

X-RAY PHOTOELECTRON SPECTROSCOPIC STUDY OF IRON, COBALT, NICKEL, COPPER, AND PLATINUM*

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Densities of states and core-electron energy levels of Fe, Co, Ni, Cu, and Pt were studied by means of x-ray photoelectron spectroscopy. The density-of-states results are in good agreement with similar data from other experimental techniques and with theory, but do not agree with the results of early ultraviolet photoemission work on Fe, Co, and Ni. The core levels of Fe metal and Co metal do not show exchange-induced splittings.

X-ray photoelectron spectroscopy (XPS) can in principle provide a rather direct determination of $N(E)$, the density of states near the Fermi level,¹ as well as very precise information on core-electron binding energies.^{1,2} We have applied this technique to the metals Fe, Co, Ni, Cu, and Pt.

The densities of states of these metals have been investigated in recent years by ultraviolet photoemission spectroscopy (UPS), ion-neutralization spectroscopy (INS), and soft-x-ray emission spectroscopy (SXS). All five metals have been investigated by at least one technique, as follows: Fe (UPS³), Co (UPS⁴), Ni (UPS,⁵⁻⁷ INS,⁸ and SXS⁹), Cu (UPS,^{10,11} XPS,¹ SXS,^{12,13} and INS⁸), and Pt (UPS¹⁴). The earliest UPS results for Ni⁵ did not show a dominant peak in the density of states near the Fermi level, in disagreement with INS,⁸ SXS,⁹ and theory.¹⁵ The UPS results^{3,4} for Fe and Co, respectively, were very similar to those of Ni and also disagreed with simple band theory. The UPS method alone gave a large peak at $\sim E_F - 5$ eV for Fe,³ Co,⁴ and Ni,⁵ and at $\sim E_F - 7$ eV for Cu.¹¹ More recent UPS work on Ni^{6,7} agrees much better with theory and with the results of other techniques. Spurious surface effects seem to have been responsible for the dominant feature in the earliest UPS work on Ni.⁵⁻⁷ A summary of these results is shown in Fig. 1. The possible causes of the discrepancies between different techniques have been discussed in detail elsewhere.^{4,6-9,16} Thus the experimental situation was not certain and it was of considerable interest to compare UPS results to those of XPS, a closely related technique for which the large photon energy should decrease any modulation of the electron spectra by the final density of states, relaxation phenomena, or other many-body effects.

In addition, the core levels of ferromagnetic Fe, Co, and Ni should be split by the exchange interaction with the unfilled d shell.¹⁷ Unrestrict-

ed Hartree-Fock (UHF) calculations on free atoms indicate that this core polarization gives

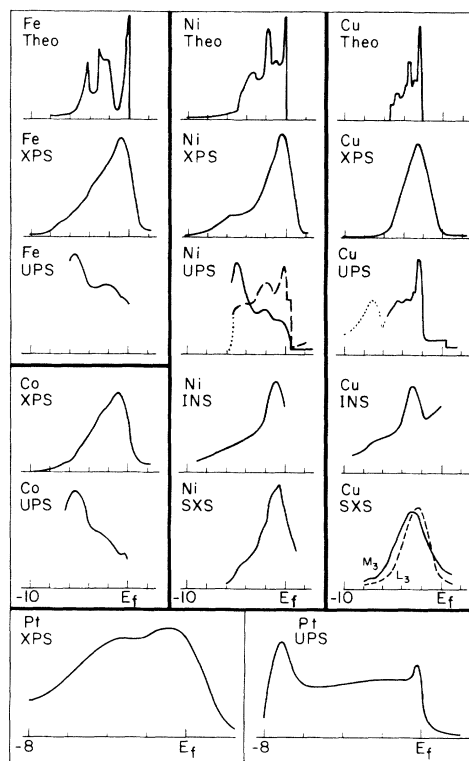


FIG. 1. Summary of some experimental and theoretical studies related to the density of states near the Fermi level (E_F). The experimental data do not strictly represent the density of states, but rather a transition density appropriate to each experimental technique. Data other than XPS have been obtained from the following: Fe Theo., J. F. Cornwell, D. M. Hum, and K. G. Wong, Phys. Letters **26A**, 365 (1968); Fe UPS, Ref. 3; Ni Theo., Ref. 15; Ni UPS, Ref. 5 (solid), Ref. 7 (dotted); Ni INS, Ref. 8; Ni SXS, Ref. 9; Cu Theo., J. C. Phillips and F. M. Mueller, private communication; Cu UPS, Ref. 11; Cu INS, Ref. 8; Cu SXS, M_3 , Ref. 12; Cu SXS, L_3 , Ref. 13; Co UPS, Ref. 4; and Pt UPS, Ref. 14. Ordinate scales are arbitrary but base line corresponds to zero for all cases. Abscissas in units of eV.

rise to a considerable difference between the binding energies of spin-up and spin-down electrons. In particular this difference for iron in the $d^6 5D$ state is approximately 3 eV for the 2s and 2p subshells and 10 eV for the 3s and 3p subshells.¹⁸ In metallic iron and cobalt these figures must be scaled down by 0.56 and 0.43, respectively, to account for the smaller magnetic moments per atom. Although UHF calculations no doubt overestimate these differences by neglecting correlations between electrons of unlike spin,¹⁷ there is reason to believe that UHF estimates should be at least within a factor of 5 of the fully correlated values.^{19,20} Chemical bonding effects of an ionic nature have also been found to be small.¹⁹ As the overall linewidths of x-ray produced photoelectron lines from core levels are 1-3 eV, such splittings are in principle detectable by XPS. We have therefore examined the spectra originating in the $2p_{1/2}$, $2p_{3/2}$, 3s, and 3p levels of solid Fe and Co to check for such splittings.

The XPS technique has been described elsewhere.^{1,2} Mg $K\alpha$ x rays (1253.6 eV) were used to excite electrons into continuum states, and they were magnetically analyzed in the Berkeley iron-free spectrometer. The total instrumental linewidth including x-ray width was ~ 1.0 eV. Since the photoelectrons originate primarily from sites near the surface,^{1,2} the sample surfaces were cleaned continuously by heating them in $\sim 10^{-2}$ -Torr hydrogen atmosphere. At this pressure and the elevated temperatures of our experiments, the presence of hydrogen should not adversely affect our results. The surface cleanliness was monitored by following the oxygen 1s photoelectron line as indicated in Fig. 2. At the lower temperatures the iron 3p line is double because oxide formation chemically shifts the core levels in atoms near the surface. At higher temperatures the intensity of the oxygen "line" (oxide + H_2O + O_2 + CO_2) decreases and the iron 3p line narrows to a width characteristic of iron metal. Structure is even resolvable in the oxygen 1s line, the right peak probably being due to the more weakly bound adsorbed gases. All runs were made in temperature regions for which the oxygen line had negligible intensity (700-950°C) and the core levels had stable widths. No significant changes were detectable in the distributions near the Fermi level of Fe and Co in the range 550-925°C. Thus XPS is unable to detect the effect of the ferromagnetic transition on the density of states. This insensitivity of $N(E)$ has

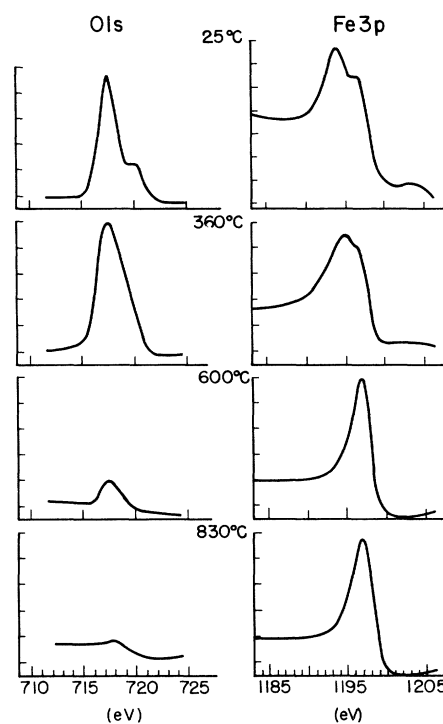


FIG. 2. Effect of hydrogen and increased temperature on the oxygen 1s and iron 3p photoelectron lines. The abscissa is electron kinetic energy. The ordinate scale for all O 1s spectra is the same.

been observed in previous UPS⁵ and INS⁸ studies on Ni.

An XPS spectrum for Cu near the Fermi level is shown in Fig. 3. The uncorrected result is just the experimental spectrum. The tail on the left side is due to inelastic scattering, and the peak on the right side arises from the Mg $K\alpha_{3,4}$ satellite x-ray lines. The corrected spectrum has been obtained by operating on the uncorrected data with an inverted response function $R^{-1}(E)$, where $R(E)$ was obtained empirically from the experimental profile of naturally sharp 3p core levels in the same sample. As the kinetic energies of electrons from the selected core levels were only 5-10% less than those of electrons from the valence band, the scattering characteristics of the two should be very nearly the same. Thus, the $R^{-1}(E)$ correction is straightforward and accurate. Also, we note that the resolvable features of any of the corrected XPS spectra of Fig. 1 were easily visible in the uncorrected spectrum, so that the correction serves primarily to define more accurately the width of the d bands for the metals investigated. The Pt results of Fig. 1 are uncorrected as Pt has no relatively

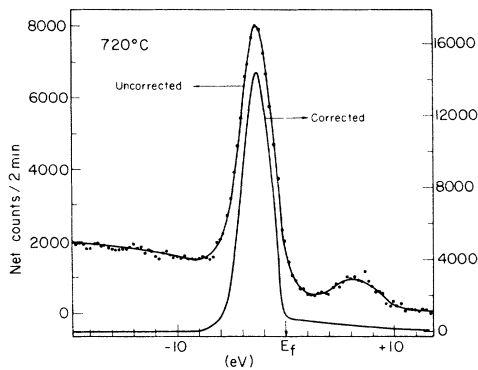


FIG. 3. Correction of a Cu XPS spectrum for the effects of scattering and satellite x-ray lines. A constant background of 4900 counts/2 min was subtracted from both spectra to give the net counts.

isolated core level for use in deriving $R(E)$. The corrected XPS spectra should thus very directly reflect the properties of the density of states, modulated by transition probabilities appropriate to the x-ray photoelectric process. The accuracy of location of the Fermi level is $\sim \pm 0.5$ eV for all metals.

Figure 1 summarizes the results of various experiments and includes theoretical predictions for Fe,²¹ Ni,¹⁵ and Cu.²² In comparing our Co results with other work, we note that the temperatures of our measurements ($>550^\circ\text{C}$) were above the hcp-to-fcc transition point. The UPS results are for hcp. On the basis of these results we make the following conclusions: (1) Where comparisons are possible, XPS results are in good agreement with those of INS, SXS, and one-electron theory and (2) the agreement between UPS and XPS is fair for Pt and Cu, but poor for Fe, Co, and Ni (solid curve). [We note however, that our results are in good agreement with recent UPS measurements for Ni (dotted curve),^{6,7} Fe,²³ and Co²³ made under better surface conditions than early work,³⁻⁵ although for Ni the peak at ~ -5 eV is enhanced in the UPS results relative to the shoulder appearing in our work.] (3) The peaks in the UPS results at ~ -5 eV for Fe, Co, and Ni and ~ -7 eV for Cu would appear to be due to spurious effects and could introduce a strong distortion of the UPS distributions away from those reflecting the initial density of states. (4) Spurious effects of the type discussed in conclusion (3) are less important in XPS than in UPS, although the absolute resolution of XPS is at present lower by approximately a factor of 2.

The results of Fig. 2 indicate no core-polariza-

tion splitting of the $3p$ level of iron at $T/T_C \sim 0.7$ and there is also no apparent decrease in linewidth as T increases to $\sim T_C$, where such polarization should disappear. The spin-orbit splitting in this level is calculated²⁴ to be ~ 1.6 eV and the linewidth of each of the two components (including instrumental contributions) is ~ 2.5 eV. Similar results were obtained for the $2p_{1/2}$, $2p_{3/2}$, and $3s$ levels of iron and for the same four core levels in Co. Ni was studied only in the paramagnetic state as its Curie temperature is too low to permit freeing the surface of adsorbed contaminants. Our results thus indicate either that the XPS technique is incapable of detecting core-polarization effects or that the detailed many-body interactions in the solid decrease the splittings by a factor of 5-10 from the Hartree-Fock free-atom values. Further work is underway to clarify this problem. We can set a tentative upper limit of ~ 1 eV on any exchange-induced splitting observable by photoelectric processes in Fe and Co metal.

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MICROWAVE COMBINED RESONANCES IN GERMANIUM: g FACTOR OF THE FREE HOLE

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We have observed combined spin-cyclotron resonance in the $M_J = \pm \frac{1}{2}$ valence bands of uniaxially stressed Ge from which we obtain directly the first measurement of the free-hole g factor, $g_{\bar{h}} = 2\kappa = 7.20 \pm 0.08$.

Rashba and Sheka¹ have predicted that in semiconductors which lack space-inversion symmetry the usual cyclotron-resonance selection rule can be violated to allow a "combined resonance," an electric dipole transition between Landau levels accompanied by a simultaneous spin flip. Subsequently, it has been suggested that a combined resonance could occur in other, less restrictive situations, for instance, in bands which lie in close proximity to one another, i.e., non-parabolic bands.² As an example attributed to the latter, combined resonance was observed recently in the conduction band of InSb by McCombe, Bishop, and Kaplan³ at high magnetic fields in the spectral region around 500 cm^{-1} . We report here an observation of a combined resonance under substantially different conditions, namely in the hole bands of the centrosymmetric semiconductor Ge at low magnetic fields using millimeter-wavelength radiation. This experiment confirms in detail the effect predicted by Gurgenshivili⁴ and Hasegawa⁵ and yields the first measurement of the free-hole g factor in Ge.

From the degenerate $J = \frac{3}{2}$ valence band edge of Ge an analog of a narrow band gap can be created by a uniaxial compressive stress which splits the band edge into two pairs of Kramers doublets $M_J = \pm \frac{1}{2}$ (up) and $M_J = \pm \frac{3}{2}$ (down). In the presence of both external magnetic field and applied stress the band edge is described by the 4×4 effective-mass Hamiltonian^{6,7}

$$\mathcal{H} = \mathcal{H}_k + \mathcal{H}_e, \quad (1)$$

where \mathcal{H}_k is the Luttinger Hamiltonian⁸ and \mathcal{H}_e is a stress Hamiltonian.⁹ For stress T along the [111] axis the strain energies of the $\pm \frac{1}{2}, \pm \frac{3}{2}$ states at $\vec{k} = 0$ are given by the eigenvalues of \mathcal{H}_e ,

$$\pm \epsilon_0 = \pm \frac{2}{3} D_{u'} T / 2c_{44}, \quad (2)$$

where $D_{u'}$ is the Kleiner-Roth deformation potential and c_{44} is an elastic stiffness constant.

For large deformations when the $\pm \frac{1}{2}$ and $\pm \frac{3}{2}$ substates of Eq. (1) are sufficiently well separated, it is possible to project from Eq. (1) the 2×2 submatrix spanning the space of $M_J = \pm \frac{1}{2}$, yielding⁴

$$\begin{aligned} \mathcal{H}_{\pm \frac{1}{2}} = & \hbar \omega_c (a^\dagger a + \frac{1}{2}) + \frac{\hbar^2 k^2}{2m_3} + \kappa \beta H_0 \sigma_z \\ & + C \frac{(\hbar \omega_0)^2}{2\epsilon_0'} \frac{k_H}{s^{1/2}} (a \sigma_+ + a^\dagger \sigma_-). \end{aligned} \quad (3)$$

Here, k_H is the component of \vec{k} along \vec{H}_0 , $\omega_0 = eH_0/mc$, $s = eH_0/\hbar c$, $\sigma_\pm = \frac{1}{2}(\sigma_x \pm i\sigma_y)$, where σ_x , σ_y , and σ_z are the Pauli matrices, and a^\dagger and a are, respectively, the step-up and step-down operators for the Landau quantum number n . The constant C depends only on the band parameters γ_2 and γ_3 of the Luttinger Hamiltonian.

The first three terms in Eq. (3) representing the zeroth-order ($T \rightarrow \infty$) Hamiltonian give the conventional Landau ladder scheme with spin splitting; the last term, which has the form of a quasi spin-orbit coupling between Landau states and spin, is responsible for the combined reso-