

Free-atom-metal shifts in the $M_{4,5}N_{4,5}N_{4,5}$ Auger spectra of Ag, Cd, In, Sn, Sb, and Te

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Experimental and theoretical free-atom-metal shifts have been determined for the $M_{4,5}N_{4,5}N_{4,5}$ Auger spectra of elements from $_{47}\text{Ag}$ to $_{52}\text{Te}$. The experimental shift values have been obtained either from direct measurement of free-atom-metal shifts (Ag, Cd), from measurement of molecular-vapor-metal shifts (Sb, Te) combined with semiempirically calculated free-atom Auger energies, or from comparison between calculated or measured atomic and separately measured solid-state Auger spectra (In, Sn). It is found that the free-atom-metal shifts remain almost constant through these elements in contradiction to most earlier theoretical predictions. The thermochemical model has been applied to calculate free-atom-metal shifts in the Auger spectra, and good agreement with experiment is found. The theoretical shift values have also been calculated using the self-consistent-field density-functional formalism and the results are found to agree very well with the experiment.

I. INTRODUCTION

The shifts in the kinetic energies of photoelectrons and Auger electrons from free atoms and metallic species have been the object of considerable interest during the last few years. Also the situation in respect to the theoretical side has to date been rather unsatisfactory. The advances in theory have clearly suffered from the lack of reliable experimental tests. There have been rather few accurate measurements for both vapor and metal phases of the same element. The different reference energy levels commonly used for vapor and solid-state measurements cause further complications and inaccuracies for energy difference values.

The purpose of this work is to present more accurate experimental and calculated shift values for the $M_{4,5}N_{4,5}N_{4,5}$ Auger spectra of consecutive elements from Ag to Te. Free-atom $M_{4,5}N_{4,5}N_{4,5}$ Auger energies have been reported for Ag,¹ Cd,^{2,3} In,⁴ I,^{5,6} and Xe.⁷ Direct atom-metal shift has been observed previously⁸ for Cd and in this work we have measured it also for Ag. Tin has low vapor pressure and is therefore difficult to handle experimentally whereas antimony and tellurium vaporize as Sb_4 and Te_2 molecules. Indium and tin have also very low melting points which make their simultaneous measurement in vapor and solid phases with our present experimental setup impossible. Therefore direct free-

atom-solid-metal results are not available for In, Sn, Sb, and Te. In order to obtain the free-atom-metal shift values for these elements we will use the existing experimental atomic Auger energies of neighbor elements for semiempirical calculation of these energies for Sn, Sb, and Te. Then using solid-state Auger energies for Sn and our measured molecular-vapor-metal shift values for Sb and Te good estimates for free-atom-metal shifts are obtained. For In the shift is obtained from separate measurements for atomic vapor and solid metal.

The free-atom-solid-metal Auger shifts are usually calculated assuming simply that the screening charge occupies the first unfilled atomic orbitals. Good agreement with experimental values has been found in some cases, e.g., for Mg, Zn, and Cd,^{8,9} but there are also clear indications of disagreement. Calculated values applying this exciton model increase much more rapidly with Z than experimental values in going from Cd to Te.¹⁰ Therefore we have used two different calculational methods. First we extend the thermochemical model, which has been successfully used to calculate free-atom-metal photoshifts, to the Auger shifts. In this method the shift values are calculated from directly measurable thermochemical quantities; cohesive energies, ionization potentials, and work functions. As for the second, more theoretical approach, the Auger shifts are calculated applying the self-consistent-field (Δ SCF) density-functional formalism.

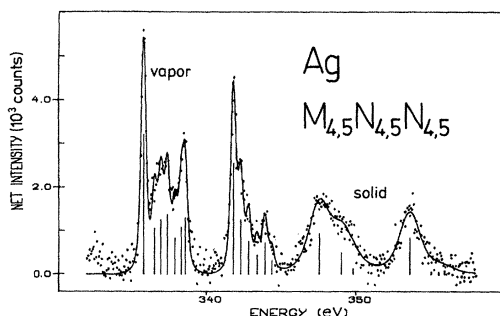


FIG. 1. $M_{4,5}N_{4,5}N_{4,5}$ Auger spectra of silver obtained simultaneously from free atoms and solid metal.

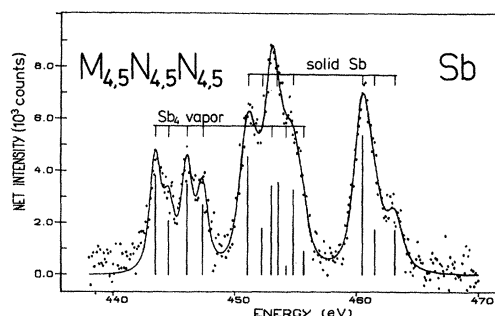


FIG. 3. $M_{4,5}N_{4,5}N_{4,5}$ Auger spectra of antimony from vapor and solid phases.

II. EXPERIMENTAL PROCEDURE AND RESULTS

The spectrometer and the experimental setup for simultaneous measurement of Auger electron spectra from vapor and solid surface has been described elsewhere.¹¹ The principle involved is to measure the solid-state spectra from the continuously condensing surface on the thin partially cooled needle located inside the vapor oven and obtain the vapor spectra simultaneously from the surrounding metal vapor. Auger electrons have been excited by incident electrons with typical energies of 3 keV. A standard pulse counting method has been used applying a microprocessor based spectrometer control and counting system.

The experimental spectra of Ag, Sb, and Te are shown in Figs. 1–3. The shift values are determined from a least-squares-fitting procedure using Voigt functions as the standard line shapes. The experimental results are shown by points and the fits to the data by solid curves. The positions of the bars in the fit represent energies and their heights relative intensities. The determined shift values are given in Table I and in Fig. 4.

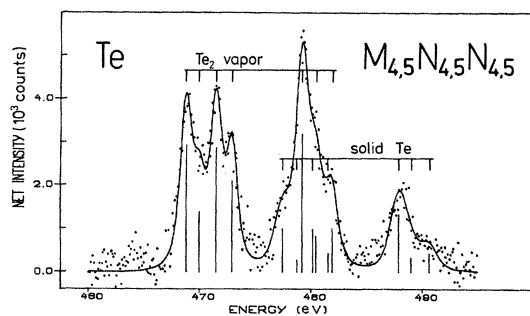


FIG. 2. $M_{4,5}N_{4,5}N_{4,5}$ Auger spectra of tellurium from vapor and solid phases.

For each element in this study the shift value is obtained as the mean value from two or three separate measurements with different vapor-solid intensity ratios. The rather poor statistics of the separate spectra (Figs. 1–3) mainly arises from the difficulties to keep the intensity ratio between vapor and solid contributions as a constant for longer measurement periods.

III. DISCUSSION

A. Comparison of Auger spectra from metals and vapors

The $M_{4,5}N_{4,5}N_{4,5}$ Auger spectrum of free silver atoms has been studied previously.¹ Comparison

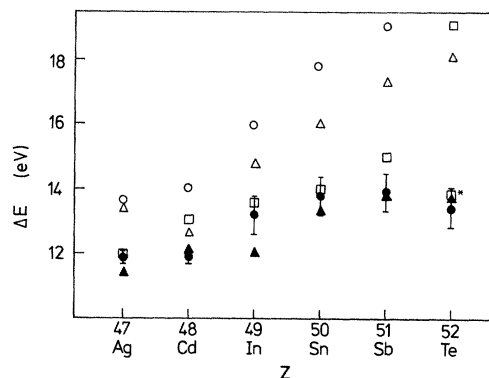


FIG. 4. Experimental and calculated Auger energy shifts (eV) for the studied elements using vacuum level as the common energy reference level. Squares represent the calculations according to thermochemical model, solid triangles the calculations carried out with Δ SCF method, open triangles the calculations using Shirley's model (Ref. 10), and open circles the calculations using Hartree-Fock hole-state procedure (Ref. 10). Solid circles are experimental values. (*See footnote h in Table I.)

TABLE I. Calculated and experimental $M_5N_{4,5}N_{4,5}$ (1G_4) Auger energies and free-atom-metal Auger shifts (in eV).

	$E(M_5N_{4,5}N_{4,5}; ^1G_4)$ Free atom			$\Delta E(M_5N_{4,5}N_{4,5}; ^1G_4)$		Expt.
	Semiemp.	Calc. ΔSCF^a	Expt.	Thermochem.	Calc. ΔSCF	
Ag	335.85	340.8	335.80(25) ^b	12.0	11.5	11.8
Cd	361.10	366.1	361.4(5) ^c	13.2	12.1	11.8
In	385.75	391.7	385.65(20) ^d			
InCl			386.35(20) ^d			
InCl ₃			386.50(20) ^d			
In (solid)			402.85(15) ^e	13.5	12.0	13.1
Sn	410.75	417.5				
SnCl ₂			411.79 ^e			
Sn (solid)			428.85(15) ^e	14.0	13.3	13.7
Sb	437.25	444.2				
Sb ₄			443.50 ^f			7.52 ^g
Sb (solid)			454.90 ^e	15.1	13.7	13.8
Te	464.20	471.1				
Te ₂			468.80 ^f			8.67 ^g
Te (solid)			481.80(15) ^e	19.0 (13.9) ^h	13.8	13.3
I	491.65		491.95 ⁱ			
I ₂			495.20 ⁱ			3.25
Xe	520.30		520.05 ^j			

^a ΔSCF Auger energies for free atoms are for the transition between the hole states $3d \downarrow \rightarrow 4d \uparrow^2$ (see Sec. III E).

^bReference 1.

^cReference 3.

^dReference 4.

^eReference 10.

^fReference 12(a).

^gDirect experimental values for molecule-solid shifts.

^hCalculated using instead of the ionization potentials of Xe the average values from ionization potentials of I and Cs.

ⁱReferences 5 and 6.

^jReference 7.

with the corresponding solid-phase spectrum reveals an essential difference between the spectra: the solid-state spectrum has quasiatomic fine structure according to the splitting of the $4d^8$ configuration, whereas the free-atom spectrum has fine structure according to the $4d^8 5s$ configuration. It has also been observed that the solid-state spectrum has anomalously low intensity for the high-energy 3F components in the $M_5N_{4,5}N_{4,5}$ group. In the fit of the mixed vapor-metal spectrum of Ag we have used seven components for free atom and three components for solid-state spectra in both M_4 and M_5 groups (Fig. 1). In the vapor spectrum the strongest peaks in the groups arise primarily from the fine-structure components originating from the 1G parent line, but in the solid-state spectrum the 1G_4 line is dominant. Thus the different fine structures of solid and free-atom spectra are not expected to cause appreciable inaccuracy in the energy shift value of 11.75

eV, which is determined as the energy difference of these main components. We believe that the inaccuracy of the shift value is ± 0.1 eV which is mainly caused by the inaccuracies involved in the fitting procedure.

Cadmium has as a free atom a closed ground-state electronic structure. The fine structure of the atomic Auger spectrum is thus due to two final-state holes produced by the Auger process, and the corresponding fine structure also exists in the solid-state spectrum. An energy shift value of 11.80 ± 0.1 eV was obtained in an earlier work.⁸

For indium the situation is similar to silver: the atomic spectrum reveals much more fine structure due to influence of the open passive $5p$ outer shell. In respects to the energy shift value 13.4 eV given in Ref. 4 the accuracy is essentially lower (± 0.5 eV) because it is obtained from two separate measurements in vapor and solid phase with different reference en-

ergy levels requiring the correction with a rather inaccurate work-function value. A second contribution to the inaccuracy arises from different fine structures of atomic and metallic spectra. The spectrum of atomic indium⁴ has so many overlapping line components from different parents that the accurate determination of the position corresponding to 1G_4 component is difficult.

The spectra of antimony and tellurium both from molecular vapors (Sb_4 and Te_2) and from solids reveal the same energy splitting (Figs. 2 and 3). This is in agreement with the observation cited in several papers,¹² namely, that if the final two-hole states are in the inner initially filled shells, the spectra for free molecules or even for solids are essentially the same as those for free closed-shell atoms, except for the effects due to extra-atomic relaxation and vibrational broadening. A energy shift between molecule and solid of 7.50 and 8.65 eV was obtained for antimony and tellurium, respectively, as a mean value for energy shifts of different line components.

B. Evaluation of the atomic Auger energies for Sn, Sb, and Te

In order to obtain atomic Auger energies for Sn, Sb, and Te we used the $3d$ and $4d$ one-electron binding energies and calculated hole-hole interaction energies in a simple three step model. The kinetic energies of $M_{4,5}N_{4,5}N_{4,5}$ (1G) lines are thus given by the $3d$ binding energy minus twice the $4d$ binding energy minus the Coulombic interaction energy for (1G) line plus the atomic rearrangement or relaxation energy. Semiempirical $3d$ binding energies have been published recently, e.g., by Johansson and Mårtensson.¹³ There are, however, some discrepancies between the experimental and these α -fitted energy values for silver and cadmium. For this reason and in order to avoid several fittings to the experimental values we will use the relaxed-orbital relativistic Hartree-Fock-Slater values of Huang *et al.*¹⁴ for both $3d$ and $4d$ binding energies. Thus it is obvious that calculated values deviate from true experimental values but the deviations can be expected to be systematic and almost linear as the function of Z . The Coulombic final-state interaction energies applying intermediate coupling have been calculated using a standard method with the numerical values of Slater integrals tabulated by Mann.¹⁵ When both Coulombic interaction and especially atomic relaxation energies¹⁶ are observed to vary very linearly as the function of Z we can combine possible linear errors in the calculated binding energies and in the hole-hole interaction energies to the atomic relaxation energies to form one linear correction. With the aid of this correction the calculated atomic Auger energies are fitted to the experimental values of Ag, Cd, and In on the lower Z values and of I and Xe on higher Z

values. The atomic Auger energies are then readily extracted for the intermediate elements Sn, Sb, and Te. The results for atomic Auger energies are given in Table I. We will note that this procedure delivers semiempirical atomic Auger energies which are based on more numerous experimental values than if the energies are fitted only by Cd and Xe. We believe that true experimental values for intermediate elements are within ± 0.5 eV, of the given energies.

The discussed method to evaluate atomic Auger energies yields absolute energy values in two-hole representation. The free-atom spectra of elements Ag, In, Sn, Sb, Te, and I reveal more fine structure due to the coupling of the vacancies produced by the Auger process to the open outer shell than the spectra of free closed-shell atoms Cd and Xe, as also pointed out in Sec. III A. The experimental Auger energies are determined with respect to the strongest component of the group, therefore in the case of open-shell spectra the energy shift between this component and the 1G_4 component of the two-hole representation should be taken into consideration. The exact determination of this energy shift requires the knowledge of the intensity distribution of components of open-shell spectra. Because this is a very difficult and laborious task, we have not taken into account the correction arising from different fine structures in our energy estimations. We assume the inaccuracies from this source in regards to the free-atom-metal energy shift values plotted in Fig. 4 to be less than 0.5 eV.

C. Molecular Auger shifts

For homonuclear molecules chemical binding-energy shifts can be assumed to be small and binding energy as well as Auger energy shifts are mainly due to the extra-atomic molecular relaxation effects. For molecular iodine the Auger shift 3.25 eV was directly measured.⁵ From the estimated atomic Auger energies and measured molecular energies we now obtain molecular Auger shifts of 4.6 eV for Te_2 and 6.25 eV for Sb_4 molecules. In the case of indium the experimental values are available for atomic In and for $InCl$ and $InCl_3$ molecular vapors. The observed Auger energy shifts are very small (0.7 eV for $InCl$ and 0.85 eV for $InCl_3$). This can be qualitatively understood as a result of a chemical and relaxation shift which in these cases are about the same size but affect the Auger energies in opposite directions. Again for $SnCl_2$ molecular Auger shift of 1.0 eV is obtained.

D. Application of the thermochemical model to calculate free-atom-metal Auger shifts

The thermochemical model based on Born-Haber cycle and equivalent core approximation was applied

to calculate the binding-energy shifts between free atoms and corresponding solid metals to our knowledge for the first time by Jen and Thomas.¹⁷ Very recently Johansson and Mårtensson^{13,18} have used the same but slightly modified procedure. In both studies rather good agreement between experimental and calculated photoshifts have been found. The Auger process forms a more sensitive test for extra-atomic relaxation models because of its more polarizing double hole final state. Therefore it is interesting to apply the same model also to Auger shifts.

The extension of the thermochemical model from photoemission to Auger emission is rather straightforward. Again complete screening of core holes is assumed. Then equivalent-cores approximation can be used and the shift values are evaluated from thermochemical data. The Born-Haber cycle for calculation of the Auger shifts is shown in Fig. 5 with the corresponding cycle for photoemission.^{13,18} The essential differences are the added Auger electron emission step (3), exchange of Z to $Z + 2$ core in the core exchange step, and two stages in the neutralization process with corresponding first and second ionization potentials of $(Z + 2)$ atom. Thus we obtain for the Auger energy shift between metal and free atom, neglecting the core exchange and impurity solution energies, and referring the energies to Fermi level in the metal and to the vacuum zero in free atoms

$$\begin{aligned} \Delta E &= E_F^m(jkl) - E_V^f(jkl) \\ &= E_F^m(j) - E_V^f(j) + E_{IP_1}(Z+2) + E_{IP_2}(Z+2) \\ &\quad + E_{\text{vap}}(Z+2) - E_{\text{vap}}(Z) \end{aligned} \quad (1)$$

When the Auger energies from metallic and atomic state have the same reference energy level, the work function ϕ must be subtracted from the right side of Eq. (1). The binding-energy shift $E_F^m(j) - E_V^f(j)$ can then be calculated from the inner cycle of Fig. 5.

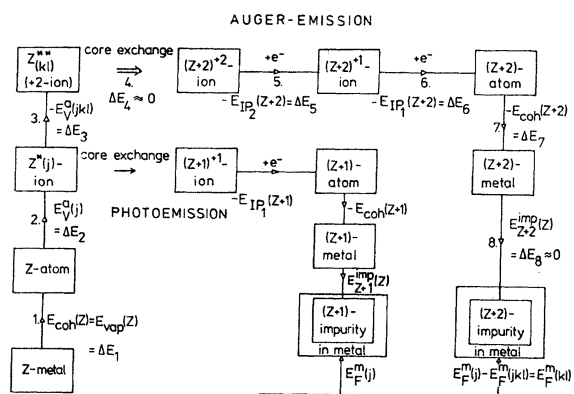


FIG. 5. Thermochemical model for free-atom-metal Auger shifts.

The calculated results for the studied elements are given in Table I and Fig. 4 using values from Ref. 19 for vaporization energy, work function, and ionization potentials.

E. ΔSCF calculation of free-atom-metal Auger shifts

We have applied the self-consistent spin-density-functional method^{20,21} to calculate the free-atom-metal Auger energy shifts. As a detailed description of these and related calculations are the subject of a forthcoming paper,²² we will provide only a short discussion here.

The method we use is reminiscent of the work by Almladh and von Barth²³ and of Bryant and Mahan²⁴ for x-ray absorption in metals and of the work by Lang and Williams²⁵ concerning core holes in atoms chemisorbed on metal surfaces. In short, four total energy calculations are carried out for each element: (i) free atom with an initial ($3d$) core hole; (ii) free atom with two final ($4d$) core holes; (iii) atom in metal with an initial ($3d$) core hole; (iv) atom in metal with two final ($4d$) core holes. Note that in the metallic case in going from (iii) to (iv) one electron is added at the Fermi level to preserve overall charge neutrality. The Auger shift (when both the atomic and metallic Auger energies are referenced to vacuum level) is then obtained from the total energy differences and the metal work function ϕ ¹⁹:

$$\Delta E = (E_{(iii)} - E_{(iv)}) - (E_{(i)} - E_{(ii)}) - \phi \quad (2)$$

The free-atom calculations were carried out using a nonrelativistic spin-polarized atomic program, with the Gunnarsson-Lundqvist²⁶ local spin-density approximation for exchange and correlation. We defer to discussion related to local density theory and open inner-shell structure (excited states^{25,27}) to a planned forthcoming paper.²² For the metallic calculations, the atom-in-jellium-vacancy²⁸ model was adopted. The metallic environment of the electron-emitting atom was mimicked by a uniform background of charge with a spherical cavity in it. The volume of this cavity is equal to the Wigner-Seitz cell volume in the solid phase. The uniform background density can be calculated from the metal valency (which runs from 1 to 6 for Ag through Te) and the Wigner-Seitz cell radius. The atomic nucleus is placed in the center of the vacancy, and the spin-density functional equations are solved self-consistently for the combined system. In addition to bound (core) states at the central atom, there is a band of delocalized states occupied up to the metal Fermi energy; the latter states are responsible for "extra-atomic" relaxation shift in the Auger energies. For the excited states with one or two core holes, the same spin configura-

tions as in the free-atom calculations were chosen: for the initial state, one $3d$ hole; for the final state, two $4d$ holes in relative spin triplet state. All charge and spin densities were taken spherically symmetric, which amounts to solving the radial equations self-consistently for the relevant spin-orbital occupation numbers. Consequently the calculated absolute values of the Auger kinetic energies correspond approximately to the M_4, M_5 group averages for the $^3P, ^3F$ final-state assignments. These average Auger energies for the free atoms are given in Table I; they are in reasonable agreement with the experiment. Moreover, while the approximations made (including the local spin-density approximation) affect the position of any given Auger line, both for free atoms and for atoms in metal, the difference between the two energies is much less sensitive to them. This is because "intra-atomic" terms largely cancel each other out and the shift is mainly brought about by environmental effects. Also the shifts of the various line components are known to be similar.¹⁰ It is also noteworthy that the computer programs for the free atom and the atom embedded in metal are identical in the sense that the latter reduces to the former as the background density (and the Fermi energy) approaches zero.

The calculated results for the Auger shifts are given in Table I. The agreement with the experimental values is remarkably good, especially when one considers the simplicity of the model. One should also note that there are no adjustable parameters in the calculation.

F. Comparison between experimental and calculated free-atom-metal shifts

Inspection of the present experimental and calculated values (in Fig. 4) clearly shows that the experimental values fall into a narrow energy range of 11.8–13.8 eV throughout the studied series. The values calculated¹⁰ applying the exciton model increase strongly from 12.2–18 eV as a function of Z .

The increase of calculated values applying the thermochemical model is much weaker and the agreement with experiment is good for Ag, Cd, In, and Sn and still satisfactory for Sb. The value for Te, deviates strongly from the experimental one. For this anomalous behavior there are some obvious reasons: For Te, the rare-gas Xe is the $(Z + 2)$ element. It is apparent that the thermochemical model does not work well in this anomalous situation because a closed-shell rare-gas atom is the $(Z + 2)$ counterpart for an open-shell solid element. Examination of numerical values of different terms in Eq. (1) shows that the sum $E_{IP_1}(Z + 2) + E_{IP_2}(Z + 2)$ clearly has the largest contribution to the calculated shift values. This sum of ionization potentials has higher values for closed-shell rare gases than for the neighboring elements. Because the thermochemical model does not take into account the specific electronic structure of the studied element it may be justified to use for $E_{IP_1}(Z + 2) + E_{IP_2}(Z + 2)$ of rare gas, e.g., the average from the corresponding values of $(Z + 1)$ and $(Z + 3)$ atoms. Thus the calculated value for Te is also shown in Fig. 4 and agrees very well with the experimental value. It should be noted that Te is a very poor metal compared with the other studied elements.

The interesting feature, the near constancy of the free-atom-metal Auger shift for the six consecutive elements from the periodic table under investigation here, is also borne out by the Δ SCF calculations. The Auger shift can be thought of as the sum of a chemical shift (which reflects the changes of the initial core-hole level brought about by the environment) and a relaxation shift due to the screening of the final two-hole state. We note that the former is nearly constant as a feedback mechanism ties it to the Fermi level: the higher the metal Fermi energy the more charge flows inside the central atom, raising the initial level. On the other hand, the relaxation shift is also fairly constant, as its main contribution arises from the extra-atomic part in the metal, which is constrained by electrostatic sum rules.

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