

# Summary Abstract: Surface dynamics of rare gas crystals

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(Received 17 October 1984; accepted 27 November 1984)

In this paper we present preliminary results dealing with the surface dynamics of ordered rare gas overlayers physisorbed on a Ag(111) substrate. The overlayers examined were 1, 2, 3, and 25 layer (111) oriented films of Ar, Kr, and Xe. Experiments with physisorbed rare gas films on other metal surfaces have been reported by Mason and Williams.<sup>1</sup> However, in this paper we report for the first time, to our knowledge, how the surface phonon relations evolve on a layer-by-layer basis from monolayer to bulk across the Brillouin zone. Our experimental results were obtained using the angle resolved time of flight (TOF) of inelastically scattered He. Inelastic He scattering is a good technique for probing these weakly bound systems because of its surface sensitivity, excellent energy resolution ( $\sim 250 \mu\text{eV}$ ), and because the momentum of the incident beam is of the right order of magnitude to probe the entire Brillouin zone for the low energy modes of these materials. A complete description of the experimental procedure and apparatus will appear in forthcoming publications.<sup>2</sup>

Thermodynamic and structural information for rare gas overlayers on Ag(111) was already available from LEED ex-

periments<sup>3,4</sup> and theoretical calculations.<sup>5</sup> These form hexagonal structures that are azimuthally aligned but incommensurate with the surface. Overlayers were grown on a cryogenically cooled Ag(111) crystal with a low pressure dosing beam by controlling the crystal temperature, beam pressure, and dosing time. The ordering and lattice constants were checked using elastic He diffraction. The angular profiles obtained in these diffraction runs indicate that the coherence lengths of these overlayers are only slightly less than that of the Ag substrate ( $\sim 100 \text{ \AA}$ ). When an experiment on a particular overlayer was completed, the number of layers was confirmed by temperature programmed thermal desorption. By controlling the rate of the temperature ramp, the monolayer desorption peak occurred separately from any of the multilayer peaks. Therefore, the coverage could be quantitatively determined by comparing the total integrated signal to that of the monolayer.

The data were analyzed by first fitting the TOF peaks with a nonlinear least squares routine. Examples of the data and the fits are shown in Fig. 1. The arrows indicate the TOF of elastically scattered He. In general, there was always a peak at this position, which we attribute to incoherent scattering from crystal defects. The well resolved peaks show that with

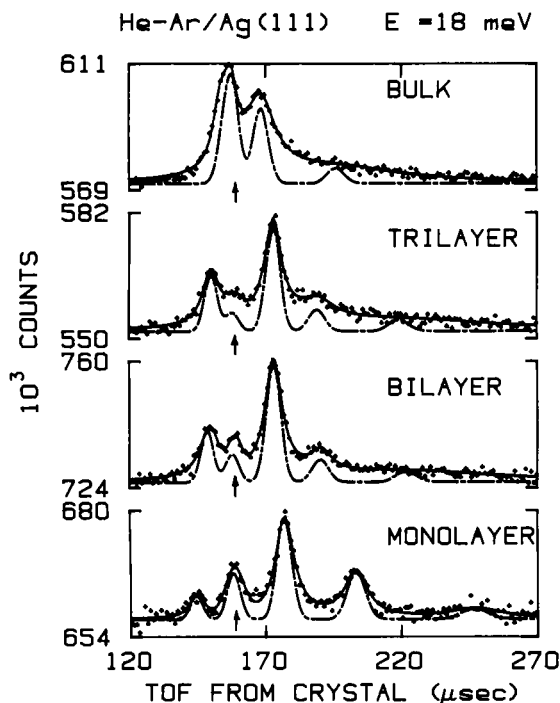


FIG. 1. TOF spectra of the Ar overlayers studied at a surface temperature of 21 K and an incident beam energy of 18 meV. Crosses are the experimental data, solid lines are least squares fits to the data, and dashed lines are computer simulations which have been arbitrarily scaled for presentation purposes. These dashed lines are computer simulations which are forward convolutions of the instrument function with the phonon dispersion curves, assuming that the inelastic transitions have delta function energy widths. Arrows indicate position of elastic incoherent scattering. The spectra were collected for 1 h with  $1 \mu\text{s}$ /channel resolution at an incident angle of  $45^\circ$ . The detector angle was, from top to bottom,  $42^\circ$ ,  $39^\circ$ ,  $40^\circ$ , and  $50^\circ$ .

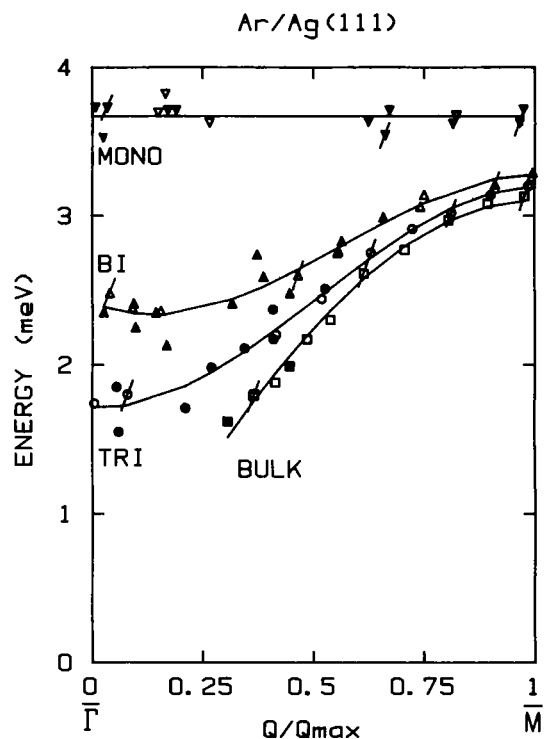


FIG. 2. Dispersion curves of the Ar overlayers from  $\bar{\Gamma} \rightarrow \bar{M}$ . Open symbols are for energy loss of the beam, closed symbols are for energy gain. Representative error bars are shown for energy and momentum loss features (with respect to the He beam) which occurred in the first zone. Solid lines are polynomial fits to the data.

an 18 meV incident beam, single phonon events are the predominant inelastic scattering channel. To give an idea of the probabilities for inelastic scattering, the large energy loss peak of the monolayer has an intensity which is  $\sim 1 \times 10^{-3}$  of the specular beam, and  $\sim 1 \times 10^{-5}$  of the incident beam. The intensities of the principal modes observed do not vary by more than a factor of 5 from zone center to edge ( $\bar{\Gamma} \rightarrow \bar{M}$ ). The difference in the flight times for these peaks compared with the elastic TOF (determined at the specular angle) was used to determine the phonon energies. With this information, and the incident and detector angles, the momentum exchange with the surface was calculated. Most of the experiments were done at an incident angle of  $45^\circ$ , and the Brillouin zone was probed by varying the detector angle.

Figure 2 is a reduced zone plot of the dispersion relations for Ar in the  $\bar{\Gamma} \rightarrow \bar{M}$  direction. This figure clearly shows that inelastic He scattering experiments can be used to quantitatively probe how the surface vibrations of thin films evolve, on a layer-by-layer basis, from monolayer to bulk. This also indicates how the forces present at the surfaces of thin supported films vary with increasing distance of the surface from the substrate. The same qualitative features have also been seen for Kr and Xe.

The monolayer  $SP_1$  mode (the only monolayer mode observed) is found to be dispersionless within experimental error. This indicates that the adsorbed atoms are behaving as independent Einstein oscillators, moving in an uncorrelated fashion in the surface potential well. Only the single phonon inelastic events corresponding to the energy loss and gain peaks adjacent to the elastic position in Fig. 1 are plotted in Fig. 2. This monolayer frequency gives the curvature at the equilibrium position, an essential piece of information for constructing the interaction potential. Temperature dependent studies show that the relative intensities of the single phonon creation and annihilation peaks vary in a manner consistent with statistical expectations. There are also two

other peaks in the monolayer spectrum of Fig. 1, corresponding to phonon creation, with energies twice and three times the fundamental. Due to the nearly harmonic nature of the rare gas-surface holding potential, we are at this time unable to determine the relative importance of overtone and multiphonon excitations in explaining these energy loss features. As further overlayers are added, the amount of dispersion increases as lateral interactions become systematically more important. Again, note that only the energy gain and loss features immediately adjacent to the elastic time of flight in Fig. 1 were used in constructing the multilayer dispersion curves shown in Fig. 2.

Lattice dynamics calculations have been carried out which well represent our experimental dispersion curves.<sup>6</sup> These calculations demonstrate the adequacy of using known gas phase pair potentials for modelling the interactions present in condensed rare gas films, and the importance of the substrate in modifying the phonon frequencies. Work is currently in progress to determine the inelastic scattering probabilities from the TOF spectra.

*Acknowledgments:* We would like to thank B. Hall, D. Mills, J. Black, M. Klein, and L. Bruch for their theoretical assistance. This work was supported in part by the ONR and the NSF-MRL at The University of Chicago. S. J. S. also acknowledges support from a Camille and Henry Dreyfuss Foundation Young Faculty Grant, and is the recipient of an Alfred P. Sloan Research Fellowship.

<sup>1</sup>B. F. Mason and B. R. Williams, *Surf. Sci.* **139**, 173 (1984).

<sup>2</sup>K. D. Gibson and S. J. Sibener (to be published).

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<sup>4</sup>J. Unguris, L. W. Bruch, E. R. Moog, and M. B. Webb, *Surf. Sci.* **109**, 522 (1981).

<sup>5</sup>L. W. Bruch, *Surf. Sci.* **125**, 194 (1983).

<sup>6</sup>K. D. Gibson, S. J. Sibener, B. Hall, D. L. Mills, and J. Black (to be published).