and will have two possible orientations of easy axes with respect to each other—perpendicular and parallel in the ratio of 2:1, respectively. The actual distribution of exchange interactions will acquire structure, and the assumption that it scales with concentration will break down. There could be an increase in the probability of low exchange fields over what is expected in a random system, and a concentration-independent linear term in the specific heat may be observed over the concentration range of 0.5 to 10 at.% impurity.

In conclusion, the approach described above where near-neighbor clusters are responsible for the low-temperature specific heat observed in dilute magnetic alloys avoids the objections to previous models and provides a simple explanation of the linear term in the specific heat.

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Optical Reflectance Spectroscopy of Surface States in H_2 Chemisorption on W(100)*

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Surface reflectance spectroscopy is used to determine optical transitions associated with the electronic structure of a W(100) surface during H_2 chemisorption. Correlation with photoemission and field-emission data attributes these transitions to excitations from intrinsic and adsorbate-induced levels to final states at the Fermi energy.

Our understanding of the electronic structure of clean solid surfaces has been greatly advanced in the past few years by electron spectroscopies which measure the density of filled electron states near the surface. For example, in the case of H_2 chemisorption on W(100), uv photoemission spectroscopy (UPS)[1-3] and field-emission spectroscopy (FES)[4] have revealed intrinsic surface states on the clean surface and adsorbate-induced surface levels which depend on the adatom identity and binding state. A valuable complement to this filled-state information which would more fully characterize the surface electronic structure is its optical excitation spectrum, indicating, e.g., to what empty final states the filled surface levels are excited and at what energies empty surface orbitals might exist.[5] Although optical absorption bands involving surface states on Si and Ge have been observed for photon energies $\hbar\omega$ below the fundamental absorption edge E_g,[6] no optical determination of prominent surface excitation energies on opaque samples ($\hbar\omega > E_g$ for semiconductors) has yet been reported.

That optical reflectance can provide useful information on surface electronic structure has been shown by McIntyre's work on metal surfaces in electrolyte solutions.[7] The effects of (sub-) monolayer chemisorption on the optical properties of a clean opaque surface in ultrahigh vacuum (UHV) have been observed by ellipsometry.[8] We recently demonstrated that these effects can also be observed in ultrahigh vacuum by differential reflectance measurements and suggested the possibility of a versatile surface reflectance spectroscopy (SRS) in which surface excitation energies could be determined optically.[9] We report here the results of such SRS studies of H_2 chemisorption on W(100), which reveal a complex coverage dependence of the surface electronic structure and yield its characteristic optical transition energies. These energies show a correlation with UPS and FES data which suggests that the transitions are excitations from the filled intrinsic and adsorbate-induced surface orbitals to final states concentrated primarily at the Fermi energy E_F.

Measurements were carried out at room temperature on a W(100) ribbon sample maintained in ultrahigh vacuum ($<10^{-9}$ Torr). Following a brief resistance heating to ~2100°K to produce an atomically clean surface, H_2 was admitted into the chamber at fixed pressure. The resulting reflectance changes caused by chemisorption on the clean surface were measured in the range $0.6 < \hbar\omega < 4.8$ eV using a rotating light-pipe reflectometer.[10]

The dependence of ΔR on exposure was measured at various $\hbar\omega$. Using recently reported sticking probabilities for the $W(100)+H_2$ system,[11] the results were converted to give the coverage dependence $\Delta R(\Theta)$.[12] Representative coverage curves are shown in Fig. 1.[13] Structure appears clearly in these spectra at $\Theta = 0.19$ and 0.26, which are shown by vertical lines in the figure dividing the curves into three regions I, II, III. The changes in optical response per adatom [indicated by the slope $S \equiv d(\Delta R)/d\Theta$] at specific Θ values arise from differences in surface electronic structure of the various adatom binding states.

A variety of well-known experiments indicate the presence of two binding states of H_2 on W(100).[11] Initially adatoms adsorb in the β_2 state, but after $\Theta \cong 0.19$ formation of a second state β_1 begins and exists to saturation. This would suggest the following simple interpretation of, e.g., the 1.40-eV curve in Fig. 1. The constant slopes $S_{\rm I}$ and $S_{\rm III}$ in regions I and III are characteristic of the reflectance change per adatom (at 1.4 eV) for adsorption in the β_2 and β_1 states, respectively. In the intermediate region II ($0.19 < \Theta < 0.3$), $S > 0$ since additional adatoms convert previous β_2 states to β_1 states (note $S_{\rm III} > S_{\rm I}$) and also contribute directly with slope $S_{\rm III}$. The curves for large $\hbar\omega$ can be explained in the same way. However, for intermediate $\hbar\omega$ (2.67 and 3.25 eV), no combination of $S_{\rm I}$ and $S_{\rm III}$ can produce the large slope observed in region II. Furthermore, if at large coverage all atoms already on the surface were in the β_1 state and further adatoms also went into the β_1 state, all curves should extrapolate to $\Delta R = 0$ at $\Theta = 0$, which is not the case at intermediate $\hbar\omega$. These SRS results imply that a more complicated, Θ-dependent surface electronic structure exists after $\Theta = 0.19$, as seen also in UPS.[3]

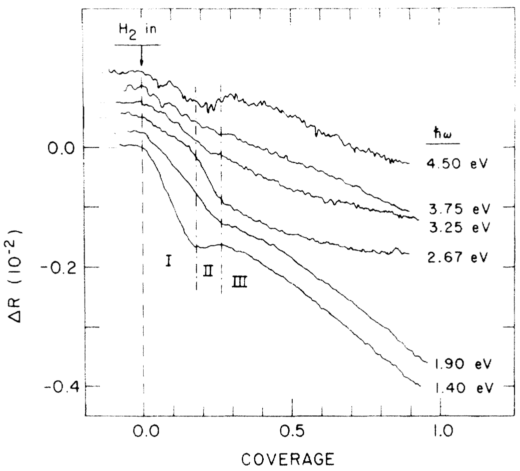

FIG. 1. Coverage dependence of reflectance changes ΔR at several photon energies $\hbar\omega$ for H_2 adsorption on W(100). The origin ($\Delta R = 0$ at coverage $\Theta = 0$) is displaced upwards as shown for $\hbar\omega > 1.40$ eV.

The dependence of relative reflectance changes $\Delta R/R$ on photon energy $\hbar\omega$ for coverages $\Theta = 0.19$ (β_2 state) and $\Theta = 1.00$ (the saturated surface) is shown by the data points in Fig. 2. Over most of both spectra $\Delta R/R < 0$ with a minimum value near 1.5 eV, but at lower $\hbar\omega$, ΔR becomes positive. This low-energy structure dominates both spectra and is, within experimental error, the same below 1.0 eV for $\Theta = 0.19$ and $\Theta = 1.00$. Thus for $\hbar\omega < 1.0$ eV, no significant further changes in reflectance (and therefore in surface electronic structure) take place after $\Theta = 0.19$. At higher $\hbar\omega$ weaker structures are evident which do change with Θ.

In order to extract information about the local electronic structure of the surface region, we use the model of McIntyre and Aspnes,[14] which represents the surface region as a uniform surface layer of (sub)monolayer thickness d ($\ll \lambda$, the wavelength of light) having complex dielectric function $\hat{\epsilon}^s(\omega) = \epsilon_1^s(\omega) + i\epsilon_2^s(\omega)$. Then $\Delta R/R$ is related to changes $\Delta\hat{\epsilon}^s$ in $\hat{\epsilon}^s(\omega)$, caused in the pres-

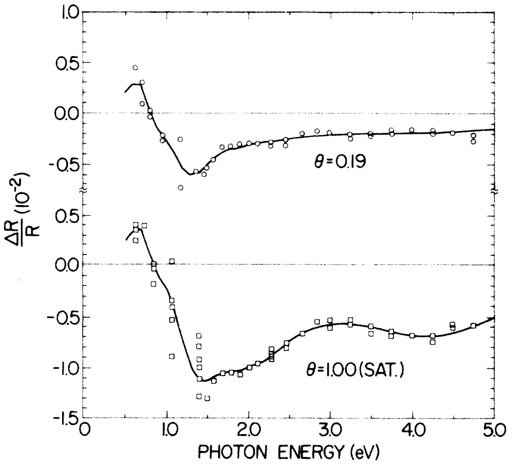

FIG. 2. Spectral dependence of relative reflectance changes for $\Theta = 0.19$ and 1.00. The theoretical (solid) curves are obtained from an oscillator fit of $\hat{\epsilon}^s$ to reproduce $\Delta R/R$ data points.

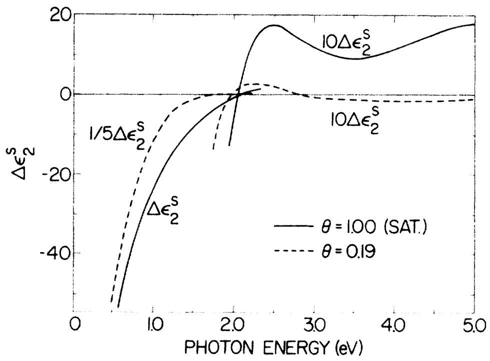

FIG. 3. Imaginary part of the change in surface dielectric function, $\Delta\epsilon_2^s$, for $\Theta = 0.19$ and 1.00.

ent case by chemisorption, by[7]

$$\frac{\Delta R}{R} = -\frac{8\pi d}{\lambda}\,\frac{\epsilon_2^b \Delta\epsilon_1^s - (\epsilon_1^b - 1)\Delta\epsilon_2^s}{(\epsilon_1^b - 1)^2 + (\epsilon_2^b)^2}, \qquad (1)$$

where $\epsilon_1^b(\omega) + i\epsilon_2^b(\omega)$ is the dielectric function of the underlying bulk. To obtain a picture of the structure in $\Delta\hat{\epsilon}^s(\omega)$ from the $(\Delta R/R)(\omega)$ data, we assumed a model $\Delta\hat{\epsilon}^s$ composed of a few Lorentzian oscillators and adjusted the oscillator parameters to produce an optimum fit of the calculated $\Delta R/R$ spectra [Eq. (1)] to the experimental data. Values for $\hat{\epsilon}^b$ are known,[15] and the thickness d, which enters (1) as a simple scale factor, was assumed to be 5 Å for $\Theta = 1.00$ and 1 Å for $\Theta = 0.19$. The calculated $(\Delta R/R)(\omega)$ spectra obtained in this way are shown by solid curves in Fig. 2.

Figure 3 shows the resulting spectral dependence of $\Delta\epsilon_2^s$ for $\Theta = 0.19$ and 1.00. The structures, consisting of a strong negative contribution at low $\hbar\omega$ and weaker peaks at higher $\hbar\omega$, show the presence of prominent optical excitations of the surface electronic structure. The strong dip at low $\hbar\omega$ dominates both spectra and produces the structure below 1.5 eV in Fig. 2. Note that $\Delta\epsilon_2^s(\Theta = 0.19) \sim 5\Delta\epsilon_2^s(\Theta = 1.00)$ at low $\hbar\omega$. This occurs because changes in surface electronic structure and reflectance for $\hbar\omega < 1.0$ eV are essentially complete at $\Theta = 0.19$, but within the model these changes must be averaged over the surface layer thickness to determine the surface dielectric function $\hat{\epsilon}^s$. (If the changes continued uniformly with Θ, $\Delta\epsilon_2^s$ would be constant with Θ, and $\Delta R/R$ would increase linearly with d.) It is unlikely that adatom-induced modifications of the Drude contribution to $\hat{\epsilon}^s$ can account for the structure at low $\hbar\omega$.[16] Instead, we tentatively attribute the low-energy dip in $\Delta\epsilon_2^s$ to adsorbate-induced quenching of strong optical transitions in the surface electronic structure. These transitions are most likely excitations from the intrinsic surface states on W(100) seen in UPS[1,2] and FES[4] 0.4 eV below E_F (which are quenched by the presence of an adsorbate and disappear completely by $\Theta \cong 0.25$ for H_2 adsorption) to final states at the Fermi energy. The large magnitude of the intrinsic surface-state dip in $\Delta\epsilon_2^s$, of order ϵ_2^b for the W substrate, suggests that near the surface a considerable portion of the Drude oscillator strength of the metal is shifted into the intrinsic surface-state excitations. The predominance of optical coupling of these states to final states at E_F may explain the apparent decrease in strength of photoemission from these states relative to the bulk with increasing photon energy.[1]

Above 2 eV, $\Delta\epsilon_2^s$ shows peaks at 2.5 and 5 eV for $\Theta = 1.00$ and at 2.2 eV for $\Theta = 0.19$. These are associated with new optical transitions in the surface region which are characteristic of the hydrogen/tungsten chemisorption bonds. Although one might expect similar transitions in electron energy-loss measurements, no H_2-induced loss peaks have yet been observed.[17] We concentrate on the $\Theta = 1.00$ structures, which are more clearly resolved. UPS measurements[3] show that saturation coverage of H_2 on W(100) causes enhanced emission from levels about 2.4 and 5.0 eV below E_F, energies which match our optical transition energies. This marked correlation implies a simple interpretation—that the 2.5- and 5-eV optical transitions both involve final states at E_F, as suggested for the low-$\hbar\omega$ structure; then the position of initial states corresponds to the adsorbate-induced levels observed by UPS. The final states at E_F are probably tails of extended (Bloch) states of the metal as modified at the surface.

SRS results for chemisorption of CO and O_2 on W(100)[18] support these interpretations. Similar features appear at low $\hbar\omega$ as expected for optical excitations of the intrinsic surface states,[1,2] while the energies of chemisorption-induced optical transitions above 2 eV depend on the adsorbate identity and match the position below E_F of filled adsorbate-induced levels seen in UPS.[3] The agreement obtained between UPS and SRS for a simple model of the optical transitions (single band of final states at E_F) lends additional credence to the SRS analysis. Although other final states are not required to explain the SRS data for simple gas adsorption on W(100), the possible observation of empty surface orbitals in other systems remains an open question, and further measurements are needed. The SRS experiments may prove particularly valuable for investigations of adsorption and surface reactions at higher pressures and elevated temperatures, a practical regime for catalysis where electron spectroscopies cannot be used.

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