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PHYSICS AND CHEMISTRY DEPARTMENTS
AND
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PROJECT TITLE:

He Atom-Surface Scattering: Surface Dynamics of Insulators, Overlayers and Crystal Growth.

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I. PROJECT SUMMARY

Investigations in this laboratory have focussed primarily on the surface structure and dynamics of ionic insulators, on epitaxial growth onto alkali halide crystals and multiphonon studies. Six major areas have been worked on this past year: 1) The surface dynamics of RbCl has been re-examined. Having now measured the optical mode lying in the gap between the acoustic and optical bulk bands, we are better able to compare the experimental results with the theoretical treatments employing relaxed and unrelaxed RbCl surfaces. 2) In collaboration with theorists at the Max Planck Institut für Strömungsforschung, Göttingen, Germany, we have developed a simple force constant model which provides insight into the dynamics of KBr overlayers on NaCl(001), a system with a large lattice mismatch. When the KBr/NaCl(001) results are compared to similar dynamical modeling of Na/Cu(001) and NaCl/Ge(001) experimental results done by others, it is clear that a microscopic understanding of growth and thin layer dynamics is now formulated and it is in agreement with experimental data. It further allows us to move to the next obvious step which is to develop a microscopic model for strain at an interface, a situation for which experimental results exist. 3) We have completed epitaxial growth experiments for KBr onto RbCl(001). Slab dynamics calculations using a shell model for this system with very small lattice mismatch are being carried out in collaboration with Professor Manson of Clemson University and with Professor Schroeder in Regensburg, Germany. 4) Extensive experiments on multiphonon scattering of helium atoms onto NaCl and, particularly, LiF have been carried out and the theory has been developed to a rather advanced stage by Professor Manson. It is expected that this work will permit the extraction of much more information from time-of-flight spectra than is currently possible. In a related application, we have shown with Professor Manson that the theoretical model provides a very good description of the multiphonon scattering from organic films. 5) Work in this laboratory has started on self-assembling organic films on gold (alkyl thiols/Au(111)). We have begun to prepare and characterize the gold crystal; one of the group members has spent two weeks at the Oak Ridge National Laboratory learning the proper Au(111) preparation techniques. 6) One of our students has spent several weeks at the Oak Ridge National laboratory carrying out neutron scattering experiments on NiO, measuring both bulk phonon and magnon dispersion curves. These experiments represent the start of the next stage of our effort on metal oxides.

Work planned for the next year is directed into two major areas: the dynamics and epitaxial growth of metal oxides which represent a very important class of ionic insulators and the dynamics of the head groups of alkyl thiols which self-assemble on gold (and other noble metals). In addition to oxides like MgO and NiO, the latter of which has transitions to magnetically ordered phases, we plan to examine several perovskites such as $KTaO_3$, and both homo- and heteroepitaxy on some of these materials will be studied. We expect in the case of the alkyl thiols to begin another line of investigation into growth as it is possible to deposit an overlayer which would chemically bond to the alkyl chains. Another potentially interesting system for growth studies with direct technological implications is the transition metal dichalcogenides which form "natural" two-dimensional materials.

II. PROJECT

A. Introduction

Interfaces are among the most fundamentally interesting and technologically fertile of physical and chemical environments. However, they are also among the most difficult to investigate, particularly for insulating materials. A host of well-developed surface science techniques employing electron and ion scattering[1] run into severe problems with non-conducting materials and similar difficulties are encountered in Scanning Tunneling Microscopy (STM).[2] Even light scattering relying on novel and sophisticated approaches that are important in studying adsorbate molecules have only limited applicability to probing interfaces.[3]

One approach that does not suffer in application to insulators is high-resolution Helium Atom Scattering (HAS).[4-8] The low-energy He atoms are electrically neutral, non-penetrating and non-reactive. Hence, they are sensitive only to the outermost layer and are totally non-destructive to the surface. Since coherent atom scattering is exquisitely sensitive to the presence of defects on crystalline surfaces, the details of the crystal growth mechanism and the formation of interfaces may be probed in real time by monitoring the specular beam intensity as a function of incident wavevector, of coverage and the deposition parameters (substrate temperature, deposition rate and deposition energy).[6-8] Further, He atom diffractive scattering can be employed to determine the geometry and other structural features of the surface at any point during the growth, and these features can also be studied as a function of the deposition parameters.[9,10] HAS instruments capable of time-of-flight (TOF) measurements can, in addition, examine the inelastic atom scattering intensity and thereby investigate the surface dynamics of the interface including modifications of surface forces that result from the growth.[9-12]

B. Helium Atom Scattering

When He atoms collide with a crystal surface, both elastic and inelastic events take place. The coherent elastic scattering arises from specular reflection and Bragg diffractive scattering.[13-16] The location of the Bragg peaks depends on the dimensions of the unit cell on the surface, and the intensities of the elastic peaks can be related back to the "corrugation" in the atom-surface potential.[14,15]

An additional mechanism for the scattering of He atoms is related to the defects on the surface. This aspect of HAS is only now becoming recognized as a powerful method for observing processes which destroy or modify order on the surface. Defect sites, including isolated adsorbates and terrace steps, give rise to diffuse (*i.e.*, incoherent) elastic scattering which shows up as loss of intensity in the specular and Bragg peaks, broadening of these coherent peaks, and as large elastic signals at non-Bragg scattering angles in measurements of the inelastic scattering.[7,8,13,17-20]

The inelastic scattering can be considered to result from the interaction of the He atoms with higher-order terms of the interaction potential, which account for the surface phonons and for the bulk phonons projected onto the surface.[5,16] Thus, the inelastic scattering contains the surface dynamics.

The HAS instrument used by our group and to be employed in the proposed work is shown schematically in Figure 1. Briefly, it is composed of several ultra high vacuum (UHV) chambers connected together and has a fixed geometry design: The axis connecting the nozzle beam source and the crystal target makes a 90° angle with the axis connecting the target and the detector. The main features are the nozzle beam source which produces a nearly monoenergetic ($\Delta E/E \approx 2\%$) He beam; the manipulator in the scattering chamber which holds the crystal target; the time-of-flight (TOF) section needed for energy analysis of the pulsed He beam; and the detector, consisting of an electric quadrupole mass spectrometer and a computer-controlled data acquisition system.[4,21]

For the alkali halides each target crystal was cleaved in air and then inserted into the vacuum chamber. The chamber was baked to achieve UHV conditions, and the target was cleaned by sublimation as determined by angular distribution measurements and inelastic studies which could be compared with previous measurements of this same surface. However, for the metal oxide experiments proposed here, the targets will be prepared by cleaving *in situ*.

For the alkali halide deposition experiments, the appropriate second alkali halide crystal was heated so that sublimation could take place from a broad effusive source[22] and a shutter was opened to expose the source to the target crystal (Figure 1). A thickness monitor, not shown in Figure 1, was used to confirm the thickness of the deposited layer. For the proposed metal oxide epitaxy, metal and oxygen atom beams will be employed.

For the alkali halide growth studies three types of measurements were made with this HAS instrument: 1) intensity *vs.* deposition thickness for the specular and Bragg peaks, which were carried out under a variety of experimental conditions in real time; 2) angular distributions of the scattered He at different coverages and for various deposition rates, He atom wavevector and surface temperature parameters; and 3) time-of-flight (TOF) measurements at different coverages. The first type of measurement was carried out in real-time, while the latter two were carried out after interrupting the deposition with the shutter. It was found that the growth could be turned on and off repeatably if the substrate temperature was not too high.[9,10] For the experiments on growth of metal oxides, similar measurements will be carried out.

C. Results

1. Dynamics of RbCl(001)

Experiments have been carried out on the cleaved RbCl(001) surface in the <100> direction.[23] Both the Rayleigh wave and a surface optical mode lying in the gap between the bulk acoustic and optical bands (the S_2 mode) were observed. The measured surface dispersion branches were compared with model calculations of surface dispersion for both a relaxed and an unrelaxed RbCl (001) surface. The calculated Rayleigh mode dispersion is found to be very nearly the same in both models and agrees well with the experimental results. However, the experimental optical mode data appear to fit the calculations only in part for each model. A comparison of the RbCl results with previously measured surface dispersion curves for KBr (which has very nearly the same lattice parameters and mass) shows that their dynamics are largely the same, but with significant differences for part of the S_2 mode close to the zone center and for the crossing resonance. See Figures 2 and 3.

2. *Dynamics of a KBr Overlayer Grown on NaCl(001)*

The results of HAS experiments on the dynamics of thin epitaxially grown films (two, three, four and seven monolayers) of KBr on NaCl(001)[10] have been interpreted by a simple force constant model.[24] The model treats the KBr overlayer with force constants between the K^+ and K^+, Br^- and Br^-, and K^+ and Br^- nearest neighbor ions, which are obtained by fitting the bulk dispersion curves; the NaCl surface is treated as a rigid wall coupled to the KBr by a second pair of force constants. The latter set are found to be "softer" than the former, which is consistent with a weakened interaction between the KBr and NaCl layers due to the large lattice mismatch (~17%). The model predicts, in agreement with the data, that the frequency of the Rayleigh wave should be finite at the zone center ($\bar{\Gamma}$ point) and approach zero as $1/N^{1/2}$, where N is the number of overlayers of KBr. See Figure 4. This agrees with a comparison of of NaCl/Ge(001) work and Na/Cu(001) results.[25,26] A more recent interpretation of the Na/Cu(001) study indicates that it represents a case where the interface binding is much larger than that between the Na atoms, leading to "organ pipe" modes, which have different vibrational characteristics.[26,27] For example, the Rayleigh wave should be finite at the zone center ($\bar{\Gamma}$ point) and approach zero as 1/N, where N is the number of overlayers of Na. The weaker bound overlayer cases, KBr/NaCl(001) and NaCl/Ge(001) behave similarly and have a $1/N^{1/2}$ dependence.

3. *Heteroepitaxy- KBr/RbCl(001)*

HAS experiments have been employed to study the growth of KBr onto a cleaved RbCl(001) surface[28] in the temperature range ~180 - 220K. Unlike the KBr/NaCl system above, the lattice mismatch here is very small (~0.2%). The oscillations in the deposition curves show the characteristic behavior of layer-by-layer growth. However, the analysis of the data indicates that the step height of the first layer is different from that of subsequent layers, 3.71 Å compared with 3.32 Å expected from the bulk lattice spacing. The results also suggest that the growth mode in this temperature range is to form numerous small islands initially, which then merge together with continued deposition. At the same time the defect density is very low for the first monolayer, but it increases with the number of layers grown. Analysis of the TOF spectra for the one monolayer film yields surface phonon dispersion branches consisting of the Rayleigh wave, a longitudinal resonance and a surface optical mode lying in the gap between the bulk optical and acoustic bands. The Rayleigh wave appears very nearly the same as that for cleaved RbCl and KBr (001) surfaces (very similar to each other), the other branches are significantly softened. The proper approach for interpreting these ionic crystal results is to use the shell model as was done by de Wette and coworkers.[29,30] For the KBr/NaCl(001) case above, one would need to use a unit cell that includes the superlattice of 28Åx28Å which at present is very difficult. However, for the KBr/RbCl(001) case of this paragraph we have a collaboration with Professor U. Schroeder at Regensburg, Germany, where we are attacking the experimental results with the shell model approach.[31] Early comparisons on the dispersion curves appear to be in agreement. This work includes also a collaboration with Professor J. R. Manson at Clemson University and our goal is to not only understand the dispersion curves, but to try checking the spectral density of surface phonons in the model with the experimental TOF spectra. See Figures 5 and 6.

4. *Multiphonon Scattering Experiments*

A theoretical model for the multiphonon helium atom scattering from surfaces has been been developed by this group with Professor J. R. Manson of Clemson University.[32-34] It has been found to give very good agreement with experiments that have been carried out in this laboratory on NaCl.[33] The importance of this model is not only does it give us the proper interpretation of multiphonon scattering, but it shows us how to interpret from multiphonon scattering results, the form factor which we need when we want to extract the spectral density of phonon states from single phonon TOF spectra.[34] Until this work, the TOF spectra have been used mostly for the spectroscopic determination of phonon energies. Now it is possible to extract the spectral densities of the surface phonons as well. It makes use of the fact that the single phonon spectra can be modeled theoretically as a product of four functions, a form factor, a Debye-Waller term, a structure factor and the spectral density.[34] In times past one had to assume functional forms for the form factor and the spectral density which meant it was difficult to argue that the assignments were truly unique. Our multiphonon model allows us to measure the form factor enabling us to find the spectral density function by fitting the single phonon spectra. As a thorough test of the model we have just completed an extensive investigation of the multiphonon scattering of helium from LiF. The data analysis from this work is just getting started.

Another application of this model was recently made by one of us (JGS) and Professor Manson in showing that it can reproduce quite well the energy distribution measurements of the scattering from a thin organic Langmuir-Blodgett film.[35] This is rather important for us regarding the experiments proposed below on the alkyl thiol/gold system. This is because the model describes how to interpret the dynamics, which lets us explore the conditions which are required to carry out single phonon experiments and how to interpret them for given incident beam conditions, surface temperature and alkyl thiol molecule used. See Figure 7.

5. *Organic films on Metals*

Work is just beginning in this laboratory on studies of the dynamics of alkyl thiols on gold (and possibly on other noble metals). Organic films are of considerable interest because a basic knowledge of their preparation and properties could serve as a guide toward understanding biological films, spacer lubrication layers, organic coatings and possibly new thin film dielectric materials. Professor M. E. Derrick is working with us on this project under an NSF Visiting Professorship for Women grant. To date we have been able to prepare and characterize a gold (111) surface using Auger Electron Spectroscopy (AES) and LEED and are about to prepare and characterize a target of $CH_3(CH_2)_{15}SH/Au$. Professor Derrick spent two weeks at the Oak Ridge National Laboratory, working with Dr. Zehner, learning techniques for crystal target preparation under a separate grant from SURA. We also have received samples of alkyl thiols/gold/mica prepared in the laboratory of Professor J. Schlenoff in the Chemistry Department which we plan to compare with the films grown on single crystal gold.

6. *Neutron Scattering Experiments on Metal Oxides*

One of our students spent several weeks at the Oak Ridge National Laboratory under a separate grant from SURA carrying out neutron scattering experiments on NiO. In collaboration with Dr. Harold Smith he was able to collect data on both bulk phonon and magnon dispersion curves as a function of target temperature. He is currently analyzing the results.

7. *Comment on Results*

Probably the most important result of this work is the knowledge that HAS can be used to measure the growth and particularly the dynamics of one or more monolayers. None of us would have believed this several years ago. Of nearly equal importance, is the simple force constant model used for interpreting the KBr/NaCl(001) work[24] and the other two growth studies on NaCl/Ge(001) and Na/Cu(001).[25-27] The model seems to contain the essential physics. This means we are on our way to a much better understanding of epitaxial growth and to exploring the effects of the binding of the layer, its coupling to the surface and the vibrational effects of the substrate.

D. Proposed Experiments

The crystal growth experiments at FSU have been focussed on the alkali halides because they are the prototypical ionic insulator materials. They form an ionic class of materials which have a wide range of masses, ionic sizes, crystal spacing and even have fcc and sc crystalline forms. We plan to conclude these fascinating studies and use the information gained to research ionic metal oxides both the clean surface and those undergoing homo- and heteroepitaxial growth. Additionally, the recent advances with self-assembling alkyl thiol films on Au(111) surfaces appear to offer a marvelous opportunity to study the surface structure and particularly the surface dynamics of chemisorption and growth of organic films on metal surfaces.[36-51] To investigate both of these paths, which are more intricate than alkali halide crystals, but are correspondingly more important technologically, will require further development of He atom scattering techniques and also of theoretical modeling. The two mentioned topics are very likely to keep us busy the entire year, however, we briefly mention opportunities with growth on natural layered materials, such as transition metal dichalcogenides. Ohuchi et al.[52-55] have pointed out how easily 2D metal chalcogenide materials can be grown on top of each other and because the bonding between the layers is of the van der Waal type, lattice matching difficulties can be avoided. Changing the metal or chalcogen atom may alter the electronic properties, metal coordination or the interplanar crystal structure. One of us has had extensive experience on similar layered materials and are aware of the fascinating scientific properties of the surfaces of the bulk materials so this direction would be a natural for us.[56]

1. Dynamics of and Growth on Metal Oxides

Experiments on ionic insulators such as MgO, NiO and $KTaO_3$ require only a single modification, albeit an important one, from the approach used with the alkali halides; namely, these materials need to be cleaved in vacuum. We have constructed an *in situ* cleaving device just for this purpose. We have also constructed a UHV transport cart so that prepared targets can be transfered from one chamber to another without being exposed to the atmosphere.

The initial work on these materials would begin in the Preparation Chamber, separate from the HAS instrument, where LEED and AES characterization of the target will be carried out. Then the prepared crystals can be transferred under vacuum to the HAS instrument. In most cases before starting growth investigations, we would first measure the surface dynamics of the clean crystals since only for MgO[57-62] and to a lesser extent for NiO[14,63-65] have there been any extensive surface dynamics studies.

For MgO and NiO we plan several types of growth studies: First, homoepitaxial growth of both MgO and NiO will be explored; then the deposition of NiO on MgO and the reverse will be tried. As these materials have less than a 1% lattice mismatch with each other[66] we might expect to observe similar behavior to that seen in the KBr/RbCl case summarized above. Unlike the simple sublimation technique which worked well for the alkali halides, for these growth experiments we plan to produce the oxides in the HAS instrument using a Knudsen source for the metals while co-producing O atoms as a beam from a microwave discharge source. If this method does not prove to be satisfactory, we will be able to collaborate with a group at FSU that has developed an MBE laboratory for epitaxial growth of magnetic superlattices and has already produced superlattices of NiO/Fe_3O_4.[67,68] The NiO studies will be similar to those suggested for MgO.[14,66-68]

The surface dynamics of the perovskites is expected to be extraordinarily interesting in its own right, particularly measured as a function of temperature. In general, these cubic crystals undergo a number of phase transitions, sometimes leading to ferroelectric phases, which may be different on the surface than in the bulk. $KTaO_3$ is a convenient starting point because it can be cleaved to produce a high quality surface. Further, when doped with Nd, it has many phase changes as a function of temperature which can be studied. Once the surface dynamics has been measured, then growth studies will commence. We will experiment with growing oxides like NiO that have the rocksalt structure (and a 5% lattice mismatch) and other perovskites like $BaTiO_3$ and $SrTiO_3$ which do not cleave to give good surfaces. In addition, since the lattice spacing (3.99Å) of $KTaO_3$ has very nearly the same geometry and size as that of the NaCl(001) surface, it should be very instructive to try to grow the alkali halide on the oxide.

As with our alkali halide epitaxy, the goal in these experiments is to investigate the dependence of the growth on lattice mismatch and on the interactions of the anions. Since the anions are generally much larger than the cations, and more polarizable, understanding their interactions seems like the key to understanding the process of growth.

2. *Organic Films on Noble Metals*

Chemisorption of hydrocarbon chains onto metal surfaces involves the formation of an interface and a new layer whose order depends on the ordering of the substrate and the interaction with the substrate. Since the hydrocarbons are insulators, the probe of choice with nanoscale resolution would seem to be the neutral He scattering.

Recent publications have reported studies by EELS, XPS (x-ray photoelectron spectroscopy), TPD (temperature programmed desorption), AES, and LEED which characterize monolayers of adsorbates of the general form $HS(CH_2)_nX$ or $(S(CH_2)_nX)_2$ on single crystal Au(111) surfaces, where X = CH_3, CO_2CH_3, CH_2OH, CO_2H and $CONH_2$, and n ranges up to 21.[36-48] The results show that an ordered layer is formed, which has each S bonded to a gold atom. The attached hydrocarbon chains sticks upward with a range of angles from 28° to 40° with the surface normal in an all trans configuration. Elastic He atom scattering experiments have also been carried out on these systems.[49] The diffraction patterns obtained for Au(111) show that for $CH_3(CH_2)_{21}S$ the methyl groups form a nicely ordered surface with hexagonal structure and a lattice spacing of 5.01Å. For these samples the domain sizes appeared to be $\leq$ 100Å. It should be noted that the He atoms are probing the top group of the chain and not the S-Au region at the metal surface. Our primary interest is in the dynamics since to our knowledge, only two very limited published results exist and they have not been compared to any theory.[35] Our work with Manson provides us with a model and we are poised to start these measurements.

These systems are of interest in general as self-assembling systems and for their potential through the choice of X groups for chemical synthesis. One can imagine a number of uses for an ordered hydrocarbon (or substituted hydrocarbon) layer, including the possibility of designing very specifically binding catalysts, as models for biological interfaces and membranes and for their relevance to corrosion protection and adhesion problems. Indeed, electron transfer processes in the substituted alkyl thiols/gold surface system have been studied as a model system for long-range electron transfer which may occur in cells as for example in photosynthesis.[50]

This work has begun by preparing and characterizing a Au (111) single crystal by AES and LEED in the separate Preparation Chamber. Next, the self-assembling systems will be prepared on the gold surface and similarly characterized with HAS. The first systems to be studied will have methyl as the terminal group (*i.e.*, X= CH_3). The focus of our work will be on the TOF experiments to examine the dynamics of these films. We expect to be able to characterize the interchain forces, the barrier to rotation of the terminal methyl groups and film phase transitions (if any) by measuring the time-of-flight spectra as a function of temperature. We also plan to explore the variation in these properties with some of the different X groups listed above. Because of the very low vibrational frequencies these long-chained systems have, it is very important that we can make use of the multiphonon theory in interpreting the results.

In a sense, this theory has come along at just the right time for this work even though it was developed for very different materials and with a completely different intention.

Finally, it would be exciting to deposit a layer of metal, such as Cu, or other material on top of the alkyl film, which would chemical bond *via* the X group to it. This could be accomplished either with Knudsen cells in the HAS instrument, or by using the MBE instrument in the neighboring lab or possibly by employing the new MOCVD apparatus which has recently come on-line in the Chemistry Department. Elastic He scattering experiments have already been carried out on physisorbed layers of Xe, Kr, H_2O, CH_3OH and n-hexane on $CH_3(CH_2)_{21}SH$/Au/mica.[51] Again, the TOF spectra would permit us to characterize the interactions between the new layer and the film.

3. *Future Experiments on Growth*

Two-dimensional layered materials, including the transition metal dichalcogenides, monochalcogenides and tin sulfide and selenide, also can be made to grow epitaxially.[52-55] Because the van der Waals interlayer forces are weak and the covalent intralayer forces are strong, the latter dominate the growth. The interface between layers can tolerate a large misfit which appears to be similar in some ways to that observed in the KBr/NaCl system; namely, it displays a superstructure which depends on the mismatch of the unit cells.

These materials have interesting and potentially useful electronic properties which can be varied from insulating to superconducting by changing the metal or the chalcogen. Further, intercalation compounds can be formed which have modified electronic properties. For example, depositing Cu on SnS_2 leads to diffusion of the Cu into the bulk which converts the SnS_2 semiconductor from a n-type to a p-type. On the other hand deposited Ag reacts with the surface while Au just forms a surface adlayer.[53]

One of us (JGS) has already had considerable experience with these materials, having carried out HAS studies on 2H-$TaSe_2$, 1T-TaS_2 and GaSe at the Max Planck Institute in Göttingen, Germany, and is quite familiar with preparing clean surfaces of them.[56]

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IV. Figure Captions

1. Schematic of the apparatus showing the relation of the Beam source with nozzle and chopper, the Scattering Chamber with crystal target and evaporation source and the Detector with the quadrupole mass spectrometer.

2. Surface phonon dispersion for RbCl(001) in the <100> direction compared to the theoretical calculations of de Wette and co-workers shown as segmented lines. The open triangles are the results of this work and the solid circles are taken from a previous measurement in this laboratory [J. Vac. Sci. Technol. A **7**, 2094 (1989)]. In the top panel no relaxation is included in the calculation [Phys. Rev. B **14**, 1167 (1977)] while in the bottom panel relaxation is included [Phys. Rev. B **35**, 5783 (1987) and private communication].

3. A comparison of the surface phonon dispersion for the "mirror" pair of RbCl (solid triangles, this work) and KBr (open circles and triangles, from this lab, [Reference 21]). The shaded bands and curves are theoretical calculations for KBr explained in the reference.

4. Surface phonon spectral density of states for vibrations normal to the surface in the case of a) two, b) three, c) four and d) seven KBr monolayers on a rigid NaCl substrate. The intensity of the peaks is represented logarithmically by the length of the horizontal line calculated for the value of Q at the center of the vertical slice. The closed and open points are the experimental values, representing strong and moderate intensity TOF peaks, respectively. The V_i label the longitudinal, z-directed vibrational modes at the zone center. For larger phonon wavevectors, the mode labeled V_1 joins the Rayleigh mode. Because of the simplicity of the model, only the Rayleigh mode is fit. The fit to the optical modes needs the more involved shell model approach.

5. A comparison of the surface phonon dispersion for 1 monolayer of KBr on RbCl(001) with that of cleaved KBr(001). The open points are from previous measurements of cleaved KBr(001) as in Figure 3 [Reference 21]. The closed points are from this work. The shaded bands and the curves are theoretical calculations described in the reference.

6. A comparison of the surface phonon dispersion for 1 monolayer of KBr on RbCl(001) with that of cleaved RbCl(001). The open points are from the measurements shown in Figure 2. The closed points are from this work.

7. Plot of a time-of-flight spectrum, converted to energy transfer, for a monoenergetic He atom beam (30meV) scattered from an arachidic acid/methyl stearate monolayer surface at 130 K [from Vogel and Wöll, J. Chem. Phys. **84**, 5200 (1986)]. The narrow peak shows the energy width of the incident He atom beam including instrumental broadening. The solid smooth curve is the fit from our multiphonon theory assuming an effective end-group mass of 15 amu.

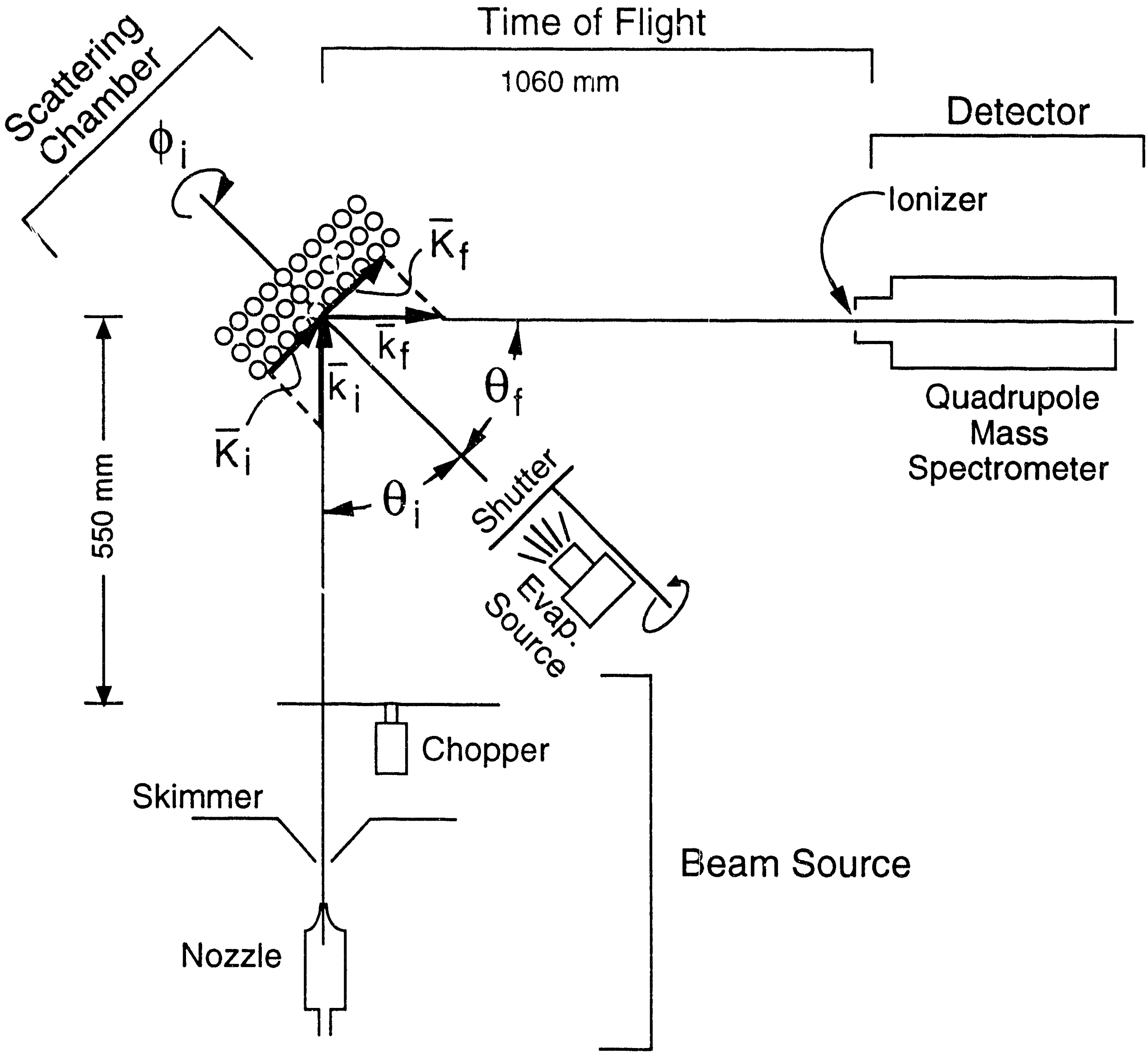


Figure 1

SKO 01 9KF REV 8KF

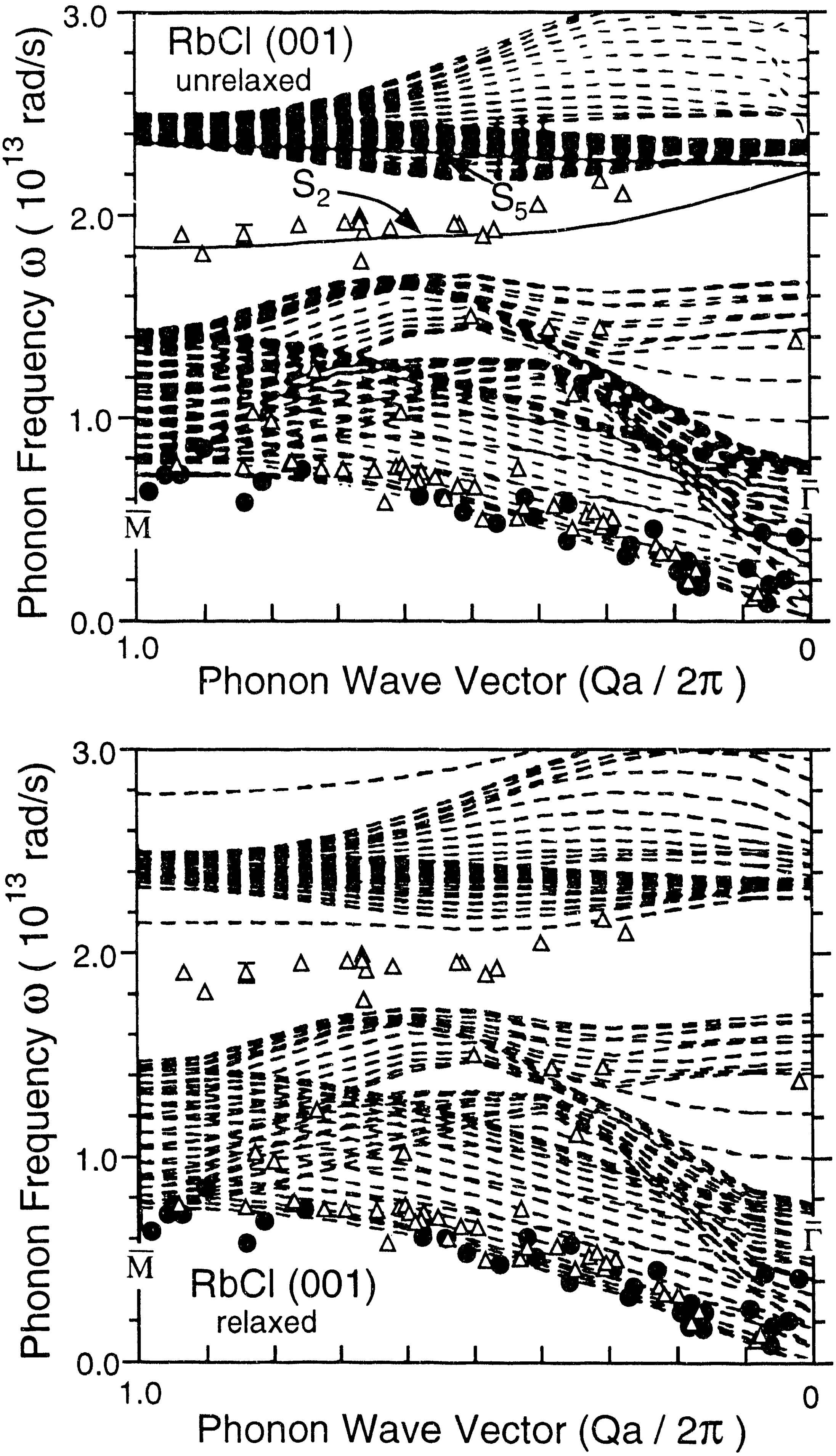

RbCl (001)
unrelaxed
S₂
S₅
3.0
2.0
1.0
0.0
Phonon Frequency ω (10¹³ rad/s)
M̄
Γ̄
1.0
0
Phonon Wave Vector (Qa / 2π)
RbCl (001)
relaxed

Figure 2

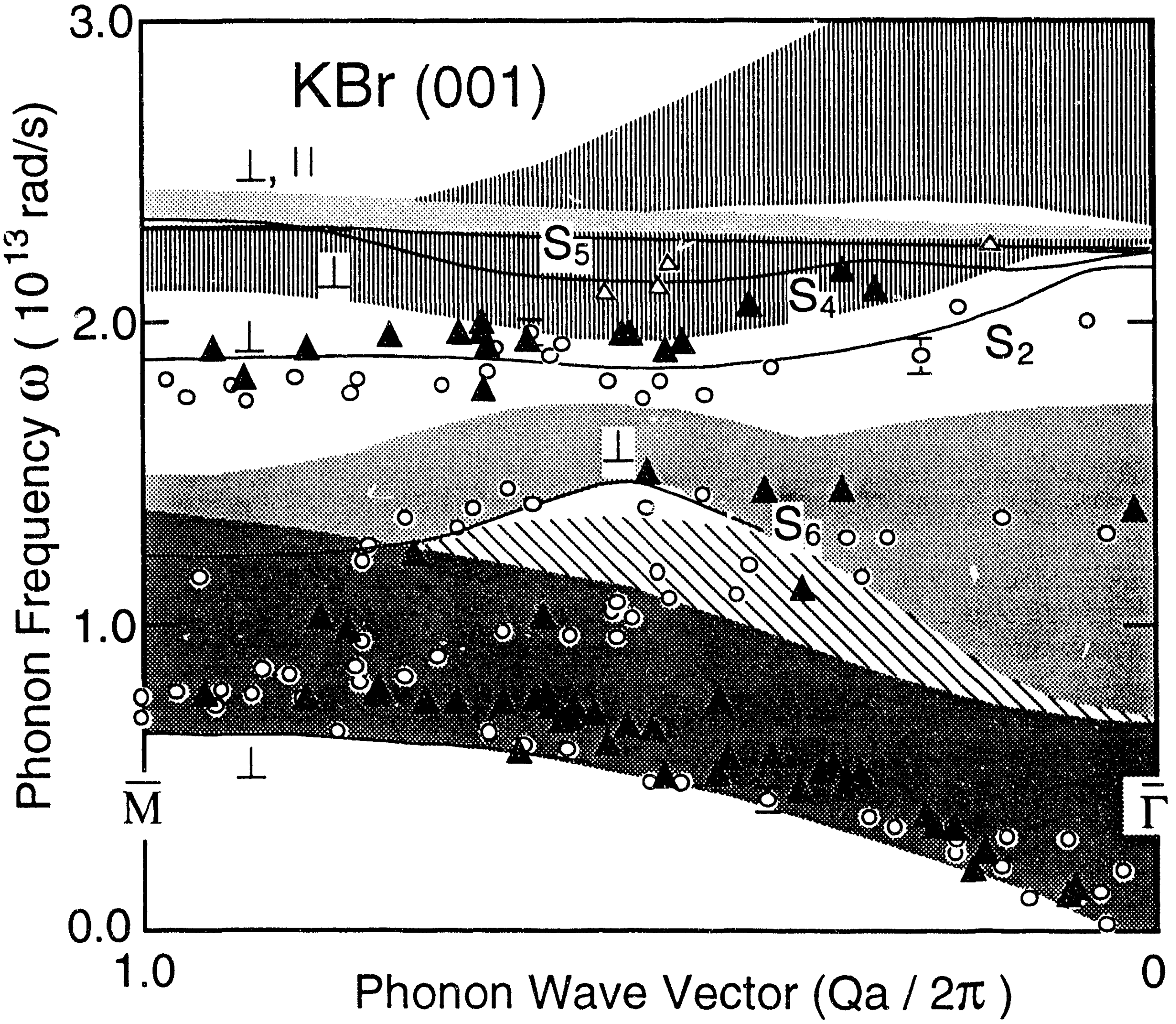


Figure 3

SKOFRONICK 8color 9KF

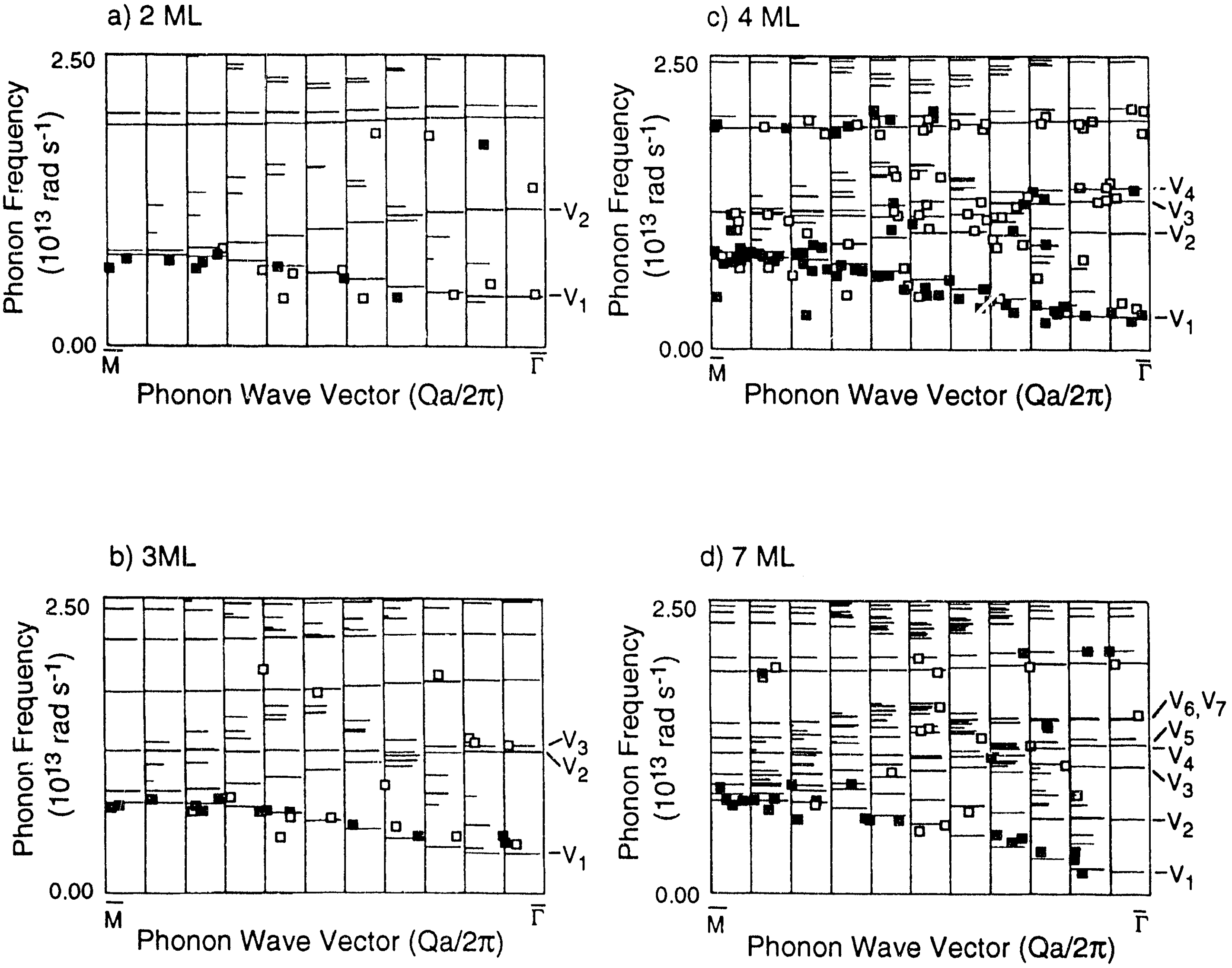

a) 2 ML
2.50
0.00
Phonon Frequency (10^{13} rad s^{-1})
M̄
Γ̄
Phonon Wave Vector (Qa/2π)
V$_2$
V$_1$
c) 4 ML
2.50
0.00
Phonon Frequency (10^{13} rad s^{-1})
M̄
Γ̄
Phonon Wave Vector (Qa/2π)
V$_4$
V$_3$
V$_2$
V$_1$
b) 3ML
2.50
0.00
Phonon Frequency (10^{13} rad s^{-1})
M̄
Γ̄
Phonon Wave Vector (Qa/2π)
V$_3$
V$_2$
V$_1$
d) 7 ML
2.50
0.00
Phonon Frequency (10^{13} rad s^{-1})
M̄
Γ̄
Phonon Wave Vector (Qa/2π)
V$_6$, V$_7$
V$_5$
V$_4$
V$_3$
V$_2$
V$_1$

Figure 4

SKOFRONICK 8 rev BKF

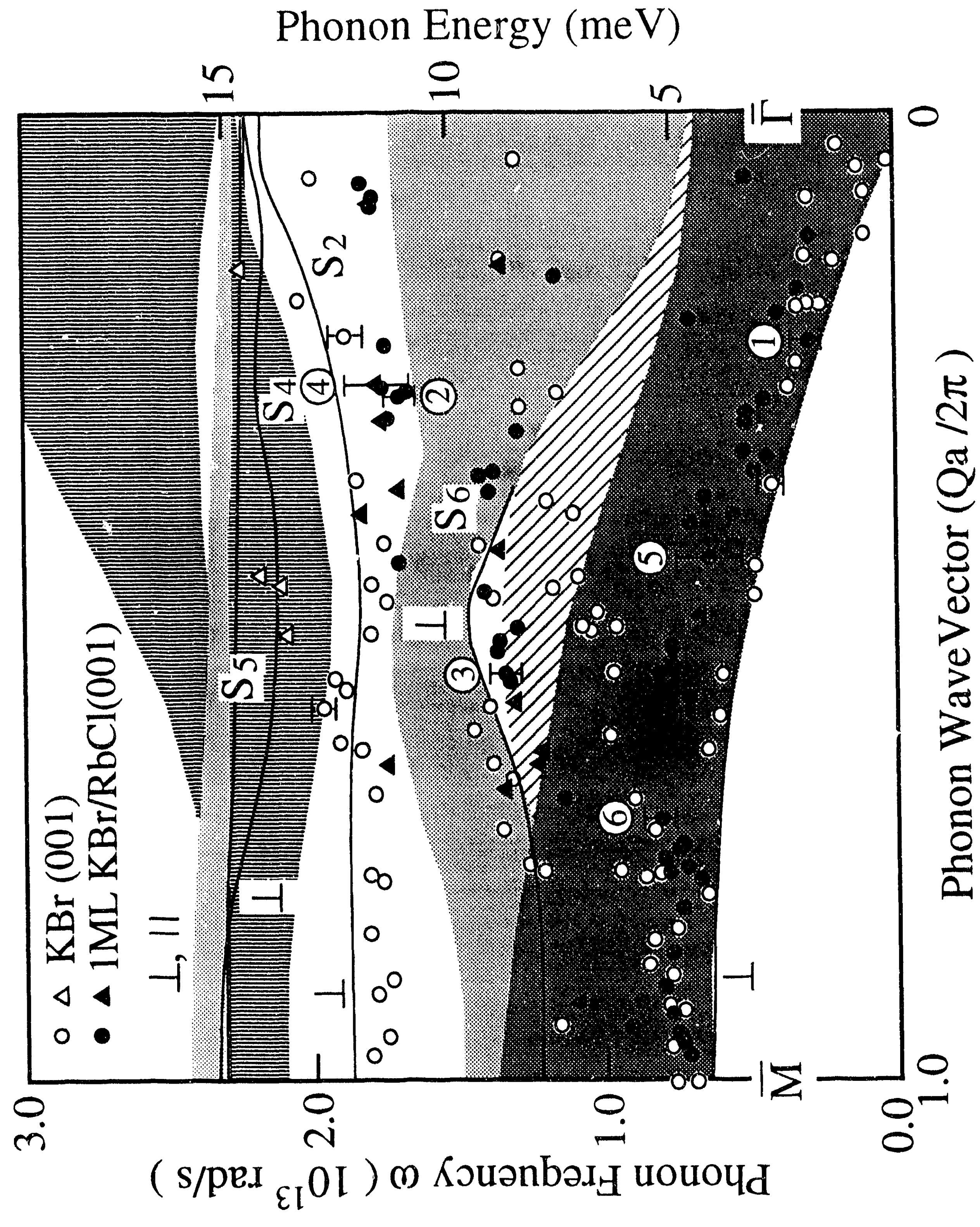


Figure 5

SKOFRONICK 8 BKF

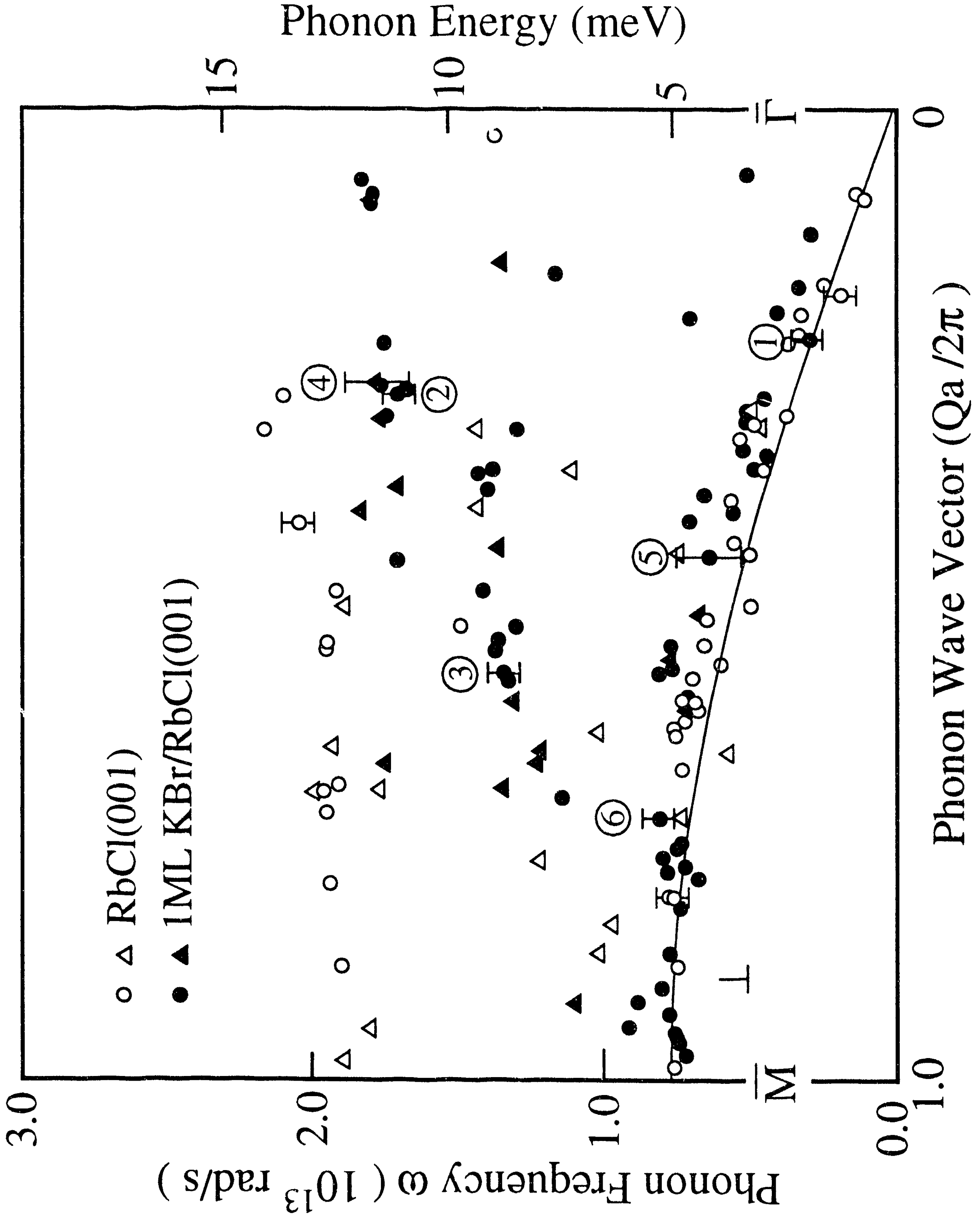
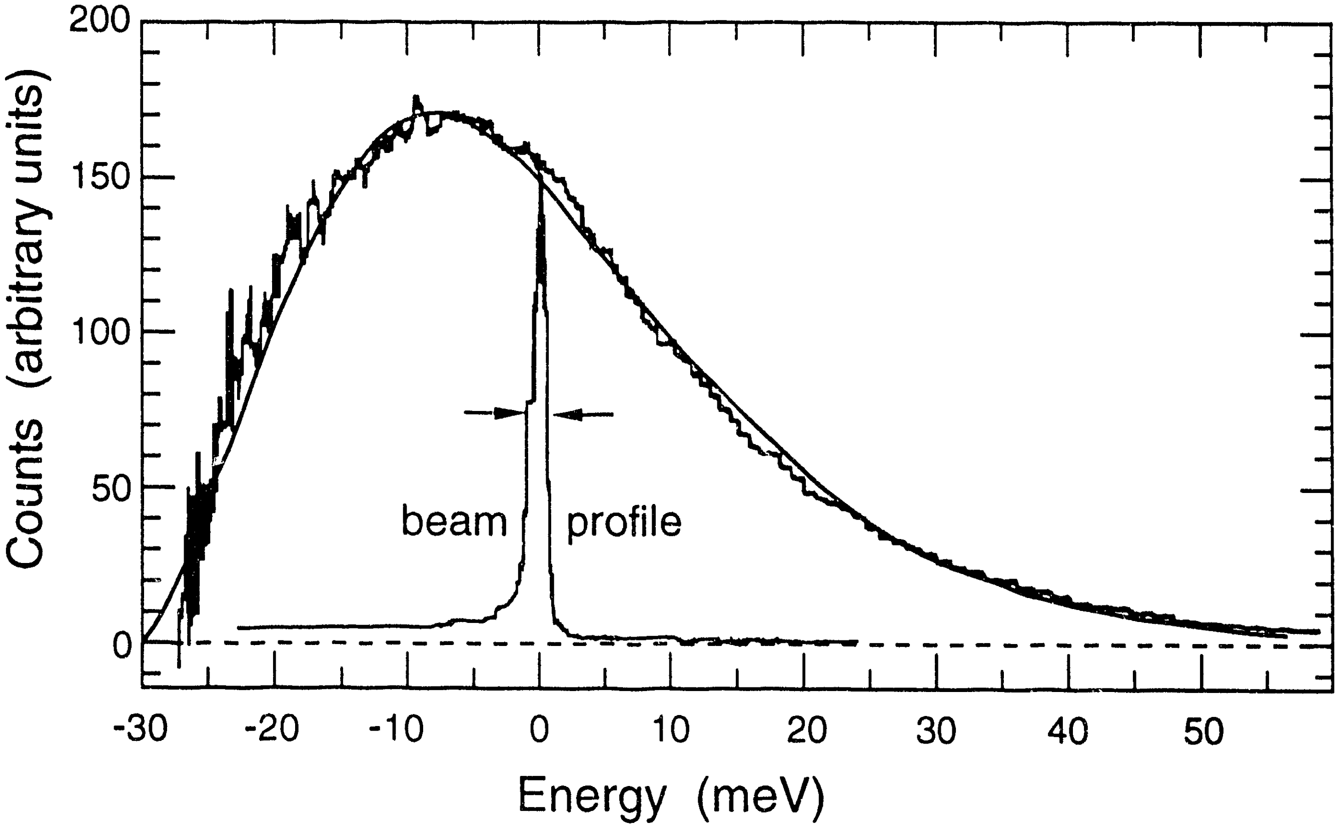


Figure 6



200
150
100
50
0
Counts (arbitrary units)
-30
-20
-10
0
10
20
30
40
50
Energy (meV)
beam
profile

Figure 7

V. FACILITIES AND PERSONNEL

The support facilities for this project include the Machine and Electronic shops of both the Physics and Chemistry Departments. The employees of these shops are paid by the State of Florida and are normally available on a first-come-first-serve basis. In addition, the Center for Materials Research and Technology (MARTECH) which the State has set-up and funded at FSU, has technical and scientific personnel who are experienced in growing and handling crystals and thin films, and in operating an ESCA surface analysis station. More recently, a program of Molecular Beam Epitaxy has been developed here to make and study magnetic superlattices. In addition, there are facilities for X-ray, scanning electron microscope, ellipsometric and IR examination of crystal samples which are readily available to us on a limited basis. A MOCVD facility is now operating in the Chemistry Department. With the location of the new National High Field Magnetic Laboratory in Tallahassee, additional facilities and expertise are becoming locally available.

The Florida State University also has established the DOE-FSU sponsored Supercomputer Computations Research Institute (SCRI) which has a Cray Y-MP and a highly parallel Connection Machine. This facility is very well suited for collaborative ventures between our group and visiting theorists.

The current scientific personnel consist of the co-principal investigators, JGS (Physics Department) and SAS (Chemistry Department), and five dedicated graduate students, J. Baker, J. Hernandez, G. G. Bishop, E. S. Gillman and J. Duan (all in Physics). Our first two students G. Chern (Physics) and W. P. Brug (Chemistry) have completed their doctoral dissertations. Dr. Chern is currently beginning as an assistant professor at a university in Taiwan. Dr. Brug is working with the environmental research group at the Los Alamos National Laboratory. Duan has just finished his Ph.D. dissertation and is writing up parts of it for publication. Bishop is a fifth year student and has worked on temperature-dependent, multiphonon experiments and is currently carrying out experiments on NiO. Gillman is a fourth year student and has been working on characterizing several metal crystal surfaces including a stainless steel alloy crystal, an α-Fe(110) crystal and most recently a Au(111) crystal which will be used in the experiments on self-assembling organic films. He has developed a new X-ray alignment and polishing device, which improves greatly the ability to work with vicinal surfaces. He has also built a new high temperature target holder for the metal crystals. Hernandez and Baker are third year students. Hernandez has begun work on the alkyl thiol/Au system while Baker carried out the neutron scattering experiments at the Oak Ridge National Laboratory under the guidance of Dr. Harold Smith.

Professor M. Elizabeth Derrick of Valdosta State College, Georgia, has has been awarded an NSF "Visiting Professorship for Women" grant to spend most of this year (June, 1992-March, 1993) working full time on the alkyl thiol/gold system. She spent two weeks at ORNL training with Dr. David Zehner on the experimental techniques needed to prepare Au(111).

We have had a number of undergraduates in our laboratory for periods of a semester through the Chemistry Department Honors Program and for summers through the Undergraduate Research Participation grants from the NSF to the Physics Department. This past summer (1992) Chris Banbury of Western Kentucky University worked with us through the Physics Department's grant.

VI. COLLABORATIONS

We have had a long-standing collaboration with the group directed by Professor J. Peter Toennies at the Max Planck Institut für Strömungsforschung in Göttingen, Germany, including a NATO grant for cooperative efforts between our group, the Göttingen group and the theory group of Benedek and Miglio in Milan, Italy. This grant has been extended for another year. The model development for the dynamics of a KBr overlayer on NaCl was carried out with theoreticians in the MPI group.

We have a collaboration with Dr. Harold Smith at the Oak Ridge National Laboratory which involved the neutron scattering experiments on NiO with our student, Mr. Baker. Financial support for this work, mostly for travel, was awarded by the Southeastern University Research Association (SURA).

To interpret and understand the results of HAS experiments requires close collaboration with theorists. As an example of this, we note the collaborative effort in the temperature-dependent, multiphonon scattering model with Professor J. R. Manson of Clemson University and in the recent calculations on KBr/RbCl by Professor Schroeder of Regensburg. We intend to remain associated, in addition, with Professor Celli at the University of Virginia, a pioneer in surface-scattering theory, who is currently helping us understand the buckling behavior of our KBr/NaCl(001) layers and with Professor F. W. de Wette at the University of Texas, Austin, who has developed the slab dynamics technique for surface dynamics calculations and is interested in the surface lattice dynamics of ionic insulators.

VII. ACTIVITIES OF THE INVESTIGATORS

The principal effort of both of us has been to extend the techniques of He atom scattering, which have proven so successful as a probe of the dynamical behavior of surfaces, to the investigation of crystal growth. We have built on our experience with the alkali halides to study homo- and heteroepitaxy in this family of materials and plan to continue this effort and to expand into other insulators families. The construction of the instrument is complete and we are very pleased with the results so far. It will be modified by adding a mechanical refrigerator so the target temperature can be lowered to approximately 30K for the alkyl thiol work.

In addition, we and our students have been active in the surface science community this year, having attended and given papers at various international meetings. These include 1) the 1992 Florida Chapter of the ACS held in Cocoa, FL; 2) an invited paper at the Schloss Ringberg conference in Germany in May, 1992; 3) an invited paper at the XIVth International Symposium on Molecular Beams in Asilomar, California, in June, 1992; 4) the American Chemical Society national meeting in Washington, D. C. in August and 5) the 1992 national meeting of the

American Vacuum Society held in Chicago. Further, we and our students have presented papers at several regional meetings and both PI,s have given colloquia and seminars here at FSU. We have also submitted abstracts for papers to be presented at meetings early next year.

Finally, one of us (JGS) has worked at the MPI in Göttingen this year in connection with the NATO grant, which resulted in a paper on the multiphonon treatment of organic films which has been submitted to *Physical Review*. In addition a review on HAS studies on layered materials has been done in collaboration with Professor J. P. Toennies.

A. Papers Published, In-Press or Submitted in 1991-1992.

1. "Homoepitaxial Growth Investigated by High-Resolution He Atom Scattering: NaCl onto NaCl(001)", J. Duan, G. G. Bishop, E. S. Gillman, G. Chern, S. A. Safron and J. G. Skofronick, J. Vac. Sci. Technol. A10, 1999 (1992).

2. "Epitaxial Growth of KBr onto NaCl(001) by High Resolution He Atom Scattering", J. Duan, G. G. Bishop, E. S. Gillman, G. Chern, S. A. Safron and J. G. Skofronick, Surf. Sci. 272, 220 (1992).

3. "Surface Lattice Dynamics of NiO(001) by Inelastic He Atom Scattering", W. P. Brug, G. Chern, J. Duan, G. G. Bishop, S. A. Safron and J. G. Skofronick, J. Vac. Sci. Technol. A10, 2222 (1992).

4. "Multiphonon Inelastic Scattering of Helium Atoms from Crystal Surfaces", G. G. Bishop, W. P. Brug, G. Chern, J. Duan, S. A. Safron and J. G. Skofronick, Phys. Rev. B (in press, preprint included).

5. "Surface Dynamics of Epitaxially Grown KBr Overlayers on a NaCl Substrate", S. A. Safron, G. G. Bishop, J. Duan, E. S. Gillman, J. G. Skofronick, N. S. Luo and P. Ruggerone, J. Phys. Chem. (submitted, preprint included).

6. "Investigation of Epitaxial Growth via High Resolution Helium Atom Scattering: KBr onto RbCl", S. A. Safron, J. Duan, G. G. Bishop, E. S. Gillman and J. G. Skofronick, J. Phys. Chem. (submitted, feature article, preprint included).

7. "Measurement of the Surface Dynamics of RbCl (001) via High Resolution He Atom Scattering", G. G. Bishop, J. Duan, E. S. Gillman, S. A. Safron and J. G. Skofronick, J. Vac. Sci. Technol. (submitted, preprint included).

8. "Multiphonon Effects in Thin Organic Films", J. R. Manson and J. G. Skofronick, Phys. Rev. B. (submitted).

9. "Helium Atom Scattering Studies of the Surface Phonons of Layered Materials", in Surface Properties of Layered Structures, Kluwer Academic Publishers, Dordrecht, The

Netherlands, Ed. by G. Benedek, Fall (1992).

B. Seminars and Posters Presented in 1991-1992.

1. "Studies of the Heteroepitaxial Growth of KBr onto RbCl via He Atom Scattering", G. G. Bishop, J. Duan, E. S. Gillman, S. A. Safron and J. G. Skofronick, Florida Section of the American Chemical Society, Cocoa Beach, FL, April, 1992.

2. "Epitaxial Growth of Alkali Halides Investigated by High-Resolution Helium Atom Scattering", S. A. Safron, J. Duan, G. G. Bishop, E. S. Gillman and J. G. Skofronick, Florida Section of the American Chemical Society, Cocoa Beach, FL, April, 1992 (invited).

3. "Epitaxial Growth of Alkali Halides Studied by He Atom Scattering", J. G. Skofronick, J. Duan, G. G. Bishop, E. S. Gillman and S. A. Safron, Sixth Workshop on Surface Phonons, Schloss Ringberg, Germany, May, 1992 (invited).

4. "Epitaxial Growth of Alkali Halides Investigated by High-Resolution Helium Atom Scattering", S. A. Safron, J. Duan, G. G. Bishop, E. S. Gillman and J. G. Skofronick, American Chemical Society national meeting, Washington, D. C., August, 1992.

5. "Watching Crystals Grow Layer-by-Layer", S. A. Safron, Florida State University, September, 1992.

6. "High-Resolution He Atom Scattering Experiments on Layered Materials", J. G. Skofronick, Florida State University, October, 1992.

7. "Measurement of the Surface Dynamics of RbCl (001) via High Resolution He Atom Scattering", G. G. Bishop, J. Duan, E. S. Gillman, J. Baker, J. Hernandez, S. A. Safron and J. G. Skofronick, American Vacuum Society national symposium, Chicago, IL, November, 1992.

8. "Surface Physics as seen by Helium Atom Scattering", Colloquium in Physics, March 5, 1992.

9. "Surface Physics Using Helium Atom Scattering", Steinhatchee UF/FSU meeting on April 11, 1992.

C. Proposals and Grants Other than DOE.

1. "Structure and Dynamics of Chemisorption through He Atom Scattering on Crystalline

Surfaces", National Science Foundation Visiting Professorship for Women, with M. E. Derrick, June, 1992- February, 1993, funded $96,700.

2. "Dynamics of Crystal Surfaces, Both Clean and with Adsorbates", NATO, with J. P. Toennies, 1990-1991, funded $5447. Renewed for 1992-1993, funded $4,500.

3. "FSU/ORNL Cooperative Research Program in Surface Science Studies", SURA, Summer, 1992, funded $4,400.

4. "Synthesis and Properties of Oxide Films, Interfaces and Superlattices", NSF, (with other faculty in MARTECH), 1993-1996, pending $2,058,493.

5. ACS/Petroleum Research Fund Type-AC grant, ACS-PRF, 1993-1996, pending, $75,000.

END

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