

LETTER TO THE EDITOR

Direct measurement of vapour-metal shifts in photo- and Auger electron spectra of Zn and Cd

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Abstract. Photo- and Auger electron spectra have been measured simultaneously from vapour and solid metal for both zinc and cadmium by using Al K α x-ray excitation. The differences in the shifts of Auger and photoelectron spectra have been determined with essentially improved experimental accuracy from directly observed vapour-metal shifts.

The vapour-metal shifts of photo- and Auger electron energies, expected to arise mainly from the electronic extra-atomic relaxation in metals, have been the object of many theoretical and experimental studies during the last few years (Shirley 1972, Kowalczyk *et al* 1974, Larkins 1977, Matthew and Perkins 1978, Wagner 1975, Weightmann 1976, Williams and Lang 1978, Hoogewijs *et al* 1977). There are, however, few measurements for vapours and the relative accuracy of existing experimental shift values is rather poor because the kinetic energies of solid state and vapour spectra have usually been measured with different spectrometers, using different reference energy levels. The solid state spectra have mostly been energy-calibrated against the Fermi level and vapour spectra against the vacuum level. Hence the experimental shifts directly involve, in addition to the inaccuracy of two different measurements ($\geq 2 \times 0.2$ eV), the rather high inaccuracies of the work function values (0.1–0.5 eV) for example. In order to improve the experimental accuracy for determination of shift values we have developed a new technique for simultaneously measuring both vapour and solid phase spectra under experimental conditions which are made as similar as possible.

The difference of the shifts of Auger and photoelectron spectra or difference in Auger parameter introduced by Wagner (1975) is a very useful quantity, because all possible static potentials of vapour and solid samples are exactly the same for Auger and photoelectrons and hence cancel out from the difference of the shifts. Furthermore, it most directly correlates with calculated extra-atomic relaxation energies, providing a good test for different theoretical models of extra-atomic relaxation energies of metals. The background level in x-ray excited electron spectra is always much lower than in electron beam excited Auger spectra, making observation of weak signals easier. Therefore we have undertaken to apply x-ray excitation for these shift measurements. X-rays have the important advantage of also providing the shifts of photoelectron lines. The disadvantage of the x-ray excitation is the substantially lower intensity of Auger electrons compared to electron beam excitation.

The experimental set-up for simultaneously measuring photo- and Auger electron

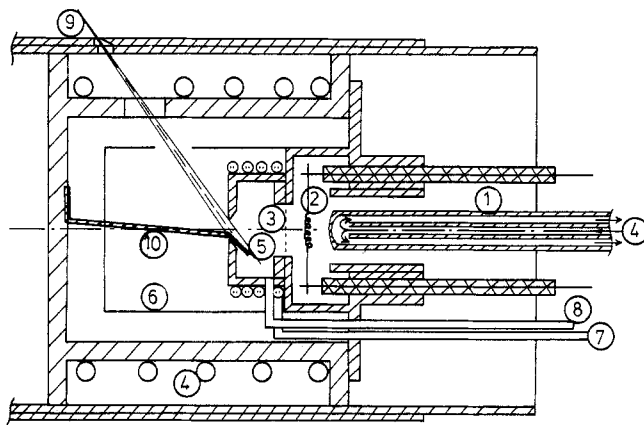


Figure 1. Experimental set-up for measuring simultaneously vapour and solid phase Auger and photoelectron spectra: 1 anode; 2 filament; 3 Al window; 4 water cooling; 5 sample cell; 6 heat radiation shield; 7 heating resistance; 8 gas inlet; 9 analyser; 10 cooled rod.

spectra from vapour and solid surface is shown in figure 1. The principle involved is to observe the solid state spectra from the condensing surface on the thin partially cooled rod located inside the vapour oven and the vapour spectra from the surrounding metal vapour. The spectrometer has been described elsewhere (Väyrynen and Aksela 1979) in more detail.

The measured photo- and Auger electron spectra of zinc and cadmium are shown in figures 2–5. 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 solid curves represent fits to the data. The vertical lines reveal the positions and the relative intensities of components used in the fits. The determined shift values are given in table 1. The measurements were done using both brass and stainless steel ovens but no significant differences in the shift values were observed, showing that the shifts are not affected by the work function of the oven material when the oven is covered inside by the metal to be studied. During these measurements the resolution of the spectrometer has been rather low (0.15%) in order to increase the intensity of the detected electrons. Therefore, and because of the small number of dominating lines, the Auger spectra have been fitted in this study with three or four components in each group. The resolution has been, however, sufficient for determination of the shifts between corresponding strongest line components in different measurements within 0.02 eV. The Auger spectra of Zn and Cd were previously analysed in detail (Aksela and Aksela 1974, Aksela *et al* 1974).

Table 1. Experimental and calculated photo- and Auger electron shifts (eV).

	Level	ΔE_{photo}		Auger transition	ΔE_{Auger}		$\Delta E_{\text{Auger}} - \Delta E_{\text{photo}}$	
		Exp.	Calc.		Exp.	Calc.	Exp.	Calc.
Zn	L ₂	3.25 (10)						
	L ₃	3.15 (10)	5.46	L _{2,3} M _{4,5} M _{4,5}	13.10 (10)	15.98	9.9	10.5
Cd	M ₄	3.00 (10)						
	M ₅	2.95 (10)	5.17	M _{4,5} N _{4,5} N _{4,5}	11.80 (10)	14.28	8.9	9.1

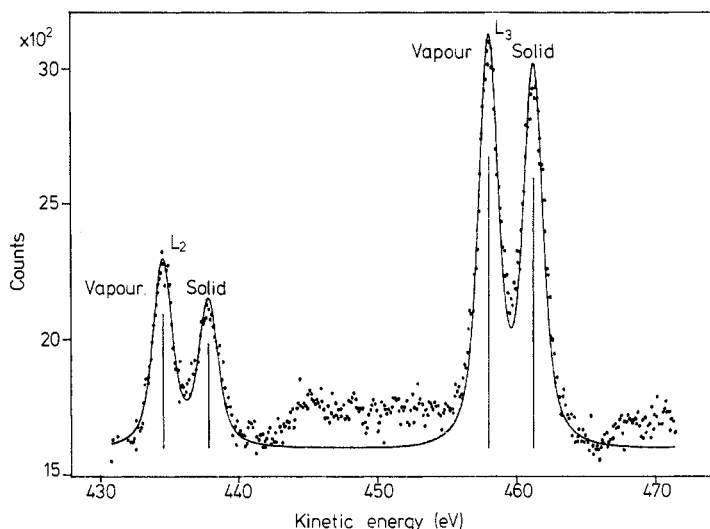


Figure 2. Vapour-metal $L_{2,3}$ (AlK α) photoelectron spectra of zinc. Full curve and vertical bars represent a least-squares fit to the experimental points.

The observed photo and Auger energy shifts may have several sources: extra-atomic relaxation of the conduction electrons in metals associated with the formation of core holes; possible changes in electron configuration on going from free atoms to solid metal; initial state chemical shifts of neutral species due to rearrangement of valence electrons during formation of solid metal and possible electrostatic potential differences of the electron-emitting atoms in vapour and solid samples. For zinc and cadmium there should be no configuration changes, and chemical shifts are also expected to be small. If we are considering the difference between Auger and photoelectron shifts, then possible shifts arising from different static potentials, surface dipole and charging

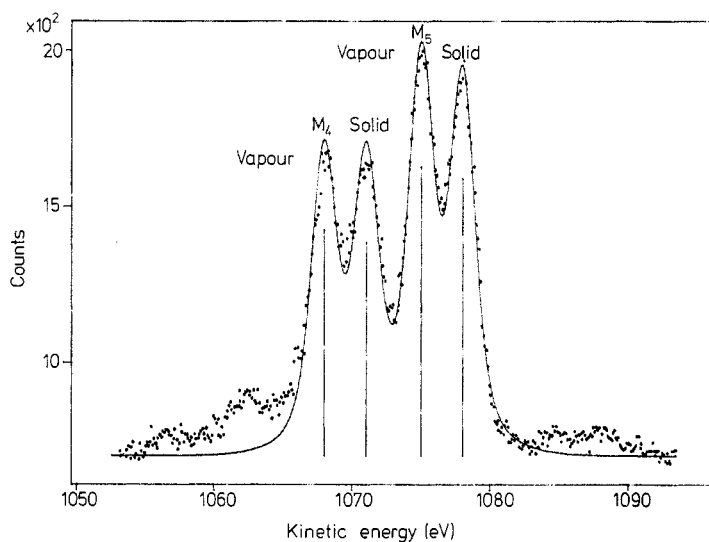


Figure 3. Vapour-metal $M_{4,5}$ (AlK α) photoelectron spectra of cadmium.

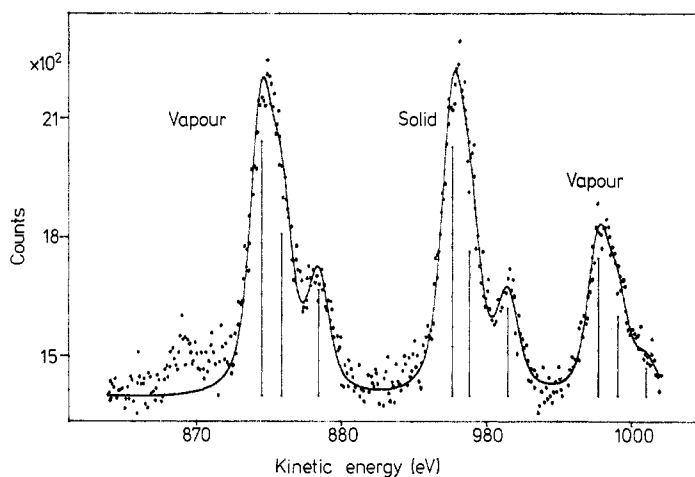


Figure 4. Vapour-metal $L_{2,3}M_{4,5}M_{4,5}$ Auger electron spectra of zinc.

potentials are cancelled. Also the initial state binding energy shifts are cancelled if they are equal for the core levels participating in the transitions. Thus the determined changes in the Auger parameter should be done entirely by extra-atomic relaxation effects.

For comparison with experimental values we have calculated the extra-atomic relaxation energies for photo- and Auger electrons of metallic Zn and Cd using Hartree-Fock hole state procedure. Applying the common approach for the screening of a core hole in metal it is assumed that the screening charges occupy the first unfilled orbitals. For the spectra of this study these are 4p or 5p orbitals for Zn and Cd respectively. The values for the shifts obtained using the Hartree-Fock program of Fischer (1978) are presented in table 1.

Our results can be compared with the experimental photoelectron shifts of Banna *et al* (1978) for Zn and Cd and with the calculated extra-atomic relaxation energies of Hoogewijs *et al* (1977) for Zn. The values of Banna *et al* are 0.4 eV lower for Zn and

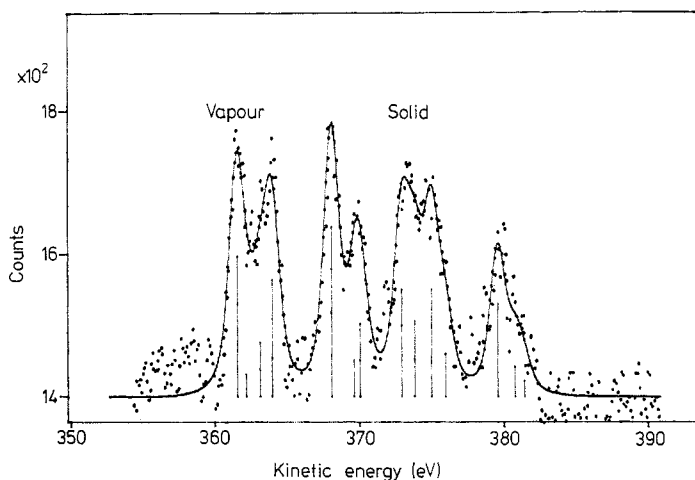


Figure 5. Vapour-metal $M_{4,5}N_{4,5}N_{4,5}$ Auger electron spectra of cadmium.

0.4 eV higher for Cd photoshifts than ours. The inaccuracies given by Banna *et al* are, however, much higher than ours arising from the problems involved in two different measurements as discussed above. Our values also follow the trend shown by calculated values in that the extra-atomic relaxation energies decrease with increasing atomic number. This is supported by photoshift 2.7 eV for Hg measured by Svensson *et al* (1976). The calculated extra-atomic relaxation energies of Zn are identical with corresponding values of Hoogewijs *et al* (1977), whereas there are no other calculated values by this method so far as we know for Cd.

It is, however, as noted earlier, more reliable to consider the changes of the Auger parameter which are to a first approximation affected only by the extra-atomic relaxation phenomena. Thus we find that the agreement for both Zn and Cd between the experimental and calculated shifts of the Auger parameter is surprisingly good.

In conclusion, we have measured free-atom- and metal photo- and Auger electron energy shifts for Zn and Cd with high experimental accuracy. In particular, the difference of the Auger and photoelectron shifts has been obtained very reliably by the applied method, providing good test objects for the further theoretical development of extra-atomic relaxation theories.

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