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Analysis of Gas Phase Clusters Made from Laser-Vaporized Icosahedral Al-Pd-Mn

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ABSTRACT

Laser vaporization of an icosahedral Al-Pd-Mn sample with detection by time-of-flight mass spectrometry is used to probe metal clusters made from the alloy. After sample vaporization, clusters form by gas aggregation and may contain several to hundreds of atoms. Multi-photon ionization/fragmentation of these clusters yields mass spectra showing many cluster sizes with enhanced intensity. Clusters are identified at masses near those of pseudo-Mackay and Bergman clusters; however, these clusters do not appear special relative to neighboring clusters. Results of this study and its relationship to the proposed cluster structures in quasicrystalline materials are discussed.

INTRODUCTION

Both pseudo-Mackay icosahedral (PMI) and Bergman type cluster models have been proposed as a basic motif for the quasicrystalline structure [1,2]. Many experiments have been done which provide support for cluster models. Quasicrystals are known to have low thermal and electrical conductivity. Measurements of these properties suggest a hierarchical localization. This would be consistent with electron localization inherent to a cluster-based structure [3]. Studies of cleavage properties and plasticity have been interpreted within the context of stable clusters as structural sub-units [4,5]. In addition, neutron scattering studies were performed on the liquid melt of quasicrystal-forming alloys during the solidification process [6]. In these studies short-range icosahedral order was identified.

The cluster models proposed do begin to describe the bulk quasicrystalline structure; however, such models require clusters to be overlapping and interlaced. It is difficult to explain how these clusters could assemble in an energetically favorable way. A cluster jellium model has been proposed to describe the structure growth [3]. In this model the inflation is driven by attempts to obtain a stabilizing closed-shell electronic configuration for the clusters.

It may be useful to investigate quasicrystal structure with experiments designed to probe isolated metal clusters. An understanding of the fundamental interactions between atomic species in the clusters may provide insight regarding electronic and geometric stability. Additionally, studying the chemical properties of the clusters may aid our understanding of the metal surface since the clusters have a high percentage of surface atoms.

The method of laser vaporization is used in our study. After vaporizing the sample, the atoms condense into clusters, which are subsequently detected by time-of-flight mass spectrometry (TOF-MS). This technique has proven to be very successful for the study of both electronic and geometric structure of gas phase metal clusters. This method has been used in the past to investigate the electronic properties of small alkali clusters. The experimental evidence from that study was described in detail using a cluster jellium model [7]. Studies have also been done which probe cluster geometry. They show that some systems adopt icosahedral symmetry

[8]. Studying quasicrystals by this method has the potential to provide important information regarding local electronic and geometric structure.

In this paper we present the initial results of our study. If Bergman or PMI clusters are inherently stable they may exist outside of the bulk quasicrystalline structure. Attempts were made to detect gas phase Bergman or PMI clusters from laser vaporized icosahedral Al-Pd-Mn.

EXPERIMENTAL

Clusters are made by laser vaporization of a quasicrystalline target rod in the cluster source. This is coupled with the flow tube reactor where the vaporization plume is cooled, and clusters form from the condensing atoms. Figure 1 shows a schematic of the cluster source and flow tube reactor. The target rod is vaporized using a pulsed 2.33 eV Nd-YAG laser, delivering ~10 mJ/pulse. The laser enters the cluster source through a quartz window and is focused on the target rod. The target rod is rotated and translated to prevent the laser from burning a hole in its surface. Most evidence suggests that the vaporization plume consists principally of neutral atoms, although small amounts of ions and larger species may be present [9]. The target rod is positioned perpendicular to the 0.32 cm i.d. flow tube through which a helium carrier gas continuously flows at ~20 Torr. Following each laser pulse, the resulting vaporization plume is very hot. The plume is rapidly cooled by the helium flow as it is carried through the flow tube reactor. Calculations show that the heat is essentially dissipated to the channel walls in a time that corresponds to a travel distance of 0.5 cm down the flow tube; therefore, a concentration of supersaturated metal atoms is quickly established and clusters begin to form [9]. Experiments show that cluster growth terminates by the time the plume has traveled ~4 cm down the flow tube reactor [10].

Figure 2 shows a schematic diagram of the instrument. The clusters leave the flow tube reactor through a 1 mm diameter nozzle and expand into stage I, which is held at 10^{-3} Torr. The clusters are formed into a molecular beam as they pass through a 2.5 mm diameter conical skimmer and enter stage II which acts as a differential pumping chamber held at 10^{-4} Torr. Finally, the cluster beam enters stage III where it is ionized and detected by time-of-flight mass spectrometry (TOF-MS).

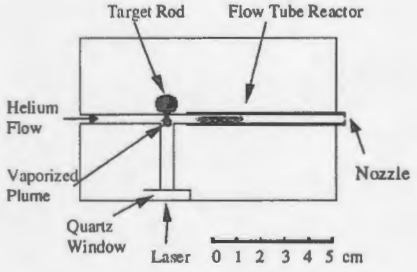

Figure 1. Schematic diagram of vaporization source and flow tube reactor

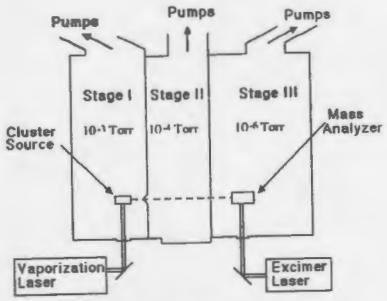

Figure 2. Schematic diagram of instrument

Multi-photon ionization is done using a 4.03 eV XeCl laser at high fluence. The firing of the laser is delayed with respect to the vaporization laser to allow time for the packet of clusters to travel to stage III. The TOF-MS is oriented perpendicular to the cluster beam above the ionization region. Due to this configuration, electrostatic deflector plates are required to extract the ions. They are accelerated at 3 kV down a 1 m flight tube. For a given deflector plate setting a cluster mass range corresponding to 20μs of flight time is detected; therefore, the entire spectrum is put together by joining mass range sections recorded at the appropriate deflector settings. The TOF-MS is also equipped with a reflectron. This is a series of retardation plates at the end of the flight tube that directs the ions back toward a detector at the front of the flight tube. This allows the ions to travel a total of 2 m, and provides a longer flight time, energy focussing, and better resolution. The ions are detected with a microchannel plate detector. Data are acquired and signal averaged over thousands of laser shots to improve signal-to-noise ratios.

An important consideration in this experiment is the isotopic abundance of species in the target rod. Although Al and Mn have single isotopes, Pd contains five significant isotopes. When dealing with multi-atom clusters, the mass distribution of a cluster will significantly broaden with the number of Pd atoms in the cluster. This is demonstrated in figure 3. The upper spectrum shows a distribution of clusters containing up to three Pd atoms. The lower spectrum

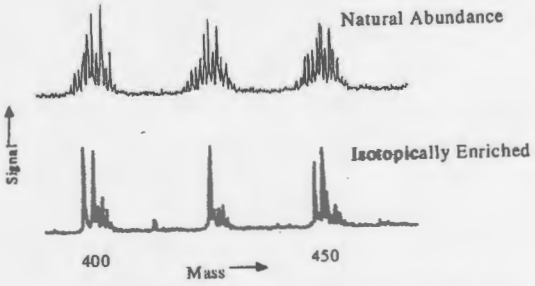

Figure 3. Time-of-flight mass spectra of clusters made from a natural Al-Pd-Mn target (upper), and an isotopically enriched Al-^{106}Pd-Mn target (lower).

shows the same mass region using a target rod with isotopically enriched Pd. By comparison, the upper spectrum is considerably complicated by isotopic substructure. This broadening and isotopic substructure decreases the resolvable mass limit. Using an isotopically enriched target rod eliminates these effects and significantly increases the resolvable mass limit.

The sample was prepared using the ^{106}Pd isotope. First the Al and Mn were pre-alloyed by arc melting at the ratios of Al 80.3 (v)% and Mn 19.7 (v)%. The resulting Al-Mn ingot was alloyed with the ^{106}Pd isotope at the proportions ^{106}Pd 51.46 (w)% and Al-Mn 48.54 (w)%. The ingot acquired by this final alloying process was quasicrystalline, as verified by x-ray diffraction. The laser ablation apparatus required the sample to be rod shaped with specific dimensions. To do this, the quasicrystalline ingot was ground into a powder and loaded into a custom made crucible. The crucible was spray formed using yttria-stabilized zirconia. This was sealed under argon in a tantalum can and sintered at 775°C for 24 hours. The final sample was a 2.83 cm rod that was 3.11 mm in diameter.

RESULTS

In this experiment, clusters were mass analyzed after a multi-photon ionization event. Multi-photon ionization provides a cluster with so much energy that it fragments into stable daughter ions. Experiments have shown that these ions do not decay further from the time they enter the TOF tube until they hit the detector. Clusters were detected with mass values matching PMI and Bergman clusters. This is shown in figure 4. The baseline becomes very noisy at these

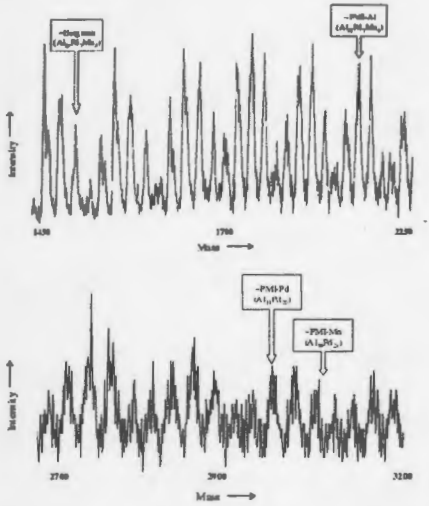

Figure 4. Mass spectra of multi-photon ionized clusters. Labels indicate where we would expect to find PMI and Bergman clusters. Masses for PMI clusters were calculated based on compositions described by Janot [5].

high masses because we are approaching the detection limit of the instrument. The peak broadening is due to random velocity vectors produced during fragmentation. At present, the clusters have not been characterized further. It is likely that these clusters are only mass coincident with PMI and Bergman clusters. They may not match the geometry and could even be of different composition. Nonetheless, if a particular cluster, such as PMI or Bergman, were especially stable, we would expect to see a peak of much greater intensity relative to neighboring peaks. These spectra show no indication of exceptional stability. Instead, many stable clusters have been produced in relatively similar quantities. This may indicate a pattern of stability over a large range of cluster sizes.

CONCLUSIONS

We have presented the initial results of our investigation of gas phase clusters formed by laser vaporization of icosahedral Al-Pd-Mn. Although clusters appear at mass values coincident with PMI and Bergman clusters, they are not especially stable relative to the surrounding masses. Further studies are required to conclusively determine cluster geometries and compositions.

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