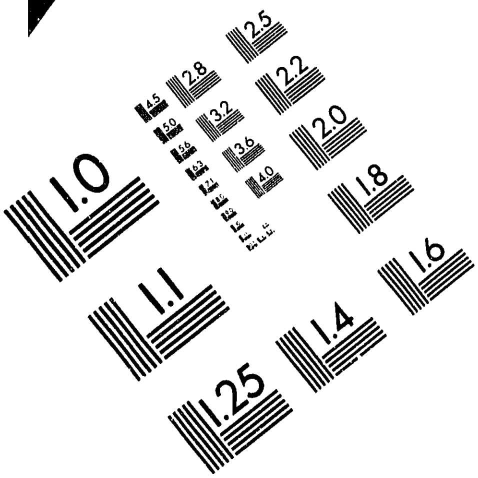

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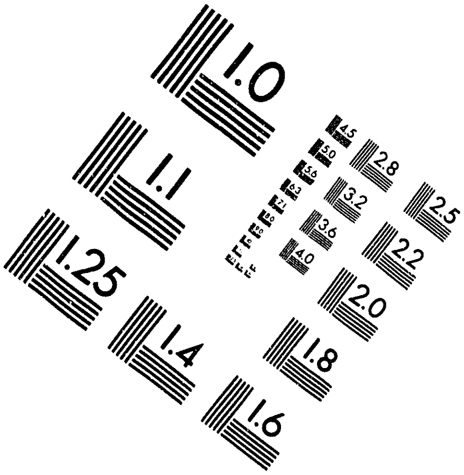

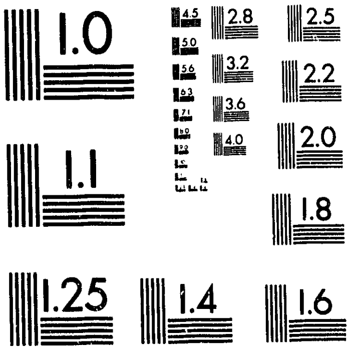

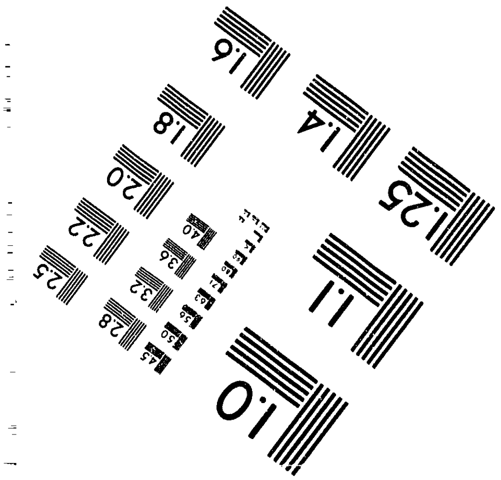

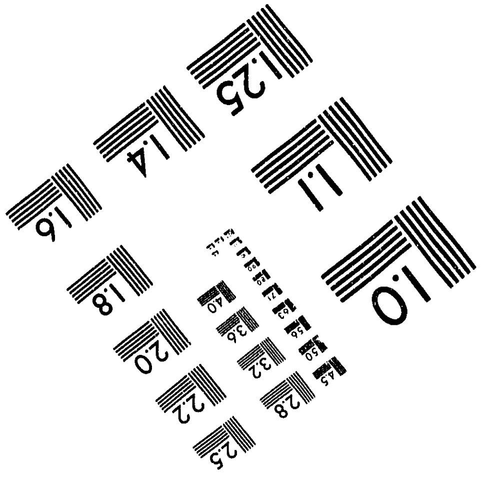

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FIRST-PRINCIPLES STUDIES OF PHASE STABILITY AND THE STRUCTURAL AND DYNAMICAL PROPERTIES OF HYDROGEN-METAL SYSTEMS

FINAL REPORT/~~RENEWAL APPLICATION~~

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SUMMARY

During the current funding period, we have carried out first-principles calculations for the hydrogen-yttrium system using the pseudopotential method within the local density functional approximation (LDA). A variety of intriguing properties of this system have been examined for an extended concentration range. In particular, we have studied the nature of hydrogen pairing in the solid solution phase (α-YH_x) and identified the connection with electronic structure. The vibrational spectra, diffusion barrier, and migration path were also investigated. We have also studied the binding characteristics for different interstitial sites and the (420)-plane ordering of octahedral hydrogen in β-YH_{2+x} within the lattice gas model. The temperature-composition phase diagram was calculated by the cluster variational method with the multibody interactions extracted from the total energies of related ordered structures. Moreover, the discovery of Peierls distortions in YH_3 explained the unusual hydrogen displacements found in neutron diffraction and the possibility of an excitonic insulating ground state was speculated.

Several new improvements in the calculational techniques have also been developed and investigated. These include the study of separable nonlocal pseudopotentials, the new scheme to calculate the full phonon spectrum, and the development of new distance-dependent tight-binding parameters.

With the success in the hydrogen-yttrium system, we propose continuing the study for other metals, in particular, the hydrogen-niobium and hydrogen-palladium systems which have the body-centered and face-centered cubic structures respectively. Since the three dimensional lattice will be changed, the optimal interstitial site for hydrogen will also be different. This will in turn affect the diffusion behavior, vibrational modes, possibility of ordering, and much more. The purpose of the study will be to identify the trend in various physical properties when the number of d electrons is increased and crystal structure changed.

We also plan to extend the study to hydrogen in metal thin films. There are currently several experimental groups working on these systems and several new features have been discovered. High quality samples can be grown with modern epitaxial methods and many properties can be studied with greater experimental control. In particular, the effect of strain on the structural and dynamical properties of the hydrogen-metal thin film system will be investigated.

INTRODUCTION

Hydrogen is by far the most abundant element in the universe. It forms alloys and compounds with many metals and is the smallest and the simplest impurity that can be implanted into a metal host. The change in the electronic, structural, and mechanical properties of the parent metal upon absorbing hydrogen is often dramatic[1,2,3]. It reacts exothermically with many transition and rare-earth metals to form metallic, semimetallic, and semiconducting compounds at various compositions without definite stoichiometry. The large solubility and high mobility and the complex properties involved make the hydrogen-metal system particularly interesting and challenging in both technological applications and basic research.

There are many immediate and potential applications of the hydrogen-metal system in the energy related industry. There have been many interests in using it as the storage medium of hydrogen. Hydrogen is an attractive energy source since it has the highest density of energy per unit weight and is essentially *nonpolluting*. A nickel/metal-hydride rechargeable battery has also been developed and has a potential to replace the traditional battery containing cadmium which is an environmental threat. Other applications include the use of the hydrogen-metal systems as energy conversion devices and as moderator, reflector, and control materials in fusion reactors because of the large proton density and metallic properties. In addition, hydrogen embrittlement of metals has been the second most important reason of material failure after corrosion.

The study of the hydrogen-metal system is also motivated by the scientific challenge it presents. It is an intriguing system in which two distinctly different constituents, hydrogen being light and very mobile and the metal relatively passive, intermix and interact strongly with each other. Hence the hydrogen-metal system is a prototype for studying the fundamental properties of light interacting particles in a three-dimensional lattice (the lattice gas model). As the composition or temperature varies, there exist disorder-disorder, order-disorder, and order-order phase transitions. There are also accompanied by metal-semiconductor transitions in some region. Moreover, the extremely large mobility of hydrogen is of central concern whenever materials applications are considered. The diffusion mechanism is of particular interest in this system.

There have been numerous experimental studies stimulated by various aspects of hydrogen technology[1,2,3]. The hydrogen-metal system is an interdisciplinary topic attracting researchers from physics, chemistry, materials science, metallurgy, etc. The techniques of measurements are diverse, including nuclear magnetic resonance (NMR), neutron scattering and diffraction, photoemission and inverse photoemission spectroscopy, x-ray emission and absorption, etc. Various properties of hydrogen in metals have been measured, such as the preferred location, local vibrational mode, diffusion barrier, electronic states, specific heat, electrical resistivity, and many more.

The rich experimental information has made the hydrogen-metal system a testing ground for new theoretical models. Theoretical studies will not only contribute to a better understanding of the unusual physical phenomena and properties, but also predict possible interesting applications. In particular, the knowledge at the microscopic level of the underlying energetics and interaction mechanisms is essential in studying the structural and dynamical properties of the system. Changes in the electronic structure of metals due to the absorption of hydrogen need to be investigated if related physical and chemical properties are to be understood. A series of band structure calculations have provided valuable information on the basic properties of the hydrogen-metal systems[4].

First-principles studies have proved to be a powerful approach in explaining and predicting the properties of many materials. In recent years, these theoretical calculations have become very accurate in providing the information on the energetics and electronic structure of the system. In particular, the formalism of the local-density-functional approximation (LDA)[5] coupled with norm-conserving pseudopotentials[6] has been successfully applied to the study of the structural and electronic properties of many solids, surfaces, and clusters and has yielded excellent results. This method is generally regarded as nonempirical, since once the density functional method is adopted, the only remaining input required for the calculation of the ground state properties is the atomic number and geometry. It is intended in the current study to apply this state-of-the-art computational technique to the hydrogen-metal system and to gain a more systematic understanding of the numerous anomalous and interesting properties observed.

PROGRESS REPORT (9/15/90 - 9/14/93)

Our major efforts in this period have concentrated on the study of the various phases of the yttrium-hydrogen system which belongs to a general class consisting of hydrogen and rare-earth metals. A variety of intriguing properties are thoroughly examined over the whole composition range (up to 3 hydrogens per metal). The most important and distinct part of the current work is that a new understanding of some of the features is achieved by studying the peculiar electronic structure, by analyzing the individual energy contributions to the total energy, and by examining the wave functions. In particular, these findings include the nature of hydrogen pairing in the solid solution (α) phase, the mechanism of lattice contraction and the (420)-plane ordering of hydrogen in the β phase, and the identification of the charge density waves and possible excitonic insulating phase in YH_3. In addition, we have also conducted some developmental works on the theoretical techniques, including an improvement of the pseudopotential method, a new method to calculate the full phonon dispersion, and the development of new tight-binding total energy models for use in larger systems. The results are summarized in the following subsections. A list of all the refereed papers (published and submitted) resulting from these studies is given at the end of the section. Some of the preprints are attached at the end of this proposal.

A. Calculation of the Structural Properties of Yttrium

With the recent development of *soft* pseudopotentials, we chose to use the plane wave basis set to carry out the calculation. The advantages of using this complete and orthogonal basis set have been well recognized. Previous problems have been associated with the slow convergence for transition metals. Therefore we first tested the computational methods by studying the structural properties of elemental yttrium and the results were encouraging. Good convergence is obtained with an energy cutoff of 30-40 Ry. It is also found that special care is necessary to handle the outer core in these early transition metals. The effect of using different exchange-correlation potentials is also investigated (Paper 1).

B. Dynamical Properties and Hydrogen Pairing in α-YH_x

Elemental yttrium is in the hexagonal close-packed (hcp) structure. For a low concentration of hydrogen, a solid solution is formed (the so-called α phase) with hydrogen occupying the tetrahedral sites in the metal lattice. It is well established that hydrogen dissolved in the hcp rare-earth metals exhibits an unusual short-ranged ordering which is closely related to the high stability of the α phase at low temperature. In addition, there have been quite a few neutron scattering results available for the local vibrational modes in this system. We first considered the ordered structures $YH_{0.5}$, $YH_{0.25}$, and $YH_{0.167}$ with hydrogen occupying two different kinds of interstitial sites: the tetrahedral (T) and octahedral (O) sites. A lattice expansion is found in the system due to the presence of hydrogen and largely results from the minimization of the kinetic energy. The binding energy difference between these two sites is about 110 meV and the occupation of tetrahedral sites is energetically more favorable. This is consistent with the conclusion of neutron scattering experiments.

We have also studied the dynamical properties of this system and calculated the local vibrational frequency from the potential surface for the protons. The anharmonic and anisotropic nature of the potential surface is well characterized in the study. Interesting results are found when the hydrogen atom is moved along the c-axis between two adjacent tetrahedral sites. The potential energy curve consists of two anharmonic wells with a barrier of about 190 meV. This double-well potential forms a one-dimensional quantum system and we can calculate the energy eigenvalues by solving the Schrodinger equation for the proton. From these eigenvalues, the local vibrational modes can be identified. We found the fundamental frequency to be around 100 meV which is in good agreement with the experimental observation.

Moreover, the pairing energy in the bulk is calculated for the first time from first principles and it shows that the pairing of hydrogen through the intermediate metal atom is indeed energetically favorable. From the analysis of the wave functions and electronic structure, it is concluded that the pairing of hydrogen has an electronic origin. The results are summarized in Papers 7 and 14.

C. Phase Stability and Electronic Properties of β-YH_{2+x}

When more hydrogen is absorbed, a dihydride phase starts to form and the metal lattice transforms from the hcp to the face-centered cubic (fcc) structure. In YH_2, hydrogen occupies the tetrahedral sites almost exclusively. With more hydrogen dissolved, the octahedral sites start to be occupied. In this study, we are mainly interested in the bonding characteristics of hydrogen in these high concentration phases. Depending upon the symmetry of the interstitial sites, the hydrogen s electron will interact with different states of the metal d orbitals. First-principles calculations have been performed for a series of ordered structures for the octahedral hydrogen. It was found that the volume expansion from Y to YH_2 was mainly due to the minimization of the kinetic energy of the extra electrons, while the contraction from YH_2 to YH_3 came from maximizing the s-d interaction at the octahedral site (Paper 15).

We have also implemented the cluster variational method (CVM) to study the phase diagram of this system. The interaction energies were obtained from about 10 different supercell calculations. This approach provided a parameter-free treatment of phase transitions in an Ising-like lattice gas model. We have predicted that the $D0_{22}$ structure is a low energy phase and the absolute phase boundary was calculated (Paper 12). This same ordered structure was observed in TbD_{2+x} in neutron diffraction experiments.[7]

D. Peierls Distortions in Hexagonal YH_3

In the trihydride phase, the hexagonal lattice is again favored and the yttrium atoms are transformed back to the hcp structure. However, the positions of the hydrogen atoms exhibit some unusual relaxations. It has been found from our calculation that in YH_3 the octahedral hydrogen atoms move down to the metal plane in order to offset the relaxations of tetrahedral hydrogen. If the periodicity of the compound is the same as the hcp metal, the material is a semimetal, with electron pockets located at the K points and holes at Γ. Because of the electron-phonon interaction, the system is subject to a Peierls instability and a gap can be opened up when the symmetry is broken.

We have searched for the optimal relaxation of hydrogen atoms as well as examined the electronic structure in details. From some earlier neutron diffraction data on HoD_3[8], it is expected that the unit cell for YH_3 be tripled to a $\sqrt{3} \times \sqrt{3}$ lattice. The energy of the "frozen in" local vibrational wave of hydrogen has been minimized to determine the nature and amplitude of the displacements. This involved a series of total energy calculations as well as investigations of the electronic structure. The HoD_3-type structure was found to be energetically more stable than the cubic structure and the transformation of the hydrogen sublattice was identified as Peierls distortions resulting from the special features of the electronic structure and the strong electron-phonon interaction. A gap between one set of bands was opened, but with the other set of electron and hole bands crossing near the Fermi level, the LDA calculation yielded a semimetal. The final electron and hole pockets were centered at Γ and very close to be isotropic. This made us speculate that the true many-body ground state might be an excitonic insulating state. Using the results from the exciton theory and the LDA band parameters, an estimate of the energy gap and the semimetal-semiconductor transition temperature was made. The results were summarized in Papers 10 and 16.

E. Phase Diagram of Hydrogen on Ru(0001)

It is commonly believed that chemisorbed hydrogen occupies the threefold hollow sites on close-packed metal surfaces. As temperature and concentration vary, different ordered and disordered phases may become stable. Assuming a two-dimensional lattice gas model, we studied the thermodynamical properties of this chemisorption system. The cluster variation method (CVM) was used to evaluate the free energy of the system. At high temperature, hydrogen atoms occupy the hollow sites randomly and form a disordered phase. As temperature is lowered, several ordered structures are found, including the 2×2, $\sqrt{3} \times \sqrt{3}$, and 2×1 structures. The phase diagram was calculated and a concentration-dependent effective pair interaction was found to be needed in order to explain the asymmetry in the phase diagram. By assuming a simple piecewise linear dependence on the chemical potential, we have reconstructed an asymmetric phase diagram which agrees well with experiment (Paper 4).

F. Developments of Theoretical Techniques

We have carried out some developmental work on computational techniques. The first one was on the improvement of the pseudopotential method. The pseudopotential approximation is designed to eliminate the need to explicitly account for the core electrons and the accuracy of this method can be improved by increasing the number of so-called reference energies. In many of the current schemes the nonlocal potential operator becomes non-Hermitian when the number of reference energies is more than one. In our study we proposed a scheme to construct a Hermitian nonlocal potential with the scattering properties matched directly to the all-electron results as closely as possible. Although it is an approximate operator, the transferability can be improved systematically in the construction. This will greatly simplify the nonlocal operations in large-scale computations (Paper 2).

Previously, the full dispersion of phonons (elementary excitations of lattice vibrations in solids) was obtained only from model fitting, or from the computation of linear response functions. Direct *ab initio* calculations have been performed only for isolated symmetry points and along symmetry lines. We have proposed a new method to derive the spectrum by reconstructing the real-space force constant matrices from the projection along several symmetry directions. Thus one needs to perform only a limited number of supercell calculations for the planar force constants. The dynamical matrix at any arbitrary wave vector can then be determined and the full phonon spectra can be obtained completely from first principles for both metals and semiconductors (Papers 3 and 6).

Even with the current computational facilities, there still exist systems that are too large to be handled by first-principles calculations. Some reliable models are needed and the tight-binding method is a widely used one especially for transition metals and semiconductors. The distance and environmental dependence of the overlap integrals for the orbitals has not been examined systematically. As a first-step investigation, we have carefully determined these parameters for Si and Ge by fitting to the energy band dispersions and total energy curves obtained from first-principles calculations (Paper 5). With these transferable parameters, we have studied the effects of strain on the surface reconstruction of Si(111) and Ge(111), where an interesting surface structural transition is observed during the epitaxial growth (Paper 8). Extensions of this study to transition metals are under development.

G. Publications Resulting from this DOE Grant

1. Y. Wang and M. Y. Chou, "Pseudopotential Plane-Wave Calculation of the Structural Properties of Yttrium", Phys. Rev. B **44**, 10339 (1991).
2. M. Y. Chou, "Reformulation of Generalized Separable Pseudopotentials", Phys. Rev. B **45**, 11465 (1992).
3. S. Wei and M. Y. Chou, "*Ab initio* Calculation of Force Constants and Full Phonon Dispersions", Phys. Rev. Lett. **69**, 2799 (1992).
4. S. N. Sun and M. Y. Chou, "Asymmetric Phase Diagram and Coverage Dependent Effective Pair Interactions of Hydrogen on Close-Packed Metal Surfaces", Surf. Sci. **280**, 415 (1993).
5. J. L. Mercer, Jr. and M. Y. Chou, "Tight-Binding Total Energy Models for Silicon and Germanium", Phys. Rev. B. **47**, 9366 (1993).
6. S. Wei and M. Y. Chou, "First-Principles Calculation of Force Constants and Full Phonon Dispersions", in *Materials Theory and Modelling*, ed. by J. Broughton, P. Bristowe, and J. Newsam (Materials Research Society, Pittsburgh, 1993), p. 641.
7. Y. Wang and M. Y. Chou, "Theoretical Study of the Binding Properties and Electronic Structure of Hydrogen in Yttrium", Z. Phys. Chem. (in press).
8. J. L. Mercer, Jr. and M. Y. Chou, "Energetics of Si(111) and Ge(111) and the Effect of Strain", Phys. Rev. B. **48** (in press).
9. M. Y. Chou, S. Wei, and D. Vanderbilt, "Comment on 'Should all Surfaces be Reconstructed?' ", Phys. Rev. Lett. (in press).
10. Y. Wang and M. Y. Chou, "Peierls Distortions in Hexagonal YH_3", submitted to Phys. Rev. Lett.
11. Y. H. Chen and M. Y. Chou, "Continuous Feedback Approach for Controling Chaos", submitted to Phys. Rev. Lett.
12. S. N. Sun and M. Y. Chou, "First-Principles Study of Phase Stability in fcc YH_{2+x}", preprint.
13. S. Wei and M. Y. Chou, "Surface Energy Anisotropy of fcc Metals", preprint.
14. Y. Wang and M. Y. Chou, "Pseudopotential Total Energy Study of α-YH_x", preprint.
15. Y. Wang and M. Y. Chou, "Energetics and Electronic Properties of β-YH_{2+x}", preprint.
16. Y. Wang and M. Y. Chou, "Structural and Electronic Properties of Hexagonal Yttrium Trihydride", preprint.

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Appendix G. Preprints

"First-Principles Study of Phase Stability in fcc YH_{2+x}"

"Pseudopotential Total Energy Study of α-YH_x"

"Energetics and Electronic Properties of β-YH_{2+x}"

"Structural and Electronic Properties of Hexagonal Yttrium Trihydride"

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