STUDIES OF TRANSITION METAL AND OVERLAYERS DYNAMICS AND MAGNETISM BY HE AND SPIN-POLARIZED METASTABLE HE BEAM SPECTROSCOPIES

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Progress Report
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Technical Progress Report
for the Period October 1, 1990-September 30, 1991
to the
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I. Accomplishments:

A. Experimental results

1. Investigation of Quantum Delocalization of H on the Pd(111) Surface:

We have measured the surface phonon dispersion of the clean Pd(111) surface in the surface temperature range $350^\circ\text{K} < T, < 450^\circ\text{K}$ and at 50% H coverage in the temperature range $180^\circ\text{K} < T, < 150^\circ\text{K}$. This was made possible by the incorporation of the closed-cycle He refrigerator we installed last year. The purpose of these measurements was to look for dynamical evidence of the delocalized motion of H on the Pd(111) surface.

In the case of the clean surface measurements we found two modes (Fig 1.a): A Rayleigh mode below the continuum band-edge which was slightly softer than that measured in the presence of H, and a longitudinal resonance (LR) mode, which was consistently absent in the presence of H. The recovery of the LR mode for the clean surface indicates that an effective quench of this mode occurs even at coverages as low as 5%. This picture would support quantum delocalization of H motion on this surface as well as on other close-packed metallic surfaces such as Pt(111) where the quenching of the LR mode at full coverage was reported.

The measurements performed around 50% coverage, however, did not reveal any clear signature that reflects the nature of the H motion.

Moreover, in lattice dynamics slab calculations we were able to reproduce the stiffening of the Rayleigh mode near the Brillouin zone boundary and its anomalous overlap with the bulk continuum edge at long wavelengths in the presence of hydrogen (Fig. 1.b), by treating the H motion adiabatically. In this model H is introduced in the surface region at the octahedral surface and subsurface sites. The motion of H atoms is simulated by massless particles, with the subsequent elimination of the H degrees of freedom; in the tradition of the bond-charge and shell models. This had two consequences: an effective increase in the Pd-Pd force constants and a moderate flattening of the Rayleigh branch. The former raised the Rayleigh branch from its position in the clean surface dispersion, while the latter resulted in pushing it to overlap with the bulk continuum near the zone center where its surface character was preserved because of mismatch with the bulk force constants.

We are currently preparing a new comprehensive manuscript where we are compiling all these new results together with a more detailed description of the results that appeared in

a Physical Review Letter last June. This paper will be ready in a few weeks and will be submitted to Physical Review.

Our focus now will be on the H system itself rather than searching for indirect signatures for the H delocalized quantum motion in the dynamical properties of the underlying Pd surface. A detailed outline of planned work is given in section III.

Fig. 1.a

Clean Pd

■▲: experimental data
solid curves: slab calculations

Fig. 1.b

H/Pd(111)

■▲: experimental data
solid curves: slab calculations

2. Investigation of the Structural and Dynamical Trends in the Growth of Cu Overlayers on Pd(111) Surface:

We have started the investigation of the Cu/Pd(111) system using the retractable evaporator we constructed last year. The first phase of the measurements we report here was focused on determining the growth mode as a function of evaporation rates and of surface temperature, which was controlled by the closed-cycle refrigerator. An initial calibration of the evaporation rates as a function of evaporation temperature and evaporator-sample geometry was performed using Auger and LEED diagnostics. These measurements provided preliminary indications that a layer-by-layer growth is taking place in the first and second overlayers at room temperature. Further Cu depositions were carried out in the temperature range $90^\circ\text{K} < T_e < 300^\circ\text{K}$. In the low temperature region the deposition was hampered by a high rate of sticking of contaminants, mainly CO, H₂O and hydrocarbons, emitted from the heated evaporator body which has limited the ambient pressure during evaporation to 10^{-9} torrs. However, a gradual reduction in this ambient pressure is taking place and we expect to be able to study the low temperature regime shortly.

We have carried out structural studies of the growth of the Cu overlayers using elastic He beam scattering. In these measurements we monitored the variation in the intensity of the specular beam with deposition time. We observed periodic oscillations in the specular intensity (Fig. 2), typical of a layer-by-layer growth mode. Moreover, these measurements have provided a better handle on the evaporation parameters, since they were able to clearly establish a calibration of layer growth against deposition times, and hence provide reliable values for single layer evaporation times.

Having determined the systematics of the evaporation parameters, we turned our attention to the region of the first layer growth. Preliminary LEED measurements showed streaking of the Pd diffraction peaks during the deposition of the first layer which is indicative of a large unit cell. We are currently focusing on the details of this structural phases that characterizes the first layer growth. We are capitalizing on the high sensitivity and resolution of elastic He scattering to reveal the a detailed picture of this structure. Special search is being done for the presence of a discommensuration phase similar to those observed on the reconstructed Au(111) surface.

Fig. 2.

Cu/Pd(111)

Specular intensity vs. deposition time

3. Investigations of the Magnetic Structure of the NiO(100) Surface Using Spin-polarized Metastable He Beam Scattering:

Initial measurements of the intensity in the specular scattering channel of surviving metastable He atoms has been met with limited success because of the poor signal-to-noise ratio. We believe that it can be attributed to two factors. The poor quality of the NiO crystal used, since it has never been properly characterized. The presence of surface imperfections and dopant impurities is expected to enhance the decay probability of the metastable atoms. We have recently purchased a high quality NiO single crystal from Scientific International for which we had requested supplemental funds a few months ago.

The second limiting factor is insufficient intensity of the incident beam. To deal with this problem we augmented our self-consistent electron optics design program with the capability of incorporating a more detailed model of the magnetic field used to confine the electron beam within the excitation region. The results were quite revealing. They demonstrated that while the magnetic field confines the electron beam in the excitation region it leads to the development of a hollow beam profile during the transition of electron beam through the focusing cathode-anode region. This is contrary to our intended design where we expected that the penetration of the magnetic field into that region would be tailored to enhance the focusing process. This finding now provides a logical explanation for the observed peaking of the metastable intensity at low magnetic field strength: an increase in the magnetic field, which should enhance the confinement, leads instead to further expulsion of the electron beam from the axis region and in turn the excitation becomes confined to thinner sheaths (Fig 3.a,b). We resolved this problem by incorporating a thin mu-metal ring designed to provide the desired magnetic field profile in the cathode-anode region. The improvements introduced in the electron optics program allowed the incorporation of the mu-metal ring into the simulations and thus provided the necessary details of the ring design (Fig 3.c). We have completed the modification of the electron gun and are in the process of testing the new configuration.

Finally, we concluded from previous LEED investigations that the presence or absence of 1/2-order peaks in the diffraction spectra of NiO(100) is contingent upon whether the surface cleavage was performed in air or vacuum. It is certain that air cleavage destroys the 1/2-order peaks pointing to the fact that tiny remnants of residual contamination or defects may lead to the removal of the reconstructed phase associated with these fractional

order peaks, be it geometrical or magnetic. We are, therefore, requesting capital equipment allocations for purchasing a UHV crystal cleaver.

B. Computation and Theory:

1. Reconstruction and Growth on Metallic fcc(111) Surfaces:

Spurred by our experimental work on the growth of fcc metal overlayers on fcc(111) surfaces we have expanded our investigations of the reconstruction of fcc(111) surfaces beyond the previous work on gold. We have thus studied what we may call generic classes of fcc(111) metal surfaces and overlayers. These studies evolved around the adoption of a parameterized interatomic potential that exhibits the necessary features typical of metallic elements such as Friedel oscillations and a core softened by metallic screening. By varying the parameters of these potentials we were able to simulate surfaces and overlayers with quite different temperature behavior providing a rich assortment of structures and structural transitions. The first of a series of papers based on the results of this work has been submitted to Physical Review Letters. However, it is worth mentioning that two high temperature surface structural phases reproduced the right sequence and details of the diffraction spectra reported in X-ray scattering from the reconstructed Au(111) surface. The structural details of these high temperature phases are quite unexpected, they revealed that the domain walls change direction from the $\langle 112 \rangle$ in the striped low temperature phase to the $\langle 110 \rangle$ leading to a diamond then a triangular pattern (Fig. 4). This has been completely missed by all previous speculations.

2. The Structure and Dynamics of a Pb/Cu(111) System:

The growth of Pb on Cu(111) was shown to exhibit a series of incommensurate phases in the first layer, culminating in a structure slightly compressed from its natural bulk. Moreover, recent He scattering results by the Göttingen group showed that the second and third layers grow simultaneously, they also measured the phonon dispersion curves as the growth of the thin film proceeded. The ensuing spectra exhibited a rich variety of unexplained and provocative features which have led us to embark on simulating this system in attempt to find the origin and mechanisms responsible. We have thus constructed an embedded atom potential for the Cu substrate and are currently dealing with a similar yet more difficult construction of the Pd potential.

We have adapted our computer codes to the Connection Machine and the Cray III, and extended the system size to 50,000 particles, so far, which allowed the investigation of surface islands of about 10,000 particles.

Fig. 4.

Temp = 0.00 $\langle 110 \rangle \rightarrow$

III. Publications

1. *Evidence of Quantum Motion of Hydrogen on Pd(111) Surface in He-Diffraction Data*, C-H Hsu, B.L. Larson, M. El-Batanouny, C.R. Willis, and K.M. Martini, Phys. Rev. Letts. **66**, 3164 (1991).
2. *Reconstructed Phases and Structural Transitions on fcc(111) Metallic surfaces*, R. Ravelo and M. El-Batanouny, submitted to Phys. Rev. Letts.
3. *Proposal of Metastable Spin-Polarized He as a Probe of Antiferromagnetic Transition Metal Oxide Surfaces*, Anna Swan, W. Franzen, M. El-Batanouny, and K.M. Martini, Mat. Res. Soc. Proc. **208**, 273 (1991).
4. *Evidence of Quantum motion of Hydrogen on Pd(111) in He-Diffraction Data*, C-H Hsu, B.L. Larson, M. El-Batanouny, C.R. Willis, and K.M. Martini, Mat. Res. Soc. Proc. **208**, 63 (1991).
5. *A Cryogenic Two-Axis UHV Manipulator Using a Closed-Cycle Refrigerator*, V. Kollias, W. Franzen, and M. El-Batanouny, to be submitted to Rev. of Sci. Instrum..
6. *Evidence of Delocalization and Quantum Motion of Hydrogen on Pd(111) Surface in He-Diffraction Data*, C-H Hsu, B.L. Larson, M. El-Batanouny, C.R. Willis, and K.M. Martini, to be submitted to Phys. Rev.

Talks and Presentations

1. *Evidence of Quantum Motion of Hydrogen on Pd(111) Surface in He-Diffraction Data*, M. El-Batanouny, Colloquim, Worcester Polytechnic Institute, January 1991.
2. *Evidence of Quantum Motion of Hydrogen on Pd(111) Surface in He-Diffraction Data*, M. El-Batanouny, Seminar, Dept. Applied Science UCD/Livermore, May 1991.

III. Planned Research

1. Further Possibles Investigation of the quantum motion of H on Pd(111) Surface:

The inelastic He scattering measurements reported in section I, mark the completion of investigating indirect signatures of the H dynamics and correlating these signatures with quantum motion.

Recent photon absorption results of magnetoplasma excitations in correlated electron gas, confined in quantum wells, have demonstrated that *roton-like* excitations are not an exclusive property of correlated Bosonic systems, such as liquid He, but do appear even in typical fermionic systems. The signature of the rotonic modes is the well known dip in the excitation dispersion curve at a wavevector characteristic of the interaction length. We have deduced from the line shapes in our elastic He diffraction data a lorentzian line shape whose intensity increases with decrease in H coverage yet its linewidth remains constant (8-9Å) for all coverages. We believe that this reflects the presence of a correlation hole which is a manifestation of the interaction length scale, and may be suggestive of the presence of roton-like excitations. Consequently, we would like to investigate such possibilities. The best probe for these investigations would be inelastic electron scattering in the impact regime, where we have the appropriate energy and momentum, and the necessary scattering cross-section. We are currently in communication with Peder Estrup at Brown University to arrange using his HREELS spectrometer in a collaborative effort.

We are also still planning to make use of the high intensity Infrared beam-line at the National Synchrotron Light Source at BNL in order to provide yet another perspective to the investigation of the H/Pd(111) system. The tunability and high intensity of this source allows the measurements of H adatom excitations on metal surfaces as has been demonstrated recently by Chabal *et al.* for the. The application of this technique to H/Pd(111) will be equivalent to the investigation of the electronic energy bands of crystalline solids using optical and UV photons. Such measurements when carried out in the dilute regime would be complementary to the electron energy loss work.

Thus the larger picture will be comprized of pure phonon dispersion curves at full coverage followed by a roton-bearing dispersion curves at medium coverages and ending in band-like transitions at very low coverages.

2. Investigating the Structural and Dynamic trend in the Growth of Cu, Ag, and Co Overlayers on Pd(111):

We shall continue with the He elastic diffraction measurements of the first layer structure of Cu on Pd(111) focusing on the possibility of being mediated by uniaxial dislocations (or discommensurations) which the streaking in the LEED diffraction spots seems to indicate. Subsequently, will study the stability of this structural phase with temperature by measuring the corresponding phonon spectra. This will be followed by a similar investigation with coverage which will carry us into the second monolayer where we will repeat the same scenario. We anticipate to study this system up to the fourth monolayer unless we observe anomalous behavior in the the growth of thicker layers.

After the completion of the Cu/Pd(111) system investigation we will study the Ag/Pd(111) system. where the lattice misfit is smaller but has the opposite sign, namely, Ag has a bigger atomic diameter ($d_{Ag} = 2.88\text{\AA}$, $d_{Pd} = 2.75\text{\AA}$). Moreover, Ag is quite softer than Cu. The investigations will again focus on several aspects: first, the temperature dependence of both the structure and the phonon spectra of the first overlayer will be investigated using He scattering. Special attention will be given to interdiffusion and alloying in this layer which will mark an upper limit in the sample temperature for our studies. Second, we shall investigate the nature of the multilayer growth and the underlying dynamical aspects using again the combination of elastic and inelastic He scattering; bearing in mind the sensitivity of the phonon spectra in the ultra-thin film to the details of its structure and the structure of its interfacial boundaries.

The last metal overlayers to be studied on Pd(111) will be Co films which has a natural hcp crystal structure, with atomic diameter of $2.51\text{\AA}$ or a misfit of -9.5%. In this case the misfit is on the borderline of layer-by-layer growth. We are, therefore, interested in how this growth might proceed in the first layer, and what would the stacking sequence be. The procedures we will follow will be similar to those described for Cu and Ag.

It is worthwhile reiterating here that in carrying out the recent surface phonon measurements of the H/Pd(111) system an overall instrument resolution of ~ 1.5 meV full-width-half-maximum has been achieved. With good linewidth fitting it can provide line resolutions of about 0.5 meV. These instrument numbers are far better than the actually measured inelastic peak linewidths which tend to be of the order of 4.0-5.0 meV or more. We should also stress that the success of investigating the dynamics of overlayer growth lies mainly in

the coupling of experimental measurements with highly sophisticated modelling capabilities, which we definitely have.

3. Investigating the magnetic structure of NiO with Spin-polarized Metastable

He beam scattering:

After completing the current improvements on the metastable atom exciter we will orient and slice the NiO crystal boule we purchased into thin rods with a $\langle 001 \rangle$ axis. This will be done with a diamond wheel saw. We are also building a special sample holder that will facilitate the rod cleavage in the UHV chamber, yet allow azimuthal rotation.

Subsequently we will proceed with the planned investigation of the feasibility of measuring the long-range structural order of the surface electron spins on the NiO(100) surface by the scattering of spin-polarized metastable He beams.

iii. Computation and Theory:

We shall continue to provide the computational support for the problem of metal overlayer growth. In that respect we shall follow the scenario outlined last year in our progress report. Our developed MD codes are most suitable for handling thin films since they treat the substrate and the surface/film differently: while the substrate is treated as a slab with periodic boundary conditions subject to a Nosé-Hoover thermostat, the surface/or thin film is treated as an island, with free boundary conditions, in contact with the substrate which acts as a regulated thermal bath. This allows the free deformation of the island subject to a constant temperature. The fact that the evolution of the island structure is extremely sensitive to the details of the interatomic potentials employed provides us with a valuable tool to understand the different possible manifestations and consequences of these details.

The investigation of the Pb/Cu(111) system will be pursued using embedded atom potentials. This will provide a means of classifying this type potential against our generic classes. Moreover, unraveling the rich variety of features in the phonon spectra of the Pb/Cu(111) system is quite challenging and is expected to be the pilot work for the subsequent investigations of the Cu/Pd(111), Ag/Pd(111), and Co/Pd(111) systems. Finally, we should reiterate that our codes are well equipped with efficient algorithms to compute the phonon dispersion curves for any film configuration which facilitated comparison with experimental data and convergence on the right structure.

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