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6. AUTHOR(S) P. Jena, S.N. Khanna and B.K. Rao			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Virginia Commonwealth University Box 568, MCV Station Richmond, VA 21298			
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13. ABSTRACT (Maximum 200 words) A study was made of the electronic and structural properties of atomic clusters and defects in metals. Five main areas were considered: (i) magnetism of clusters, low dimensional systems and transition metal superlattices, (ii) interaction of hydrogen with metals and hydrogen absorption around metal ions, (iii) defects and defect complexes, (iv) electronic structure of LiMgH ₃ class of compounds and (v) super-shell structure in clusters. The final report provides an outline of the accomplishments in each of these areas as well as the professional accomplishments.			
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A. During the above three year period we have worked on the availability of electronic and structural properties of atomic clusters and defects, in metals. Five main areas were considered: (i) magnetism of clusters, low dimensional systems and transition metal superlattices, (ii) interaction of hydrogen with metals and hydrogen absorption around metal ions, (iii) defects and defect complexes, (iv) electronic structure of LiMgH₃ class of compounds and (v) super-shell structure in clusters. In the following we provide a brief outline of our accomplishments in each of these areas as well as our professional accomplishments.

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B. SUMMARY OF THE IMPORTANT RESULTS.

(i) Magnetism of Low Dimensional Systems, Transition Metal Superlattices and Clusters.

Considerable effort was devoted to understanding the effect of size, dimensionality and temperature on the magnetic moment of transition metal systems^{1,2,7,9,27}. These include Fe, Co and Ni forming chains, planes, slabs of varying thickness, clusters, and bulk containing vacancies, impurities and vacancy-impurity complexes. Since the existing theories are designed to study periodic systems, we developed a new method by combining ab-initio and real-space tight binding methods^{1,2}. We found that the magnetic moment of an atom is primarily governed by the local coordination and that chains are more magnetic than planes which are more magnetic than

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bulk. Our studies on chains of finite number¹² of atoms showed that the Ni chains containing odd number of atoms had higher moments than even number chains. This quantum size effect¹² persists in chains having up to 20 atoms at which point the moments approach the asymptotic limit. The appearance of a non bonding orbital at the Fermi energy was found to account for the larger moment in odd atom chains.

Calculations were carried out on magnetic clusters modelled as fragments of the bulk². It was found that for ferromagnetic materials like Fe, Co, or Ni, the clusters have higher moment than bulk and the moment on an atom approaches the bulk limit when an atom is surrounded by three neighboring shells. We also found that mono-layers and small clusters of non magnetic elements are magnetic like V are magnetic¹⁹.

Stern-Gerlach experiments on Fe_n and Co_n clusters in beams showed that these clusters have much lower magnetic moments per atom than the bulk. This observation defied the theoretical predictions of higher magnetic moment in smaller sizes. We resolved this apparent paradox^{18,22} by showing that small clusters behave like paramagnetic atoms and that the observed small moment is a consequence of the superparamagnetic relaxation at the cluster temperatures. Our model explained the experimental data on the size and temperature dependence of the magnetic moment and has since been used by various experimental groups to explain their experiments. We also studied the magnetic behavior of small clusters with spins coupled antiferromagnetically^{26,28}. Here we

showed that the geometry had a strong effect on the observed behavior. While cuboctahedric clusters had well defined ground states, the icosahedric clusters have frustrated free spins due to the underlying lattice and hence will behave as paramagnets.

We have also studied the magnetism in transition metal superlattices²⁹. Experimentally the Fe layers separated by Cr spacer layers have been found to couple antiferromagnetically. To understand this finding, we have studied the magnetic coupling between Fe layers separated by spacer layers consisting of 3d transition metal elements (Sc, Ti, V, Cr, Fe, Co, Ni and Cu) by using the self-consistent density functional theory and discrete variational method. The coupling between the Fe layers is ferromagnetic in all cases except for Cr where this coupling alternates from ferro magnetic to antiferromagnetic depending on whether the spacer layers are odd or even. Furthermore the spacer layers involving Sc, Ti and V are antiferromagnetically coupled to Fe while Co and Ni layers are coupled ferromagnetically. These findings are the subject of experimental investigations in various labs.

(ii) Interaction of Hydrogen with Metals and Hydrogen Absorption Around Metal Ions

In most metals hydrogen precipitates at low temperatures to form an ordered hydride phase. A departure from this common occurrence was first observed in resistivity experiments in rare-earth metals (Sc, Y, etc.). The ability of these materials to retain hydrogen in solid solution down to absolute zero was

completely unexpected and gave rise to a flurry of experimental studies involving neutron-scattering, nuclear magnetic resonance and channelling. The above anomaly was shown to be due to the pairing of hydrogen, although the structural origin of the pairs remained a debatable issue.

Using clusters of Y as a model of the bulk, we calculated for the first time self-consistently the energetics^{3,14} of a pair of hydrogen atoms located at adjoining tetrahedral (T) and octahedral (O) sites, T-T sites and T sites mediated by a metal atom. The last configuration was found to be energetically most stable in agreement with all available experimental data. Subsequent calculations have confirmed our results. The binding energy of the pair thus calculated was used in a lattice gas model^{6,20} to predict the temperature dependence of the fraction of H atoms involved in pairs. This prediction has now been verified in inelastic neutron scattering experiments.

Hydrogen absorption in metals is extremely important for industrial applications. We have carried out quantum chemical calculations²⁵ including correlations to study the amount and nature of hydrogen uptake by a Li atom in neutral as well as in ionic form. We have found that while the neutral Li atom cannot bind more than one hydrogen atom, the cation can bind a large number of hydrogen atoms in molecular form. This contrasting behavior originates from the fact that the bonding of hydrogen with neutral Li is covalent while that with the cation is primarily caused by polarization. The bonding of hydrogen with the Li ion exhibits

dual nature. The first H_2 molecule binds to the anion dissociatively while the subsequent H_2 molecule can only exist in a "physisorbed" state. Our findings have just been confirmed by Prof. Bowers at UCLA who has been able to attach up to $7H_2$ molecules to a C_o^+ ion.

(iii) Defects and Defect Complexes in Metals:

Using the density functional theory and the embedded cluster model, we addressed a long standing problem of the effect of carbon impurities on the migration and trapping of vacancies in Fe. We calculated¹¹, self-consistently for the first time, the energetics of carbon-vacancy complexes in Fe as a function of distance separating the carbon atoms and the vacancy along different crystallographic directions. Carbon was found to prefer an off-center site from the vacancy irrespective of its direction from the vacancy center. The equilibrium site of carbon was one where it was coordinated to three Fe atoms in its nearest neighbor shell. Multiple decoration of vacancies by carbon was also found to be possible. Our results were consistent with positron annihilation experiments. We argued that positron annihilation spectroscopy cannot provide the geometry of the defect complex and that experiments more sensitive to the geometry of the carbon-vacancy complexes are needed to compare with our theory. We showed that the bonding of carbon to iron atoms was not caused by charge transfer between the atoms, but rather had a magnetic origin.

We were the first to resolve an apparent conflict⁶ between the perturbed angular correlation (PAC) experiment and the kinetic

model concerning the equilibrium site of In on Cu (100) and the clustering of In atoms at elevated temperatures. A comparison of the calculated and experimental result for the electric field gradient (EFG) and asymmetry parameter (η) led to the conclusion that In occupies the substitutional terrace site on Cu (100) surface. The migration and clustering of In atoms at elevated temperatures obtained from the same experiment was explained in a kinetic model by assuming In atoms to lie on a surface that has over 90% vacant sites. Clearly if In occupied the substitutional terrace site, other sites on the same surface are not empty but occupied by Cu-atoms. Thus, there was a conflict between the assumed equilibrium In site and the nature of diffusion of In at higher temperatures. This conflict was resolved⁵ by calculating the energies of In occupying the on-top site, bridge site and the substitutional terrace site. In each case the distance of In from the substrate was varied to minimize the energy. We found that the bridge and substitutional sites compete for In trapping, with the bridge site being slightly favored over the substitutional site. As the sample is annealed, some of the In atoms in bridge sites migrate to the substitutional terrace site where efg is observed. The clustering arises as the In atoms at the bridge sites move freely and interact with the In atoms at the terrace site. Subsequent to our calculation, the bridge site for In was identified experimentally.

Encouraged by the success of the cluster model in depicting the electronic structure and binding at surfaces, we turned our

attention to understanding the nature of bonding^{8,16} at the interface of metal matrix composites (Al/SiC). There has been considerable debate concerning whether the bonding is due to charge transfer or diffusion of atoms across the interface. Recently, experiments involving Auger and electron loss spectroscopies have been used to determine the mechanism of formation of the Al/SiC interface. Annealing at moderate temperatures was found to cause aggregation of Al at C-rich sites. Furthermore, a shift of the Al 2p level to higher binding energy and Si 2p level to lower binding energy was also observed. We have demonstrated¹⁶ through SCF-LCAO-MO calculation that all of these results can be understood by studying energies, electron charge transfer, bond lengths, and core-level shifts of Al-Al, Al-C, Al-Si and Si-C dimers. Our results also revealed that the bonding at the interface can be explained by a charge transfer mechanism.

Disordered materials constitute an extreme form of defects. We have looked¹⁷ at the electronic conduction in disordered metals and alloys. We developed an electronic transport scheme which could permit dc and ac conductivity calculations, could be applied to the localized and extended regimes, and could be combined with ab-initio tight binding scheme to allow ab-initio transport calculations. We used the Kubo-Greenwood formula for conductivity and the theory of orthogonal polynomials. The new formulation, developed within the tight-binding model, provides a systematic expansion beyond the random phase approximation and permits studies of ac, dc conductivities, magnetoresistance and the correlation

functions (velocity-velocity correlation function). Since the formulation is carried out in real space, it can be applied to disordered systems with ease. We have used our approach to study the canonical site-diagonal disordered cubic lattice, and the results are in perfect agreement with other approaches. We are now planning to use it to perform studies on clusters and quasicrystals.

(iv) Electronic Structure of LiMgH₃ Class of Compounds

The possibility of LiMgH₃ class of materials showing superconductivity at elevated temperatures has attracted considerable interest. We have calculated²³ the lattice spacing and the electronic structure of LiMgH₃, NaMgH₃ and LiCaH₃ by modelling these hydrides as clusters with modified perovskite structure and using the self-consistent field linear combination of atomic orbitals -- molecular orbitals theory. This yields lattice constants of 3.47 Å, 3.53 Å and 4.07 Å for LiMgH₃ and LiCaH₃ respectively. The electronic structure of LiMgH₃ is characteristic of an insulating material. The gap at the Fermi energy in the density of states of LiMgH₃ is, however, significantly less than that of LiBeH₃ and is insensitive to moderate changes in the interatomic spacing. On the other hand, LiCaH₃ and NaMgH₃ are both found to exhibit metallic character with the Fermi energy lying in regions of high electron density of states.

(v) Super-Shell Structure in Clusters

We examined the possibility that clusters may exhibit super-shell structures²¹ with orbital angular momentum, $\ell > 6$, that has long

been predicted for nuclei. We have estimated an upper limit for the number of atoms by comparing the energy difference between the highest occupied and the lowest unoccupied state with the crystal field splitting of the cluster. The former was obtained by solving the Schrödinger equation for a spherical potential well with hard walls, while the latter is obtained from the band structure of the solid. The results indicate that shell structure may persist in clusters containing as many as a million atoms. Experimentally the super-shell structure has already been seen in clusters of 500 atoms.

C. LIST OF PUBLICATIONS

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2. M.R. Press, S.N. Khanna and P. Jena: Magnetism and local order: II. Self-consistent cluster calculations. Phys. Rev. B. 40, 399 (1989).
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"Interfaces in Metals and Ceramic Composites", ed. by R.Y. Lin, R.J. Arsenault, G.P. Martins and S.G. Fishman (T.M.S., Pittsburg, 1990) pg. 333.

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17. D. Mayou, S.N. Khanna and F. Cyrot-Lackmann, "A new approach to electronic transport in disordered systems with strong scattering", *J. Non-cryst. Sol.* 117, 413 (1990).
18. J. Merikoski, J. Timonen, M. Manninen and P. Jena: Ferromagnetism in small clusters, *Phys. Rev. Lett.* 66, 938 (1991).
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21. M. Manninen and P. Jena: Electronic shell structure and the crystal field splitting in simple metal clusters, *Euro. Phys. Lett.* 14, 643, (1991).
22. "Magnetic behavior of clusters of ferromagnetic transition metals", S.N. Khanna and S. Linderoth, *Phys. Rev. Lett.* 67, 742 (1991).
23. Y. Li, B.K. Rao, T. McMullen and P. Jena: Electronic structure of LiMgH_3 class of compounds. I. cluster calculations, *Phys. Rev. B* 44, 6030 (1991).

24. M. Yussouff, B.K. Rao and P. Jena: Reverse isotope effect on the superconductivity of PdH, PdD and PdT. Phys. Rev. B (submitted).
25. B.K. Rao and P. Jena: "Hydrogen uptake by an alkali metal ion", (Submitted to Europhys. Lett.)
26. B.V. Reddy and S.N. Khanna, "Effect of geometry on magnetism in small antiferromagnetic clusters", Phys. Rev. B. 45, 10103 (1992).
27. S.N. Khanna and P. Jena, "Magnetism of finite systems: From Clusters to Crystals" in Physics and Chemistry of Finite Systems: From Clusters to Crystals ed. by P. Jena, S.N. Khanna and B.K. Rao (Kluwer Acad. Pub. 1992, p. 709).
28. B.V. Reddy and S.N. Khanna, "Magnetism in small antiferromagnetic clusters" in "Physics and Chemistry of Finite Systems: From Clusters to Crystals" ed. by P. Jena, S.N. Khanna and B.K. Rao (Kluwer Acad. Pub. 1992, p. 799).
29. B.V. Reddy, S.N. Khanna, P. Jena and M.R. Press, "Magnetic Properties of Transition Metal Superlattices", (Submitted).

C. PROFESSIONAL ACTIVITIES

Our work has received international recognition as evidenced by numerous invitations to speak at conferences, give colloquia and chair scientific sessions at international meetings. Following is

a summary of our activities during the past twenty-four months. Activities of each of the P.I and co-P.I.'s are listed separately.

P. Jena

Invited to speak at the following conferences:

Virginia Academy of Sciences	1989
Gordon Conference on Metal Hydrides	1989
International Center for Theoretical Physics Trieste, Italy	1989
DOE Panel on "Fundamental Issues in Hydrogen Materials Interaction"	1990
TMS Annual Meeting	1990
APS March Meeting	1990
International Conference on "Low Density Metals" Trieste, Italy	1990
Materials Research Society Meeting on "Clusters and Cluster Assembled Materials" Boston, MA	1990
International Conference on "Complexities in Physics - entering the 21st Century" Stockholm, Sweden	1990
International Symposium on "Metal-Hydrogen Systems", Banff, Canada	1990
Chinese Materials Research Society Meeting, Beijing (declined)	1990
U.S./Japan Workshop on "Novel Micro-cluster Assemblies", University of Maryland	1991
Member, Advisory Board, International Symposium on Atomic and Nucleonic Clusters, Finland	1991
Eight Colloquia in Universities across the U.S.A.	

S.N. Khanna

International Conference on Hydrogen in Metals, Banff, Canada, Sept. 3-7, 1990.

Acta Metallurgica Conference on Materials with Ultrafine Microstructures, Oct. 1-5, 1990.

Materials Research Society meeting in Boston, Nov. 26-30, 1990.

International Conference on Nuclear and Atomic Clusters 1991, Turku, Finland, June 3-7, 1991.

Gordon Research Conference on "Hydrogen - Metal Systems", July 15-19, 1991.

Gordon Reserach Conference on "Metal and Semiconductor Clusters", Aug. 5-9, 1991.

B.K. Rao

Symposium on Current Trends in Physics, Institute of Physics, India, 1989.

Symposium on Atomic and Molecular Physics, Hyderabad, India, 1990.

East Coast Conference on Atomic Clusters and Cluster Ions, American Chemical Society, Baltimore, 1991.

Organization of Workshops and International Conferences

1. Annual Reserach Workshop of the Electronic Structure Group, 1989, 1990, 1991.
2. International Conference on "Correlations in Electronic and ATomic Fluids", Trieste, Italy, 1989.
3. International Symposium on the Physics and Chemistry of Finite Systems: From Clusters to Crystals, October, 1991.
4. Gordon Conference on Hydrogen-Metal Systems, July, 1991. P. Jena is the Vice-Chairman of this conference.

DEGREES EARNED BY STUDENTS

Weldon Webb, M.S., 1990.
Brian Constance, M.S., 1989.
Liu Feng, Ph.D., 1990.
Scott Weber, M.S., 1991.
Budda Reddy, M.S., 1991.

PERSONNEL SUPPORTED

P. Jena (Summer support)
S.N. Khanna (Summer support)
B.K. Rao (Summer support)
L. Magaud (Postdoc)
M. Challa (Postdoc)
F. Liu (Postdoc)
B. Reddy (Graduate Student)
A. Caro (Visitor)

COLLABORATION

C.N.R.S., Grenoble, France - Prof. F. Cyrot-Lackmann
I.P.E., E.P.F.L., Lausanne, Switzerland - Prof. J. Buttet
Helsinki University of Technology and University of Jyvaskyla,
Finland - Profs. R.M. Nieminen and M. Manninen
University of Manitoba - Prof. J.M. Vail
Michigan State University - Prof. S.D. Mahanti
University of Virginia - Prof. L. Bloomfield