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Adsorbate-Induced Angle Averaging of Cu(111) Photoemission Spectra

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The adsorption of Cs on Cu(111) produces major changes in the Cu 3d-band part of angle-resolved photoelectron spectra recorded at $\hbar\omega = 16.8$ and 21.2 eV. The angular dependence is much reduced and the spectra are quite similar to those obtained from polycrystalline Cu. We associate this behavior with a strong incoherent scattering by the adsorbate.

While uv photoelectron spectroscopy can provide useful information about the electronic structure and adsorbate geometry of chemisorption system,¹ much still remains to be learned about the process of photoemission from such systems. One interesting question concerns the transmission through the surface layer into vacuum of photoelectrons excited from initial states in the substrate valence band. This part of the process is important particularly if electronic levels introduced by the adsorption coincide in energy with the substrate valence band. It may then be difficult to determine whether the observed changes of photoelectron spectra recorded at a certain emission angle are associated with the new chemisorption levels or with a modified escape probability for the electrons from the substrate: The latter, for example, may be due to diffraction by an ordered overlayer.² From a theoretical viewpoint the transmission problem should be soluble by low-energy electron-diffraction (LEED) type calculations, although very lengthy ones considering the generally complicated angular distribution of the optically excited electrons, incident on the surface layer. A difficulty met with in this connection is that the starting point for the calculation of the optical excitation spectrum may be uncertain. Based on photoemission data from an oxygen-exposed Cu(111), Shevchik *et al.*³ recently suggested that the electron wave-vector conservation rule is not applicable in the direction perpendicular to the surface for optical transitions oc-

curing within the emission depth of the photoelectrons.

The present results suggest that one major change induced by adsorption may be described in quite simple terms. The spectra measured for the Cu(111)/Cs adsorption system can be well understood within the framework of direct optical transitions in the bulk of the Cu(111) crystal, if it is assumed that the Cs layer acts as a filter which transmits the electrons in an increasingly diffuse manner as the coverage is increased. The diffuse transmission corresponds to an integration over emission angles brought about by quasi-elastic scattering of the electrons into the detection angle. When approximately half of a full monolayer of Cs or more is adsorbed, the spectra show little variation with emission angle at the photon energies investigated, $\hbar\omega = 16.8$ and 21.2 eV. The influence of scattering may be large for the present system since, according to LEED calculations,⁴ Cs is a relatively strong scatterer of low-energy electrons. If the adsorbate scatters strongly enough, most of those photoelectrons, which are excited optically in the substrate, will be scattered as they pass the surface layer. In such a case, the angular distribution of emitted electrons will depend on the atomic order in the adsorbed layer. Randomly distributed atoms can scatter the electrons through any angle into the detector, which then measures an angle-averaged spectrum. The range of angles sampled via scattering will be more restricted the higher the de-

gree of order in the overlayer.

The Cu(111)/Cs system allows attention to be focused on the transmission properties of the adsorbate. The substrate has a well-known electronic structure. There is a weak electronic interaction between substrate and adsorbate leaving the adsorbate valence levels largely unaffected. The most important change is a Friedel resonance type of broadening. This is accompanied at low Cs coverage by a transfer of most of the alkali valence charge to the substrate.⁵⁻⁷ Apart from the shift of a fractionally occupied Cu(111) surface band to lower energy in order to accommodate the transferred Cs valence electron,⁸ there is little change of the electronic structure of the substrate upon Cs adsorption. This is evident from the very detailed agreement between the measured and calculated angle-integrated uv photoemission spectra from Cs-coated Cu for $\hbar\omega < 11$ eV.⁹ The calculations are based on the assumption that only direct optical transitions between bulk energy bands are important and that Cs-covered Cu may be treated as Cu with a clean surface and a reduced work function. Another advantage of the Cu(111)/Cs system is the small overlap between the energy of the outer electrons of the adsorbate with the Cu valence band. The substrate emission is dominated by the 3*d* band located between 2 eV and 5 eV below the Fermi level (FL) and thus well separated from the Cs 5*p* electrons approximately 12 eV below the FL as well as from the resonance-broadened 6*s* valence level which extends to about 1 eV below the FL.⁸ A further important feature of the Cu(111)/Cs system is that adsorbed amounts are easily monitored via the characteristic coverage dependence of the work function.¹⁰ Since the adsorbate is uniformly distributed over the surface, a coverage change corresponds to a variation of a relatively well-defined nearest-neighbor distance.^{10,11}

We measure angle-resolved photoelectron spectra using a π -segment cylindrical-mirror electron-energy analyzer accepting electrons emitted within a cone having an opening angle of around 2°. The detected electron beam is located in the plane of incidence making a fixed angle of 138° with the direction of the incoming light. The incidence angle is therefore 42° when electrons are collected in the direction normal to the sample. The azimuthal angle is fixed (45° away from $[\bar{2}, 1, 1]$) whereas the polar angle may be changed by turning the sample. Cs is evaporated from a glass ampoule broken in vacuum onto a Cu(111) crystal, which is cleaned by Ar⁺ bombardment

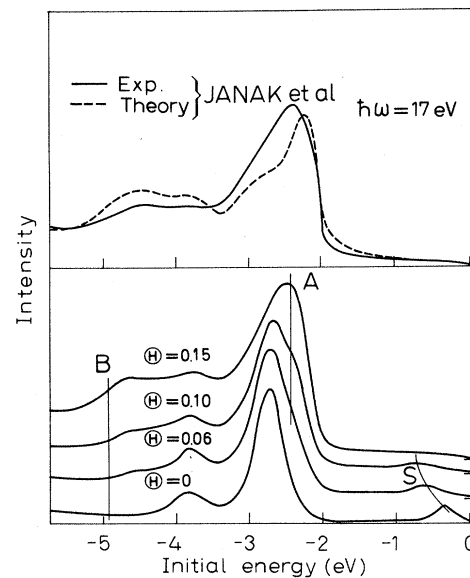


FIG. 1. Photoelectron energy distributions for $\hbar\omega = 16.8$ eV of Cu(111) with different Cs coverages θ , recorded in the direction normal to the sample (lower panel). The upper panel shows measured (full drawn) and calculated spectra (Ref. 12) for a polycrystalline Cu film.

(2 μ A, 250 eV, 10 h) and heating (400°C, $\frac{1}{2}$ h). The Cs coverage is determined from the known work-function reduction, which is measured by the diode method using a three-grid LEED display system.

Upon adsorption of monolayer amounts of Cs on Cu(111), major changes of the photoelectron energy spectra are observed (Fig. 1, lower panel). The coverage values θ , where θ is defined to be 0.25 for a close-packed $p(2 \times 2)$ layer,¹⁰ are indicated in the diagram. The spectra are plotted against initial electron energy with zero energy corresponding to the FL. The shift of the surface-state peak, labeled S, to lower initial energy has been studied in detail previously with use of photon energies below 6 eV.⁸ Here we discuss the influence of adsorbed Cs on the Cu 3*d*-band region between 2 eV and 5 eV below the FL. Two new features appear here, labeled A and B. The highest coverage value shown in $\theta = 0.15$. At higher coverage no changes of interest in the present context are observed. There is a moderate (~30%) loss of Cu 3*d*-band emission intensity as the Cs coverage is increased from zero to 0.15.

We associate the observed changes of the angle-resolved photoemission spectra with a quasielastic scattering of the electrons from the Cu 3*d* band as these pass the adsorbate layer. The con-

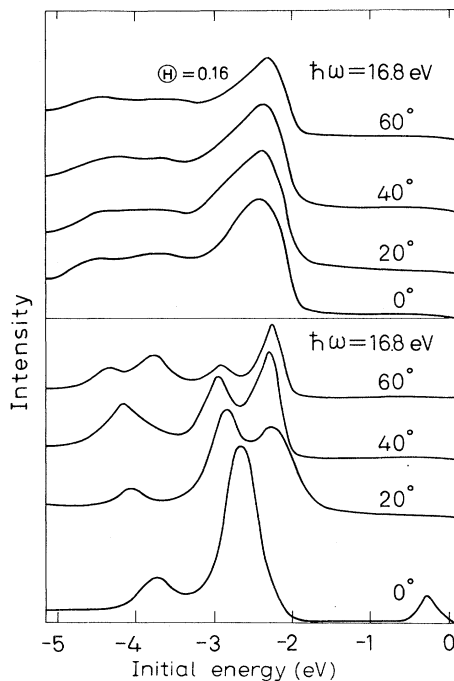


FIG. 2. Photoelectron energy spectra recorded at different polar angles from Cu(111) (lower panel) and Cu(111) with a Cs coverage $\theta = 0.16$ (corresponding to 65% of a full Cs monolayer). The azimuthal angle is fixed and 45° away from $[2, 1, 1]$.

clusion is based on the small dependence of spectral structure on polar emission angle (Fig. 2, upper panel) for coverages above 0.15. Furthermore, there is good agreement between the present results for high Cs coverages and the spectrum recorded by Eastman and Grobman¹² at nearly the same photon energy for a polycrystalline Cu sample (Fig. 1, upper panel). Together with the experimental spectrum at $\hbar\omega = 17$ eV is shown the angle-averaged spectrum predicted by Janak, Williams, and Moruzzi¹² from calculations based on wave-vector-conserving transitions between Cu bulk energy bands. In this report, we show spectra measured at $\hbar\omega = 16.8$ eV, but the same conclusions can be drawn from data taken at $\hbar\omega = 21.2$ eV.

Contributions to the angular integration observed for a Cs-covered Cu(111) crystal may be obtained from coherent as well as incoherent scattering by the adsorbate. The uniformly distributed Cs atoms produce a cone of diffracted electrons around an incident beam making the (00) spot on the LEED screen appear at the center of a diffraction ring.¹⁰ A calculation of the number of electrons falling on the detector therefore involves a summation over all directions half a dif-

fraction-cone angle away from the detection angle. Previously, diffraction effects have been observed to give an enhanced emission in certain directions for a crystal with an ordered overlayer.² With the mechanism suggested above, new structure may appear in photoelectron spectra even when the adsorbate layer is not an ordered one. Only in special cases, however, can a summation over such a limited range of emission angles be expected to make the spectrum similar to that obtained by integration over all emission angles. Therefore it appears likely that the incoherent quasielastic scattering, corresponding in LEED to the diffuse background around the diffraction ring, makes an important contribution to the recorded spectrum. In view of the polar-angle dependence of spectra recorded for clean Cu(111) (Fig. 2 lower panel), the electrons must be scattered through a wide range of angles to account for the angular averaged character of the spectrum recorded for Cs-covered Cu(111).

A comparison between different adsorbates regarding the importance of the elastic scattering is not straightforward since there are usually additional effects contributing to the spectral changes. As an example one may take the copper-oxygen system, which has been studied extensively.^{3, 13-17} The Cu spectra are modified here by the emission of electrons from chemisorption levels at the low- and high-energy edges of the Cu 3d band and by the lack of emission from the Cu(111) surface state, which is wiped out as the copper-oxygen bond is formed. Photoemission spectra measured after an oxygen exposure of 10^3 L ($1 \text{ L} = 10^{-6} \text{ Torr sec}$) showed a strong angular dependence in the Cu 3d-band range of initial energies.³ This is consistent with the present results since only a small fraction of the surface is covered by oxygen at this exposure.¹⁸ The relatively strong damping upon oxygen adsorption of an s, p-band emission peak¹⁶ is probably a combined effect of the rearrangement of the electronic energy levels in the surface region and the type of scattering discussed here. The s, p-band peak was observed only at particular emission angles and should therefore be especially sensitive to scattering.

In summary, we find that new structure, which is not due to chemisorption levels, can appear in angle-resolved photoelectron spectra from an adsorbate-covered crystal. As a result of strong scattering by the adsorbate, the spectra recorded for Cs-covered Cu(111) show little angular dependence and are similar to the angle-integrated

spectrum.

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Tetramethylammonium Copper Chloride and *tris* (Trimethylammonium) Copper Chloride: $S = \frac{1}{2}$ Heisenberg One-Dimensional Ferromagnets

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The magnetic susceptibilities of powdered samples of $\text{Me}_4\text{NCuCl}_3$ (TMCuC) and $[(\text{CH}_3)_3\text{NH}]_3\text{Cu}_2\text{Cl}_7$ (TTMCuC) have been measured. Both compounds behave like one-dimensional $S = \frac{1}{2}$ Heisenberg ferromagnets which are weakly coupled antiferromagnetically to adjacent chains. For TMCuC, we obtained $J/k = 30$ K with $|J'| \lesssim 0.003$ K; the ratio $|J'/J|$ is the lowest yet found for a ferromagnetic $S = \frac{1}{2}$ chain. For TTMCuC, we obtained $J_{\text{FM}}/k = 50$ K, with $|J'/J_{\text{FM}}| \lesssim 10^{-4}$, and $J_{\text{AFM}}/k = -10$ K for the antiferromagnetic chains also present.

The magnetic properties of low-dimensional materials continue to be of much interest to physicists and chemists.¹ Of the many possible combinations of space dimensionality, spin dimensionality, and spin quantum number, one combination which has been conspicuous by the lack of suitable realizations is the one-dimensional (1D) spin- $\frac{1}{2}$ Heisenberg ferromagnet. The majority of studies on one-dimensional magnetic systems have been on antiferromagnets, with emphasis on $S = \frac{5}{2}$ Heisenberg (Mn^{2+}), $S = \frac{1}{2}$ Ising (Co^{2+}), and $S = \frac{1}{2}$ Heisenberg (Cu^{2+}) systems. The general lack of one-dimensional ferromagnets, particularly for $S = \frac{1}{2}$ where quantum effects are expected to be most pronounced, has been unfortunate. Recently we reported two pseudo-one-dimen-

sional ferromagnets,² $\text{CuCl}_2 \cdot \text{DMSO}$ [$\text{DMSO} \equiv (\text{CH}_3)_2\text{SO}$] and $\text{CuCl}_2 \cdot \text{TMSO}$ [$\text{TMSO} \equiv \text{C}_4\text{H}_8\text{SO}$] with a strong intrachain coupling, $2J/k$, of ~ 80 – 90°K but the extent of interchain coupling ($|J'/J| \sim 10^{-2}$) was large enough to preclude their study as ideal systems. The structural insight gained in these studies prompted us to investigate two additional compounds where the interchain coupling, J' , could be expected to be minimized.

The results presented in this paper indicate that $(\text{CH}_3)_4\text{NCuCl}_3$ (TMCuC) is the most one-dimensional $S = \frac{1}{2}$ Heisenberg linear chain ferromagnet yet reported. The other compound discussed here, $[(\text{CH}_3)_3\text{NH}]_3\text{Cu}_2\text{Cl}_7$ (TTMCuC), contains a similar set of linear $(\text{CuCl}_3)_n$ chains with ferromagnetic interactions and very small inter-