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Fragment spin multiplicities in the fission $Ag_{23}^{2+} \rightarrow Ag_{12}^{+} + Ag_{11}^{+}$

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We examine the fragment spin multiplicities in the fission $Ag_{23}^{2+} \rightarrow Ag_{12}^{+} + Ag_{11}^{+}$ using the jellium model which allows axially symmetric deformations and fission. The fission is investigated along two fission paths, one leading to two prolatelike fragments and the other resulting in two oblatelike fragments. It is shown that the former path produces the low-spin $Ag_{11}^{+}(S=0)$ and the low-spin $Ag_{12}^{+}(S=\frac{1}{2})$, but the latter path produces the high-spin $Ag_{11}^{+}(S=1)$ and the high-spin $Ag_{12}^{+}(S=\frac{3}{2})$. Therefore the ratio of fission barriers along the two different paths will be estimated from the abundance ratio of two different spin fragments.

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The shell model for simple metal clusters explains the magic numbers seen in the mass abundance spectra as the shell closing numbers for the valence electrons in a spherical effective potential [1]. For example, the magic number 8 corresponds to the closed shell configuration $1s^2 1p^6$, and the magic number 20 corresponds to the closed shell configuration $1s^2 1p^6 1d^{10} 2s^2$. Clusters with open shell configurations are unstable; thus they may be reactive just as open shell atoms are. Saito and Ohnishi considered Na_{19}, whose valence electron configuration is a closed shell configuration plus one s electron, as a giant alkali-metal atom and studied the fusion $2Na_{19} \rightarrow Na_{38}$ using the jellium model in order to explain the relatively high abundance of Na_{38} in the mass abundance spectrum [2].

Clusters with open shell configurations often have deformed stable shapes. The deformation is due to the Jahn-Teller effect where the splitting of the degenerate levels caused by the deformation lowers the total energy. The splitting patterns of the degenerate levels depend on the symmetry of the deformation. For example, a prolate deformation will split $1p$ levels into 2σ and 1π levels in energy increasing order while an oblate deformation will split them into those in the reversed order [3]. The splitting patterns for d levels also depend on whether the deformation is prolate or oblate. It is known for a transition-metal atom in a crystal field that the spin multiplicity of the atom depends on the splitting pattern of the d levels. If we make an analogy between a metal cluster with d electrons and a transition-metal atom, and consider the deformation as something corresponding to the crystal field, it is natural to think that the spin multiplicity of the cluster may depend on the deformation of the cluster.

In a previous study of the fission of doubly charged silver clusters, we noticed that in some cases the fission barrier to two oblatelike fragments is comparable to the fission barrier to two prolatelike fragments [4]. Then the fragments from these two different fission paths may result in products with different spin multiplicities. If this is the case, the ratio of fission barriers along the two different paths will be estimated from the measured abundance ratio of two different spin fragments, which will be a great help in obtaining a reliable model for metal cluster fission processes. In this Rapid Communication we consider the fission $Ag_{23}^{2+} \rightarrow Ag_{12}^{+} + Ag_{11}^{+}$ using the jellium model and show that the spin multiplicity of fragments indeed depends on the fission path.

The valence electron configuration in the spherical effective potential for Ag_{12}^{+} is $1s^2 1p^6 1d^3$ and that for Ag_{11}^{+} is $1s^2 1p^6 1d^2$. In a prolately deformed potential the $1d$ levels will split into 3σ, 2π, and 1δ levels in energy-increasing order, but in an oblate potential they may split into 1δ, 3σ, and 2π levels in energy-increasing order. Therefore Ag_{11}^{+} will have $S=0$ if the deformation is prolate and $S=1$ if the deformation is oblate according to Hund's rule. The spin multiplicity of Ag_{12}^{+} is a little more complicated. If the deformation is prolate, Ag_{12}^{+} will have $S=1/2$. For the oblate deformation Ag_{12}^{+} will have $S=1/2$ if the splitting between the 1δ and 3σ levels is large, but will have $S=3/2$ if the splitting is small.

We examine the fission $Ag_{23}^{2+} \rightarrow Ag_{12}^{+} + Ag_{11}^{+}$ using the jellium model where valence electrons are moving in a uniform positive background [5,6]. We solve the jellium model by the Kohn-Sham density-functional procedure [7,8] using the local spin density functional of Perdew and Zunger [9]. The Kohn-Sham equation is solved by the discrete variable representation [10] using zeros of the sine function as the basis for the z coordinate and the zeros of the Bessel function of the zeroth order as the basis for the ρ coordinate, where $\rho = \sqrt{x^2+y^2}$. The problem of almost degenerate energy levels is handled by broadening the occupation numbers using the finite temperature distribution. The temperature is set to 100 K for the present calculations. The details of the numerical method will be found elsewhere [11].

The shape of the background jellium is defined by the following shape function:

$$\rho_s(z) = s\{[1-(z/s)^2][A + 2\alpha B z/s + B(z/s)^2\}^{1/2}, \quad (1)$$

where A, B, and α are parameters for elongation, neck formation, and asymmetry, respectively, and s is the scaling parameter to maintain constant volume of the jellium. The volume of the jellium is calculated as the product of the

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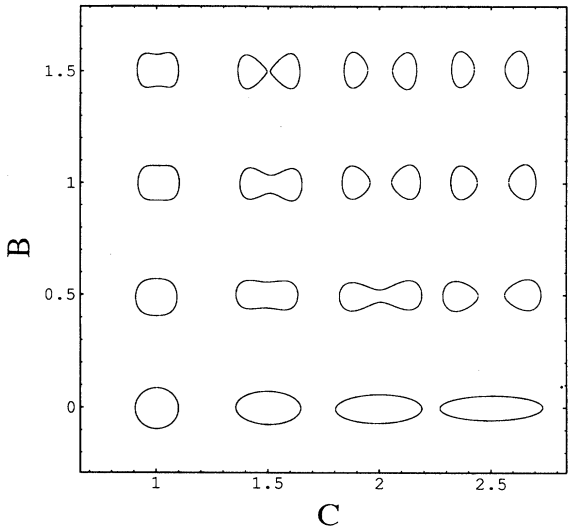

FIG. 1. Shapes of the background jellium at various values of B and C for $Ag_{23}^{2+} \rightarrow Ag_{12}^{+} + Ag_{11}^{+}$ ($\alpha = 0.0116$).

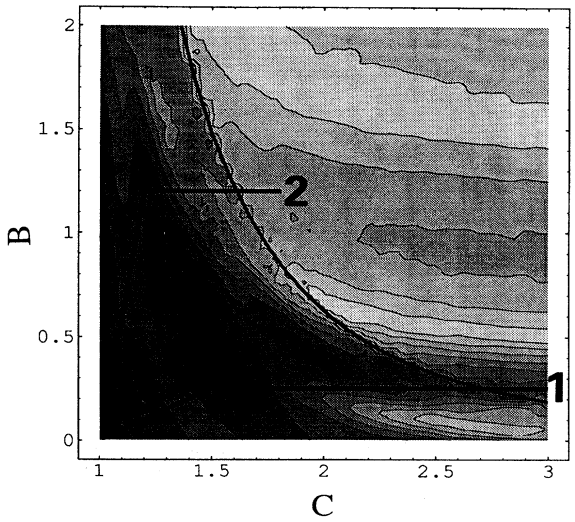

FIG. 2. Contour plot of the total energy for $Ag_{23}^{2+} \rightarrow Ag_{12}^{+} + Ag_{11}^{+}$ by the shell correction method. The zero of the energy is the liquid drop energy at $C=1$, $B=0$. The contours are from 1 to 9 eV with a spacing of 1 eV. The gray levels of the shading run from black to white with increasing energy. The lines denoted by 1 and 2 are path 1, $B=0.5(C-1), 1 \leq C \leq 1.5$ and $B=0.25, 1.5 \leq C \leq 3$; and path 2, $B=6(C-1), 1 \leq C \leq 1.2$ and $B=1.2, 1.2 \leq C \leq 1.75$, respectively. The solid curve is the fission line.

number of atoms in the cluster and the volume of the sphere of the Wigner-Seitz radius r_s (3.02 a.u. for silver). The surface of the jellium is defined by $\rho_s(z)=\rho$. This is a modified version of the one used in nuclear physics [12]. The modification is made so that the ratio of the volumes of the fragments is constant on the fission line

$$B = 1/C^3(0.2+\alpha^2), \tag{2}$$

where $C=(A+B/5)^{-1/3}$ is another elongation parameter. We are going to use C for the elongation parameter instead of A from now on. The asymmetric parameter α is fixed depending on the fragments volume ratio as

$$N_1/N_2 = (\alpha-1)^4(4+\alpha)/(\alpha+1)^4(4-\alpha), \tag{3}$$

where N_1 and N_2 are the numbers of the atoms in fragment 1 and fragment 2, respectively.

In Fig. 1 the shapes of the jellium at various values of B and C are depicted. In Fig. 2 the two fission paths we have considered are depicted, where path 1 leads to two prolate-like fragments and path 2 leads to two oblatelike fragments. These two paths have small fission barriers according to the total energy estimate by the shell correction method. The shell correction estimate of the total energy is also depicted in Fig. 2 together with the fission line.

Here we briefly summarize the shell correction method we have employed [4,12,13]. In the shell correction method the total energy is a sum of the liquid drop energy and the shell correction. We calculate the liquid drop energy as a sum of the volume energy, the surface energy, and the Coulomb energy. Because the volume energy is constant through the fission process, it is omitted. The surface energy is given by

$$E_{surf} = \sigma S, \tag{4}$$

where σ is the surface energy per area and S is the surface area. We simply adopt the bulk value for σ (900 erg/cm^2 for silver).

The Coulomb energy is calculated by treating the liquid drop as an ideal conductor. Then the electric charge distributes only on its surface. The Coulomb energy is given by

$$E_{Coulomb} = \begin{cases} eZ\phi/2 & \text{before fission,} \\ eZ_1\phi_1/2 + eZ_2\phi_2/2 & \text{after fission,} \end{cases} \tag{5}$$

where Z, Z_1, and Z_2 are charges on the parent cluster and its fragments, respectively, and ϕ, ϕ_1, and ϕ_2 are the electrostatic potentials for them, respectively.

The shell correction is the energy fluctuation from the average arising from the inhomogeneous distribution of the valence electron levels. It is given by

$$E_{shell} = \sum_{i=1}^{\infty} n_i\epsilon_i - \int_{-\infty}^{\epsilon_F} \epsilon\Gamma(\epsilon)d\epsilon, \tag{6}$$

where ϵ_i and n_i are the energy and the occupation number of the ith orbital for an electron in the effective potential, $\Gamma(\epsilon)$ is a smooth density of states of the electron levels in the same potential, and ϵ_F is the Fermi energy associated with the smooth density of states. We use a cavity potential with the shape of the jellium as the model potential for the effective potential. The semiclassical density-of-states formula by Balian and Bloch [14] is used for $\Gamma(\epsilon)$.

In Fig. 3 the total energy along path 1 is depicted. The zero of the energy is taken at $C=0$ for both the jellium calculation and the shell correction estimate. The jellium splits at $C=2.72$. There is a local minimum around $C=1.8$. The barrier between the spherical position and the minimum at $C=1.8$ is 1.0 eV. The total energy at the minimum is -1.1 eV, and the barrier between the minimum and the fragmentation is 0.1 eV; thus the internal energy of 1.2

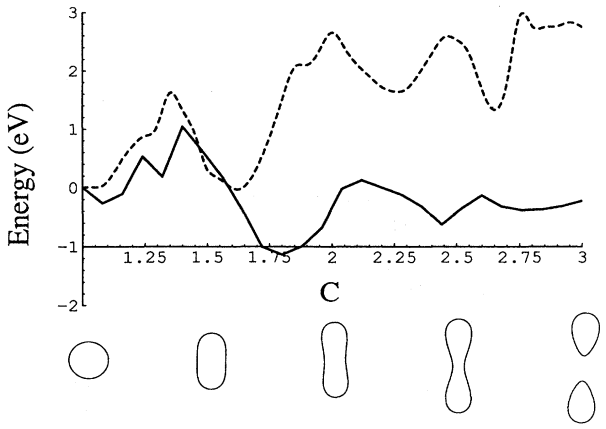

FIG. 3. The total energy along path 1 by the jellium model (solid line) and by the shell correction method (dashed line). The shapes are at $C=1$, 1.5, 2, 2.5, and 3.

eV is needed for the fission from this minimum. If the cluster resides around the spherical position, the internal energy of 1.0 eV is enough for the fission. The agreement between the shell correction estimate and the jellium estimate is good around $C=0$, but the former goes much higher than the latter as C increases. The present shell correction method neglects the spill-out of electrons outside the jellium and the curvature contribution to the liquid drop energy. It is apparent that these must be incorporated to improve the shell correction estimate. Also it is known that the simple jellium model underestimates the surface tension for silver because it fails to satisfy the mechanical equilibrium condition [15]. The jellium model must be improved to satisfy the mechanical equilibrium condition [16,17].

The total energy along path 2 is shown in Fig. 4. The jellium splits at $C=1.61$. There is a local minimum at $C=1.3$ with the total energy 0.8 eV. The barrier between the spherical position and the local minimum at $C=1.3$ is 1.6 eV. The barrier between this local minimum and the fission is 1.5 eV. Therefore if the cluster resides in these local minima, the internal energy of 0.7 eV is enough for the fission. The agreement between the shell correction estimate and the jellium estimate is good around $C=0$, but again the former goes higher than the latter as C increases.

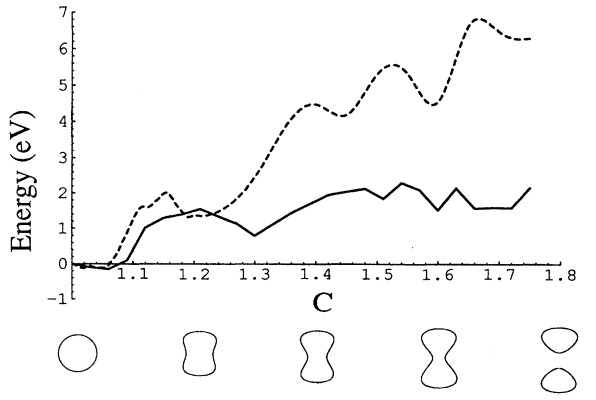

FIG. 4. The total energy along path 2 by the jellium model (solid line) and by the shell correction method (dashed line). The shapes are at $C=1$, 1.2, 1.4, 1.6, and 1.8.

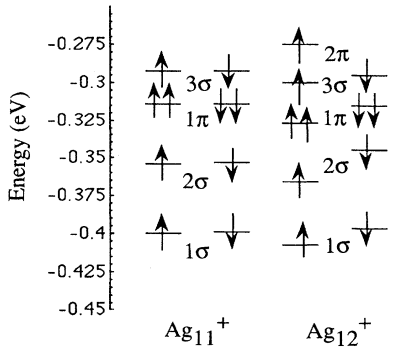

FIG. 5. The orbital energies of Ag_{11}^{+} and Ag_{12}^{+} at $C=2.76$ along path 1.

The orbital energies of Ag_{11}^{+} and Ag_{12}^{+} at $C=2.76$ along path 1 are depicted in Fig. 5. Prolatelike deformations split $1p$ levels into 2σ and 1π in energy-ascending order, and 3σ is the lowest among the split $1d$ levels. The valence electron configuration for the fragment Ag_{12}^{+} is $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2 2\pi^1$ and that for the fragment Ag_{11}^{+} is $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2$. Therefore the fragment Ag_{12}^{+} is in the low-spin $S=1/2$ state and the fragment Ag_{11}^{+} is in the low-spin $S=0$ state.

In Fig. 6 the orbital energies of Ag_{11}^{+} and Ag_{12}^{+} at $C=1.66$ along path 2 are shown. Oblatelike deformations split $1p$ levels into 1π and 2σ in energy-ascending order and 1δ is the lowest of the split $1d$ levels. The fragment Ag_{12}^{+} has the valence electron configuration $1\sigma^2 1\pi^4 2\sigma^2 1\delta^2 3\sigma^1$, resulting in the high-spin $S=3/2$ state. The fragment Ag_{11}^{+} has the $1\sigma^2 1\pi^4 2\sigma^2 1\delta^2$ configuration, resulting in the high-spin $S=1$ state.

Now we examine the possibility of the production of the high-spin Ag_{12}^{+} or Ag_{11}^{+}. If Ag_{23}^{2+} is in the prolatelike deformed minimum around $C=1.8$ along path 1, the internal energy needed for the fission to two prolatelike fragments is 1.2 eV, but that to two oblatelike fragments is 2.6 eV. Therefore most of the products will be the low-spin Ag_{12}^{+} and the low-spin Ag_{11}^{+}. But if the fission starting with Ag_{23}^{2+} re-

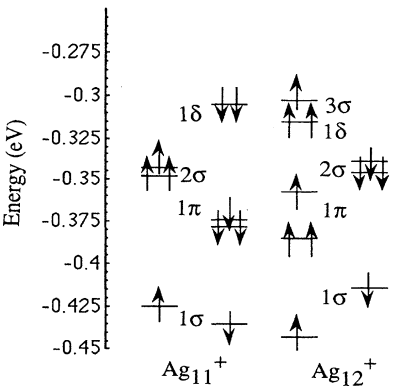

FIG. 6. The orbital energies of Ag_{11}^{+} and Ag_{12}^{+} at $C=1.66$ along path 2.

sides around the spherical position, then the internal energy needed for the fission to two prolatelike fragments is 1.4 eV and that to two oblatelike fragments is 1.6 eV. Therefore there will be a significant amount of high-spin Ag_{12}^{+} and high-spin Ag_{11}^{+} in the products.

Our fission barrier estimate is based on the jellium calculation, which is known to underestimate the surface tension for the silver crystal surface. Therefore the real fission barrier may be different from the estimate presented in this work. But the spin multiplicity of the fragment will be correctly described by this model because it arises from the shell structure of the valence electrons. Note also that the existence of more than one spin state for a simple metal cluster cannot be described by the present shell correction method.

Now we consider a possible way to make spherical Ag_{23}^{2+}. It may be produced by the electron attachment of Ag_{23}^{3+}. Because Ag_{23}^{3+} has the magic number 20 valence electrons, it should be spherical. The fissility parameter $f=E_{Coulomb}/2E_{surf}$ calculated by the spherical liquid drop model is 0.49 for Ag_{23}^{3+}. Therefore it is metastable according to the liquid drop model prediction [18]. By adding an electron to Ag_{23}^{3+} it will be possible to start the fission $Ag_{23}^{2+} \rightarrow Ag_{12}^{+} + Ag_{11}^{+}$ from the spherical position.

There may be many different ways that the high-spin Ag_{12}^{+} or Ag_{11}^{+} can be formed. It will be worth checking the existence of the high-spin Ag_{12}^{+} or Ag_{11}^{+} in the conventional metal cluster sources.

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