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|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------|----------------------------------------------|---------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------|--------------------|
| 1a. REPORT SECURITY CLASSIFICATION<br>Unclassified                                                                                                                                                                                                                                                                                                                                                           |       |                                              | 1b. RESTRICTIVE MARKINGS<br>DTIC FILE COPY                                                        |                                                                                                     |                    |
| 2a. SECURITY CLASSIFICATION AUTHORITY<br>ELECTE                                                                                                                                                                                                                                                                                                                                                              |       |                                              | 3. DISTRIBUTION/AVAILABILITY OF REPORT<br>Approved for public release;<br>distribution unlimited. |                                                                                                     |                    |
| 2b. DECLASSIFICATION/DOWNGRADING SCHEDULE<br>25 1989                                                                                                                                                                                                                                                                                                                                                         |       |                                              | 5. MONITORING ORGANIZATION REPORT NUMBER(S)<br>ARO 22655.19-PH                                    |                                                                                                     |                    |
| 4. PERFORMING ORGANIZATION REPORT NUMBER(S)<br>D C3                                                                                                                                                                                                                                                                                                                                                          |       |                                              | 5. MONITORING ORGANIZATION REPORT NUMBER(S)<br>ARO 22655.19-PH                                    |                                                                                                     |                    |
| 6a. NAME OF PERFORMING ORGANIZATION<br>Virginia Commonwealth Univ                                                                                                                                                                                                                                                                                                                                            |       | 6b. OFFICE SYMBOL<br>(If applicable)         |                                                                                                   | 7a. NAME OF MONITORING ORGANIZATION<br>U. S. Army Research Office                                   |                    |
| 6c. ADDRESS (City, State, and ZIP Code)<br>Richmond, VA. 23220                                                                                                                                                                                                                                                                                                                                               |       |                                              |                                                                                                   | 7b. ADDRESS (City, State, and ZIP Code)<br>P. O. Box 12211<br>Research Triangle Park, NC 27709-2211 |                    |
| 8a. NAME OF FUNDING/SPONSORING ORGANIZATION<br>U. S. Army Research Office                                                                                                                                                                                                                                                                                                                                    |       | 8b. OFFICE SYMBOL<br>(If applicable)         |                                                                                                   | 9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER<br>DAAG29-85-K-0244                                 |                    |
| 8c. ADDRESS (City, State, and ZIP Code)<br>P. O. Box 12211<br>Research Triangle Park, NC 27709-2211                                                                                                                                                                                                                                                                                                          |       | 10. SOURCE OF FUNDING NUMBERS                |                                                                                                   |                                                                                                     |                    |
|                                                                                                                                                                                                                                                                                                                                                                                                              |       | PROGRAM ELEMENT NO.                          |                                                                                                   | PROJECT NO.                                                                                         |                    |
|                                                                                                                                                                                                                                                                                                                                                                                                              |       | TASK NO.                                     |                                                                                                   | WORK UNIT ACCESSION NO.                                                                             |                    |
| 11. TITLE (Include Security Classification)<br>Electronic Structure and Properties of Defect Complexes in Metals                                                                                                                                                                                                                                                                                             |       |                                              |                                                                                                   |                                                                                                     |                    |
| 12. PERSONAL AUTHOR(S)<br>Purusottam Jena                                                                                                                                                                                                                                                                                                                                                                    |       |                                              |                                                                                                   |                                                                                                     |                    |
| 13a. TYPE OF REPORT<br>Final                                                                                                                                                                                                                                                                                                                                                                                 |       | 13b. TIME COVERED<br>FROM 9/25/85 TO 9/24/88 |                                                                                                   | 14. DATE OF REPORT (Year, Month, Day)<br>November 1988                                              |                    |
| 15. PAGE COUNT<br>23                                                                                                                                                                                                                                                                                                                                                                                         |       |                                              |                                                                                                   |                                                                                                     |                    |
| 16. SUPPLEMENTARY NOTATION<br>The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.                                                                                                                                           |       |                                              |                                                                                                   |                                                                                                     |                    |
| 17. COSATI CODES                                                                                                                                                                                                                                                                                                                                                                                             |       |                                              | 18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)                 |                                                                                                     |                    |
| FIELD                                                                                                                                                                                                                                                                                                                                                                                                        | GROUP | SUB-GROUP                                    | Electronic Structure, Defect Complexes, Metals, Disordered Systems, Clusters . (sign)             |                                                                                                     |                    |
|                                                                                                                                                                                                                                                                                                                                                                                                              |       |                                              |                                                                                                   |                                                                                                     |                    |
| 19. ABSTRACT (Continue on reverse if necessary and identify by block number)<br>Work has been confined to three different areas. These include:<br>(i) Defect complexes - Interaction of hydrogen with vacancies, substitutional impurities, impurity-vacancy complexes, and lattice strain. Also studied are the interaction of He with metals, electric field gradient produced by impurities at host over |       |                                              |                                                                                                   |                                                                                                     |                    |
| 20. DISTRIBUTION/AVAILABILITY OF ABSTRACT<br><input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS                                                                                                                                                                                                                                       |       |                                              | 21. ABSTRACT SECURITY CLASSIFICATION<br>Unclassified                                              |                                                                                                     |                    |
| 22a. NAME OF RESPONSIBLE INDIVIDUAL                                                                                                                                                                                                                                                                                                                                                                          |       |                                              | 22b. TELEPHONE (Include Area Code)                                                                |                                                                                                     | 22c. OFFICE SYMBOL |

cont'd → sites in cubic metals, positron annihilation in clean voids, as well as those containing rare-gas atoms and impurities, and the effect of lattice relaxation on the positron lifetime.

(ii) Disordered Systems - Electronic states, magnetic behavior and the electrical transport in metal-metalloid glasses; role of metalloids in affecting the electronic spectrum; stability and glass forming ability of metallic glasses.

(iii) Clusters - Equilibrium geometries, stability, electronic structure, and properties of neutral and charged micro-clusters consisting of up to ten atoms.

The theoretical methods used cover a wide range of techniques starting from the simple jellium model to effective medium approximation, tight-binding model, and the self-consistent field linear-combination of atomic orbitals-molecular orbital (SCF-LCAO-MO) method.

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|--------------------|-------------------------------------|
| Accession For      |                                     |
| NTIS CRA&I         | <input checked="" type="checkbox"/> |
| DTIC TAB           | <input type="checkbox"/>            |
| Unannounced        | <input type="checkbox"/>            |
| Justification      |                                     |
| By                 |                                     |
| Distribution /     |                                     |
| Availability Codes |                                     |
| Dist               | Avail and/or Special                |
| A-1                |                                     |



**FINAL TECHNICAL REPORT**

**PROJECT TITLE:** ELECTRONIC STRUCTURE AND PROPERTIES OF DEFECT  
COMPLEXES IN METALS  
**GRANT NO:** DAAG29-85-K-0244  
**PERIOD:** 1985-1988

During these three years, our work has been confined to three different areas. These include:

(i) Defect complexes - Interaction of hydrogen with vacancies, substitutional impurities, impurity-vacancy complexes, and lattice strain. Also studied are the interaction of He with metals, electric field gradient produced by impurities at host sites in cubic metals, positron annihilation in clean voids, as well as those containing rare-gas atoms and impurities, and the effect of lattice relaxation on the positron lifetime.

(ii) Disordered Systems - Electronic states, magnetic behavior and the electrical transport in metal-metalloid glasses; role of metalloids in affecting the electronic spectrum; stability and glass forming ability of metallic glasses.

(iii) Clusters - Equilibrium geometries, stability, electronic structure, and properties of neutral and charged micro-clusters consisting of up to ten atoms.

The theoretical methods used cover a wide range of techniques starting from the simple jellium model to effective medium approximation, tight-binding model, and the self-consistent field linear-combination of atomic orbitals-molecular orbital (SCF-LCAO-MO) method. Most of these calculations are

fully self-consistent with exchange and correlation potentials approximated either by the local density or by the Hartree-Fock configuration interaction (HF-CI) methods. Our work has resulted in forty-one publications. Following is a brief description of the main research results.

**(i) Defect Complexes:**

Considerable effort was concentrated in the study of the interaction of hydrogen with metal-defects. These problems are particularly interesting<sup>1</sup> not only because metal-hydrogen systems are technologically important, but also because there are many puzzling fundamental issues to be resolved. For example, how important are the zero-point vibrations of hydrogen on measured properties?<sup>2</sup> Do lattice defects such as vacancies, impurities, and impurity-vacancy complexes affect hydrogen diffusion?<sup>1,3</sup> What roles do lattice strain and electronic mechanisms play in trapping hydrogen in impure solids?<sup>4</sup> What are the equilibrium sites of hydrogen?

We have studied these problems in simple and transition metal hosts by modelling the imperfect system as a cluster<sup>5</sup> of finite size as well as by using the effective medium theory.<sup>6</sup> The former method takes into account all the non-linear, non-local interactions correctly within the cluster. The latter, on the other hand, approximates the total energy functional but takes fully into account the zero-point motion of hydrogen<sup>2</sup> and the extended host. While the cluster calculations are time consuming and tedious, the effective medium theory (EMT) is

simple to use and can be applied to a large number of systems with complicated defect configurations. A comparison of results obtained from these methods gives one confidence in interpreting the results.

As an illustration, we note that the effective medium theory predicted<sup>7</sup> hydrogen to be trapped at an off-center vacancy site. Our HF cluster calculations of a positive muon (a light isotope of hydrogen) in Li-vacancy system confirmed<sup>8</sup> this observation. We also made a detailed comparison<sup>9</sup> between total energy curves of a He-atom interacting with a metal using both HF-cluster method and effective medium theory (EMT). The calculations provide the range of He-metal distances over which the EMT results are accurate.

A recent experiment<sup>10</sup> on muon spin rotation in uniaxially strained Fe revealed significant shift in the muon internal field compared to that in pure Fe. Using the EMT we studied<sup>11</sup> the effects of lattice relaxation, quantum motion, and uniaxial strain on the internal field at a positive muon site in Fe. Our results showed a significant statistical population shift between the interstitial sites due to strain, and accounted for the observed frequency shift<sup>10</sup> quantitatively. We also predicted that the muon precession frequency shift in strained Fe should scale as  $1/T$  ( $T$  = temperature in  $^{\circ}\text{K}$ ). This has subsequently been verified in a muon-spin rotation experiment.<sup>12</sup>

The prevailing hypothesis<sup>13</sup> concerning hydrogen defect interaction in metals was that the long range strain fields produced by defects are primarily responsible for hydrogen trapping. We studied<sup>14</sup> the binding energies of hydrogen and its isotopes to substitutional impurities in Ti, Cr, and V in Nb by taking explicitly into account, the electronic effects associated with the wave mechanics of the hydrogenic interstitials and the lattice distortion they create. The difference in the electronic structure between impurity and host atoms was shown to be largely responsible for the trapping of hydrogen. Results were in good agreement with inelastic neutron scattering experiments.<sup>15</sup> The effects of lattice distortion created by the substitutional impurities on hydrogen trapping was later compared<sup>4</sup> with those due to electronic interactions in a self-consistent study of Ti and Cr impurities in V. Both lattice strain and short range electronic effects were found to play a role in hydrogen trapping. In V Ti system, the elastic strain due to lattice expansion and softening induces hydrogen trapping. In V Cr system the lattice hardens. Consequently, the strain field does not favor hydrogen trapping and over compensates electronic effects. The observed decrease in the hydrogen diffusion in V Cr, however, was found not to be due to trapping, but due to the increase in the activation barrier for diffusion. Our results helped to clarify the experimental situation.<sup>16</sup>

Followed by the success of our treatment, we studied the

interaction of hydrogen and deuterium in Ni irradiated by In, where a perturbed angular correlation experiment had just been carried out.<sup>17</sup> The results revealed that substitutional In did not trap hydrogen, while that decorated by vacancies did. Furthermore, the binding energy of H with In-vacancy complexes was independent of H concentration. To understand this, we studied<sup>18</sup> the energetics of H and D interacting with monovacancies, substitutional In impurity, a complex of four vacancies, and in In-four vacancy complex in Ni. We found that substitutional In does not trap hydrogen, while the vacancies and vacancy-complexes do-in agreement with experiment.<sup>17</sup> The presence of In inside vacancy-complexes had no noticeable effect on hydrogen binding energy. Unlike in Fe, Nb, and V hosts,<sup>4,11,14</sup> the hydrogen distribution in Ni In-vacancy complexes was found to be primarily localized.

Calculations of electronic properties of metals and metal hydrogen systems were also carried out<sup>19,20</sup> using a molecular cluster representation. Studies as a function of cluster-size revealed that while the equilibrium lattice constant could be calculated with as few as 20 atoms in a cluster, properties such as cohesive energies and hydrogen binding energies did not converge rapidly as cluster size increased. In the course of our studies, we also discovered<sup>20</sup> an interesting limitation of the cluster model in predicting equilibrium site of hydrogen. The results depended not only on the choice of cluster size but also on the cluster geometry. This illustrated the important role of

cluster surface effects on the hydrogen site preference. This result is expected to have a significant impact on future modeling of defects by clusters. Using electronic structure calculations, we also established, for the first time<sup>21</sup>, the equilibrium separation between a pair of interacting hydrogen atoms in metals and showed that it agreed with the empirical distance<sup>22</sup> obtained from a systematic analysis of all stable hydrides. This calculation also revealed that the hydrogen atom could form a H<sub>2</sub>-like "molecule" inside a metal if enough energy was available for the hydrogen to overcome the activation barrier. This prediction seems to be borne out in some recent neutron scattering experiments.<sup>23</sup>

The positron annihilation technique<sup>23</sup> has proved to be an important tool in studying vacancy-like defects. Some of our efforts were directed toward the study of dependencies of electronic properties and positron lifetimes on the size of clean and rare-gas decorated voids. We began by carrying out self-consistent calculations of the electron density distribution in voids in fcc metals (Al, Cu) based upon the jellium<sup>24</sup> as well as a discrete lattice model.<sup>25</sup> The lifetime of positrons and the angular correlation of annihilation photons in clean voids and voids decorated with rare-gas (He, Ar, Kr) impurities were calculated<sup>26</sup> using the local density distribution. The positron annihilation characteristics showed a strong dependence on the void size as well as on its impurity decoration. The results were compared with experimental data<sup>27</sup> and clearly showed the



important role these calculations could play in identifying the particular morphology of a defect complex inside which the positron is annihilating. We also showed<sup>28</sup> that the relaxation of neighboring atoms around a void in Mo was a non-monotonic function of void size, and in the case of a mono-vacancy could have a significant effect on the trapped positron lifetime. The inclusion of these effects brought theory into quantitative agreement with experiment.<sup>29</sup>

One of the most interesting examples of showing the strength as well as the limitations of positrons in providing information on defect complexes is the study of carbon-vacancy complexes in Fe. Experimental measurements<sup>30</sup> of the positron lifetime in electron irradiated pure and carbon-doped Fe as a function of temperature show various lifetimes believed to be characteristic of vacancies, vacancy migration and the formation of carbon-vacancy complexes. Using the density functional theory and the embedded cluster model, we have calculated the binding energies of carbon-vacancy complexes in Fe as a function of distance separating the carbon atom(s) and the vacancy along different crystallographic directions. Carbon is found to prefer off-center sites from the vacancy and maintains a constant distance of  $3.35a_0$  from the nearest Fe atom(s) independent of its direction from the vacancy center. This distance agrees closely with that in stoichiometric  $\text{Fe}_3\text{C}$ . Our results suggest that the equilibrium site of carbon is one where it is coordinated to three Fe atoms in its nearest neighbor shell. Further decoration

of vacancies by more than one carbon atom has been found to be energetically favorable. The bonding of carbon to iron atoms is not mediated by charge transfer between the atoms, but rather has a magnetic origin. Positron lifetimes at vacancies and vacancy-carbon complexes have also been calculated for various configurations. Our results provide an excellent account of the positron data. For single C impurity in a vacancy we find that the positron lifetime is isotropic with respect to the location of C inside the vacancy. This shows that positron lifetime cannot be used to pinpoint the location of impurities.

The last class of problems studied in this category is the electric field gradients produced by impurities at host atom sites in cubic metals. The loss of cubic symmetry at host sites is not only due to the difference in the host and impurity charge, but also due to the lattice strain<sup>31</sup> created by the displacement of atoms around the impurity. Despite the vast amount of experimental data<sup>32</sup> published on this subject, a systematic theoretical study was lacking. We developed a comprehensive theory<sup>33</sup> valid at all distances that involves electronic and strain contributions. The former was calculated self-consistently in the spherical solid model<sup>34</sup> while the latter used a point ion model.<sup>31</sup> We studied a large number of impurities in Al. The results compared very well with the available experimental data<sup>32</sup> and represent the most exhaustive study of efg undertaken in recent years.

### (ii) Disordered Systems

Electronic structure studies of amorphous NiP alloys were undertaken in order to elucidate the electronic and magnetic behavior, electrical transport and the stability of metal - metalloid class of glasses. While our initial work<sup>35</sup> employed non-self-consistent single site Korringa-Kohn-Rostoker coherent potential approximation (KKR-CPA), our recent studies<sup>36</sup> have been based on self-consistent density functional approach. The main focus of our work has been the disappearance of magnetism<sup>37</sup> and the change in the sign of Hall coefficient in NiP glass<sup>38</sup> as the P concentration is increased beyond 18%. The central issue has been the role of metalloids (P) in these glasses. Earlier theories conjectured<sup>39</sup> that the metalloids acted as charge donors; the role of P was to donate electrons to Ni d-band. While such a model could apparently account for many observed behaviors, direct photo-emission experiment<sup>40</sup> showed no indication of d-band filling in these glasses. This conflict could not be resolved in any simple manner within the existing theoretical models (based on rigid-band arguments) as it was inconceivable that the magnetism could be changed without adding electrons to fill d-holes.

Our recent studies<sup>36</sup> carried out within the local spin-density framework have resolved the above controversy. We have proposed a new model for the nature of electronic states in NiP glass. We showed that the metalloid (P) sp-states interact

closely with the host (Ni) states and produce changes in the electronic spectrum. The change occurs in a manner where the majority spin d-electrons are converted into minority spin d-electrons, keeping the total number of d-electrons almost constant. This sets up a mechanism by which the alloy demagnetizes itself, maintaining the overall charge neutrality. Our calculated density of electronic states show features in agreement with photoemission experiment. We have also looked into the question of the glass forming ability<sup>39</sup> of these glasses around 20% metalloids.

We also collaborated in an experimental study of the room temperature Hall resistivity of electro-deposited amorphous  $\text{Ni}_{1-x}\text{P}_x$  ( $0.15 < x < 0.26$ ).<sup>41</sup> We proposed that the observed change in sign of the classical Hall coefficient could be attributed to a decrease in sp density of states at the Fermi energy which would permit d-holes to dominate the conductivity and; therefore, could probably account for the observed effect.

(iii) Clusters:

Our studies of the modeling of clusters as fragments of crystalline studies led us into a novel area of research in the last three years. This field of clusters<sup>42,43,44</sup> is quite different from what we discussed earlier. Here we no longer look at clusters as a model of an infinite system by assuming the interactions to be governed by the local environment, but treat them as a new state of matter intermediate between atoms and solids. Rapid advancement in experimental techniques<sup>45</sup> have

enabled researchers to produce clusters of atoms of varying sizes and composition. These clusters exhibit unusual size specific features<sup>46</sup> concerning their stability, ionization threshold, polarizability, electronic and vibrational properties. A systematic study of these clusters could not only reveal how crystals grow from agglomeration of atoms but their size-specific properties may aid in designing new cluster materials with desired properties.

We have undertaken an ambitious task of understanding theoretically the structural and electronic properties of homo- and hetero- nuclear clusters in neutral and charged states. Most of our calculations to date have used Hartree-Fock configuration interaction (HF-CI) scheme.<sup>47</sup> We are presently pursuing studies using the local density approximation to the density functional theory.<sup>48</sup> One of our objectives is to see to what extent local density methods can provide meaningful results when compared with the ab initio HF-CI method. This is particularly important in systems such as clusters where the electron density is not a slowly varying function.

One of the most fundamental quantities in clusters from a theoretical point of view is the geometry of the ground state. We have derived<sup>49</sup> these structures for alkali metals (Li, Na), alkaline-earth metals (Be, Mg), Al, C, and compound clusters<sup>5</sup> ( $\text{Li}_n$  Mg,  $\text{Li}_n$  Na, and  $\text{Li}_n$  Al) by minimizing the total energy of the clusters and requiring that the gradient forces at constituent atoms vanish. We have found that the equilibrium geometries of

clusters, in general, are neither as compact nor as symmetric as they could be. A simple picture based upon a molecular orbital theory of bonding and antibonding was developed<sup>51</sup> to account for the general shapes of metal clusters. Two effects are found to dominate the process leading to the equilibrium geometry. These are the Jahn-Teller effect that lowers the energy by removing structural degeneracy and the Hund's rule coupling that lowers the energy by removing the spin-degeneracy. These two effects often oppose each other and are responsible for many novel features concerning magnetic and topological order.<sup>52</sup> For example, we have found that for planar clusters Jahn-Teller effects dominate over Hund's rule, resulting in clusters with lowest spin-multiplicity. The situation is reversed in three-dimensional clusters which assume a magnetic character. Furthermore, the higher spin-multiplet cluster is found to exist in a meta-stable state. We have illustrated this effect in  $\text{Li}_4$ ,  $\text{Na}_4$ , and  $\text{C}_4$  clusters and it may have potential industrial application. Experimental verification of this novel prediction is being awaited. Further theoretical studies along these lines are being planned.

The total energies of the clusters at their global minima were used to explain<sup>49</sup> their relative stabilities. The results were compared with the "magic numbers" (ie. the number of atoms for which pronounced peaks exists in the mass spectra). We pointed out various difficulties in interpreting the "magic numbers" based upon total energy considerations alone. We showed

that an unambiguous way to determine the "magic numbers" is by mass-selecting a cluster and studying<sup>53</sup> its fragments as it is forced to break up. We found that, energetically, the most favorable fragmentation channel is the one that contains, as one of the fragments, the most stable cluster. This observation is borne out by experimental data.<sup>54</sup> We also calculated<sup>49</sup> the vertical and adiabatic ionization potentials. The former corresponds to the singly charged cluster whose geometrical structure is identical to the neutral one while the latter corresponds to one where the cluster is allowed to relax after ionization. Our results explained the odd-even alternation in the experimental ionization potentials.

We also studied the stability and fragmentation channels of multiply charged metal clusters.<sup>55</sup> We showed that "magic numbers" associated with singly charged alkali metal clusters are 3, 9, 21,...as opposed to 2, 8, 20...seen in neutral clusters. A recent experiment has verified our prediction for singly charged  $Rb_n$  clusters. We found that as electrons are removed successively from a cluster, the electrostatic repulsion between the holes may overcome the cohesive energy of the cluster, leading it to fragment into smaller species - much like the situation in nuclear fission. We noticed that these fragmentation products were unequal in size, although they carried equal charges. The hole charge, upon multiple ionization, was shared by the constituent atoms. Our theoretical

studies of multiply charged metal clusters are the first ones in the field.

An energetically unstable, multiply charged cluster may not always spontaneously fragment into smaller species. There may be barriers against such dissociation. We discovered this while systematically studying the stability of doubly charged transition metal dimers.<sup>55</sup> The study revealed the existence of energy barriers against spontaneous dissociation and unravelled situations where two equally charged atoms can attract! The barrier heights are found to be intimately connected with the electronic structure of the constituent atoms. For example, in  $\text{Ni}_2^{++}$ , the barrier height for dissociation into two  $\text{Ni}^+$  ions is zero whereas for  $\text{Mo}_2^{++}$ , it is as much as 2 eV. The presence of high barriers against fragmentation can lead to extremely large life-times and thus observable meta-stable clusters. Our results agree with a recent experiment<sup>56</sup> in  $\text{Mo}_2^{++}$ .

We were among the first groups to theoretically study the effect of a foreign atom on the geometrical structure and stability of an otherwise homo-nuclear cluster.<sup>50</sup> Self-consistent calculations were carried out for  $\text{Li}_n\text{Mg}$ ,  $\text{Li}_n\text{Al}$ , and  $\text{Li}_n\text{Na}$  clusters. It was found that replacing a Li atom by a Na atom had no effect on its initial geometry or stability. The effects of Mg and Al were, however, quite dramatic on the structure of Li cluster, but had no adverse effect on its stability. The latter was found to be due to a the lowering of energy levels unaccompanied by any level changes when a foreign



atom was added. The results agree very well with experiments<sup>57</sup> on parent  $K_n$  clusters. Subsequent calculations<sup>58</sup> have verified our conclusions.

To enrich our understanding of the physics and chemistry of this rapidly expanding field, we organized in 1986 the highly successful international symposium on the Physics and Chemistry of Small Clusters. The results were published<sup>62</sup> by Plenum in a 955 page book under the auspices of the NATO-ASI series.

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### **C. Other Activities:**

- Organized the International Symposium on the Physics and Chemistry of Small Clusters in 1986.
- Invited speaker at international conferences in India, Argonne National Lab, Heidelberg, Richmond, Tokyo, and AIME meeting in Orlando.

-Invited to chair meetings at the American Physical Society, Gordon Conference, and international conferences in Tokyo, Heidelberg and Argonne.

-Dr. Jena was the recipient of the 1987 Distinguished Scholar award at Virginia Commonwealth University.

#### D. Personnel Supported:

P. Jena (P.I.) Summer 1986, 1988  
 S. N. Khanna (Co-P.I.) Summer 1986, 1987, 1988  
 D. Shillady (Faculty Assoc.) Summer 1986, 1987  
 B. K. Rao (Faculty Assoc.) Summer 1987, 1988  
 G. Das (Faculty Assoc.) Summer 1986  
 M. R. Press (Postdoctoral Fellow) 1986-1988 (Fulltime)  
 E. Blaisten Barojas (Visiting Prof.) 1987-1988 (Fulltime)  
 L. Feng (Graduate student) Summer 1987

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