The physics of simple metal clusters: experimental aspects and simple models

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The study of simple metal clusters has burgeoned in the last decade, motivated by the growing interest in the evolution of physical properties from the atom to the bulk solid, a progression passing through the domain of atomic clusters. On the experimental side, the rapid development of new techniques for producing the clusters and for probing and detecting them has resulted in a phenomenal increase in our knowledge of these systems. For clusters of the simplest metals, the alkali and noble metals, the electronic structure is dominated by the number of valence electrons, and the ionic cores are of secondary importance. These electrons are delocalized, and the electronic system exhibits a shell structure that is closely related to the well-known nuclear shell structure. In this article the results from a broad range of experiments are reviewed and compared with theory. Included are the behavior of the mass-abundance spectra, polarizabilities, ionization potentials, photoelectron spectra, optical spectra, and fragmentation phenomena.

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I. INTRODUCTION

In this age of miniaturization of electronic devices, there is an increasing need to understand the properties of metallic structures with dimensions of the order of nanometers. Metal clusters are particles composed of a countable number of atoms, starting with the diatomic molecule and reaching, with a vaguely defined upper bound of several hundred thousand atoms, into that interesting size range.

Metal clusters are not new. In fact, the glaziers of the Middle Ages discovered how to produce beautiful stained glasses by special treatments of metal-containing glasses. In fact, the earliest investigations are perhaps due to Rayleigh, who recognized that the colors of stained glasses were due to the scattering of light by small metal particles embedded in the glass. His work was followed by an extensive electrodynamic treatment by Mie (1908), which is relevant even today. From those early investigations through the 1970s, much of the metal cluster work concentrated on related systems, where small metal particles were precipitated in glasses and investigated for their electromagnetic properties (Kreibig, 1970).

During the 1960s and 1970s, new cluster sources were developed to produce clusters composed of only a few atoms in the gas phase (Robbins *et al.*, 1967). It seemed that these particles had properties that were unrelated to the bulk. This might be expected from either a molecular or a solid-state point of view, since for these very small particles the surface is important. Even for a cluster with 1000 atoms, about a quarter of the atoms lie on the surface, so that its properties may be importantly modified compared with the bulk.

Because of the large fraction of surface atoms, it is clear that when the cluster is embedded in a matrix of some kind, additional complexity is introduced. Hence an understanding of the properties of isolated clusters of well-defined size in the gas phase is an essential first step towards a description of embedded clusters, which some day may well be of technological importance. These considerations lead to several pioneering investigations giving birth to the now very rich field of cluster physics.

Up to the early 1980s clusters were primarily thought of as small molecules. There was little reason to expect patterns relating the properties of clusters with different sizes or of different metals; as for molecules, every cluster was considered to be essentially unique. In those days the most carefully studied clusters were indeed very small, with at most about a dozen atoms, and no obvious order was discerned. Much larger particles were believed to be essentially bulklike, and the surface was thought to scatter electrons randomly. Hence complex molecular electronic structure was expected to give way to bulk structure, where the increasing complexity ultimately warranted a statistical description (Kubo, 1962).

However, this changed in late 1983 when Walter Knight's group, with Keith Clemenger, Walt de Heer, and Winston Saunders, produced and detected clusters of alkali metals with up to about 100 atoms. They immediately recognized that there was a striking order: the electronic structure of these clusters appeared to reflect that of a spherical potential well (Knight *et al.*, 1984). This fundamental principle was inferred from little more than the cluster abundance spectra: clusters in which the number of valence electrons matched the spherical shell-closing numbers were produced more abundantly, as seen in Fig. 1. By a striking coincidence, Ekardt (1984a, 1984b) independently and virtually simultaneously predicted this shell structure in his model for alkali clusters using the jellium approach, in which the clusters are considered to be uniformly positively charged spheres filled with electrons. Earlier, Martins *et al.* (1981) also had recognized similarities between the electronic orbitals from a molecular calculation with those from a jellium picture.

We now know that these characteristic abundance patterns persist up to very large sizes: electronic shell structure is observable even for clusters with several thousand atoms, as recently made evident by Sven Bjørnholm and his collaborators (Pedersen *et al.*, 1991) and by other groups.

After those early discoveries, electronic shell structure was observed in many simple and noble-metal cluster systems. The initial observations of the electronic shell structure and the theoretical development of the shell model have been reviewed by de Heer, Knight, *et al.* (1987). From then on the development was rapid. Experimentally the electronic shell structure was verified in the electronic response properties (ionization potentials, polarizabilities, collective excitations, etc.), and the jellium model was further developed to a high degree of sophistication.

However, a sphere is a reasonable approximation only for electronically closed-shell clusters. For open-shell clusters the spherical shape is unstable towards distortions due to the Jahn-Teller effect (Jahn and Teller, 1937),

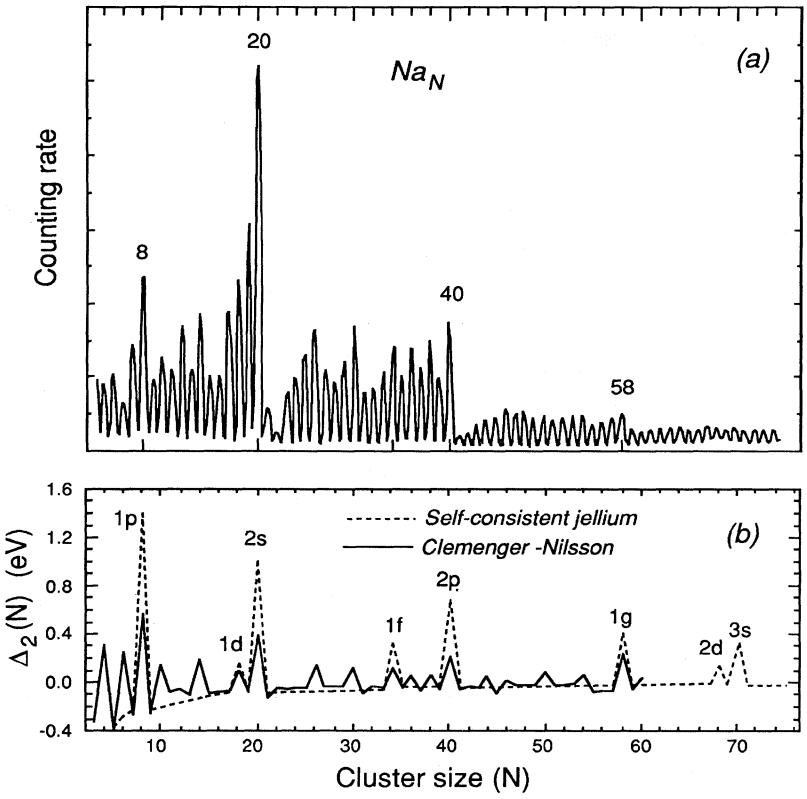

FIG. 1. Sodium cluster abundance spectrum: (a) experimental (after Knight *et al.*, 1984); (b) dashed line, using Woods-Saxon potential (after Knight *et al.*, 1984); solid line, using the ellipsoidal shell (Clemenger-Nilsson) model (after de Heer, Knight, Chou, and Cohen, 1987).

which has important and readily observable consequences. More recent self-consistent models now take this into account, but it was already recognized by Clemenger (1985a, 1985b). Noting that a very similar situation existed for nuclei, he adapted the deformed nuclear shell model of Nilsson (1955) to alkali clusters and found that virtually all the fine structure in the spectrum of Fig. 1 could be related to predictions from this model.

The experimental fact that to first order the detailed ionic core structure is not as important, and that the electrons may be considered to be nearly free and confined in a potential well, can be exploited at various levels. In the self-consistent jellium model, the ionic cores are considered to provide a uniformly charged positive background, and the electronic structure is subsequently calculated using various approximations for the interacting electron gas. However, even thus simplified the many-body problem is still far from trivial, as evidenced by the vast literature based on the jellium model alone. At a much lower level are the "hook and crook" approaches so dear to experimentalists who usually cannot wait for accurate theoretical predictions. For metal clusters, in particular, these have been extremely useful for providing very reasonable first-order interpretations of experimental data. In this review we shall heavily rely on descriptions of this kind. There is no intended implication that these methods can provide much more than rudimentary descriptions. Nevertheless, very often when conceiving and developing an experiment, all the experimentalist wants is a basic understanding of the physical properties involved, with reasonable quantitative estimates.

The review projects an experimentalist's point of view and attempts to present as clear a picture as possible of the experimental situation. However, rather than presenting a dry summary of experimental results, I have tried to unify them as much as possible by relating the observations with the simplest possible models. Of course this has the risk of trivializing the enormously complex many-body problem, which these clusters, after all, represent. I emphasize that this is by no means my intention. The models presented here serve the same purpose they do in all branches of physics, that is, to organize the experimental observations and to establish elementary relationships between observed effects at the most basic level.

Section II introduces the basic concepts of the electronic shell model based on the Clemenger-Nilsson model, and predictions of this model are compared with experiment throughout. I believe that this model and its concepts are so important that it warrants this degree of attention. Details of the model with several applications are given in the appendices. General experimental techniques are reviewed in Sec. III. The discussion is continued with six more or less self-contained sections, each one treating a specific cluster property (Secs. IV–IX). In each of these sections the experimental data are presented, discussed, and compared both with simple models and with detailed calculations.

A serious attempt has been made to touch on the most important developments in the field, but the review is by

no means exhaustive. Often when earlier experimental results have been refined or appended with newer ones, only the more current results are explicitly mentioned, with the understanding that the development can be traced from the cited work. By no means is any judgment on the importance of the earlier work implied. I apologize for any instances in which work was overlooked. Furthermore, in order to achieve as uniform a presentation as possible, figures have often been redrawn from published data, thereby introducing slight distortions. For accurate values, the reader is urged to consult the original figures.

Theory is treated only peripherally. In fact the review originally consisted of two parts, an experimental and a theoretical one. It was decided, however, that it is more reasonable to have two complementary reviews. The theoretical counterpart by Matthias Brack (1993) treats the theory of simple metal clusters in detail and follows this review.

This work covers only one aspect of the vast field of cluster science. For a brief but wide-ranging overview, the reader should consult the recent (although not completely up-to-date) review by Sugano (1991). Among other things, that work treats metal, semiconductor, molecular, and inert-gas clusters. Other invaluable sources of information on all aspects of cluster physics are the proceedings of the ISSPIC conferences (International Symposium on Small Particles and Inorganic Clusters), held at Lyon in 1976 (ISSPIC 1, 1977), at Lausanne in 1980 (ISSPIC 2, 1981), at Berlin in 1984 (ISSPIC 3, 1985), at Aix-en-Provence in 1988 (ISSPIC 4, 1989), at Konstanz in 1990 (ISSIPC 5, 1991), and at Chicago in 1992 (ISSPIC 6, 1983). Additional sources are the proceedings of two conferences at Richmond in 1986 and 1991 (Jena, Rao, and Khanna, 1987; Jena, Khanna, and Rao, 1992). Reviews relating to topics discussed in this work are cited in the text.

II. SHELL MODEL FOR SIMPLE METAL CLUSTERS

For monovalent simple metals, the conduction band is approximately free-electron-like and the Fermi surface is nearly spherical. For sodium, in particular, deviations from a perfect sphere are almost negligible (Ashcroft and Mermin, 1976). Correspondingly, the jellium model ignores the ionic core structure altogether and replaces it by a uniform positive background, and this approach has led to valuable insights into the electronic structure of bulk metals. Surfaces clearly require special attention. However, even assuming that the positive charge abruptly terminates at the surface gives reasonable predictions for electronic properties (Lang and Kohn, 1971). The advantages are obvious, leading to a much more manageable description than one which accounts for the ionic structure in detail.

These considerations motivate the jellium model for metal clusters. Despite the obvious objections that can be raised against such a description, especially for clusters containing only a few atoms, the results are nevertheless impressive. The jellium model for clusters is extensively treated in the theoretical counterpart of this review (Brack, 1993).

We now depart from the jellium model and develop a related semiempirical model, which is used throughout this review. This is a vastly simpler approach and is based essentially on the Sommerfeld model (Ashcroft and Mermin, 1976). In contrast with the jellium calculations, in which the electrons are treated self-consistently, the model takes for granted that a very simple effective single-particle potential (for example, a rounded spherical square well) is a good starting point.

Our aim is to obtain a qualitative description of the properties of the simple metal clusters so that properties can be calculated with a minimum of effort. Not only is this useful when reasonable quantitative values are required, but it also provides invaluable insight into the fundamental physics involved. Detailed explanations are given in the appendices, where a variety of properties are treated explicitly. Here we give only the principle ideas and establish points of contact with sophisticated calculations to give insight into the accuracy that may be expected from this model.

A. Shell model for spherical clusters

The mass-abundance spectrum in Fig. 1 suggests that to lowest order the valence electrons in sodium clusters are independent and are confined in a spherically symmetric potential. Such a potential automatically gives rise to spherical shell structure because of its symmetry, where the valence electrons successively fill the degenerate levels. As for atoms, the electronic system of a cluster with exactly the right number of electrons to complete a shell is very stable. When one more atom is added to the cluster, its valence electron will occupy a state with considerably higher energy, and hence the stability of the cluster is reduced. The reduced stability is reflected in a reduced abundance, explaining the large abundance drops after each shell-closing number in Fig. 1.

In metal cluster physics the quantum numbers follow the nuclear (i.e., not the atomic) convention, so that each shell is characterized by the radial quantum number n and the angular momentum l. For a given quantum number l, the lowest state has $n=1$, etc. Figure 2 shows the energy-level structure for three spherically symmetric wells, and it can be seen that changing the well shape not only changes the relative level spacings, but may even alter their ordering.

For comparison, Fig. 3 shows the calculated self-consistent effective single-particle potential for Na_{40} (Chou *et al.*, 1984; further examples are given by Ekardt, 1984a). The energy levels are also shown and the shell structure is clearly discernable. This particular self-consistent potential well has the shape of a wine bottle, and the energy-level spacings approximately correspond

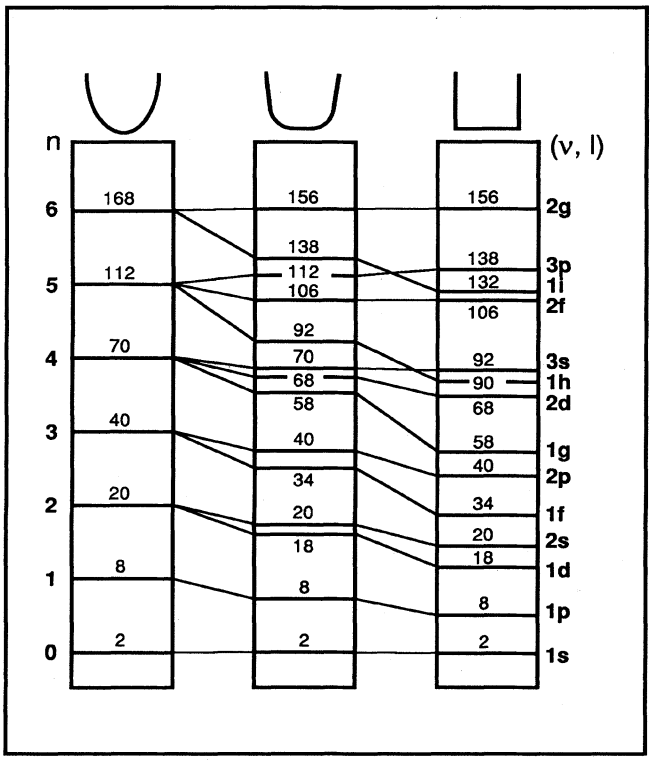

FIG. 2. Energy-level occupations for spherical three-dimensional, harmonic, intermediate, and square-well potentials. After Mayer and Jensen, 1955.

to those of the intermediate case in Fig. 2. Further, the shape of the well (as determined in the jellium model) depends on the cluster in question; however, the energy levels from one closed-shell cluster to the next are found to be closely related.

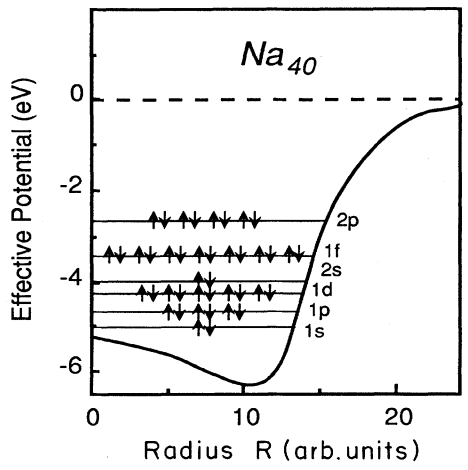

FIG. 3. Self-consistent effective potential of jellium sphere corresponding to Na_{40} with the electron occupation of the energy levels. After Chou *et al.*, 1984.

B. Ellipsoidal Clemenger-Nilsson shell model

Approximating small clusters with spheres can be only be justified for closed-shell clusters. From the Jahn-Teller theorem (Jahn and Teller, 1937) it follows that open-shell clusters must distort. As demonstrated by Clemenger (1985a, 1985b), the fine structure in Fig. 1(a) is a manifestation of these distortions. Clemenger introduced a deformable potential well that is particularly well suited to account for this effect. In fact, he simply adapted the well-known Nilsson model extensively used to estimate the shapes of nuclei (see, for example, Bohr and Mottelson, 1975).

The Clemenger-Nilsson model assumes that the effective single-particle potential is essentially that of a three-dimensional harmonic oscillator. This turns out to be a remarkably good approximation for smaller clusters (i.e., $N<20$). For larger ones, a small anharmonic distortion term is required; however, for most of the analyses here we ignore this refinement, so that the calculations become so simple that they are easily done analytically (Appendix A).

An important feature of the model is that its shape adjusts to the electronic structure while keeping the volume of the cluster fixed. In this way spheroidal clusters (i.e., with two equal axes $R_x=R_y$ and one unequal axis R_z) can be treated; details are given in Appendix A. From this model it is found that the shapes of open-shell clusters are significantly distorted. The cluster shapes and energy-level structure are represented in the Clemenger-Nilsson diagram (Appendix A, Fig. 53).

As in the spherical shell model, the spheroidal shell model predicts enhanced stabilities for closed-shell clusters. However, in addition, the spheroidal distortions cause subshell closings which are also seen in the spectra. Hence this model reproduces not only the main features but also most of the fine structure in the abundance spectrum, as shown in Fig. 1(b). Other features, for example, the abundance maximum at 12, are found in the ellipsoidal Clemenger-Nilsson model, which allows distortions along all three axes of the cluster (see below).

In Sec. IV.A.1 the relation between the abundance spectra and electronic stabilities is treated more carefully. Here we note that the correspondence provides empirical evidence that *to lowest order the fine structure is often caused by the overall shape of the cluster,* and in particular it is not necessarily due to the detailed arrangement of the ionic cores. This surprising property is the basis for the jellium model for metal clusters.

1. Cluster shapes in the ellipsoidal shell model

It is straightforward to extend the Clemenger-Nilsson model by allowing distortions along three axes. Now the shapes are either spheres, spheroids, or ellipsoids, as can be calculated with little effort (ignoring the anharmonic terms, Appendix A).

The cluster shapes are shown in Fig. 4(a) and are readi-