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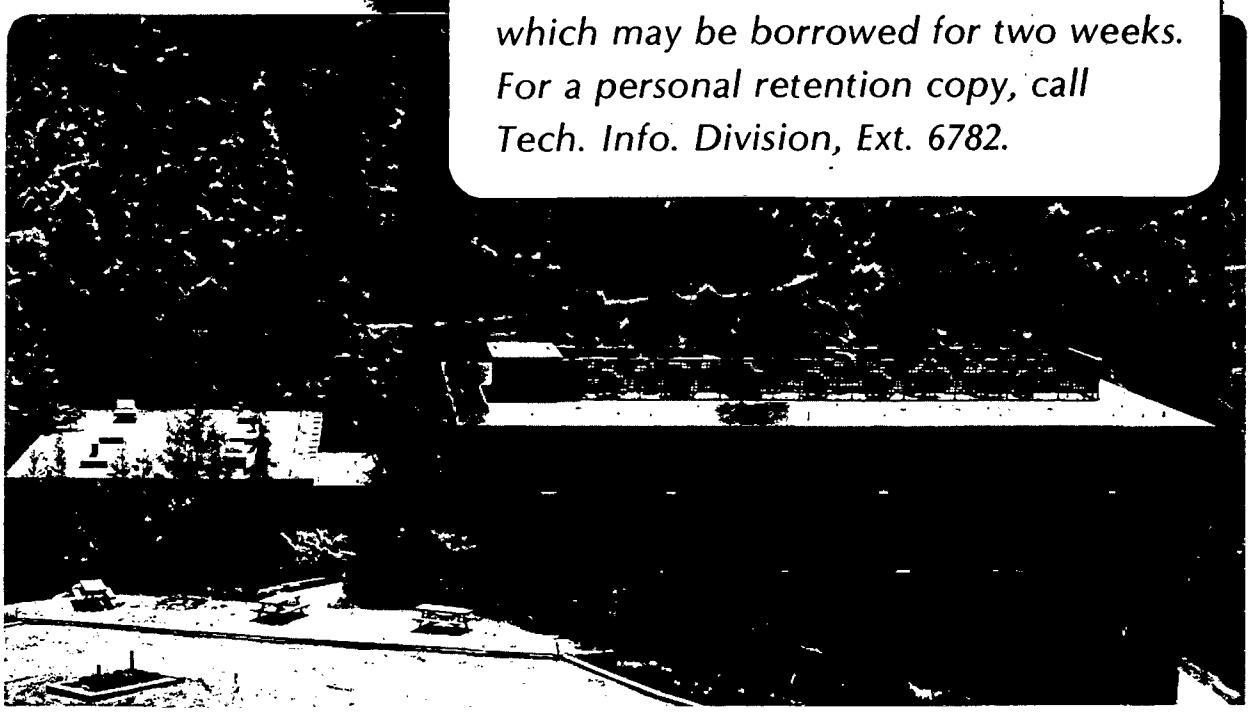

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THE OBSERVATION OF SURFACE SENSITIVE $M_{2,3}$ ABSORPTION EDGE SHIFTS BY REFLECTED ELECTRON ENERGY LOSS SPECTROSCOPY (REELS)

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We have observed that an electron beam of kinetic energy 100-200 eV is scattered from some transition metal surfaces like Ti, Fe and Ni with a strong resonant energy loss corresponding to the $M_{2,3}$ core-level excitation. Because of the low kinetic energy, the scattering is principally from the surface atomic layer, and core-level spectroscopy of just the surface atoms is therefore possible. Chemisorption of oxygen on these transition metals caused substantial shifts in the $M_{2,3}$ threshold energies which appear to be related to charge transfer bonding with the oxygen.

The measurement of core-level threshold absorption energies in materials by electron energy loss spectroscopy (EELS) is a well established technique in transmission electron microscopy (TEM).[1] In TEM, the electron kinetic energy is several keV, and the energy loss is usually observed by kinetic energy analysis of the transmitted beam. Core-level threshold energies are normally used for elemental identification in TEM or STEM instruments, but in recent years some efforts have been made to examine the fine structure above the absorption edge in energy loss spectra analogous to EXAFS.[2] There is a low energy version of EELS possible which can be conducted in the backscattering mode of a

LEED experiment[3] and which could be used to determine core-level thresholds from states 50-100 eV below the Fermi level. We refer to this low energy version of EELS as reflected electron energy loss spectroscopy (REELS). Because of the low incident kinetic energy, the scattering would be principally from the surface atomic layer, and therefore the core-level threshold energies determined by REELS would represent the core-levels of surface atoms. The surface sensitivity of REELS would be higher than with x-ray photoelectron spectroscopy (XPS) performed with conventional x-ray sources, which is the most frequently used method for measuring core-level binding energies. Core-level absorption threshold energies and XPS binding energies are, by definition, slightly different quantities, but both provide chemical state information in terms of shifts or fine structure. A comparison of the physical processes occurring in these two spectroscopies is depicted in Fig. 1. Both spectroscopies can be conducted with the same electron trajectories (photoelectrons and reflected electrons) and electron energy analyzer, e.g. a CMA with integral electron gun. In the more familiar XPS experiment, x-rays from an Al or Mg target impinge on the sample surface and excite a core electron from the sample whose kinetic energy is given by

$$KE = h\nu - E_B - \phi \qquad [1]$$

where $h\nu$ is the photon energy, E_B is the binding energy of the core-level relative to Fermi level, and ϕ is the spectrometer work function. Since $h\nu$ = 1200-1400 eV, the KE for core-levels like $M_{2,3}$ in the first row transition metals is very high, 1100-1300 eV, and the escape depth for

these photoelectrons is 10-20 Å (5-10 atomic layers) according to the tabulation of Powell.[4] In the REELS experiment, a low energy (100-200 eV) electron beam is backreflected from the surface and interactions with the surface atoms result in characteristic quantum losses corresponding to resonant absorption processes. The surface sensitivity is therefore comparable to that of LEED (2 atomic layers). One of these absorption processes is excitation of core electrons to empty states just above the Fermi level, and kinetic energy analysis of the backscattered electrons should reveal a peak at the energy appropriate for this transition. For 200 eV primary beam energy, the only core-levels accessible are those about 50-100 eV below the Fermi level, which limits the general applicability of the technique. However, a number of elements of catalytic interest have core levels which can be probed by REELS, in particular the first row transition elements from Ti to Zn (the $M_{2,3}$ core levels at ca. 40-100 eV below E_F) and the third row transition elements from Ta to Hg (the $N_{6,7}$ core levels at ca. 25-100 eV below E_F). In this letter, we present recent REELS observations for Ti, Fe and Ni, and report chemical shifts for oxygen adsorption that appear to have greater surface sensitivity than XPS chemical shifts.

REELS experiments were performed with a PHI Model 15-110 single-pass CMA with high resolution apertures (0.3% of pass energy, or about 500-600 meV for these experiments) and integral electron gun. Spectra were collected via pulse counting and signal averaging with a PDP 11/04 minicomputer. N(E) spectra were obtained by normalizing the E·N(E) signal from the CMA by E. The primary electron beam current was 20 nA and the beam voltage nominally 200 eV, but the elastic peak was observed

at 185-6 eV. The beam was defocussed to a diameter of ca. 20 μm to produce a beam intensity of 5 mA/cm^2. The inelastic energy losses were measured from the observed elastic peak. The metal surfaces were high purity (5N) polycrystalline foils pre-treated by argon ion- bombardment until no traces of oxygen, carbon or other impurities were observable in the AES spectra.

Energy loss spectra are shown in Fig. 2, and corresponding conventional XPS spectra (taken with a double-pass CMA[5]) are shown in Fig. 3. Loss peaks were observed at about the energies expected from the XPS binding energies of the $M_{2,3}$ core-levels. There is a well-recognized problem in quantitative assignment of the absorption edge energy,[6] as the edge is wide (2-4 eV or more) and often contains fine structure. For simplicity we have selected the energy midway between the valley and the peak, e.g. 65 eV in Ni, 53.7 eV in Fe, 33. eV in Ti, as the threshold energy. The fine structure occurring at energy losses above the threshold presumably corresponds to band structure effects. Oxygen dosing (120 sec) at 2 x 10^{-7} torr and room temperature produced significant shifts in the absorption edges for Ti and Fe, but essentially no change in the edge energy in Ni. The AES peak height ratios O_{510}/Ti_{387} and O_{510}/Fe_{651} were 2.2 and 3.0 respectively. According to previous electron spectroscopy studies of oxygen on these surfaces,[7,8] these AES ratios correspond to multilayer oxygen, i.e. surface "oxide" formation. The Fe spectrum shows about a 2.5 eV shift to higher energy upon oxygen adsorption, with some fraction of the Fe atoms apparently showing no shift in energy. The most dramatic effects were observed with Ti, in which the $M_{2,3}$ absorption edge was strongly attenuated and shifted into two apparent

states, one at 35 eV (ΔE = + 2 eV) and one at 38 (ΔE = + 5 eV). These are very similar to the $L_{2,3}$ chemical shifts previously reported[7] for the oxidation of Ti to TiO and to TiO_2, respectively. The 2.5 eV shift in the Fe absorption edge is also in agreement with previously measured[9] $L_{2,3}$ chemical shifts for oxidation of Fe to FeO. Dosages of 10-20 L of oxygen on Ni at room temperature would not be expected to produce NiO chemical shifts[10] and, in fact, no shift in the adsorption edge was observed. These few preliminary experiments indicate REELS may be a promising technique for determining chemical shifts at surfaces of interest in catalysis and corrosion science. The REELS experiment can be performed with standard single-pass CMA's, which makes the experiment simpler to perform than XPS.

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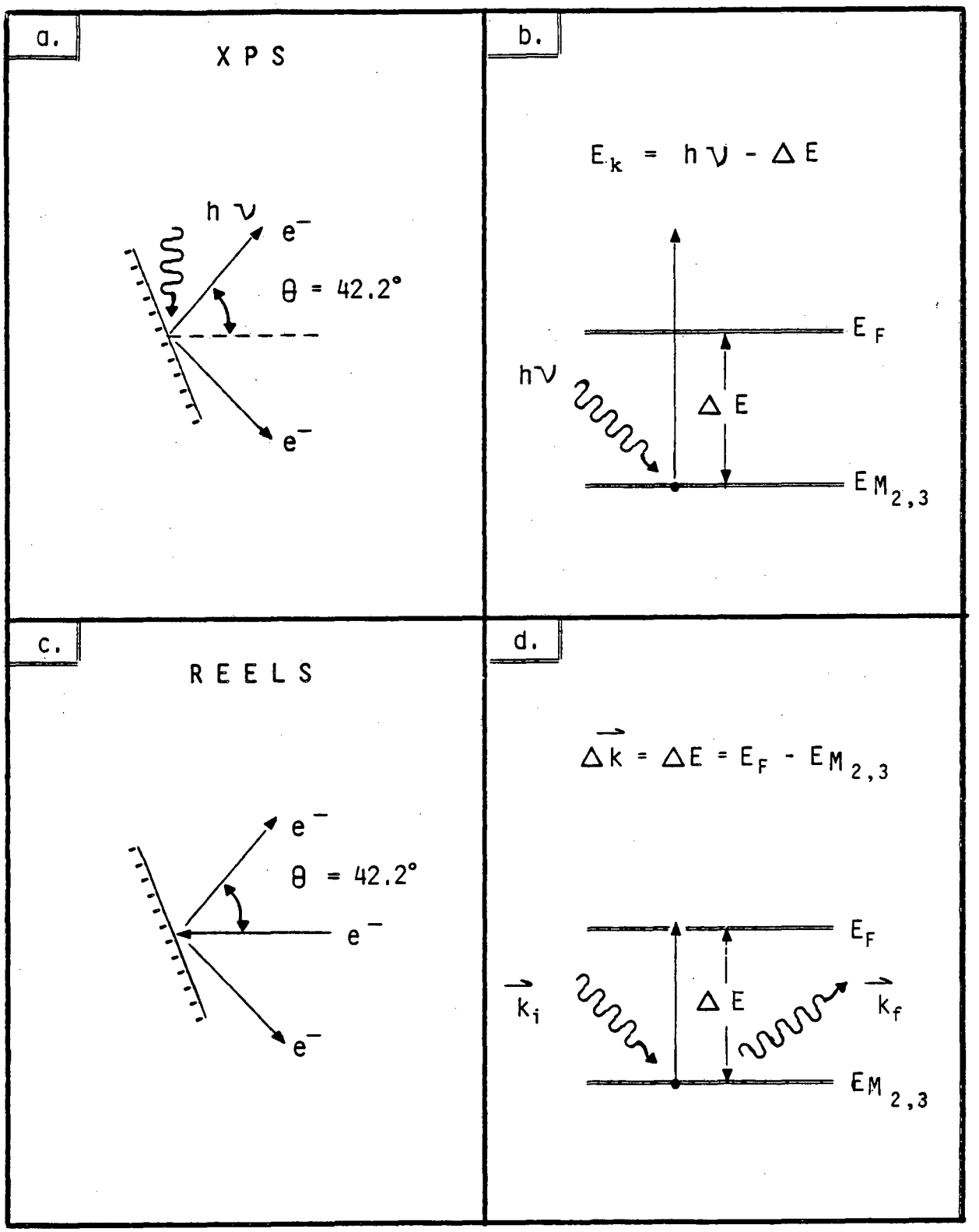
FIGURE CAPTIONS

1. Geometric and energy level relations between incident photons, the sample and ejected photoelectrons in XPS (a&b); corresponding relations between incident electrons, the sample and the reflected electrons in REELS (c&d). The same CMA is assumed for kinetic energy analysis.
2. REELS spectra for clean and oxygen dosed (a) Ni, (b) Fe, (c) Ti, for a primary beam energy of 200 eV.
3. Conventional $M_{2,3}$ XPS spectra for clean (a) Ni, (b) Fe, (c) Ti foils using a standard Mg-Kα x-ray source.



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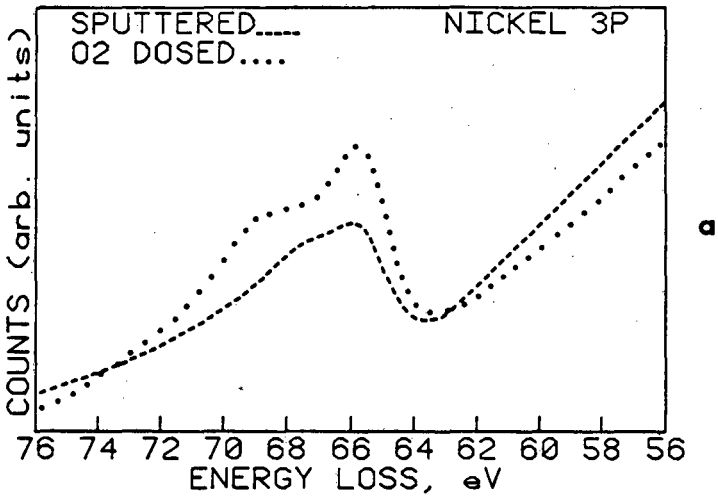

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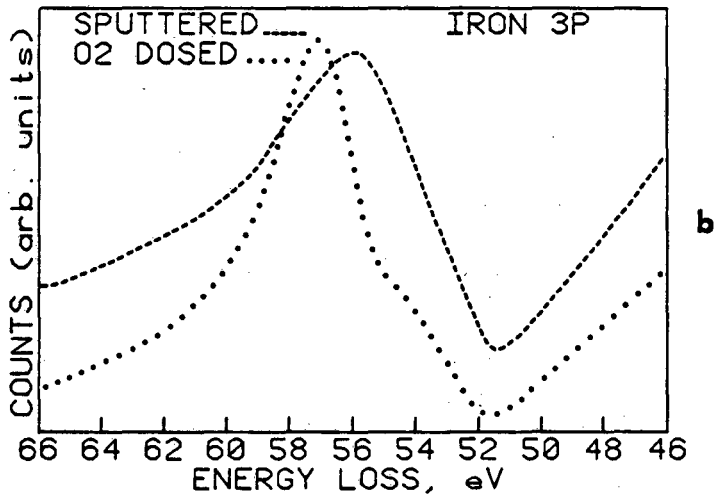

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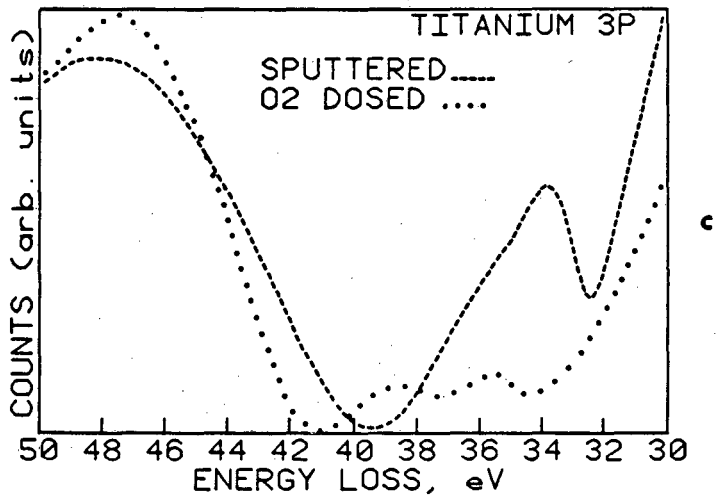

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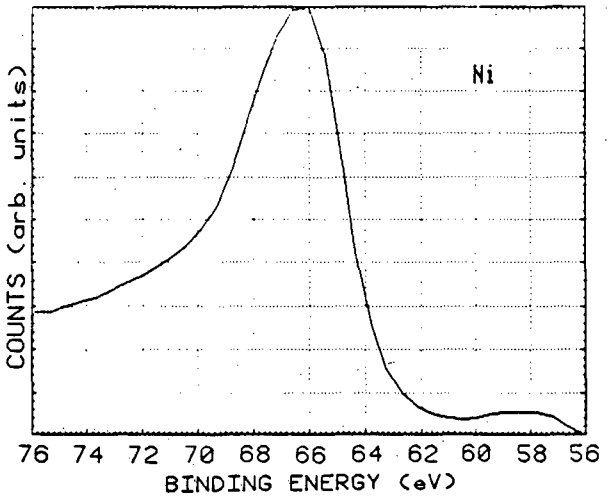

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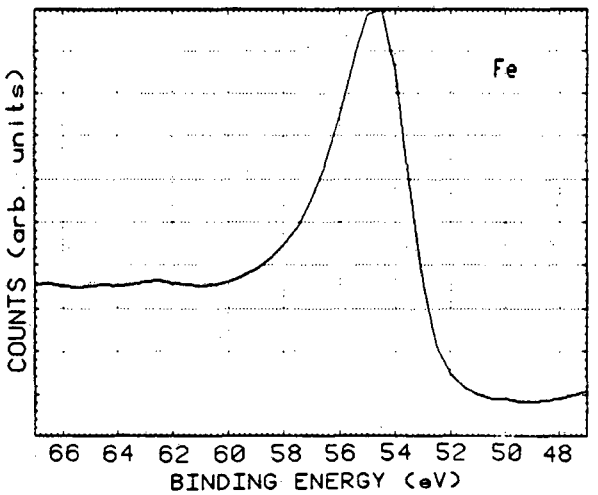

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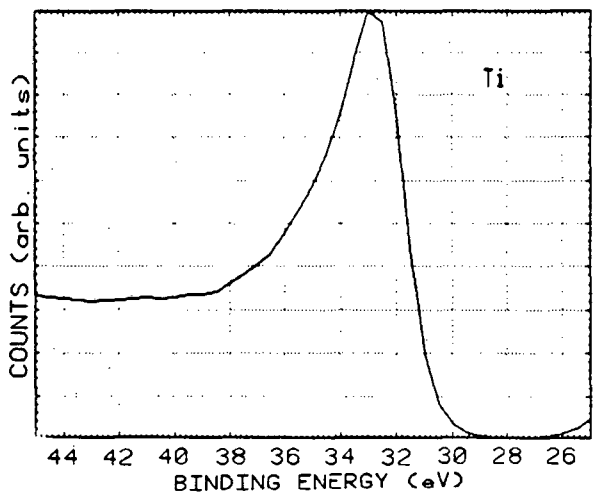

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