactorily in terms of the atomiclike two-hole final states. This finding is in good agreement with the theoretical predictions of Sawatzky²⁸ according to whom an Auger spectrum should be atomiclike if the effective hole-hole interaction energy is larger than twice the one-electron bandwidth. Thus the band effects are expected to be even smaller for the next higher elements with $4d$ electrons lying deeper in the core.

With respect to the subject matter at hand a few words about the natural linewidths $\Gamma(3d)$ and $\Gamma(4d)$ may be in order. According to Table IV the experimental $\Gamma(3d)$ values for the solids are systematically smaller than the theoretical ones. A

similar result was found in $L\alpha$ x-ray emission ($L_3-M_{4,5}$) measurements²⁹ of the elements from ^{42}Mo through ^{50}Sn . Apparently, in theory the natural width due to $3d$ Auger transition rates are overestimated by about 0.2–0.3 eV, at least, for In through Te. Instead, the theoretical $\Gamma(4d)$ values seem to be in accord with the experimental widths $\Gamma(4d)$ within the error limits quoted.

The natural widths $\Gamma(4d4d)$ of the double-hole final states are calculated from the equation

$$\Gamma(4d4d) = \Gamma(M_{4,5}N_{4,5}N_{4,5}) - \Gamma(3d)$$

by using the experimental widths of the Auger lines and the $3d$ photoemission lines. Theoretical $\Gamma(4d4d)$ values are obtained from the model of Sawatzky and from a relation $\Gamma(4d4d) = 2\Gamma(4d)$, quite commonly used in the literature, and are listed on Table IV. A comparison between theory and experiment reveals that the latter estimate is in error by a factor of 3 while Sawatzky's model is in much closer agreement.

C. Experimental extra-atomic relaxation energies

The vapor-metal shifts of the Auger lines were determined from the absolute kinetic energies of the $^1G_4$ term. The observed shifts R_e after subtracting the work functions of the metals are given in Table V. The vapor-metal shifts in this table are not directly free-atom-metal extra-atomic relaxation energies denoted by R_{ea} because they refer to shifts between the molecular and solid species. The shifts between free atoms and solids are higher by the amount of molecular extra-atomic relaxation energy R_M if no other effects are present. For the present elements, R_M is not known accurately. However, a first-order approximation for R_M may be obtained from the re-

sults of $M_{4,5}N_{4,5}N_{4,5}$ Auger measurements on atomic- and molecular-iodine vapors where a shift of 3.2 eV for R_M was found.³⁰ For tetra-atomic InCl_3 and Sb_4 and triatomic SnCl_2 R_M is probably somewhat higher, perhaps 3–5 eV. In the absence of any better estimate we assume that R_M is 3 eV for Te_2 and 5 eV for the rest of the molecules.

Chemical environment also influences the Auger spectra by changing the binding energies and tends to decrease kinetic energies for the compounds. We have found that the $M_{4,5}N_{4,5}N_{4,5}(^1G_4)$ line is shifted in InCl_3 by –6.5 eV relative to the In metal and by about –5 eV in SnCl_2 relative to the Sn metal. These shifts consist of a chemical shift R_{ch} and a change in the extra-atomic relaxation of the compounds relative to the metals. In general,

$$R_{ea} = E(Z^M) - E(Z^V) = R_e + R_M - R_{ch}, \quad (1)$$

where $E(Z^M, V)$ refers to the kinetic energies of electrons from metal (M) and atomic vapors (V). To estimate R_{ch} and R_M we made use of the results of Bahl *et al.*³¹ for Te. They found R_{ch} to be 3–4 eV for a large number of Te compounds. We have taken the average of the two values for R_{ch} both in the InCl_3 and SnCl_2 molecules and assumed $R_M \cong 5$ eV, R_{ea} in the metals amounts to about 14 eV according to Eq. (1). When taking into account fairly large uncertainties in the presented values of R_M and R_{ch} it is reasonable to suggest that R_{ea} in In and Sn is between 13 and 16 eV. For Sb and Te a correction for R_M only is required. Therefore, one obtains $R_{ea} \cong 12$ eV for Sb and Te, and this result is probably more accurate than that for In and Sn.

D. Theoretical extra-atomic relaxation energies

To obtain a theoretical estimate for R_{ea} we have followed the reasoning afforded by Shirley³² and Kowalczyk *et al.*^{33–35} Using the model of Hedin and Johansson³⁶ within the framework of the equivalent

core scheme, the extra-atomic relaxation for the $M_{4,5}N_{4,5}N_{4,5}$ Auger transitions reads

$$R_{ea} = \frac{3}{2}F_{Z+1}(4d5p) + \frac{1}{2}[F_{Z+2}(4d5p) - F_{Z+1}(3d5p)]. \quad (2)$$

Here atomic-state $5p$ orbitals are to be regarded as completely occupied screening orbitals. The quantities $F_Z(dp)$ are combinations of the two-electron Slater integrals

$$F_Z(dp) = F^0(dp) - \frac{1}{15}G^1(dp) - \frac{3}{70}G^3(dp),$$

where F^0 , G^1 , and G^3 can be evaluated from Mann's tables.³⁷

The calculated values of R_{ea} for Cd through Te are presented in Table V, column 4. Within the fairly large error limits existent for the experimental R_{ea} some agreement is evident between theory and experiment for In and Sn while a good agreement was obtained for Cd.⁶ On the contrary, the model predicts an obvious too high R_{ea} for Sb and Te. To our knowledge, there exists only one earlier investigation of R_{ea} in the range from In through Te; viz., that for Te MNN and MNO transitions.⁸ For the MNN transitions R_{ea} was reported to be between 16.1 and 17.6 eV depending on the calculation method employed. Our R_{ea} for Te is clearly below this value.

Recently, Matthew³⁸ has presented extra-atomic relaxation energies for Auger transitions by applying the excited-atom model of Williams and Lang.³⁹ In this model, R_{ea} is derived from

$$R_{ea} = \frac{3}{2}[I_2(Z+2) - I_1(Z+1)] - \frac{1}{2}[I_2(Z+1) - I_1(Z)], \quad (3)$$

where $I_n(Z+m)$ is the n th ionization potential of atom $Z+m$. The values of R_{ea} obtained from Eq. (3) are given in Table V. They seem to predict too small relaxation energies. We have computed R_{ea} also by carrying out Hartree-Fock hole-state

TABLE V. Difference R_e between the $M_{4,5}N_{4,5}N_{4,5}(^1G_4)$ line energies of the solid-phase and vapor-phase Auger spectra after subtracting the work function from the kinetic energies of electrons of the metals. Experimental extra-atomic relaxation energies, $R_{ea}(\text{expt})$, calculated from Eq. (1) are given together with theoretical R_{ea} obtained from Eqs. (2) and (3) and from HF hole-state calculations. Values in eV.

Element	$R_e(\text{expt})$	$R_{ea}(\text{expt})$	$R_{ea}(\text{theory})^b$	$R_{ea}(\text{theory})^c$	R_{ea}^{HF}
Cd ^a	12.2	12.2	12.7	8.3	14.3
In	12.2	13 to 16	14.9	9.3	16.0
Sn	12.6	13 to 16	16.1	10.4	17.7
Sb	6.9	11 to 13	17.3	10.1	19.5
Te	8.0	11 to 13	18.2	11.1	21.3

^aReference 6.

^bEquation (2), Refs. 32–36.

^cEquation (3), Ref. 38.

calculations separately for single-hole initial and double-hole final states. The screening charge is again assumed to correspond to the extra electrons (one electron for single-ionized initial state and two electrons for double-ionized final state) on the first unoccupied atomic orbitals ($5p$ for these transitions). The extra-atomic relaxation shift in this approximation is the change in the total energy of the atom caused by the addition of the screening electrons on their orbitals. The shift of Auger energies is then given by the difference of extra-atomic relaxation energies of double-hole final and single-hole initial states. The calculated values R_{ea}^{HF} are presented in Table V. It can be seen that the R_{ea}^{HF} 's are even larger than the R_{ea}^{HF} 's calculated from Eq. (2).

E. Line broadening in solids

Finally, we shall discuss the line broadening of the solid state $M_{4,5}N_{4,5}N_{4,5}$ Auger spectra. Table IV shows that the line broadening ranges from 0.08 to 0.51 eV when Γ_L of free molecules and metals are compared. Hence, the broadening effect is rather small. For instance, free Cd atoms exhibit the linewidth of 0.32 eV,⁶ and heavier Xe atoms Γ_L of 0.64 eV.¹⁰ Accordingly, a molecular line broadening is quite noticeable in the vapor-state Auger spectra for In to Te. This broadening is associated with different vibrational states of the molecules. Using a linear interpolation for atomic Γ_L between Cd and Xe the molecular line broadening is roughly one-half of Γ_L quoted in Table V. If this estimate is reasonably correct

the total solid-state line broadening appears to be 0.5 eV for In and increases with Z up to about 0.9 eV for Te. This tendency of the line broadening is substantiated by the fact that Cd exhibits the broadening of 0.47 ± 0.10 eV, as deduced from direct measurements on free Cd atoms.⁶

Our Γ_L values are much smaller than 2.1–2.3 eV reported for Te by Bahl *et al.*³¹ A reason for this discrepancy is that Bahl *et al.* have applied only three line components in each Auger group.

In conclusion, the $M_{4,5}N_{4,5}N_{4,5}$ Auger transitions of pure metals from In through Te have been measured at high resolution and compared with the corresponding Auger transitions of free molecules. This comparison was accomplished by decomposing each Auger group into six lines which can be held as a reasonable compromise between the number of components predicted in theory and the number of structures resolvable experimentally. It has been shown that the relative energies and intensities of the Auger components do not vary appreciably when measured from the vapors and the solids. All features can be accounted for by multiplet splitting of atomic two-hole final-state configuration which indicates that these transitions exhibit a quasiautomatic nature in their entirety. We have also estimated extra-atomic relaxation energies for Auger transitions and found them to be between 13–16 eV for In and Sn and between 11–13 eV for Sb and Te. The solid-state line broadening amounts to about 0.5 eV for In and increases with atomic number, being approximately 0.9 eV for Te.

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