

# Magic numbers in transition metal (Fe, Ti, Zr, Nb, and Ta) clusters observed by time-of-flight mass spectrometry

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We have measured time-of-flight (TOF) mass spectra of transition metal free clusters,  $TM_n$  (TM=Fe, Ti, Zr, Nb, and Ta and  $n$  is the number of atoms per cluster), produced by a laser vaporization source. The size resolved TOF intensities at  $n=7, 13, 15$  are much higher than those at the neighboring  $n$  values for all  $TM_n$ . Such specific  $n$  values are assigned to the magic numbers of these transition metal clusters and can be related to pentagonal bipyramid, icosahedron, and bcc structure units. The other magic numbers are observed for larger  $TM_n$ :  $n=19$  and  $23$  for Fe,  $n=19$  and  $25$  for Ti, being attributable to the polyicosahedron. The TOF spectra of Nb and Ta clusters are similar to each other and display the common magic number of  $n=22$ . © 1999 American Institute of Physics. [S0021-9606(99)01525-1]

## I. INTRODUCTION

Transition of physical and/or chemical properties from an atom to a bulk material is an attractive problem. Free clusters, which intervene between these two ultimates, have been paid much attention in the last two decades and the presence of magic number clusters has been one of the most interesting subjects. The following have been proposed for the origins of magic numbers. (i) An electronic shell structure comprises delocalized valence electrons in alkali- and noble-metal clusters: the magic numbers of  $n=8, 20, 40, \dots$  are related to the closed shells of  $n$  electrons in the spherical well potential.<sup>1</sup> (ii) A geometrically stable structure such as an icosahedron in the rare-gas atom clusters: the magic numbers of main shells are  $n=13, 55, 147, \dots$ , and those of subshells are  $n=19, 23, 25, \dots$ .<sup>2</sup> On the contrary, there have been only few reports on the magic numbers in transition metal clusters. However, Fe clusters have been intensively investigated for their chemical reactivity,<sup>3,4</sup> ionization potential,<sup>5,6</sup> photoelectron spectra,<sup>7</sup> dissociation energy,<sup>8</sup> and magnetism.<sup>9,10</sup> These results showed characteristic changes in the physical and chemical properties as a function of  $n$ .

Recently, we have found the magic numbers of  $n=13, 15, 19,$  and  $23$  in mass abundance spectra of Fe clusters,  $Fe_n$ , using a laser vaporization cluster source and a time-of-flight (TOF) mass spectroscopy.<sup>11</sup> In this report, we describe the magic numbers observed in transition metal (Fe, Ti, Zr, Nb, and Ta) clusters, and discuss them with the geometrical structures.

## II. EXPERIMENT

Metal clusters were produced from a laser vaporized cluster source similar to the one designed by Milani and de Heer<sup>10</sup> (Fig. 1). A pulsed second harmonic of Nd:YAG laser (Spectra Physics: GCR150), which was focused on a rotating metal rod, vaporized the rod surface. The focusing diameter was approximately 0.5 mm. Metal vapor thus obtained was cooled by He gas which was injected from a pulsed gas valve

(General Valve: Series 9) and synchronized with the vaporization laser. Metal clusters were formed in a small cell with  $1 \times 10^3 \text{ mm}^3$  in volume. The initial pressure in the pulsed valve was varied from 0.4 to 1 MPa to achieve suitable conditions of cluster formation for respective elements. Clusters were ejected from the source into vacuum through a 2 mm diameter nozzle. The cluster beam was passed through two 2.6 mm diameter skimmers in a two-stage differential pumping system and collimated. The mass resolved intensity of the clusters were analyzed by a linear time-of-flight mass spectrometer (TOF-MS) having similar configuration designed by Wiley and McLaren.<sup>12</sup> A distance between the cluster source and the TOF-MS entrance was about 1 m. Ion signals were detected by a microchannel plate (MCP), and accumulated in a digital oscilloscope (LeCroy: LC334) from 500 to 2000 times to reduce the statistical error. Positively autoionized clusters formed in the source were directly ejected and analyzed by the TOF-MS with no ionization process. On the other hand, neutral clusters were detected by ionization using an ArF excimer laser (Lambda Physics: COMPex100) at the entrance of the TOF-MS. In this case, autoionized clusters were deflected by a high voltage field located between the cluster source and the TOF-MS (Fig. 1).

## III. RESULTS

### A. Iron cluster

Figure 2 shows the cluster abundance spectra against  $n$  obtained by means of the TOF-MS for autoionized and positionized Fe clusters. In this figure, the intensities for clusters of  $n=7, 13, 15, 19,$  and  $23$  are much higher than those of the neighboring  $n$  values, being independent of autoionized and positionized conditions. Since these results are well reproducible within the present experimental conditions, we have called these numbers the magic numbers.<sup>11</sup>

Fe cluster has been investigated by many researchers from chemical and physical points of view. The chemical reactivity of Fe clusters changes markedly at around

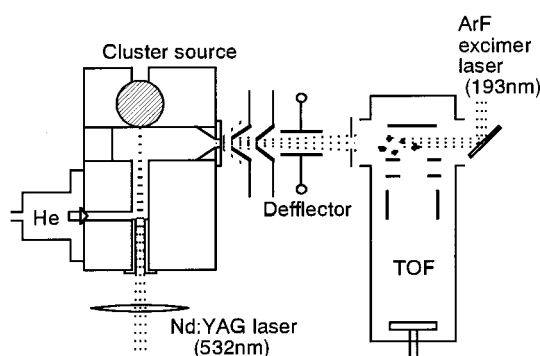


FIG. 1. Schematic drawing of the laser vaporization cluster source and the time-of-flight (TOF) mass spectrometer.

$\text{Fe}_{15}$ – $\text{Fe}_{16}$ ,  $\text{Fe}_{18}$ – $\text{Fe}_{19}$ , and  $\text{Fe}_{22}$ – $\text{Fe}_{23}$ ,<sup>4,13</sup> and structures of  $\text{Fe}_{13}$ ,  $\text{Fe}_{19}$ , and  $\text{Fe}_{23}$  are ascribed to the polyicosahedra, and that of  $\text{Fe}_{15}$  to bcc. The photoelectron spectra for  $\text{Fe}_n$  change at around  $\text{Fe}_{15}$ – $\text{Fe}_{16}$ ,  $\text{Fe}_{18}$ – $\text{Fe}_{19}$ , and  $\text{Fe}_{22}$ – $\text{Fe}_{23}$ . However, all of these structures were assigned to bcc. The inconsistency in the structure assignments is probably ascribed to the different cluster source conditions.<sup>7</sup> According to the collision induced dissociation experiment for Fe clusters,<sup>8</sup> the binding energy for  $\text{Fe}_7$ ,  $\text{Fe}_{13}$ ,  $\text{Fe}_{15}$ , and  $\text{Fe}_{19}$  are higher than the other size Fe clusters. These results agree with the magic numbers of Fe clusters observed in the present experiment.

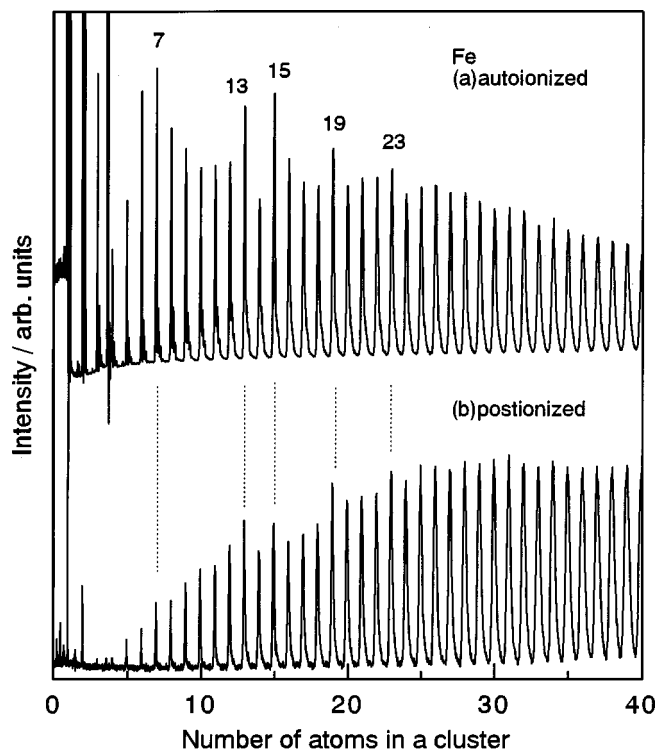


FIG. 2. TOF spectra of Fe clusters. (a) “autoionized” means the positive ion clusters directly ejected from the source, and (b) “postionized” means the neutral clusters ionized by an ArF excimer laser.

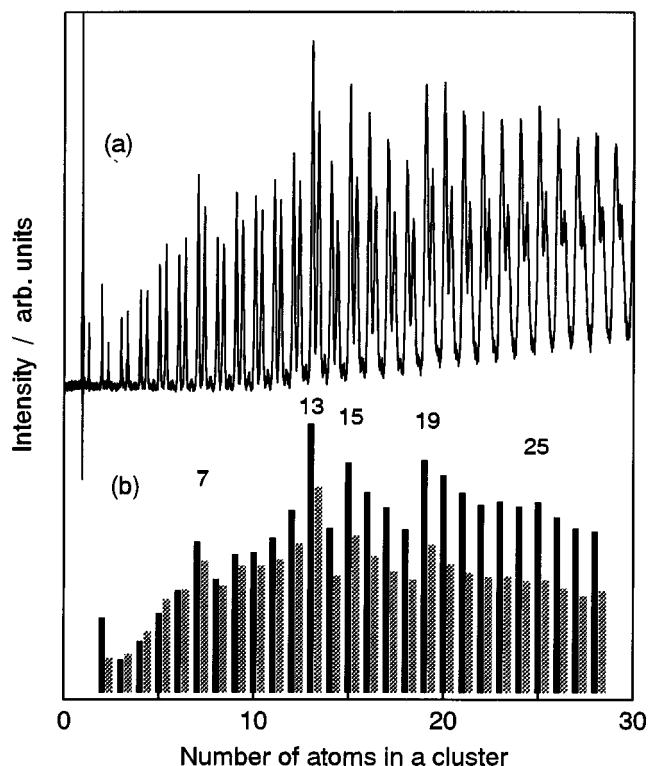


FIG. 3. (a) TOF spectrum of autoionized Ti cluster. (b) Peak height obtained from peak fitting of peaks in a spectrum (a). Solid and gray bars show the intensities of  $\text{Ti}_n$  and  $\text{Ti}_n\text{O}$  clusters, respectively.

## B. Titanium and zirconium clusters

Figure 3(a) shows the TOF spectra for the autoionized Ti clusters. In the Ti cluster spectrum, both metal and oxide clusters were detectable. Oxygen atoms included in Ti clusters mainly come from the oxidized target surface and partly from an impurity of He gas. Ti metal is so active to be used for a getter-pump and such oxygen contribution is more marked in comparison with the other elements. Since the mass-number of  $\text{Ti}_n$  reacting with three oxygen atoms, i.e.,  $\text{Ti}_n\text{O}_3$ , is the same as that of  $\text{Ti}_{n+1}$ , there is a possibility that  $\text{Ti}_n\text{O}_3$  affects the intensity of  $\text{Ti}_{n+1}$ . However, the intensity of  $\text{Ti}_n\text{O}_2$  is so weak that the influence of  $\text{Ti}_n\text{O}_3$  on the intensity of  $\text{Ti}_{n+1}$  is also negligible. Moreover, we may consider the influence of oxidization on the abundance of metal clusters through the reaction,  $\text{Ti}_n + \text{O} = \text{Ti}_n\text{O}$ . If  $\text{Ti}_n$  reacts less with O, the abundance of  $\text{Ti}_n$  is higher and that of  $\text{Ti}_n\text{O}$  is lower than others. Figure 3(b) shows peak height of  $\text{Ti}_n$  and  $\text{Ti}_n\text{O}$  clusters obtained by the peak fitting calculation of TOF spectrum shown in Fig. 3(a). As seen in Fig. 3(b), both  $\text{Ti}_n$  and  $\text{Ti}_n\text{O}$  show similar trend in the size dependent abundance, indicating that the oxidation gives no big influence on the appearance of magic numbers of  $\text{Ti}_n$ .

It has been also reported that  $\text{Ti}_n$  has higher binding energy at  $n=7, 13, 15,$  and  $19$ .<sup>8</sup> The intensities of  $\text{Ti}_{25}$  are also slightly higher than those of the neighboring ones in Fig. 3. This feature was observable under different cluster source conditions.<sup>14</sup> Therefore, we assign  $n=25$  is also the magic number for  $\text{Ti}_n$ .

Figure 4 shows the TOF spectra for the autoionized Zr cluster. The characteristic features of the TOF spectra of  $\text{Ti}_n$

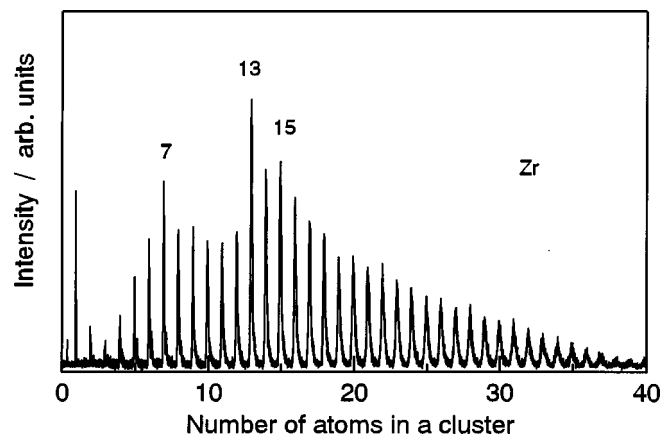


FIG. 4. TOF spectrum of autoionized Zr clusters.

and  $Zr_n$  are similar to that of  $Fe_n$ : the intensities of  $n=7, 13, 15,$  and  $19$  are higher than those of their neighbors, except  $n=19$  for the Zr cluster spectrum.

### C. Niobium and tantalum clusters

The abundance spectra of autoionized Nb and Ta clusters are shown in Fig. 4. The intensities become marked at  $n=7, 13,$  and  $15$  as observed for Fe, Ti, and Zr. It should be noted that Nb and Ta clusters show other features in the TOF spectra: the intensity becomes a minimum at  $n=19$ , gradually increases with  $n$  and becomes a maximum at  $n=22$ . The intensity at  $n=22$  is two times larger than that at  $n=19$ :  $n=22$  is a magic number for Ta and Nb. Similar features are observed from  $n=26$  (a minimum) to  $n=29$  (a maximum).

## IV. DISCUSSION

Assuming that metallic clusters are isotropic having compact structures, we qualitatively discuss the magic numbers observed in the present experiments. Since the bcc structure exists in the equilibrium phase diagrams of Fe, Ti, Zr, Nb, and Ta, it is a candidate structure of the present transition metal clusters. When one atom occupies a center of the bcc structure unit, there are eight and six atoms at the first and the second nearest-neighbor sites, respectively: the interatomic distance between the center and the first nearest-neighbor atoms differ only about 15% from that between the center and the second nearest-neighbor atoms. These 15 atoms form a geometrically stable bcc cluster, resulting in the magic number at  $n=15$  as seen in Figs. 2, 3, and 4. This magic number has been also supported by the specific chemical reactivity<sup>4,13</sup> and photoelectron spectra<sup>7</sup> for  $Fe_{15}$ .

The magic numbers of  $n=13$  and  $19$  can be attributed to the fcc structure including the first and the second nearest-neighbor atoms. However, the magic numbers from  $n=55$  to  $561$  have been observed for nickel and cobalt clusters using a near threshold photo ionization technique,<sup>15</sup> being ascribed to large icosahedron-type structures. Moreover, rare-gas atom clusters show typical magic numbers related to the icosahedron-type shell structures: the magic numbers of  $n=13, 55, 147, \dots$  originate from the main shells, and those of  $n=19, 23(25), 71, 87, \dots$  from the subshells.<sup>2</sup> Since both bulk

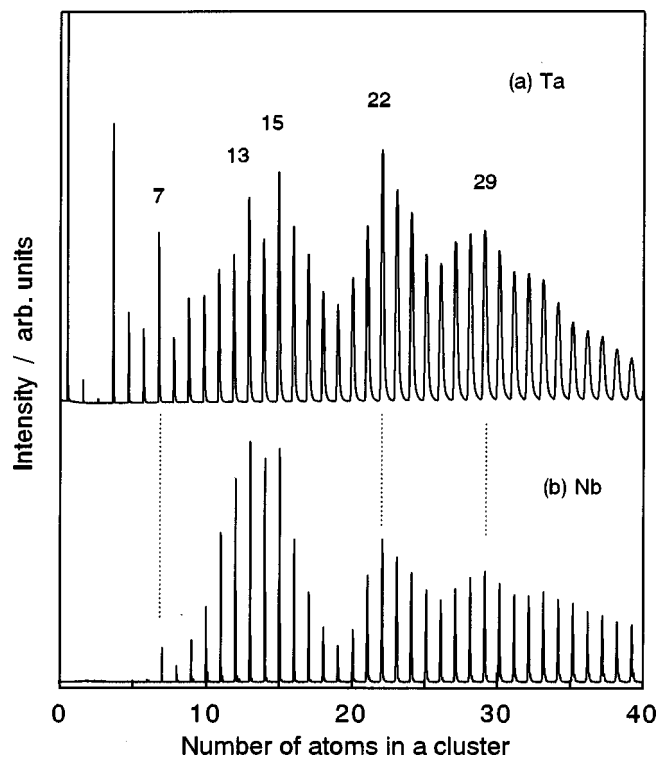


FIG. 5. TOF spectra of autoionized clusters: (a) Ta and (b) Nb.

metal- and rare-gas atom solids have isotropic and compact structures, the icosahedron-type structures are also plausible for small transition metal clusters (see Fig. 5):  $n=13, 19, 23,$  and  $25$  in small transition metal clusters,  $TM_n$ , are the icosahedron-based magic numbers. As shown in Fig. 6, the magic number of  $n=7$  is attributed to the pentagonal bipyramid which is the elemental unit of the icosahedron and the

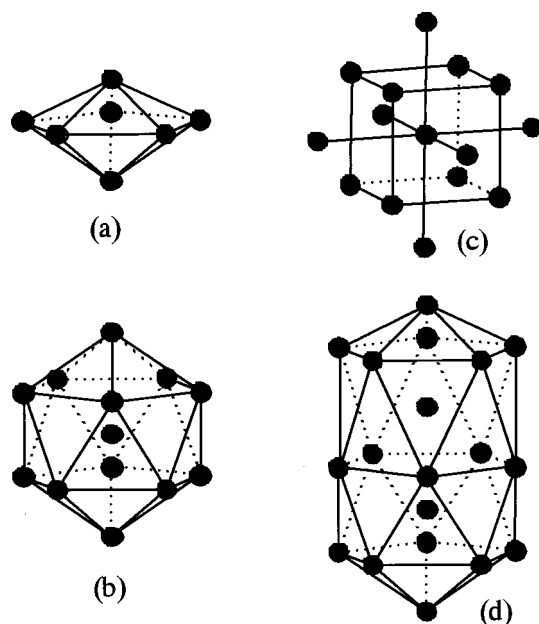


FIG. 6. Structural models for stable transition metal clusters: (a) pentagonal bipyramid ( $n=7$ ), (b) icosahedron ( $n=13$ ), (c) bcc ( $n=15$ ), and (d) double icosahedron ( $n=19$ ).

magic number of  $n = 19$  to a partial combination of the pentagonal bipyramid and icosahedral stacking.

Although the peculiar physical or chemical properties of transition metal clusters can be correlated to the magic numbers observed in the present experiments, only one report described the magic numbers in the TOF spectra of  $Fe_n$  (Ref. 16) within our knowledge. Then, we have to ask why the magic numbers can be observed in present experiment. It has been reported that large clusters are first produced by laser vaporization and they are decomposed to smaller ones.<sup>17</sup> The excess cluster energy, i.e., the high temperature and multiple charge cause fragmentation of cluster. The  $Fe_n$  and  $Ti_n$  clusters with  $n = 7, 13, 15,$  and  $19$  shows higher binding energy,<sup>8</sup> and these numbers are consistent with the magic numbers observed in the present experiment. In this context, fragmentation of the cluster is the main process to give higher abundance for stable clusters than other clusters, and the origin of this fragmentation is a key point to understand clustering process in the laser vaporization cluster source. Therefore, present results suggest that rather high cluster temperature is achieved in the laser vaporization cluster source and stable clusters thermally remain as magic number clusters in TOF spectra. On the other hand, the measurement of Fe cluster magnetic moment indicated that the cluster temperature is comparable to the nozzle temperature.<sup>18</sup> Hence, fragmentation of the cluster is no longer caused after ejecting from the cluster source. In order to confirm this argument, we need further systematic studies, such as a forming ability of magic numbers as functions of the laser intensity, the cluster source temperature, etc.

The origin of magic numbers  $n = 22$  and  $29$  for Nb and Ta cluster is unclear at this moment. However, it should be noted that Nb and Ta belong to the same Va group in the periodic table. The valence electrons may participate in their stability.

## V. CONCLUSION

There are the magic numbers in the TOF spectra of Fe, Ti, Zr, Nb, and Ta clusters produced with a laser vaporization cluster source. The common magic numbers,  $n = 7$  and  $13$ , are attributable to the pentagonal bipyramid and icosahedron, while  $n = 15$  to the bcc structural unit. The larger magic

numbers,  $n = 19$  and  $23$  ( $25$ ) for Fe and Ti are attributable to the polyicosahedra. In Fe clusters, the magic numbers are consistent with their peculiar change of chemical reactivity, photoelectron spectra, and dissociation energy. Nb and Ta clusters show other magic numbers of  $n = 22$  and  $29$ , even though the origin of these magic numbers is unclear in our experiment.

## ACKNOWLEDGMENTS

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