101

Progress Report for Project Grant DE-FG05-85ER45208

**He ATOM-SURFACE SCATTERING:
SURFACE DYNAMICS of INSULATORS, OVERLAYERS and CRYSTAL GROWTH**

Covering the Project Period from
May 1, 1991 to April 30, 1994

to the

U. S. Department of Energy

from the

HELIUM ATOM SURFACE SCATTERING GROUP

Physics and Chemistry Departments
and
Center for Materials Research and Technology
The Florida State University
Tallahassee, Florida 32306-3016

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

EXPERIMENTAL SCIENTISTS:

S. A. Safron, Professor of Chemistry
J. G. Skofronick, Professor of Physics

MASTER *ds*

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TABLE OF CONTENTS

TITLE PAGE	1
TABLE OF CONTENTS	2
I. PROJECT SUMMARY	3
II. PROJECT	4
A. Introduction	4
B. He Atom Scattering	4
C. Results	6
III. REFERENCES	10
IV. FIGURES	13
V. FACILITIES AND PERSONNEL	20
VI. COLLABORATIONS	21
VII. ACTIVITIES OF THE INVESTIGATORS	21

I. PROJECT SUMMARY

During this Project Period investigations in this laboratory have been directed primarily towards understanding the surface structure and dynamics of ionic insulators, the microscopic interactions controlling epitaxial growth and the formation of overlayers, and energy exchange in multiphonon surface scattering. Six major areas have been worked on: 1) Experiments have been carried out on the surface dynamics of RbCl and preliminary studies done on CoO and NiO. The oxide work involved the use of a new *in situ* cleaver. For RbCl we have now measured the optical mode lying in the gap between the acoustic and optical bulk bands and have been able to compare the experimental results with theoretical treatments employing both relaxed and unrelaxed RbCl surfaces. 2) Epitaxial growth and overlayer dynamics experiments on the systems NaCl/NaCl(001), KBr/NaCl(001), NaCl/KBr(001) and KBr/RbCl(001) have been performed. The large lattice mismatch ($\sim 17\%$) in the KBr-NaCl system was found to give rise to a surface superstructure which persisted until about six or seven layers had been deposited. For the small mismatch KBr-RbCl system ($\sim 0.2\%$) no superstructure was seen. 3) We have collaborated with two theoretical groups to explore models of overlayer dynamics with which to compare and to interpret our experimental results. First, with the 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 the KBr overlayer on NaCl(001), as well as other systems. As an ionic adsorbate on an ionic substrate, it also provides an important limiting case for comparison with other kinds of overlayer/substrate systems that have been examined in similar studies, such as Na/Cu(001) and NaCl/Ge(001). In addition, we have worked with Professor U. Schröder at the University of Regensburg, Germany, to compare our KBr/RbCl results with his slab dynamics calculations employing a shell model representation for this system. This is important because the shell models are considered to be the best current models for the lattice dynamics and dielectric properties of ionic insulators. Our work with this group is, thus, a first attempt to treat an ionic film/substrate system in a "realistic" framework. 4) We have carried out extensive experiments on the multiphonon scattering of helium atoms from NaCl and, particularly, LiF. The simpler models that we first proposed with Professor Manson of Clemson University have now been refined and extended to a rather advanced degree by him. This effort presents an opportunity for a definitive study of the theoretical approach. The model should permit the extraction of much more information from inelastic scattering data than is currently possible. In a related application, we have shown with Professor Manson that the model provides a very good description of the multiphonon scattering from organic films at relatively high temperatures. 5) Work has begun in this laboratory on self-assembling organic films on gold and silver surfaces (alkyl thiols/Au(111) and Ag(111)). We have begun by preparing and characterizing the gold and silver (111) surfaces by LEED and AES. One of our graduate students is at the Oak Ridge National Laboratory (Summer, 1993) working with a group that studies organic films on metals. Professor Betty Derrick of Valdosta State College, Georgia, under an NSF Visiting Professorship for Women grant has been working with us on this project. 6) Another one of our students is also at the Oak Ridge National Laboratory (Summer, 1993) continuing neutron scattering experiments on the bulk phonon and magnon dispersion of NiO and CoO which were begun last summer.

II. PROJECT

A. Introduction

Interfaces are unique chemical and physical environments and as such they are of interest both fundamentally and technologically. However, they present formidable challenges to the investigator, particularly in the case of insulating materials. A host of well-developed surface science techniques employing electron and ion scattering¹ run into severe problems with non-conducting materials and similar difficulties are encountered by researchers relying on Scanning Tunneling Microscopy (STM).² Even light scattering making use of the newest and most sophisticated methods that are important in studying adsorbate molecules has only limited applicability in probing interfaces.³

One approach that applies equally well to all types of materials, including insulators, is high-resolution Helium Atom Scattering (HAS).⁴⁻⁸ Low-energy He atoms being electrically neutral and chemically inert, interact non-destructively with the surface layer. Produced as a nearly mono-energetic beam, the atoms scatter coherently from an ordered surface giving rise to Bragg diffraction which can be used to determine the geometry and other structural features of the surface. Since coherent atom scattering is exquisitely sensitive to the presence of defects, the details of crystal growth and the formation of interfaces may be probed in real time by monitoring the specular beam intensity as a function of the incident wavevector, the coverage and the deposition parameters (*e.g.*, substrate temperature, deposition rate and deposition energy).⁶⁻⁸ Moreover, the changes in the diffraction pattern reflecting changes in the surface geometry can be studied as a function of the deposition parameters at any stage during the growth.^{9,10} HAS instruments capable of time-of-flight (TOF) measurements can, in addition, examine the inelastic atom scattering intensity and thereby investigate the dynamics of clean surfaces and modifications of surface forces due to the presence of an adlayer.⁹⁻¹²

B. Helium Atom Scattering

When helium atoms collide with a crystal surface, both elastic and inelastic events take place. The coherent elastic scattering arises from specular reflection and Bragg diffraction.¹³⁻¹⁶ The location of the Bragg peaks in angular scans of the He atom scattering intensity 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}

Defect sites, including isolated adsorbates and terrace steps, give rise to an additional mechanism for the scattering of atoms; namely, the diffuse (*i.e.*, incoherent) atom scattering. The diffuse elastic scattering shows up primarily as loss of intensity and broadening in the specular and Bragg peaks, and as large elastic signals at non-Bragg angles in TOF measurements of the inelastic scattering.^{7,8,13,17-20} This aspect of HAS is only now becoming recognized as a powerful method for observing processes which destroy or modify order on the surface.

Inelastic atom scattering can be considered to result from the interaction of the helium atoms with higher-order components 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 reflects the dynamics of the surface.

The HAS instrument used by our group has been described in detail in the literature and is shown schematically in Figure 1.²¹ The major modifications to this instrument include: 1) two separately pumped chambers for growth studies which have been mounted onto the scattering chamber and 2) a new refrigerator which can maintain the target crystal on the manipulator at about 30 K. In one of the new chambers for deposition, a simple effusive source for metal evaporation has been set up, while the other has an oxygen atom source which uses a microwave discharge. The two molecular beams are aimed to intersect at the crystal target at which point growth can occur. Vacuum valves separate the scattering chamber from the sources so that the source can be changed without opening the scattering system to air.

In addition to this instrument, we have constructed a separate Preparation Chamber which is fitted with an ion gun, LEED and Auger Electron Spectrometer (AES). We have been using this chamber to prepare and characterize the gold and silver (111) surfaces for use in the alkane thiol studies.

For the alkali halide experiments 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 before angular distribution measurements and inelastic studies were done. However, for the metal oxide experiments, the targets were prepared by cleaving *in situ*. A clean alkali halide surface could always be regenerated by subliming for about an hour at 400-500°C, depending on the compound; but the CoO and NiO surfaces, excellent immediately after cleaving in vacuum, began to deteriorate after a couple of days and could not be recovered by heating or by dosing with O₂.

For the alkali halide deposition experiments, the appropriate second alkali halide crystal was operated by heating as a broad sublimation source.²² A thickness monitor, not shown in Figure 1, was used to confirm the thickness of the deposited layer. In the preliminary growth experiments on NiO described below, the O atom source was not used and growth was attempted instead with an O₂ molecular beam.

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; 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 NiO, measurements similar to 1) and 2) were attempted.

C. Results

1. Surface Dynamics of CoO(001), NiO(001) and RbCl(001)

Shell model calculations of the surface dynamics of alkali halides have generally agreed rather well with experiments although some differences have been found. A good example of this behavior can be seen in Figure 2 for new measurements on the cleaved RbCl(001) surface in the $\langle 100 \rangle$ direction.²³ Model calculations of surface phonon dispersion for both a relaxed and an unrelaxed RbCl (001) surface were compared with the measured surface dispersion branches. 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 (S_2 mode) appear to fit the calculations only in part for each model.

Much less work has been done in the way of comparing shell model calculations with experimental results for the metal oxides having the rocksalt structure. Some results are now reported for MgO²⁴ and for NiO^{25,26} with fair agreement. The metal oxides appear to have more complex electronic interactions, especially at the surface, so that one might expect the shell model picture to be less complete than for the simpler alkali halides. In addition, the transition metal oxides have magnetic phases which may also complicate the theoretical approach. In Figure 3 we present our preliminary dispersion results for NiO and for CoO which have been carried out on (001) surfaces obtained by cleaving in vacuum. Since the surface quality deteriorates after two to three days, even at base pressures of 10^{-10} torr, only a limited number of experiments could be performed. Other NiO and CoO crystals are currently being obtained and prepared (notched for the *in situ* cleaving) to complete these preliminary investigations.

2. Epitaxial Growth

HAS has been employed to study the growth of NaCl on NaCl(001)⁹, KBr on NaCl(001)¹⁰, NaCl on KBr(001)²⁷ and KBr on RbCl(001)²⁸. As this work is nearly all published at this time, we can summarize the main features. *a)* The oscillations in the deposition curves (specular beam intensity vs. deposition time) show the behavior characteristic of layer-by-layer growth in each of these systems. *b)* In the case of the KBr-NaCl systems, the large lattice mismatch ($\sim 17\%$) leads to the formation of a superstructure during the initial stages of film growth. The diffraction patterns for adlayers between 2 and 6 or 7 layers thick have extra diffraction peaks arising from a superstructure length corresponding to 7 NaCl's and 6 KBr's; that is, $7a_{\text{NaCl}} = 6a_{\text{KBr}}$. No evidence of superstructures was found in the homoepitaxy of NaCl or in the KBr/RbCl system which has a lattice mismatch of about 0.2%. *c)* The analysis of the deposition oscillations for KBr/RbCl indicate 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. *d)* The TOF data show that after only a few layers are deposited, the surface dispersion of the film material resembles very closely the dispersion of the cleaved surface of that material. For example, see Figure 4. *e)* In all cases the growth mechanism in the temperature range 180-220 K appears to consist of two-dimensional growth with the formation of small islands initially that merge together with continued deposition as in the model of Comsa and co-workers⁷.

A detailed examination of the KBr/NaCl(001) dispersion data for 4 monolayers of KBr shows that there is an extra mode, nearly dispersionless across the surface Brillouin zone, lying at energies below the Rayleigh wave. A similar low-lying mode is found in measurements on other, non-ionic, adlayer/substrate systems where there is substantial lattice mismatching. The Table below summarizes the currently available results of lattice spacing of the substrate and the adlayer, the energy of the flat mode and the number of layers where the intensity of the mode was strongest. Speculation is that this mode occurs when sufficiently many layers have been grown that the adlayer can relieve the strain due to the mismatch by switching out of registry with the substrate into its bulk crystal structure. At this point the potential energy as a function of position for adlayer molecules may become bimodal and, hence, give rise to a low frequency vibration. The Table shows that this phenomenon has now been seen in very different materials and might therefore represent "universal" behavior. We are currently pursuing this model idea.

System ^a	$a_{\text{substrate}}$	a_{adlayer}	mode energy	layer observed
KBr/NaCl(001)	5.64 Å (fcc)	6.60 Å (fcc)	2.5 meV	4 ML
Na/Cu(001)	3.61 Å (fcc)	3.66 Å (bcc)*	1.7 meV	2 ML
Pb/Ge(111)	5.66 Å (fcc)	4.95 Å (fcc)	1.75 meV	3 ML

*Nearest neighbor distance.

^aFor KBr/NaCl(001), see Ref. 29; for Na/Cu(001) see Ref. 30; for Pb/Ge(111) see S. Schmidt, Diplom thesis, Max Planck Institut für Strömungsforschung, 1992.

3. Dynamics of KBr Overlayers on NaCl(001) and on RbCl(001)

In collaboration with theorists from the Max Planck Institut für Strömungsforschung, Göttingen, Germany, we have interpreted 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 with a simple force constant model.^{29,31} 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 (Γ point) and approach zero as $1/N^{1/2}$, where N is the number of overlayers of KBr.³² See Figure 5. This vibration is from a longitudinal wave in the z direction and the layers act like they are moving as a unit. While this model is much more "primitive" than the shell model, we have employed it here because the shell model would have required using a very large unit cell (as discussed above, a 7 by 7 NaCl lattice dimension) which is difficult to handle even with current supercomputers, and because the results can be usefully compared with similar treatments of other epitaxially grown systems. Indeed, one finds a remarkable trend in going from KBr/NaCl(001) to Kr/Ag(111) to Na/Cu(001)^{30,31}, from weak overlayer-substrate interactions to relatively strong overlayer-substrate

interactions.³²

As the lattice dimensions for KBr match those for RbCl nearly exactly, one can approximate the unit cell as having the dimensions of the RbCl substrate. In collaboration with Professor U. Schröder of the University of Regensburg, Germany, we have interpreted our KBr/RbCl results with a shell model calculation using the slab dynamics technique.³³ The model parameters for the intra-film and intra-substrate interactions were taken from the literature for bulk KBr and RbCl, respectively. The parameters at the interface between Rb^+ and Br^- and between K^+ and Cl^- were taken to be those of the bulk RbBr and KCl, respectively. The model parameters for the Rb-K and Cl-Br at the interface were adapted from the bulk values to preserve the same charge balance. The results shown, in part, in Figure 6 are satisfying, particularly for the gap mode, S_2 , considering that the model parameters have not been adjusted to fit the data and the optical mode seems to be fitted. More work is needed. Schröder and co-workers are currently re-evaluating the bulk parameters for this system to see if it is possible to obtain a consistent fit of the bulk data using the same ionic charges on both KBr and RbCl. This would both simplify the current treatment and allow for a more direct extraction of the interface forces. Other adaptations of the bulk parameters to describe the interactions at the interface are also possible and need to be explored. Further, we note that the current version does show a small outward relaxation for the adlayer, but it does not reproduce the large first adlayer spacing found in the experiments²⁸. We expect this to be corrected in the improved versions. In preliminary work in regard to this last point, Schröder's group has found that the separation between the overlayer and substrate varies critically with the binding forces. Thus, measurements such as these may prove to be a sensitive method for determining film/substrate binding forces.

4. *Multiphonon Scattering Experiments*

A theoretical model for the multiphonon helium atom scattering from surfaces has been developed by Professor J. R. Manson of Clemson University with this group.³⁴⁻³⁶ It has been found to give very good agreement with experiments that have been carried out in this laboratory on NaCl and more recently on some unpublished results on Na/Cu(001).^{34,35,37} The importance of this model is that it shows that phonon TOF spectra (related to the differential reflection coefficient) can be thought of as a product of four functions: a form factor, a Debye-Waller factor, the structure factor and the spectral density of phonon states. When applied, it provides not only a proper interpretation of multiphonon scattering intensity as a function of crystal temperature, but it also allows one to extract the form factor from multiphonon scattering data. This in turn permits the determination of the spectral density from single phonon TOF spectra.³⁶ As a thorough test of the model we have completed an extensive investigation of the multiphonon scattering of helium from LiF. The data analysis from this work is not yet completed.

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.³⁸ See Figure 7. This is a rather important result for us because we are proposing, in an accompanying renewal grant application, to carry

out dynamics studies on the alkyl thiol/noble metal systems. These long-chained molecules chemisorbed to gold also have very low energy phonons and the model describes how to extract the dynamics from the TOF spectra and the optimal operating conditions for the experiments.

5. Alkyl Thiols Films on Au(111) and Ag(111)

Work has begun in this laboratory to study the dynamics of alkyl thiol monomolecular films on gold and silver (111) surfaces. Organic molecules chemisorbed in an ordered assembly are of considerable interest because in certain respects, and depending on the composition of the molecules, the film represents a model biological membrane. In addition, understanding the properties of these films might facilitate the design of superior lubricants, organic coatings and possibly novel thin film dielectric materials. Professor M. E. Derrick has been working with us on this project under an NSF Visiting Professorship for Women grant. Although the nine-month period of the grant is ended, she plans to continue work on this project as her time permits. Professor Derrick spent two weeks during Summer, 1992, at the Oak Ridge National Laboratory, working with Dr. Zehner, learning techniques for crystal target preparation under a separate grant from SURA. This summer, 1993, one of our students has spent five weeks at Oak Ridge learning crystal surface preparation and deposition techniques with Dr. Zehner and Dr. Overbury's groups, also with a SURA grant for this purpose. To date we have been able to prepare and characterize Au(111) and Ag(111) surfaces using Auger Electron Spectroscopy (AES) and Low Energy Electron Diffraction (LEED). We have also prepared a target of $\text{CH}_3(\text{CH}_2)_{15}\text{SH}/\text{Au}(111)$ which we have sought to characterize with infra red spectroscopy. Very shortly, we expect to use HAS to examine this surface.

It is well known that gold deposited on mica forms a (111) surface. We have recently begun to characterize mica and Au/mica surfaces with HAS for use as a complementary substrate to the single crystal gold for the organic films. We also have built a vacuum deposition source for $\text{CH}_3(\text{CH}_2)_9\text{SH}$ to compare with films grown from ethanol solution for both gold substrates. Recently Professor J. Schlenoff in the Chemistry Department has given us some samples of alkyl thiols/gold/mica prepared in his laboratory, which we plan to compare with the films made in our laboratory.

6. Neutron Scattering Experiments on Metal Oxides

One of our students spent several weeks in Summer, 1992, at the Oak Ridge National Laboratory under a separate grant from SURA to carry 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. This summer, 1993, he is continuing this work with Dr. Smith under a new SURA grant. We expect that he will be able to complete the project on NiO and also obtain preliminary data for CoO. This work ties in very nicely with our efforts to measure the magnetic effects on the surface of these materials.

III. REFERENCES

1. See for examples, W. P. Woodruff and T. A. Delchar, *Modern Techniques of Surface Science* (Cambridge University Press, Cambridge, 1986) and A. Zangwill, *Physics at Surfaces* (Cambridge University Press, Cambridge, 1988).
2. For example, see P. K. Hansma, V. B. Elings, O. Marti, and C. E. Bracker, *Science* **242**, 157 (1988).
3. For examples, see *Vibrations at Surfaces*, Y. T. Chabal, F. M. Hoffmann and G. P. Williams, eds., (Elsevier, Amsterdam, 1990).
4. G. Brusdeylins, R. B. Doak and J. P. Toennies, *Phys. Rev. B* **27**, 3662 (1983).
5. J. P. Toennies, in *Surface Physics*, Springer Series in Surface Science Vol. 14, W. Kress and F. W. de Wette, eds., (Springer-Verlag, Berlin, 1991) Chapter 5.
6. J. J. De Miguel, A. Sánchez, A. Cebollada, J. M. Gallego, J. Ferrón and S. Ferrer, *Surf. Sci.* **189/190**, 1062 (1987); J. J. De Miguel, A. Cebollada, J. M. Gallego, J. Ferrón and S. Ferrer, *J. Crystal Growth* **88**, 442 (1988).
7. B. Poelsema and G. Comsa, *Scattering of Thermal Energy Atoms from Disordered Surfaces* (Springer-Verlag, Berlin, 1989); R. Kunkel, B. Poelsema, L. K. Verheij and G. Comsa, *Phys. Rev. Lett.* **65**, 733 (1990).
8. H. Xu, Y. Yang and T. Engel, *Surf. Sci.* **255**, 73 (1991).
9. J. Duan, G. G. Bishop, E. S. Gillman, G. Chern, S. A. Safron and J. G. Skofronick, *J. Vac. Sci. Technol. A* **10**, 1999 (1992).
10. J. Duan, G. G. Bishop, E. S. Gillman, G. Chern, S. A. Safron and J. G. Skofronick, *Surf. Sci.* **272**, 220 (1992).
11. C. Koziol, J. P. Toennies and G. Zhang, in *Phonons 89, Vol. 2*, S. Hunklinger, W. Ludwig and G. Weiss, eds., (World Scientific, Teaneck, New Jersey, 1990) p. 880.
12. K. D. Gibson, S. J. Sibener, B. M. Hall, D. L. Mills and J. E. Black, *J. Chem. Phys.* **83**, 4256 (1985).
13. J. P. Toennies, *J. Vac. Sci. Technol. A* **2**, 1055 (1984).
14. T. Engle and K. H. Rieder, *Structural Studies of Surfaces 91*, Springer-Verlag, Berlin, 1982, pp. 55-180.

15. H. Hoinkes, Rev. Mod. Phys. **52**, 933 (1980).
16. J. P. Toennies in *Dynamics of Gas-Surface Interactions*, G. Benedek and U. Valbusa, eds., Springer-Verlag, Berlin, 1982, pp. 208-226.
17. J. W. M. Frenken, J. P. Toennies, Ch. Wöll, B. Pluis, A. W. Denier van der Gon, and J. F. van der Veen, *Proc. of ICSOS II*, Amsterdam, June, 1987, Springer Series in Surface Sciences, Eds. by J. F. van der Veen and M. A. Hove.
18. A. M. Lahee, J. R. Manson, J. P. Toennies and Ch. Wöll, J. Chem. Phys. **86**, 7194 (1987).
19. J. P. Toennies, J. Vac. Soc. Technol. A **5**, 440 (1987).
20. J. Lapujoulade, *Interactions of Atoms and Molecules with Solid Surfaces*, Ed. by V. Bortolani, N. H. March and M. P. Tosi, pp. 381-405, Plenum, 1990.
21. G. Chern, J.G. Skofronick, W.P. Brug and S.A. Safron, Phys. Rev. B **39**, 12828 (1989).
22. Z. R. Wasilewski, G. C. Aers, A. J. SpringThorpe and C. J. Miner, J. Vac. Sci. Technol. B **9**, 120 (1991).
23. G. G. Bishop, J. Duan, E. S. Gillman, S. A. Safron and J. G. Skofronick, J. Vac. Sci. Technol. A **11**, 2008 (1993).
24. M. Mahgerefteh, D. R. Jung and D. R. Frankl, Phys. Rev. B **39**, 3900 (1989); D. R. Jung, M. Mahgerefteh and D. R. Frankl, Phys. Rev. B **39**, 11164 (1989).
25. W. P. Brug, G. Chern, J. Duan, G. G. Bishop, S. A. Safron and J. G. Skofronick, J. Vac. Sci. Technol. A **10**, 2222 (1992).
26. J. P. Toennies, G. Witte, A. M. Shikin and K. H. Rieder, J. Elect. Spectros. Related Phenom. (in press).
27. J. Duan, Ph.D. Dissertation, Florida State University, 1992.
28. S. A. Safron, J. Duan, G. G. Bishop, E. S. Gillman and J. G. Skofronick, J. Phys. Chem. **97**, 1749 (1993).
29. S. A. Safron, G. G. Bishop, J. Duan, E. S. Gillman, J. G. Skofronick, N. S. Luo and P. Ruggerone, J. Phys. Chem. **97**, 2270 (1993).
30. G. Benedek, J. Ellis, A. Reichnuth, P. Ruggerone, H. Schief and J. P. Toennies, Phys. Rev. Lett. **69**, 2951 (1992).

31. G. Brusdeylins, N. S. Luo, P. Ruggerone, D. Schmicker, J. P. Toennies, R. Vollmer and Th. Wach, *Surf. Sci.* **272**, 358 (1992).
32. N. S. Luo, P. Ruggerone, J. P. Toennies, G. Benedek and V. Celli, *J. Elect. Spectros. Related Phenom.* (in press).
33. J. G. Skofronick, G. G. Bishop, J. Duan, E. S. Gillman, S. A. Safron, D. Bonart and U. Schröder, *J. Elect. Spectros. Related Phenom.* (in press).
34. J. G. Skofronick, G. G. Bishop, W. P. Brug, G. Chern, J. Duan, S. A. Safron and J. R. Manson, *Superlattices and Microstructures* **7**, 239 (1990).
35. G. G. Bishop, W. P. Brug, G. Chern, J. Duan, E. S. Gillman, S. A. Safron, J. G. Skofronick and J. R. Manson, *Phys. Rev. B* **47**, 3966 (1993).
36. J. R. Manson, *Phys. Rev. B* **43**, 6924 (1991).
37. G. Witte, Private communications
38. J. R. Manson and J. G. Skofronick, *Phys. Rev. B* **47**, 12890 (1993).

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. Note that $\theta_i + \theta_f = 90^\circ$ and that the velocity spread of the nozzle beam $\Delta v/v \approx 1\%$.

2.

Surface phonon dispersion for $\text{RbCl}(001)$ 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 recent experiments [Ref. 23] 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 15, 1167 (1977)] while in the bottom panel relaxation is included [Phys. Rev. B 35, 5783 (1987) and private communication from F. W. de Wette].

3. Preliminary surface phonon dispersion curves for NiO (001)<110> in the top panel and for CoO (001)<110> in the bottom panel using targets which have been cleaved *in situ*. The solid lines are drawn, in part, as a guide to the eye.

4. A comparison of the measured surface phonon dispersion curves for cleaved KBr(001) (open points) [Ref. 21] and for 4 monolayers of KBr deposited onto NaCl(001) (solid points) [Ref. 10]. The solid lines are the surface localized modes and the shaded areas are the surface projected bulk bands from the calculation of Benedek and Miglio [see Ref. 21]. The major differences are that the Rayleigh wave for the 4 monolayer film does not go to zero at $\bar{\Gamma}$ [see Ref. 29] and the gap mode (S₃) for the film rises above the gap mode for the cleaved surface midway in the surface Brillouin zone. Note also the very low energy dispersionless mode near $\omega \approx 0.4 \times 10^{13}$ rad/s.

5. 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.[Ref. 29] 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_1 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. Note also the very low energy dispersionless mode near $\omega \approx 0.4 \times 10^{13} \text{ rad/s}$ for the 4 ML case.

6. Measured surface phonon dispersion curves for 1 monolayer of KBr deposited onto RbCl(001) in the $\langle 100 \rangle$ azimuth compared with a slab dynamics calculation employing a modified shell model interaction for the interface [Ref.33]. The solid lines labeled by S_n are modes localized predominantly in the surface layer while those labeled I_n are modes predominantly localized in the second and third layers.

7. Plot of a time-of-flight spectrum, converted to energy transfer, for a monoenergetic He atom beam (30 meV) scattered from an arachidic acid/methyl stearate monolayer surface at 130 K [from 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, presumably CH_3 .

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 Magnetic Field 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 used 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 four dedicated graduate students, J. Baker, G. G. Bishop, E. S. Gillman and J. J. Hernandez (all in Physics). Our first three students G. Chern (Physics), W. P. Brug (Chemistry) and J. Duan (Physics) have completed their doctoral dissertations. Dr. Chern is currently an assistant professor at Chang Kai Shek University in Taiwan. Dr. Brug is working with the environmental research group at the Los Alamos National Laboratory. Dr. Duan has just started in a program in medical physics in Jacksonville, Florida. Bishop is a fifth year student and has worked on temperature-dependent, multiphonon experiments and is currently carrying out experiments on metal oxides. 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. A patent is being sought for this device. 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. Both have spent time this summer, 1993, at Oak Ridge; Baker is currently completing his neutron scattering project with Dr. Smith, while Hernandez is learning crystal preparation techniques with the group of Dr. David Zehner and vapor deposition techniques with the group of Dr. Steven Overbury.

Professor M. Elizabeth Derrick of Valdosta State College, Georgia, has spent most of this past year (June, 1992- March, 1993) under an NSF "Visiting Professorship for Women" grant 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. In Summer, 1992, Chris Banbury of Western Kentucky University and this summer, 1993, Scott Murphy of Clemson University have worked with us through the Physics Department's grant. This summer Jim Mathies, an FSU undergrad in Physics, is also working in our laboratory. In the Spring semester, 1993, two Chemistry honors students, Chris Libbey and Albert Richardson, carried out projects with our group.

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. In addition, one of us (JGS) has published a number of papers with the MPI group, including recent work on C_{60} and TaS_2 and a review article on layered materials.

For the slab dynamics calculations using the shell model, we have begun a collaboration with Professor U. Schröder and his students at the University of Regensburg, Germany.

We have a collaboration with Dr. Harold Smith at the Oak Ridge National Laboratory which involves the neutron scattering experiments on NiO and CoO 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 generally 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. 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 Helium Atom Scattering, which have proven so successful as a probe of the dynamical behavior of surfaces, to the investigation of crystal growth and interface formation. 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. Recent experiments in this group and in others have shown that HAS is a powerful and versatile method for investigating wide-ranging structural and dynamic properties of surfaces and interfaces for all kinds of materials.

In addition, we and our students have been active in the surface science community during this project period, having attended and given papers at various local, regional, national and international meetings. These include invited papers at the Sixth Workshop on Surface Phonons, Schloss Ringberg, Germany, May, 1992; at the 1992 XIVth International Symposium on Molecular Beams in Asilomar, California, June, 1992; and at the 1993 Adriatico Research Conference: Scattering from Surfaces in Trieste, Italy, July, 1993; an invited paper for the "feature article" in the *Journal of Physical Chemistry*, published March, 1993; an invitation to present a paper and organize a session on surface vibrations for a Surface Science Symposium at the March meeting of the American Physical Society, 1994, in Pittsburgh. Further, a review of work on layered materials was published as a chapter of a book dealing with these materials.

A. Papers Published, In-Press or Submitted in the Project Period.

1. "Surface and Bulk Phonon-Assisted Resonances with Surface Bound States in the Inelastic Scattering of He Atoms on NaCl(001)", S. A. Safron, W. P. Brug, G. G. Bishop, G. Chern, M. E. Derrick, J. Duan, M. E. Dewese and J. G. Skofronick, *J. Vac. Sci. Technol. A* **9**, 1657 (1991).
2. "Surface Properties of CsF by He Atom Scattering", J. G. Skofronick, J. Duan, G. Chern, W. P. Brug, G. G. Bishop and S. A. Safron, *Surf. Sci.* **251/252**, 782 (1991).
3. "Study of the Epitaxial Growth of Single Crystal C₆₀ on Mica by Helium Atom Scattering", D. Schmicker, S. Schmidt, J. G. Skofronick, J. P. Toennies and R. Vollmer, *Phys. Rev. B* **44**, 10995 (1991).
4. "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. A* **10**, 1999 (1992).
5. "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).
6. "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. A* **10**, 2222 (1992).
7. "Helium Atom Scattering Studies of the Surface Phonons of Layered Materials", J. G. Skofronick and J. P. Toennies, in *Surface Properties of Layered Structures*, Kluwer

Academic Publishers, Dordrecht, The Netherlands, Ed. by G. Benedek, Fall (1992).

8. "Multiphonon Inelastic Scattering of Helium Atoms from Crystal Surfaces", G. G. Bishop, W. P. Brug, G. Chern, J. Duan, S. A. Safron, J. G. Skofronick and J. R. Manson, *Phys. Rev. B* **47**, 3966 (1993).
9. "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.* **97**, 2270 (1993).
10. "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.* **97**, 1749 (1993)(feature article).
11. "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. A* **11**, 2008 (1993).
12. "Multiphonon Effects in Thin Organic Films", J. R. Manson and J. G. Skofronick, *Phys. Rev. B.* **47**, 12890 (1993).
13. "He Atom Scattering Study of the Surface Dynamics of an Epitaxial One Monolayer KBr Film on RbCl(001): A Shell Model Analysis", J. G. Skofronick, G. G. Bishop, J. Duan, E. S. Gillman, S. A. Safron, D. Bonart and U. Schröder, *J. Elect. Spectros. Related Phenom.* (in press).
14. "Strong Coupling of Rayleigh Phonons to Charge Density Waves in 1T-TaS₂", G. Benedek, G. Brusdeylins, F. Hofmann, P. Ruggerone, J. P. Toennies, R. Vollmer and J. G. Skofronick, *Phys. Rev. B* (submitted).

B. Seminars and Posters Presented in the Project Period.

1. "A Time-Resolved Study of an Electromagnetic Pulsed Nozzle Beam", E. S. Gillman, J. G. Skofronick, G. G. Bishop, W. P. Brug, J. Duan and S. A. Safron, 20th Annual Symposium on Applied Vacuum Science and Technology, Florida Chapter of the American Vacuum Society, February, 1991.
2. "Homoepitaxial Growth of NaCl on NaCl (001) Single Crystal Surface by He Atom Scattering", J. Duan, J. G. Skofronick, E. S. Gillman, G. Chern, W. P. Brug, G. G. Bishop and S. A. Safron, 20th Annual Symposium on Applied Vacuum Science and Technology, Florida Chapter of the American Vacuum Society, February, 1991.
3. "He Atom Studies of the Homoepitaxial Growth of NaCl on NaCl (001) Crystal Surface", J. G. Skofronick, J. Duan, G. Chern, W. P. Brug, G. G. Bishop and S. A. Safron,

American Physical Society, national meeting, Cincinnati, Ohio, March, 1991.

4. "A Pedestrian View of Bucky-Balls", J. G. Skofronick, Max-Planck-Institut für Strömungsforschung, Göttingen, Germany, June, 1991.
5. "Investigation of Homoepitaxial Growth of NaCl onto NaCl (001) by He Atom Scattering", S. A. Safron, J. Duan, G. G. Bishop, E. S. Gillman, G. Chern and J. G. Skofronick, Gordon Research Conference "Dynamics of Gas-Surface Interactions", New Hampshire, August, 1991.
6. "He Atom Scattering Study of Layer-by-Layer Growth of NaCl on NaCl(001), J. Duan, G. G. Bishop, E. S. Gillman, G. Chern, S. A. Safron and J. G. Skofronick, The Fourth Eastern Regional Conference on Crystal Growth, American Association for Crystal Growth, Atlantic City, October, 1991.
7. "Epitaxial Growth of KBr onto NaCl (001) by High-Resolution He Atom Scattering", S. A. Safron, J. Duan, G. G. Bishop, E. S. Gillman, G. Chern and J. G. Skofronick, International Conference on Molecule-Surface Interactions, Jülich, Germany, October, 1991.
8. "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, American Vacuum Society, national meeting, Seattle, Washington, November, 1991.
9. "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, American Vacuum Society, national meeting, Seattle, Washington, November, 1991.
10. "Lattice Dynamics Study of KBr Epi-Layer on NaCl (001) by He Atom Scattering, J. Duan, G. G. Bishop, G. Chern, E. S. Gillman, S. A. Safron and J. G. Skofronick, Southeastern Section of the American Physical Society, Durham, N.C., November, 1991.
11. "Multiphonon Scattering of He Atoms from the KBr(001) and CsF(001) Surfaces", G. G. Bishop, J. G. Skofronick, J. Duan, W. P. Brug, S. A. Safron and E. S. Gillman, Southeastern Section of the American Physical Society, Durham, N.C., November, 1991.
12. "Surface Mobility of NaCl Adsorbates on the NaCl (001) Surface by Helium Atom Scattering, E. S. Gillman, G. G. Bishop, G. Chern, J. Duan, S. A. Safron and J. G. Skofronick, Southeastern Section of the American Physical Society, Durham, N.C., November, 1991.
13. "Production, Separation and Characterization of C₆₀ and C₇₀", J. Baker, B. Barnes, J. Hernandez, S. A. Safron and J. G. Skofronick, 21th Annual Symposium on Applied

Vacuum Science and Technology, Florida Chapter of the American Vacuum Society, February, 1992.

14. "Heteroepitaxial Growth Study of KBr/RbCl(001) via He Atom Scattering", J. Duan, G. G. Bishop, E. S. Gillman, G. Chern, S. A. Safron and J. G. Skofronick, American Physical Society, national meeting, Indianapolis, Indiana, March, 1992.
15. "Surface Physics as seen by Helium Atom Scattering", J. G. Skofronick, Colloquium in Physics, FSU, March 5, 1992.
16. "Surface Physics Using Helium Atom Scattering", Steinhatchee UF/FSU meeting on April 11, 1992.
17. "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.
18. "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.
19. "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.
20. "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.
21. "Watching Crystals Grow Layer-by-Layer", S. A. Safron, Florida State University, September, 1992.
22. "High-Resolution He Atom Scattering Experiments on Layered Materials", J. G. Skofronick, Florida State University, October, 1992.
23. "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.
24. "Investigation of Epitaxial Growth via High Resolution Helium Atom Scattering: KBr onto RbCl(001)", J. G. Skofronick, J. Duan, G. G. Bishop, E. S. Gillman and S. A. Safron, American Physical Society March meeting, Seattle, Washington, March, 1993.

25. "Inelastic Scattering Behavior of He from Thin Organic Films", J. R. Manson and J. G. Skofronick, American Physical Society March meeting, Seattle, Washington, March, 1993.
26. "He Atom Scattering Study of the Surface Dynamics of an Epitaxial One-Monolayer KBr Film on RbCl(001)", J. G. Skofronick, G. G. Bishop, J. Duan, E. S. Gillman and S. A. Safron, Vibrations at Surfaces VII, S. Margherita, Italy, June, 1993.
27. "Structure and Dynamics of Chemisorption through He Atom Scattering on Crystalline Surfaces", M. E. Derrick, J. Hernandez, E. S. Gillman, S. A. Safron and J. G. Skofronick, Georgia Academy of Sciences, Spring, 1993.
28. "Surface Dynamics of Epitaxially Grown Thin Alkali Halide Films by Helium Atom Scattering", J. G. Skofronick, Adriatico Research Conferences: Scattering from Surfaces, Trieste, Italy, July, 1993.

C. Proposals and Grants Other than DOE in this Project Period.

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, 1991, funded \$5,880.
4. "FSU/ORNL Cooperative Research Program in Surface Science", SURA, Summer, 1992, funded \$4,400.
5. "FSU/ORNL Cooperative Research Program in Surface Science", SURA, Summer, 1992, funded \$6,500.

*reprints + proposal
for future funding
removed.
ds*

DATE

FILMED

5 / 16 / 94

END