ent in TmAsO$_4$ either by using Raman scattering or by studying the effects of applied stress on its magnetic and optical properties. An x-ray diffraction study would be very useful for determining directly the crystal symmetry below 6 K. Another very interesting experiment would be an adiabatic nuclear demagnetization of ^{169}Tm in TmAsO$_4$, a Van Vleck paramagnet, in which full advantage could be taken of the large electronic moment with its large coupling to the nucleus present at $T < 1$ K in high magnetic fields.

*Present address: Harry Diamond Laboratories, Washington, D. C.

[1]See, for example, the review article by M. D. Sturge, in Solid State Physics, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1967), Vol. 20, p. 91.

[2]E. Cohen, L. A. Riseberg, W. A. Nordland, R. D. Burbank, R. C. Sherwood, and L. G. Van Uitert, Phys. Rev. 186, 476 (1969).

[3]L. A. Riseberg, E. Cohen, W. A. Nordland, and L. G. Van Uitert, Phys. Lett. 30A, 4 (1969).

[4]A. H. Cooke, C. J. Ellis, K. A. Gehring, M. J. M. Leask, D. M. Martin, B. M. Wanklyn, M. R. Wells, and R. L. White, Solid State Commun. 8, 689 (1970).

[5]A. H Cooke, D. M. Martin, and M. R. Wells, Solid State Commun. 9, 519 (1971).

[6]K. A. Gehring, A. P. Malozemoff, W. Staude, and R. N. Tyte, Solid State Commun. 9, 511 (1971).

[7]H. G. Kahle, L. Klein, G. Müller-Vogt, and H. C. Schopper, Phys. Status Solidi (b) 44, 619 (1971).

[8]G. Will and W. Schäfer, J. Phys. C: Proc. Phys. Soc., London 4, 811 (1971).

[9]F. Sayeta, J. X. Boucherle, M. Belakhovsky, A. Kallel, F. Tcheou, and H. Fuess, Phys. Lett. 34A, 361 (1971).

[10]J. N. Lee, H. W. Moos, and B. W. Mangum, Solid State Commun. 9, 1139 (1971).

[11]R. T. Harley, W. Hayes, and S. R. P. Smith, Solid State Commun. 9, 515 (1971).

[12]J. C. Wright and H. W. Moos, Phys. Rev. B 4, 163 (1971).

[13]R. P. Hudson and B. W. Mangum, to be published.

[14]R. W. G. Wyckoff, Crystal Structures (Interscience, New York, 1965), 2nd ed., Chap. VIII.

[15]For further details on the optical spectra see J. N. Lee, thesis, The Johns Hopkins University, 1971 (unpublished).

[16]J. C. Wright, private communication.

[17]R. T. Harley, W. Hayes, and S. R. P. Smith, in "Proceedings of the International Conference on Light Scattering in Solids, Paris, July 1971" (to be published).

[18]R. J. Elliott, K. A. Gehring, A. P. Malozemoff, S. R. P. Smith, W. S. Staude, and R. N. Tyte, in "Proceedings of the International Conference on Light Scattering in Solids, Paris, July 1971" (to be published).

Photoemission Energy-Level Measurements of Chemisorbed CO and O on Ni†

D. E. Eastman and J. K. Cashion*
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598
(Received 27 August 1971)

Photoemission energy distributions at high photon energies permit one-electron measurements of the electronic energy levels and level widths of chemisorbed gases on clean metal surfaces at fractional monolayer coverages. Chemisorbed CO on Ni exhibits energy levels at 7.5 and 10.7 eV below the Fermi level E_F while chemisorbed O on Ni shows a 2-eV width level at 5.5 eV below E_F. Upon increased oxygen exposure, a surface oxide of Ni is formed which exhibits valence bands about 8.5 eV wide.

Many studies have been reported on the configurations of adsorbed gases on surfaces and on adsorbate binding energies; however, relatively little work has been reported on the electronic energy levels of such adsorbates. Techniques which have been used include ion-neutralization spectroscopy (INS)[1] and field-emission spectroscopy.[2] In this Letter we describe the application of ultraviolet photoemission spectroscopy (UPS) to measurements of electronic energy levels of adsorbed gases on clean metal surfaces. Chemisorbed CO on Ni exhibits energy levels at 7.5 and 10.7 eV below the Fermi level E_F with en-

ergy widths of about 2 and 1 eV, respectively. We tentatively identify the -7.5-eV level with the carbon lone pair $\sigma2p$ molecular orbital involved in bonding to the Ni. Compared with gaseous CO, this level is shifted upwards in energy by about 1.5 eV (relative to the vacuum level). Likewise, the -10.7-eV level is identified as the $\pi2p$ bonding molecular orbital of CO and is shifted upwards by about 1.2 eV. Chemisorbed oxygen shows a single level of width 2 eV centered at 5.5 eV below E_F. As the oxygen exposure is increased from about 1×10^{-6} Torr sec to 25×10^{-6} Torr sec, this -5.5-eV level broadens into a

valence band about 8.5 eV wide with structure at about 5, 7, and 10 eV below E_F, and a new energy level appears at about 2 eV below E_F which is identified as the $Ni^{2+}(d^8)$ level of the surface oxide.

Photoemission measurements at $h\nu = 21.2$ and 40.8 eV were made in ultrahigh vacuum using a windowless spectrometer with a 90° cylindrical electrostatic analyzer.[3,4] The sample chamber was pumped with a 400-liter/sec noble-ion pump together with a liquid-nitrogen-cooled Ti sublimation pump, and typically reached a base pressure of 5×10^{-10} Torr. With the lamp operating at about 0.5 Torr, pressures of about 2×10^{-8} Torr of He were maintained in the sample chamber.

Photoemission energy distributions for chemisorbed CO on Ni are shown in Fig. 1. Films of Ni about 1000–2000 Å thick were prepared by evaporation (~3 Å/sec) at pressures of ~10^{-8} Torr using an electron beam gun. Curve (1) in Fig. 1(a) shows the energy distribution for a polycrystalline Ni film prepared on a smooth quartz substrate at room temperature. Emission from the d bands is observed in the energy range 0 to about 3.3 eV below E_F, and a smooth background of secondary emission due to inelastically scattered electrons is observed at lower energies. Upon one Langmuir (1 L) exposure of this film

FIG. 1. (a) Emission spectra at $h\nu = 21.2$ eV for (1) Ni, (2) Ni + 1 L exposure of CO, and (3) Ni + 7 L of CO (1 L $\equiv 1 \times 10^{-6}$ Torr sec). (b) Emission spectra at $h\nu = 40.8$ eV for (4) Ni and (5) Ni + 0.6 L of CO. All curves are plotted versus initial electron energy measured relative to $E_F = 0$.

to CO (1 L $\equiv 1 \times 10^{-6}$ Torr sec), the work function was observed to increase by +0.31 eV and curve (2) was obtained.[5] We now observe two additional levels centered at about 7.5 and 10.7 eV below E_F (cross-hatched areas). Upon further exposure, these CO-derived levels increase in amplitude and the work function increases until maximum coverage is reached at about 7 L (curve 3). Widths of about 1 eV for the −10.7-eV level[6] and about 2 eV for the −7.5-eV level are observed. The −7.5-eV level has about $\frac{1}{3}$ the emission intensity of the Ni d bands.

Similar results were obtained using a (100)-oriented Ni film prepared by evaporation onto a cleaved NaCl substrate at about 250°C. Spectra for Ni(100) and Ni(100) + 0.6-L exposure of CO are shown in Fig. 1(b) for $h\nu = 40.8$ eV. Compared with curve (1) for $h\nu = 21.2$ eV, Ni d-band emission within about 3.3 eV of E_F exhibits a different shape (due to momentum selection rules[7]), and the secondary-emission background below −3.3 eV is much lower. In curve (5), CO-derived energy levels (cross-hatched) are observed at about 7.5 and 10.7 eV below E_F with widths of about 1 and 1.8 eV, respectively, and are about 20% as intense as the background. The observation of these energy levels at two different photon energies also indicates that they correspond to occupied levels and are not due to structure in the final state or to Auger transitions.

Considerable work has been reported on annealing effects, binding energies, and surface configurations of chemisorbed CO on Ni[8] and Pd.[9] Within the framework of a molecular orbital (MO) picture, it is commonly believed[9] that CO is bound to the surface through the carbon end, with the carbon lone pair $\sigma 2p$ MO donating electrons to the d bands of Ni, the d electrons in turn being back-donated into the antibonding $\pi 2p$ MO of CO. For gaseous CO, photoemission measurements at $h\nu = 21.2$ eV give ionization potentials of 14.01 eV for the $\sigma_g 2p$ MO, 16.91 eV for the bonding $\pi_u 2p$ MO, and 19.7 eV for the $\sigma_u 2s$ MO, which has a much lower intensity.[10] Comparing with our data for chemisorbed CO, we tentatively associate the level at −7.5 eV (~12.5 eV below the vacuum level for low coverages, since $\varphi \simeq 5$ eV for Ni) with the carbon lone pair $\sigma 2p$ MO, which is shifted upwards in energy by about 1.5 eV and broadened to about 2.0 eV (full width at half-maximum). Likewise, the level at −10.7 eV (~15.7 eV below the vacuum level) is associated with the bonding $\pi_u 2p$ MO, which is shifted upwards in energy by about 1.2 eV and broadened to about 1
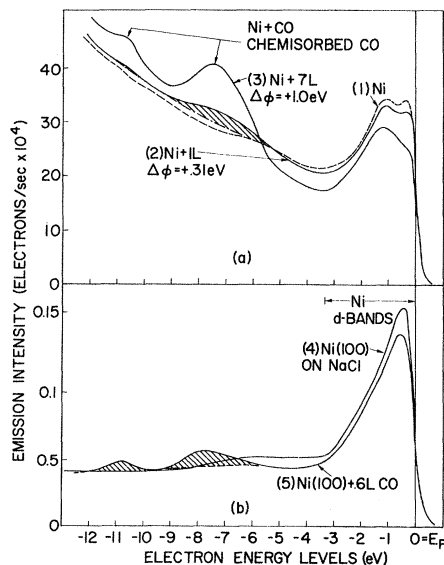
eV. The greater broadening of the −7.5-eV level is expected since it interacts more strongly with the Ni d electrons. The observed level widths for polycrystalline and (100)-oriented Ni are roughly independent of CO coverage. Electrons back-donated into the antibonding $\pi 2p$ MO of CO are not expected to be observed since their energy levels are probably just below E_F and are masked by Ni d-band emission.

The data in Fig. 1 illustrate the sensitivity of the photoemission technique for observing adsorbate energy levels. This sensitivity results from the short hot-electron scattering length, which limits the escape depth of photoemitted electrons. At $h\nu = 21.2$ eV, emission intensities of about 30 000 electrons/sec are obtained, with an rms signal-to-noise ratio S/N of about 170:1 for a 1-sec integrating time constant. Exposure to 1 L of CO results in an extra signal of about 3000 electrons/sec at −7.5 eV, and so the background noise roughly corresponds to an exposure of ~0.06 L. This detectability can be further increased by using a longer time constant. The sensitivity at $h\nu = 40.8$ eV is slightly less (with the noise corresponding to ~0.1 L) because of the much lower signal levels (~1000 electrons/ sec). However, these lower signal levels are compensated by the lower secondary-emission background. The relative amplitudes and linewidths of the CO-derived levels are also more accurately determined at $h\nu = 40.8$ eV because the energy-dependent analyzer transmission varies less rapidly at these high energies.

Our observed CO intensities are consistent with hot-electron escape-depth measurements for Ni.[11] A mean free path of about 8–10 Å (~ four monolayers) has been measured for energies about 8 eV above E_F. The scattering lengths at the higher energies involved in this work are expected to be at least as short. In order to estimate relative emission intensities, we make the rough assumptions that (a) Ni has a four-monolayer escape depth, (b) we have a monolayer of adsorbed CO (curve 3), and (c) CO and Ni have comparable absorption cross sections. We then estimate the CO intensity to be about $\frac{1}{3}$ to $\frac{1}{4}$ that of the underlying Ni. This estimate is in approximate agreement with the observed CO-emission intensity in curve (3), which is about $\frac{1}{3}$ that of Ni. Comparable escape depths and surface sensitivities are expected for other transition metals.

Comparing surface sensitivity with other spectroscopy techniques, the photoemission technique (UPS) appears to be roughly $\frac{1}{5}$ to $\frac{1}{10}$ as sensitive

as INS,[1] which mainly probes the outer surface layer. However, the effective sensitivity of UPS is increased relative to the two-electron INS technique because it is a one-electron technique, is simpler (e.g., no deconvolution), and has better resolution. Likewise, field-emission spectroscopy[2] is considerably more surface sensitive than UPS, but has the restriction of being limited to energies within a few eV of E_F. Another desirable feature of UPS is that the incident radiation does not strongly affect the surface adsorbates; no desorption of CO from Ni was observed. This is an advantage compared with techniques such as low-energy-electron diffraction (LEED) and Auger spectroscopy, for which the incident electron beam affects the adsorbed CO (Ref. 9).

Energy distributions for oxygen-exposed Ni as a function of exposure are shown in Fig. 2. In Fig. 2(a), energy distributions for Ni (curve 1) and Ni + 0.75-L exposure of oxygen (curve 2) are shown. For exposures $\lesssim 2$ L, a broad oxygen-derived level about 2 eV wide centered at 5.5 eV below E_F is seen (cross-hatched area), and the work function increases to a maximum of about $\Delta\varphi = +0.5$ eV at 2 L. This oxygen level is very similar, both in energy position and width, to that observed by Hagstrum and Becker via INS for a monolayer of O on Ni (Ref. 1).
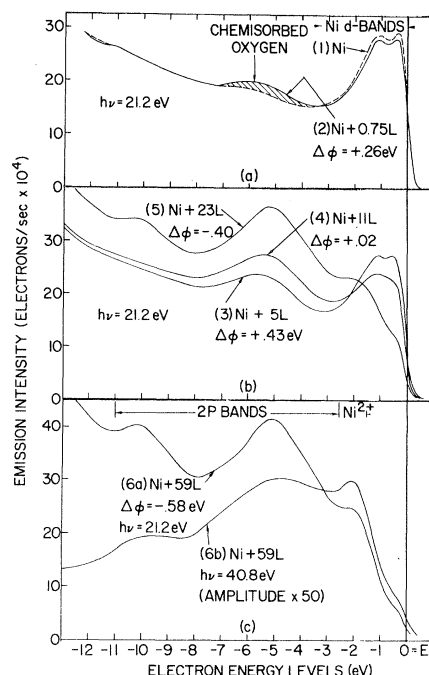
As the oxygen exposure is increased in the

FIG. 2. Emission spectra for adsorbed oxygen on Ni for various oxygen exposures.

range 7 to 25 L [Figs. 2(b) and 2(c)] the following effects are observed: (i) The oxygen-derived levels gradually increase in amplitude and broaden, (ii) the work function decreases, and (iii) Ni d-band emission within 3.3 eV of E_F decreases. At exposures of 23 L (curve 5) and 59 L (curve 6), emission from metallic Ni has diminished to $\lesssim \frac{1}{3}$ its initial value, and emission from oxygen-derived levels is seen in the range from about 2.5 to 11 eV below E_F, with structure observed at about 5, 7, and 10 eV below E_F. We associate this structure with the filled $2p$ bands of our surface oxide. A new energy level at 2 eV below E_F is seen for exposures $\gtrsim 23$ L. This level, which is more clearly seen at $h\nu = 40.8$ eV (curve 6b), is attributed to the d electrons of oxidized Ni [probably $Ni^{2+}(d^8)$]. The observed increase of this -2-eV level with increasing $h\nu$ by about a factor of 2 relative to the lower-lying $2p$ bands is consistent with emission from d states relative to p states, since the latter tend to saturate their oscillator strengths at lower photon energies.[4]

In summary, our measurements for CO and O adsorbed on Ni show that photoemission spectroscopy has considerable promise as a general technique for measuring energy levels associated with adsorption and other surface reactions. Fruitful extensions of these measurements might include the use of well-characterized single-crystal substrates, low-temperature measurements which should permit both physisorption measurements as well as chemisorption measurements of species which do not adsorb in appreciable quantities at room temperature, and, perhaps of most interest, studies of catalytic surface reactions in which surface energy levels can be measured via photoemission spectroscopy

while catalytic activities are measured via mass spectroscopy or other suitable methods.

The technical assistance of J. J. Donelon is gratefully acknowledged.

†Based in part on work sponsored by the U. S. Air Force Office of Scientific Research under Contract No. F44620-70-0089.

*Present address: University of Wisconsin–Parkside, Kenosha, Wis. 53140.

[1]H. D. Hagstrum and G. E. Becker, Phys. Rev. Lett. 22, 1054 (1969), and J. Chem. Phys. 54, 1015 (1971).

[2]E. W. Plummer and R. D. Young, Phys. Rev. B 1, 2088 (1970).

[3]J. K. Cashion et al., to be published.

[4]D. E. Eastman and M. Kuznietz, J. Appl. Phys. 42, 1396 (1971).

[5]Gas exposures were measured using a nude ion gauge next to the sample. Work function changes $\Delta\varphi$ were determined by measuring the change in width $(h\nu - \varphi)$ of the energy distribution, where φ is the work function.

[6]The amplitude of this -10.7-eV level is attenuated due to the low transmission of the electron analyzer at this low kinetic energy (~ 5 eV), and the background is mainly due to secondary emission from the analyzer. The relative amplitudes of the CO levels are shown in Fig. 1(b) for $h\nu = 40.8$ eV. All energy distribution curves are uncorrected for the analyzer transmission factor, which increases linearly with increasing kinetic energy for energies $\gtrsim 7$ eV.

[7]D. E. Eastman, J. Phys. (Paris), Colloq. 32, C1-293, (1971).

[8]M. Onchi and H. E. Farnsworth, Surface Sci. 11, 203 (1968).

[9]J. C. Tracy and P. W. Palmberg, J. Chem. Phys. 51, 4852 (1969).

[10]D. W. Turner et al., Molecular Photoelectron Spectroscopy (Wiley, New York, 1970), p. 34.

[11]D. E. Eastman and W. F. Krolikowski, Phys. Rev. Lett. 21, 623 (1968).

First-Order Transition in Chromium at the Néel Temperature*

P. R. Garnier and M. B. Salamon†
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801
(Received 13 October 1971)

A latent heat, hysteresis, and superheating and supercooling have been observed in a Cr single crystal by means of an extension of the ac calorimetric method.

Although neutron-diffraction studies revealed a first-order transition in Cr at $T_N = 311$ K,[1] other manifestations of the first-order nature are rare. The transition is usually smeared over a few tenths of a degree and looks like a second-order

phase change.[2] Recently, however, Sze and Meaden[3] have observed a large (50%) step in specific heat and a cooling plateau in a polycrystalline sample, from which they estimate a latent heat of 0.47 cal/mole. We report here the re-