

## Photoelectron spectra of Zn and Cd metals. Evidence of satellite structure

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The satellite structure in the x-ray photoelectron spectra of Zn and Cd metals has been measured with particular attention being paid to the core subshells. The interesting result of these observations is that, as for pure metals, it is possible to obtain experimental information on the unoccupied band structure through the satellites in the core spectra with the use of electron spectroscopy for chemical analysis.

Zn and Cd are hexagonal-close-packed metals with an atomic ground-state configuration  $d^{10}s^2$ . The picture that has emerged from theoretical and experimental studies is that the valence band of these metals is a free-electron-like band containing two electrons. These metals are of particular interest because of the light they throw on the electronic structure and various excitation processes in materials containing  $d$  electrons. Their properties place them between transition metals and covalent crystals such as Ge and Sn, which are representative semiconductors.

A long-standing problem for transition metals has been their itinerant (bandlike) versus localized (atomic) nature. For these metals, various theoretical studies of ground-state properties<sup>1,2</sup> and experimental measurements<sup>3,4</sup> have clearly shown that an itinerant-band picture is basically valid. For Zn metal (the more intensively studied of the two) the position of the  $3d$  bands has been the subject of some controversy among the theoreticians. This centers upon whether they lie below<sup>5</sup> or above<sup>6</sup> the bottom of the conduction band, which lies roughly 10 eV below the Fermi level  $E_F$ .<sup>6</sup> The position of the  $d$  band is important in understanding the nature of these metals. The difference in the theoretical calculations is attributed (by the authors themselves) to a different choice of the potential.

Recent accurate valence-band energy dispersion  $E(\vec{k})$  measurements<sup>7</sup> using angle-resolved photoemission spectroscopy (ARPES) techniques seem to have definitively ascertained an itinerant-band behavior for the Zn  $3d$  states analogous to the  $d$  states for other transition and noble metals (Fe, Co, Ni, Cu, and Pd).<sup>3,4</sup> This behavior confirms the results of Juras *et al.*,<sup>6</sup> according to whom the  $d$  bands, in Zn metal, lie "within" the conduction band.

We will discuss the x-ray photoemission spectra obtained in the light of the above results. Particular

care has been taken in studying the satellites appearing in the core region. This is the first observation, using electron spectroscopy for chemical analysis (ESCA), of the multielectron excitation transitions in pure metals.

### EXPERIMENTAL

The x-ray photoelectron spectra of the Zn and Cd metals were measured on an ESCA-3 photoelectron spectrometer (Vacuum Generators, Ltd.) using an  $AlK\alpha_{1,2}$  x-ray source ( $h\nu=1486.6$  eV) and a base pressure of  $1.0 \times 10^{-9}$  Torr. Commercial foils of pure metal (of 99.99% purity) were thoroughly cleaned of the surface oxide layer by prolonged sputter etching. In the figures, for convenience, the zero has been placed at the center of the main peaks or at the center of the higher  $d$  or  $p$  states in the case of doublets. The satellite bands were deconvoluted via a reasonable Gaussian fit of the experimental spectra using a DuPont 310 curve resolver. The approximate satellite peaks obtained from the deconvolution are reported in Table I.

### DISCUSSION

Existing experimental measurements reported in the literature lead to the following conclusions:

(a) The structure due to interband transitions for Zn is found as two peaks<sup>8,9</sup> occurring at about 0.9 and 1.7 eV for  $\vec{E}||c$  and about 0.2 and 1.7 eV for  $\vec{E}\perp c$ . Similarly, in Cd, a band is observed at about 1.1 eV (Ref. 10) or 1.5 eV (Ref. 11) for  $\vec{E}||c$  and at  $\sim 1.0$  eV for  $\vec{E}\perp c$ . These measurements, on single crystals or on a Cd film deposited by vacuum evaporation,<sup>11</sup> were made in reflectivity or absorptivity. For the single crystals, polarized radiation was used with the electric-field vector parallel or perpendicular to the  $c$  axis of the crystal. These experimental results are in good agreement with the optical properties of Zn and Cd investigated theoretically by

TABLE I. Experimental values of the separation energy  $\Delta\epsilon$  (eV) of the satellites relative to primary Zn and Cd peaks. The error limit can be evaluated as  $\pm 0.2$  eV.

	Cd				Zn			Calc. <sup>a</sup>	
	4d	4s	3d <sub>3/2</sub>	3p <sub>3/2</sub>	3d	3p	3s		
Main peak	0	0	0	0	0	0	0		
Satellite	2.2	2.1		2.0	1.6	1.8	1.8	2.07	$L_{1,v}-L_{1,c}$
		4.2	4.0	3.9	3.5		3.6		
		6.2	6.3		6.2	6.2	6.2	6.8	$L_{2,v}-L_{1,c}$
		7.3	7.1		8.5	8.8	8.7	8.95	$L_{1,v}-L_{1,c}$
			9.5		11.0	11.4	11.3	11.03	$M_{4,v}^+-M_{4,c}^-$
			11.3		14.2	14.0	14.2	14.27	$K_{1,v}-K_{3,c}$
					16.6	17.0	16.6		
					19.4	19.6	19.3		
					21.8	22.0	21.6		
					24.2	24.0	24.2		

<sup>a</sup>Some interband transitions calculated by Juras *et al.* (Ref. 6).

Kasowski<sup>12</sup> and calculated with use of a nonlocal empirical pseudopotential determined from Fermi-surface measurements. Because the optical absorption may be related to regions, in the band structure, where the energy bands are nearly parallel, these transitions occur along the symmetry lines  $\Gamma \rightarrow K$ ,  $\Gamma \rightarrow M$ , and  $L \rightarrow H$ .

(b)  $E(\mathbf{k})$  dispersion measurements<sup>7</sup> have demonstrated that (i) the Zn 3d states have itinerant-band behavior; (ii) the spin-orbit splitting of the Zn 3d levels occurs with  $\Delta\epsilon \approx 0.5-0.7$  eV (depending on the polarization) and the relative intensity of the doublet components, at high energy, is  $\sim 1.4$ .

(c) Atomic vapors of Zn and Cd studied by photoelectron He II spectroscopy<sup>13</sup> yield a splitting of the 3d levels of  $\Delta\epsilon \approx 0.37$  eV (Zn) and 0.7 eV (Cd).

From our x-ray photoelectron spectroscopy (XPS) measurements, we observe the spin-orbit splitting of the d levels in both Zn and Cd (Fig. 1). In the spectrum of Zn, the splitting is barely visible (approximate deconvolution yields  $\Delta\epsilon \approx 0.7$  eV), whereas in Cd, it emerges clearly ( $\Delta\epsilon = 1.0$  eV). The relative intensities observed agree with the range 1.4–1.5 assigned by Himpsel *et al.*<sup>7</sup>

Apart from d-level splitting, in Zn there is a pair of weak satellites (see arrows in Fig. 1) lying at

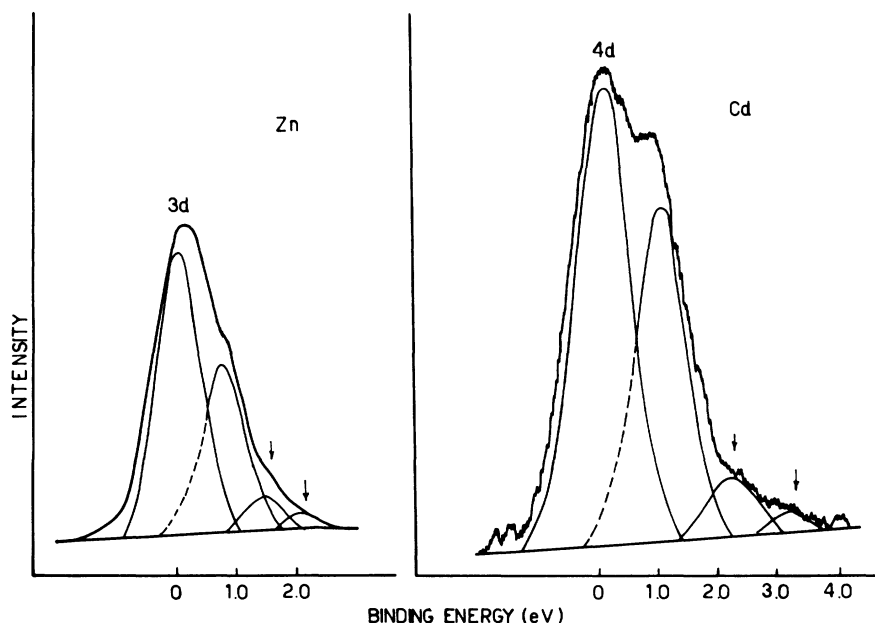


FIG. 1. XPS spectra of Zn 3d and Cd 4d bands.

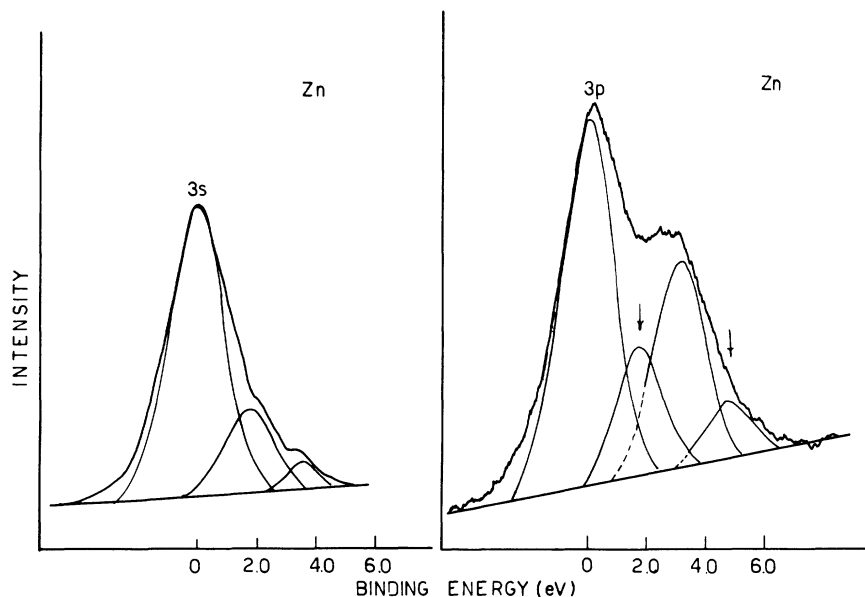


FIG. 2. XPS spectra of Zn 3s and Zn 3p bands.

$\Delta\epsilon=1.5-1.6$  eV from the respective mean peaks ( $d_{5/2}-d_{3/2}$ ) and in Cd at  $\Delta\epsilon=2.2$  eV. These satellites, observed near the 3d (or 4d) band may be rationalized in two different ways:

(a) They are transitions from  $d$  levels to the first empty levels of the conduction band. The binding energy of these transitions does, indeed, fall in this region. This type of explanation has been used by Bancroft *et al.*<sup>14</sup> for the structure observed, using the constant-initial-state (CIS) technique, close to the 5d transitions of metallic Pb.

(b) They are the first interband transition, as observed by Rubloff<sup>8</sup> and Weaver *et al.*<sup>9</sup> In this case, the value observed for Zn is in good agreement with those found by these workers, although the values for Cd are slightly higher.

#### CORE REGION

It is well established<sup>15,16</sup> that in XPS spectra of metals, and in favorable conditions, it is possible to observe the interaction between the positive core hole (created during the process) and the conduction electrons. This effect is very weak and occurs as an asymmetry on the tail of the band. Consequently, to be observable, the band must be very intense and narrow, i.e., unperturbed by other phenomena which might be present. For the case investigated here, these conditions are met only for 3d<sub>3/2</sub> band of Cd (Fig. 5; see inset).

It is also possible to detect, at the lower binding energy with respect to the main peak, a weak feature

due to a surface transition (see in Cd 4s—Fig. 3—at a binding energy of  $\sim -1.5$  eV). We will not discuss these points further, given the unsuitable conditions of our measurements.

Satellites are observed in the core region; for convenience these will be treated as two groups. Some appear very close to the main peaks (Figs. 2 and 3) and others, at the higher  $\Delta\epsilon$ , form a broad band clearly composed of an envelope of several transitions (Figs. 4 and 5).

Figure 2 shows the 3s and 3p spectra of Zn measured at high resolution. In the Zn 3s region (not disturbed by spin orbit coupling phenomena) two satellites are clearly visible at  $\Delta\epsilon$  (from main peak) 1.9 and 3.8 eV, respectively. The former is assignable to the first interband transition, lying at 1.7 eV according to Rubloff and Weaver *et al.* and the latter to another interband transition which, together with other transitions discussed below, forms a series of multielectron excitations.

Via deconvolution, the Zn 3p region also has a satellite band at  $\Delta\epsilon=1.8$  eV; the assignment of this band requires care given the possible splitting of the  $p$  level. Indeed, using accurate measurements via polarized x-ray  $K\beta_{1,3}$  emission spectra on a Zn monocrystal, Dräger and Brümmer<sup>17</sup> found a  $(\vec{E}||c)-(\vec{E}\perp c)$  shift of about 0.8 eV for the Zn atom at the lattice site of  $D_{3h}$  symmetry. The structure of the 3p level is thus split into three sublevels, which these authors attribute to different “portions” of  $3p_z$  and  $3p_{x,y}$  symmetry originates by a crystal-field effect in an environment of noncubic symmetry.

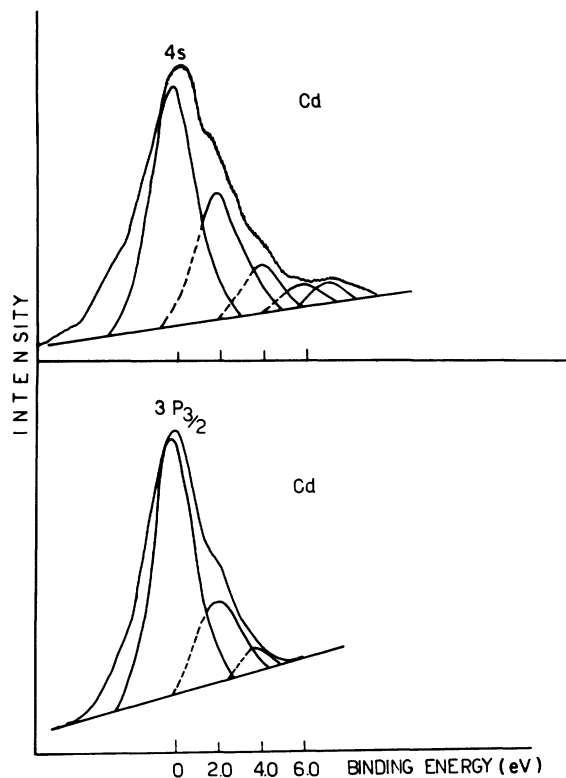


FIG. 3. XPS spectra of Cd 4s and Cd  $3p_{3/2}$  bands.

As mentioned above, in our spectra there is a satellite on each of the two principal main peaks ( $p_{3/2}, p_{1/2}$ ) with  $\Delta\epsilon = 1.8$  eV. This is a decidedly higher value than that of Dräger *et al.* but in good agreement with the first interband transition observed in Zn 3s. The resolving power of our instrument does not allow us to further investigate this peak.

Figure 3 shows the 4s and  $3p_{3/2}$  spectra of Cd. Again, a satellite is observable at  $\Delta\epsilon \approx 2.0$  eV assignable to the first interband transition; other satellites at  $\sim 4.0$ ,  $\sim 6.9$ , and  $\sim 7.3$  eV originate from transitions from the last occupied levels to the first empty levels of the conduction band (multielectron excitations).

The transitions observed at  $\Delta\epsilon > 5$  eV in the core regions (Figs. 4 and 5) are observed for the first time. As for other compounds investigated previously by us (lead, zinc, and transition-metal halides<sup>18-20</sup>) there are envelopes containing several bands. For comparison purposes, Fig. 6 compares the spectrum of Zn metal with that of ZnO, reported previously.<sup>19</sup> It is clear that in both cases a similar band envelope is present, in ZnO it is shifted to higher binding energies. Given the relatively low intensity of this band envelope, and hence high signal

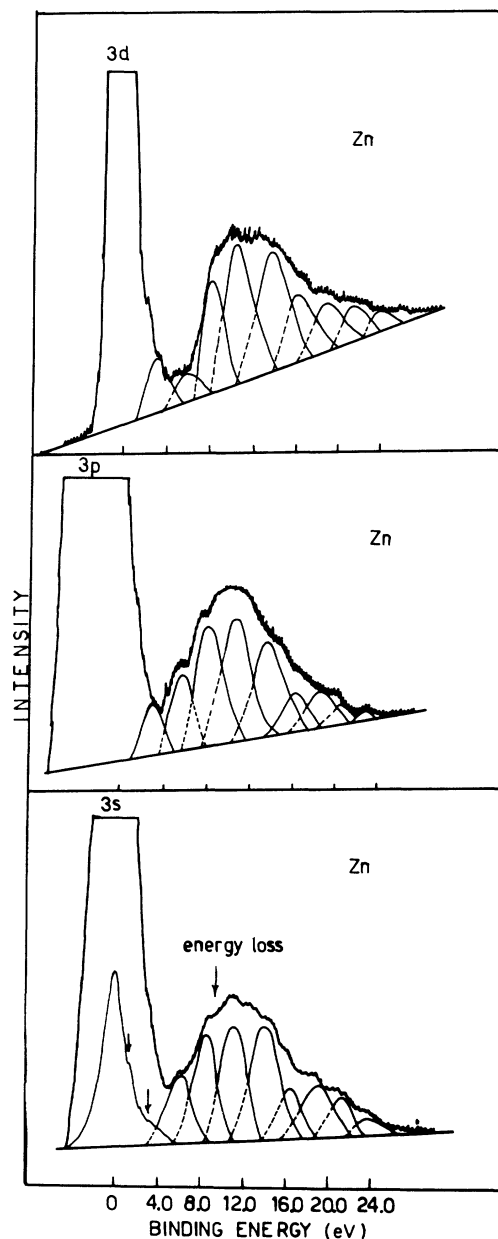


FIG. 4. XPS spectra of Zn 3d, 3p, 3s region.

amplification necessary to observe them, a quantitative analysis is precluded.

We recall that the characteristic energy-loss band of the metals falls in this region of the spectra.<sup>21-23</sup> These plasmon peaks have relatively small halfwidths ( $< 1.0$ – $2.0$  eV) and hence contribute little to the observed band envelope. The approximate (deconvoluted) positions with respect to the main peaks ( $\Delta\epsilon$ ) are listed in the table with some transitions calculated by Juras *et al.* The plasmon peaks lie roughly at the energies indicated by an arrow in the figure with—as already mentioned—small

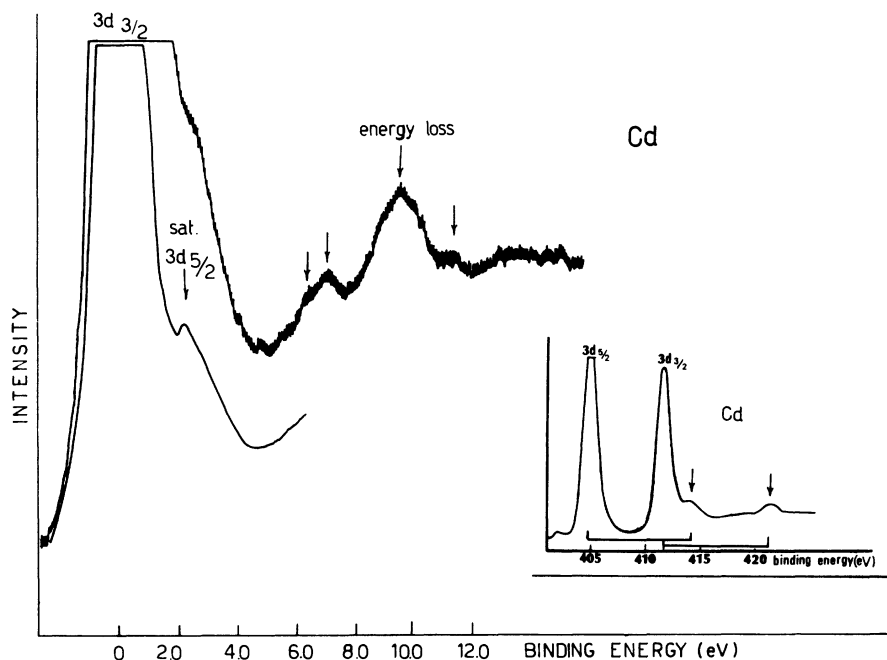


FIG. 5. XPS spectrum of Cd 3d region.

halfwidth. Consequently, the other bands, which appear in all the core regions of the spectrum at roughly the same energies, are assigned to multielectron excitations. They originate from both the  $sp$  valence levels and from the more internal  $3d$  (or  $4d$  in Cd) ones, as described in the other cases studied by us.

For Zn it was possible to observe clearly the satellites that appear in the different core levels ( $3d, 3s, 3p$ ) (Fig. 4). Conversely, for Cd only the  $3d_{3/2}$  region (given the high intensity of the main peak) was favorable for these measurements (Fig. 5). As may be observed from the complete  $3d$ -region spectrum, shown in inset of the figure, there is also the  $3d_{5/2}$  envelope (arrows) which partly overlaps the main  $3d_{3/2}$  peak. However, it is sufficiently cut off as not to interfere with the analysis of the satellites belonging to  $3d_{3/2}$  peak.

We can make the following conclusions:

(a) In all the regions examined ( $d, p,$  and  $s$ ) a transition at  $\Delta\epsilon \approx 1.8$  eV in Zn ( $\approx 2.0$  eV in Cd) is observed and assigned (in agreement with results obtained by others, via different techniques) to the first interband transition. As explained above, doubts may arise only in the case of the satellites appearing close to the  $3d$  (Zn) or  $4d$  (Cd) bands.

(b) A broad band is observed in the core regions which cannot originate exclusively from energy loss, but also involves a band envelope connected with multielectron excitations.

The interesting point of these results is that it is possible to obtain information on the unoccupied band structure via an XPS study of the core-region satellites even in the case of simple metals.

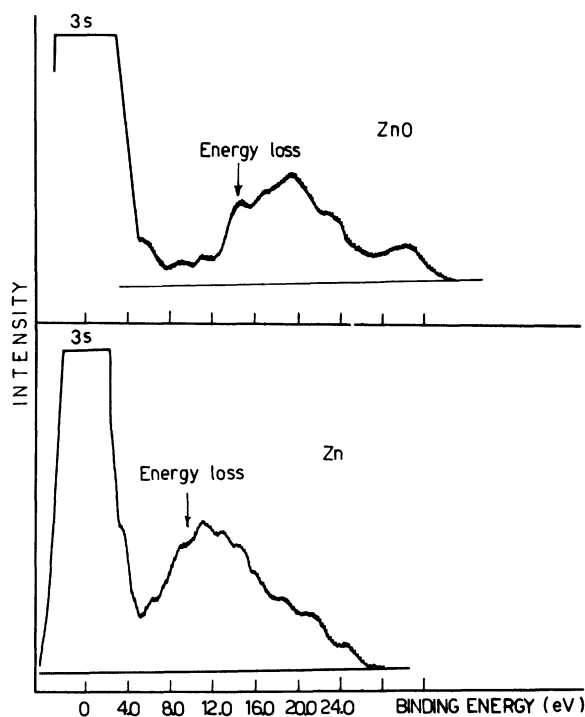


FIG. 6. XPS spectra of ZnO and Zn in the 3s region.

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