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Elemental and Molecular Clusters

Editors: G. Benedek,
T. P. Martin, and G. Pacchioni

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Preface

The 13th course of the International School of Materials Science and Technology was held in Erice, Sicily, at the Ettore Majorana Center for Scientific Culture, 1–15 July, 1987. At the suggestion of the European Physical Society, the course took the form of a summer school designed to present the fundamental concepts and methods needed to study elemental and molecular clusters. This volume is based on the lectures presented at the summer school. It has been organized into four parts: Electronic Properties, Structure, Fragmentation and Chemistry. Within each part the contributions have been ordered alphabetically by author; first the lectures followed by the seminars.

The summer school, held under the auspices of the European Physical Society, received generous support from a number of other organizations: The Italian Ministry of Education, The Italian Ministry of Scientific and Technological Research, The Sicilian Regional Government, IBM Italia, The National Research Council of Italy (CNR), The National Group for Structure of Matter, Italy (GNSM and CISM), and The Associazione Studi e Ricerche sull'Innovazione Tecnologica (ASRIT, Cameri, Italy).

Indispensable for the planning of the summer school was the support of the Director of the Ettore Majorana Center, Professor A. Zichichi, and of the Director of the International School of Materials Science and Technology, Professor M. Balkanski. We wish to express our sincere appreciation to the center staff, Dr. Alberto Gabriele, Dr. Pinola Savalli and Dr. Jerry Pilarsky for their expert assistance in all organizational matters and for their warm hospitality.

The success of a school is, in the last analysis, determined by the interest and commitment of the lecturers and participants. We are particularly grateful to the lecturers, not only for their carefully prepared formal contributions, but also for the spontaneous "evening sessions" and to all the participants for their inexhaustible enthusiasm.

Erice, August 1987 *The Editors*

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Part I

Introductory Comments

Clusters: What Are They?

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1. INTRODUCTION

How do the properties of a solid gradually evolve as atoms are brought together to form increasingly larger units? In order to answer this question one must study aggregates of atoms too large to be called molecules but still too small to have even the structure of a crystal. Recent advances in experimental methods have made possible some first explorations in this long neglected but fascinating field of study. Because these aggregates have attracted investigators /1-9/ from many branches of science and technology, a colorful but confusing array of terms has been used to describe them: small particles, microclusters, grains, oligomers, specks and microcrystals, to mention a few. Considering this state of affairs a few words of introduction might be useful addressing the questions: What are clusters? How do they differ from molecules? Why might they be of interest?

A ring of eight sulfur atoms or a tetrahedron of phosphorus atoms cannot with good conscience be called a cluster. Such stable units exist in the vapor, liquid and solid phases and have long been called molecules. Because molecules are readily available, their properties are usually well investigated. The term cluster might then be reserved

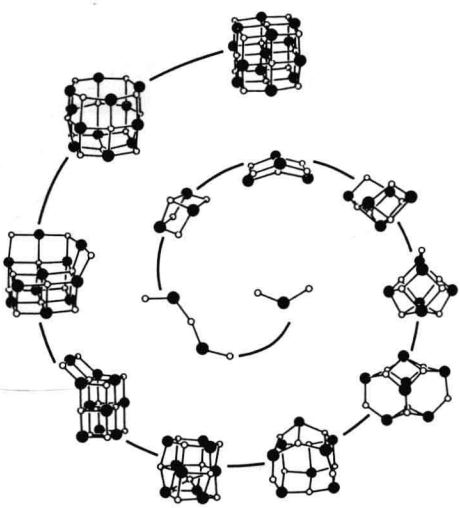

Fig.1. Calculated configurations for $Na^+(NaCl)_n$ clusters. Crystalline structures are not necessarily preferred during the first stage of growth of a solid.

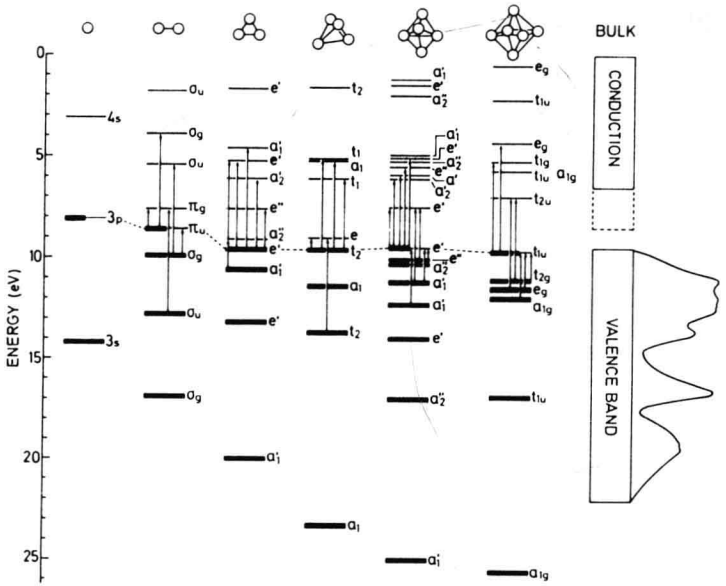

Fig.2. Calculated electronic energy levels of Si clusters having the indicated sizes and shapes.

for atom aggregates that are not found in appreciable numbers in an equilibrium vapor. Clusters, therefore, represent a new class of objects for investigation.

After a cluster reaches a critical size, it is no longer free to reconstruct each time a new atom is added. A final lattice structure becomes frozen into the cluster. This crystallization may occur for aggregates containing less than 100 atoms. Still it is convenient and meaningful to give these aggregates a new name, microcrystals, because deviations from the bulk structure can be described as a surface relaxation.

Why could the properties of clusters be of interest? For one thing we would like to understand the crystal growth process on a microscopic level. Everytime a new atom or molecule condenses onto a cluster, the atoms in the cluster completely rearrange themselves; the cluster reconstructs. We would like to know the sequence of structures a cluster assumes as it grows from a molecule into a crystal, Fig. 1.

Another reason for studying clusters is that we would like to know how the electronic band structure of a solid develops. This is represented in Fig. 2 by a simple Hückel calculation of the electronic energy levels of silicon clusters with increasing size. It is of interest to observe how the discrete levels coalesce to form bands and at what stage a distinct gap appears between filled and unfilled states.

A question often asked is, how many metal atoms are required to form a cluster that has metallic properties? One characteristic property of a metal is its optical response, the interaction with light. A single Li atom has a very simple absorption spectrum, Fig. 3. It consists of essentially one line in the visible. This absorption can be well described as a one electron transition from a 2s state to a 2p state. A lithium crystal, on the other hand, has a completely different absorption spectrum. The absorption is strong in the far-infrared, goes through a minimum in the visible and then rises again in the

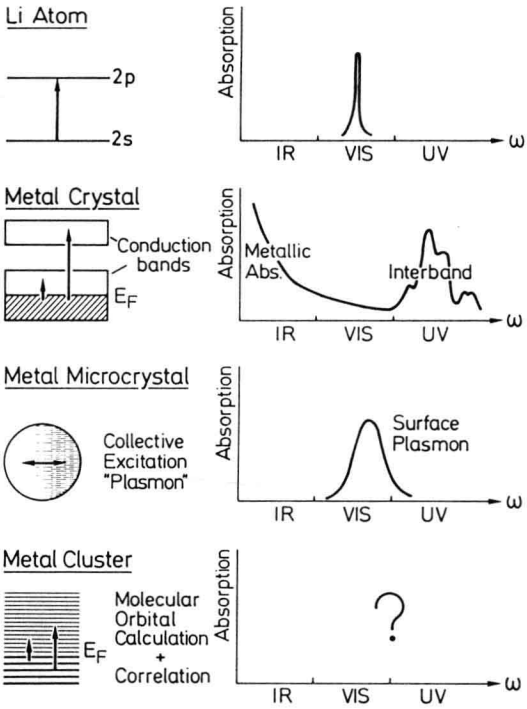

Fig.3. Absorption of light by Li in various stages of aggregation.

ultraviolet. The reason for this is that very low energy photons can excite electrons from the continuum of states just below the Fermi energy to states just above the Fermi energy. The strong uv absorption is caused by interband transitions. Suppose we chip off a small corner of the crystal, producing a microcrystal that contains only 50 atoms. Again the absorption spectrum changes completely. A relatively broad absorption maximum appears in the visible, Fig. 3. This absorption is due to a collective excitation of outer electrons, a plasmon excitation. The Li crystal also has plasmon excitations. However, in the crystal these excitations have a longitudinal character and do not couple to transverse light waves. In the microcrystal one can consider a plasmon as a collective sloshing motion of the electrons from one side of the microcrystal to the other side. It is clear that such a motion has a strong dipole moment, thus giving rise to the strong absorption band in the visible. The absorption of light by a Li atom is well described within the one electron picture. However, this picture cannot describe even qualitatively the plasmon excitations which dominate the optical response of a 50 atom cluster. Between a few atoms and 50 atoms we must completely change our way of looking at optical response. Clusters offer us the opportunity of studying this transition. Another reason for studying clusters is that the technique of cluster beam mass spectrometry offers new and convenient methods of allowing elements to react in a controlled manner and of determining the stability of the reaction products/9/.

2. CLUSTERS PRODUCED BY GAS EXPANSION

It has been known for several decades/10,11/ that when a gas under relatively high pressure (1 bar) expands into a vacuum through a small (0.1 mm) nozzle, clusters condense out of the cooled gas. The size distribution of the clusters can be controlled by varying the expansion parameters. Using this technique a large variety of gas and vapor clusters have been studied: hydrogen/12/, water/13-21/, sodium/22-27/, inert gases/28-33/ and tetracene/34,35/ to mention a few. For example, water clusters can be formed by expanding a mixture of water vapor and argon through a 0.22mm nozzle. The peak corresponding to $[H(H_20)_{21}]^+$ stands out particularly strongly in the mass spectrum. This mass spectrum is usually interpreted to indicate an enhanced stability for the 21-molecule water cluster. What does this cluster look like? Ice has a wurtzite structure where each oxygen atom is surrounded tetrahedrally by four other oxygen atoms. One, and only one, hydrogen atom is found on each bond. It is not possible to find a highly symmetric arrangement of 21 molecules within the wurtzite structure. However, using the tetrahedral bonding scheme it is also possible to construct a dodecahedral cage. In fact, such a cage has been identified in many clathrate compounds. The stability of the dodecahedron against both growth and decay could explain the strength of the n=21 peak in the mass spectrum.

3. CLUSTERS PRODUCED BY ION BOMBARDMENT

If an intense beam of high energy (5 KeV) ions Xe^+ is directed against a solid surface (CsI), secondary ions are ejected from the surface and can be detected in a mass spectrometer. These secondary ions include not only simple molecules but also large clusters containing hundreds of atoms/36-41/. A mass spectrum of $[Cs(CsI)_n]^+$ clusters produced in this way shows that the peak corresponding to the cluster $(Cs_{14}I_{13})^+$ is particularly strong. This cluster has been shown to have an enhanced stability not only for CsI but also for NaCl/41-43/ and CuBr/44/. Since this cluster is too small to be observed directly, we must rely on theoretical considerations in order to determine its structure. Stable cluster configurations can be calculated at widely varying levels of sophistication. The simplest method involves the packing of hard spheres. At the other end of the scale, stable structures can be determined by elaborate configuration interaction calculations of the total energy. Such calculations are appropriate for clusters with any type of bonding but are limited in practice to very small clusters of light atoms. The total energy of clusters with either purely ionic/45,47/ or van der Waals/48/ bonding can be determined much more simply. It is possible to define a size-independent, two-body interatomic potential. By summing this potential over all atom pairs a multidimensional total energy surface is obtained. Each minimum on this surface corresponds to a stable cluster configuration. The main computational difficulty is not to define the surface, but to find all true minima without getting trapped at a saddle point with a low curvature. Such total energy calculations indicate that $(Na_{14}Cl_{13})^+$ has more than the usual binding energy. The reason for this is quickly seen by looking at the structure of this cluster, Fig. 4. $(Na_{14}Cl_{13})^+$ is highly symmetric, resembling a portion of the rock salt structure. Calculations with parameters appropriate for the compounds CuBr and CsI indicate that the cubic cluster is responsible for the strong peaks in the mass spectra of these materials also. This is quite surprising because CuBr and CsI condense to form crystals of the zinc blende (coordination number, CN 4) and cesium chloride type (CN 8), respectively. It appears

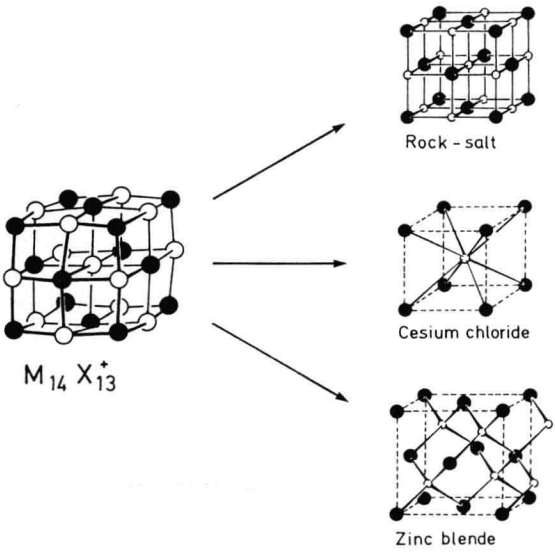

Fig.4. The most stable form of the metal halide $(M_{14}X_{13})^{+}$ and the crystal structures of NaCl, CsI and CuBr.

the rock salt form (CN 6) is energetically favored in the early stages of growth of not only NaCl but also CsI and CuBr.

4. VAPORS QUENCHED IN He GAS

Most materials when heated to a sufficiently high temperature in an inert gas atmosphere produce a dense smoke composed of microcrystals/49-52/. The size of the microcrystals varies from 10 to 1000 Å depending on experimental conditions. Recently, a time-of-flight mass spectrometric study has shown that the technique of inert gas evaporation produces not only microcrystals but also clusters containing fewer than 100 atoms/53,54/.

Not all elemental vapors produce a detectable number of clusters when quenched in He gas. Ge and Sn not only cluster easily/56-59/, but are particularly interesting because in the solid form they represent a transition from covalent to metallic bonding. Ge_n mass peaks are strong for n= 6,10,14,15 and 18, and particularly weak for n=13,17,20 and 24/60,61/. The meaning of these anomilies in the mass spectra is slowly emerging as a result of recent molecular dynamics computer simulations and ab initio calculations of the total energy /55/.

The dominant feature of the Sn mass spectrum is the weakness of a peak for n=14. In this respect Sn resembles Pb/53/. That Sn should more resemble Pb than Ge can be seen already in the solid state. Although Sn does have a low temperature semiconducting crystalline modification (α-Sn) with the diamond structure, at room temperature it is a metal with the β-Sn structure (CN 6). Once again we can only speculate as to the cause of the instability of the cluster corresponding to n=14. There

are several close-packed structures corresponding to n=13 consisting of a central atom surrounded by a complete shell of outer atoms. An additional atom, which lies on the surface of such a highly symmetric compact core, could be expected to be weakly bonded.

5. CLUSTERS BY LASER EVAPORATION

A pulsed cluster source has been developed which uses a focused laser beam for vaporization/62-65/. The vaporization is timed to occur at the peak of a high pressure He pulse. Such a source is particularly appropriate for time-of-flight mass spectrometry. It has the advantage that essentially any material can be vaporized, even carbon. The mass spectrum of C_n^+ clusters has a bimodal size distribution. For n <30 both even and odd clusters were observed. The peaks corresponding to n=3,11,15 and 19 were particularly strong.

Under certain clustering conditions the C_{60} peak completely dominates the mass spectrum/66-69/. It seems unlikely that the special stability of such a cluster can be explained on the basis of a planar six-atom ring structure or on the basis of a tetrahedrally bonded diamond structure because such structures would possess too many dangling bonds. It has been suggested that C_{60} has the shape of a football (soccerball). It is spheroidal with icosahedral symmetry.

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