with decreasing $\epsilon_g/k_B T$ and increasing $\hbar\omega_c/k_B T$.

It may be pointed out here that the present analysis is valid only for the case of very strong magnetic fields. This is because of the fact that Eq. (1) is true only for $\hbar\omega_c \gg k_B T$. Furthermore, our theory accounts only for LMR due to the nonparabolicity of the energy bands. No account has been made for the LMR due to magnetic-field–dependent relaxation time; but this was done only to emphasize the contribution of nonparabolicity to LMR. A theory which accounts for both of these sources which contribute to LMR is being worked on and the results shall be reported in a future communication.

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Evolution of Core States from Energy Bands in the $4d5s5p$ Region from Pd to Xe †

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X-ray photoemission studies were performed on the $4d5s5p$ elements Pd through Te using monochromatized Al ($K\alpha$) radiation. With increasing atomic number the $4d$ structure evolves from d bands to spin-orbit–split atomiclike core levels. Structure was observed in the $5s5p$ bands for the first time by this method. The cohesive energy was attributed to the $5p$ bands in In through Sb. Evidence for both bonding and nonbonding $5p$ bands was obtained for Te.

Most discussions of band structure in metals are predicated on the assumption that the tightly bound electrons can be regarded as belonging to separate ion cores, while those that are more loosely bound occupy valence bands. In passing beyond the end of a transition series one would expect the d bands to become narrower, fall below the Fermi energy E_F, and evolve into core levels. It is not always clear, however, just which atomic levels can be safely treated as core states and which ones must be explicitly included as part of the band structure. In this Letter we report x-ray photoelectron spectroscopy (XPS)[1] experiments addressed to this question for the $4d5s5p$ elements Pd ($Z = 46$) through I ($Z = 53$). By following the $4d_{3/2}$-$4d_{5/2}$ spin-orbit splitting from I down through Cd to Ag, one can unambiguously trace the onset of band-structure broadening. We also report the first observation by XPS of structure in the sp bands. This structure exhibits systematic changes between Cd and Te.

The specimens studied were high-purity single crystals in each case except Sb and I, for which polycrystalline samples were used. All the specimens except I were studied in a Hewlett Packard 5950A spectrometer with a monochromatic Al ($K\alpha$) x-ray source. The working pressure was always less than 5×10^{-9} Torr. Iodine was examined in the Berkeley iron-free spectrometer. Standard metallographic methods were used to produce clean surfaces. The typical procedure consisted of spark-cutting disks from single-crystal rods, mechanically polishing, and finally electropolishing just prior to insertion into the vacuum chamber. Surface purity was monitored *in situ*, and the sample was repeatedly argon etched until all impurity XPS lines were eliminated. This typically required 15 min of bombardment with a 10-μA beam of 900-V Ar+ ions. Oxygen 1s and carbon 1s spectra taken after each valence-band measurement indicate that there was no oxygen build-up. A carbon layer corresponding to $\frac{1}{10}$ the intensity of the carbon 1s line of graphite accumulated on the surface after 10 h.

Valence-band spectra are displayed in Fig. 1, and derived parameters are set out in Table I.
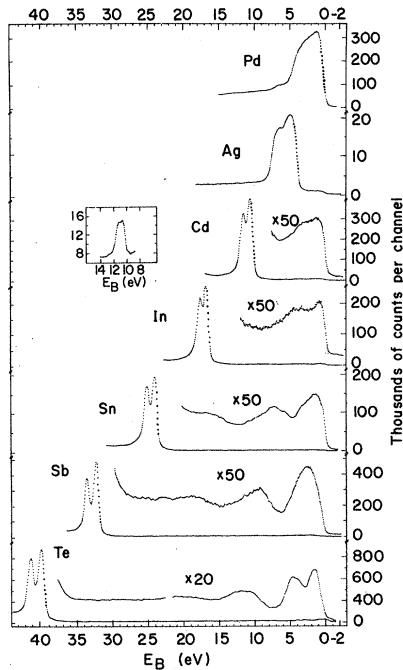
FIG. 1. X-ray photoelectron spectra of the valence-band region for Pd through Te.

The position of E_F in these spectra is known to ± 0.09 eV relative to the Fermi edge of Au, which was measured together with each sample.

In the spectra of Pd, Ag, Cd, In, and Sn, E_F appears to fall at an energy where the density of states is rather large, and the maximum slope of the leading edge is consistent with the resolution of the instrument. For each of these cases the observed slope can be obtained by folding a Fermi distribution function with a Gaussian instrumental response function of 0.55 ± 0.02 eV full width at half-maximum (FWHM). For Sb and Te there is no visible leading edge at E_F.

Doublet structure in the $4d$ shell is evident from Ag through I. The energy splitting ΔE between the two components of the doublet is plotted in Fig. 2(a). Also plotted is a theoretical splitting which was estimated by normalizing orbital energy differences taken from free-atom relativistic Hartree-Fock-Slater (HFS) calculations[2] to ΔE(Sb). That the free-atom values of spin-orbit splitting are appropriate in metals is confirmed by the good agreement of this normalized curve with the experimental splitting in gaseous Xe,[3] also shown in Fig. 2(a). The free-atom val-

TABLE I. Summary of experimental data.

	Ag	Cd	In	Sn	Sb	Te	I	Xe
Binding energy $4d_{3/2}$ (eV)	—	11.46(9)[a]	17.64(9)	24.76(9)	33.44(9)	41.80(9)	—	—
Binding energy $4d_{5/2}$ (eV)	—	10.47(9)	16.74(9)	23.68(9)	32.14(9)	40.31(9)	—	—
FWHM $4d_{3/2}$ = FWHM $4d_{5/2}$	—	0.81(18)	0.78(15)	0.83(8)	0.76(18)	0.94(2)	—	—
4d Splitting (eV)	1.6(1)	0.990(46)	0.899(10)	1.075(34)	1.254(42)	1.51(1)	1.76(16)	1.97[b]
HFS free atom 4d splittings normalized to Sb	0.59	0.73	0.88	1.06	1.25	1.48	1.72	1.98
Binding energy 5s (eV)	—	2.2(5)	4.1(4)	7.0(5)	9.1(2)	11.5(2)	—	—
FWHM 5s (eV)	—	5.0(7)	4.0(5)	5.8(5)	4.0(5)	5.3(5)	—	—
Binding energy 5p (eV)	—	—	0.75(13)	1.25(27)	2.35(25)	4.0(2) / 1.13(5)	—	—
FWHM 5p (eV)	—	—	2.0(2)	3.5(5)	3.9(2)	2.3(2) / 2.1(2)	—	—
4s/4p rel. areas	—	—	1.85	0.7	0.63	0.5	—	—
n/m	—	—	2.00	1	0.66	0.5	—	—

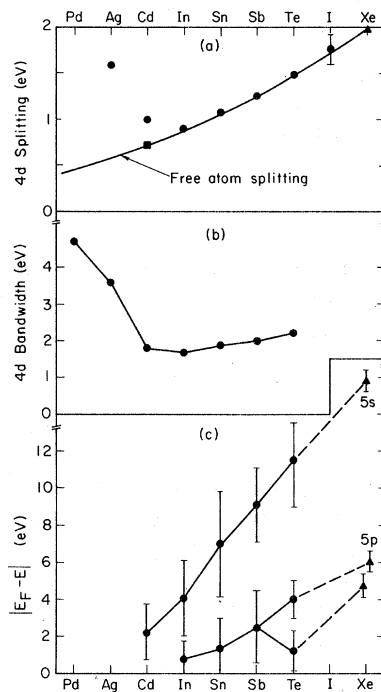[a]Errors in last place given in parenthesis.   [b]Ref. 3.

FIG. 2. (a) Comparison of the experimental $4d$ level splitting with free-atom HFS calculations; the Cd-point (rectangle) refers to the experimental value for Cd atoms sputtered onto an Au (111) surface. (b) Experimental $4d$ bandwidths. (c) Positions of the $5s$ and $5p$ bands relative to the Fermi level; the vertical bars represent the bandwidths at half-maximum. The Xe values in (a) and (c) are taken from Ref. 3.

ues are lowered 0.1 eV by this normalization. The trend from Sn to I is in excellent agreement with the theoretical curve. The intensity ratio of the two components is in each case close to 1.3, in only fair agreement with the value 1.5 expected for a $d_{3/2}$, $d_{5/2}$ doublet on the basis of multiplicity alone. For the heavier elements Sn to I, the $4d$ electrons can be assigned to the ion cores with confidence. The splitting in In may be just slightly larger than the free-atom spin-orbit splitting. For Cd the experimental splitting $\Delta E = 0.99$ eV greatly exceeds the predicted spin-orbit splitting of 0.73 eV, and is in fact even larger than the observed splitting in In. We conclude that band structure affects the $4d$ shell in Cd, at 11 eV below E_F, and is perhaps perceptible even for the $4d$ shell of In at $E_F - 17$ eV.

The spin-orbit splitting energy ΔE is a uniquely reliable parameter for detecting the onset of lattice effects because it is independent of component linewidth, which can be affected by lifetime broadening. Nevertheless, the total "$4d$ bandwidth" can also be used to study broadening by

the lattice. In Fig. 2(b) the $4d$ bandwidth (FWHM) is plotted against Z. The bandwidth drops monotonically with increasing Z across the $4d$ transition series from 6 eV in Mo (not shown) to 3.4 eV in Ag, going through a minimum at In and increasing thereafter because of spin-orbit splitting. The width in Cd is greater than in In, showing again that band-structure effects are present in Cd metal.

In the past, XPS studies of valence bands in transition-series metals have yielded little information about s and p bands.[1,4-6] This was a consequence of their small cross section for photoemission, the presence of $K\alpha_{3,4}$ lines, and bremsstrahlung in the exciting radiation. With these unwanted components removed by monochromatization, it was possible to observe for the first time a considerable amount of structure in the $5s5p$ bands of Cd, In, Sn, Sb, and Te. A detailed analysis of the spectra must await more intensive measurements and further density-of-states calculations, but the systematic variation of the $5s5p$ spectra from Cd to Te (Fig. 1) suggests a preliminary interpretation in terms of a transition from band structure to atomic core-level character for the $5s$ band with a simultaneous filling of the $5p$ band. Three systematic effects occur between Cd and Te. First, the s-p valence band, which shows structure even in Cd, resolves into two peaks in Sn and Sb and three in Te. Second, the higher-binding-energy peak, which we designate as $5s$, falls monotonically below E_F as Z increases. We designate the lower-binding-energy bands in In, Sn, Sb, and Te as $5p$. Finally, the experimental area ratio ($5s/5p$) in In to Te agrees well with the occupation number ratio (n/m) for the respective free-atom ground-state configurations $5s^n 5p^m$ (Table I).

We interpret this behavior in terms of the evolution of corelike $5s$ and $5p$ shells. Figure 2(c) illustrates the approach of the $5s$ and $5p$ bands toward the core s and p levels of Xe. The bars in Fig. 2(c) represent the widths (FWHM) of the $5s$ and $5p$ bands. In Cd through Te all bands are considerably broader than the corresponding levels in Xe. It should also be noted that the $5p$ splitting in Te is dominated by band-structure effects, yielding a splitting much larger (2.9 eV) than the spin-orbit splitting in Xe (1.3 eV). Thus, the systematic trend toward corelike levels aids assignment of the peaks, although solid-state interactions are clearly present in Cd to Te.

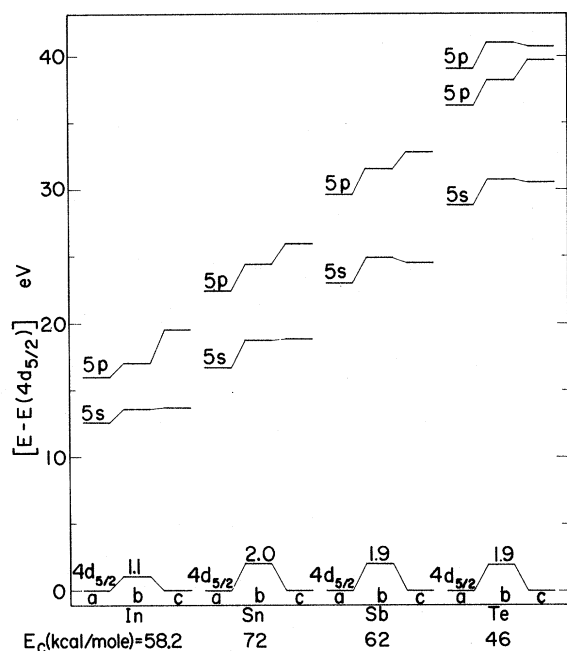Further analysis of the $4d$, $5s$, and $5p$ peak positions permits us to attribute the cohesive

FIG. 3. $5s$- and $5p$-band contributions to the cohesive energy E_c of the metals In through Te. a, experimental values; b, experimental values shifted by the $4d$ relaxation energy Δ given by Eq. (1); and c, free-atom HFS values (Ref. 2).

energy to the $5p$ orbitals. Examination of the peak positions in Cd through Te shows that the $5s$ and $5p$ binding energies are nearer the $4d$ binding energies than are the corresponding free-atom orbital energies from HFS estimates. We ascribe this discrepancy in part to the cohesive energy of the solid and, in part, to relaxation of the passive orbitals during photoemission. Valence-shell relaxation energies are usually much smaller than those of more tightly bound levels.[7] Assuming this to be true for these elements, we may calculate the d-shell relaxation shift Δ according to

$$\Delta = [E_c + n(E_{5s} - \eta_{5s}) + m(E_{5p} - \eta_{5p})]/(n + m).$$

Here E_c is the cohesive energy as taken from the works of Pitzer and Brewer[8] and Wert and Thomson,[9] $\eta_{5s,5p} = \epsilon(5s, 5p) - \epsilon(4d)$ is the difference between the s or p orbital energy and the $4d$ orbital energy in the free atom, $E_{5s,5p} = E_B(4d) - E_B(5s, 5p)$ is the corresponding measured binding-energy difference in the solid, and n and m are the numbers of $5s$ and $5p$ electrons. Figure 3 shows the results of these simple calculations. The relaxation energies range from 1.1 to 2.0 eV for the elements In to Te. The values of Δ show very good agreement with expectations. A theoretical esti-

mate of the magnitude of Δ for I may be obtained by comparing the orbital- and binding-energy estimates for the $4d$, $5s$, and $5p$ levels as given by Rosen and Lindgren[10] (their methods "A" and "B"). The result, $\Delta(I) = 2.4$ eV, agrees quite well with our values.

An important result of this analysis is that the cohesive energy is almost entirely accounted for by the $5p$ electrons. In Te there are two $5p$ peaks of equal area at binding energies of 1.1 and 4.0 eV relative to E_F. The higher–binding-energy band alone accounts for most of the cohesive energy, and it is also wider than the 1.1-eV band. These observations strongly support the model for group-VI elements in twofold coordination as discussed by Kastner.[11] In the chalcogens the valence band is formed by unshared-electron states in contrast to the tetrahedral semiconductors, in which the bonding band forms the valence band and the antibonding band forms the conduction band. We assign the 4.0-eV peak in tellurium as the bonding band and the 1.1-eV peak as the unshared or lone-pair band.

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