Spin polarization of high-symmetry clusters of simple metals in the ground state

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A calculation from "first principles" shows that the ground state of high-symmetry Na clusters corresponds to a projection of the spin magnetic moment equal to 5_{μ_B}. The effect is produced because of the characteristic features of the single-particle spectrum, which are attributable to the small deviation of the self-consistent field in the cluster from the spherically symmetric field.

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Experimental studies of 13-atom clusters of mercury in zeolite cavities indicate a complicated dependence of the magnetic susceptibility χ on the temperature T and magnetic-field intensity H.[1] In each case the samples are paramagnetic materials, and at small T and large H the magnetic moment can amount to several Bohr magnetons μ_B per cluster. As noted by the authors of Ref. 1, the explanation of such properties remains unclear, since both zeolite and massive mercury are diamagnetic materials. Setting aside the complicated question of the dependence of χ on T and H, we would like to emphasize that the ground state of high-symmetry clusters of simple metals can correspond to large values of the spin magnetic moments.

This fact is a consequence of the single-particle spectrum of valence-electron energies, which were used, for example, in calculations of Al[2] and Be[3] clusters. The single-particle levels can be collected into groups that are separated from each other by large gaps. The location of the centers of gravity of these groups is in good agreement with the discrete spectrum of a spherical potential well (PW) whose radius is equal to the cluster radius, while the bottom is lower than the first filled level. A splitting of the PW levels occurs in the spectrum of a given cluster in accordance with its symmetry. An important characteristic of the spectrum of high-symmetry clusters is the small splitting compared with the distance between the groups of levels. This situation is normal, since the behavior of the valence electrons of simple metals is determined within the atomic spheres by the weak pseudopotential field.

If a certain group of levels is not completely filled, then the ground state can be a spin-polarized (SP) state with the maximum projection of the total spin, consistent with the Pauli principle. To analyze this assumption, we chose three clusters: $Na_9(Na_1Na_8)$, $Na_{13}(Na_1Na_{12})$, and $Na_{15}(Na_1Na_8Na_6)$. We calculated their electron structure by using the self-consistent method of scattered waves in the $X\alpha$ approximation for the local exchange potential (SCA SW $X\alpha$) for various combinations of occupation numbers. All clusters had the O_h point symmetry. One atom was at the geometrical center. The interatomic distance between the nearest atoms was 7.02 at. units for each cluster. The radius of the atomic "muffin-tin" spheres was equal to 3.51 at. units. The group of 8 atoms had the (111) geometrical configuration, that of

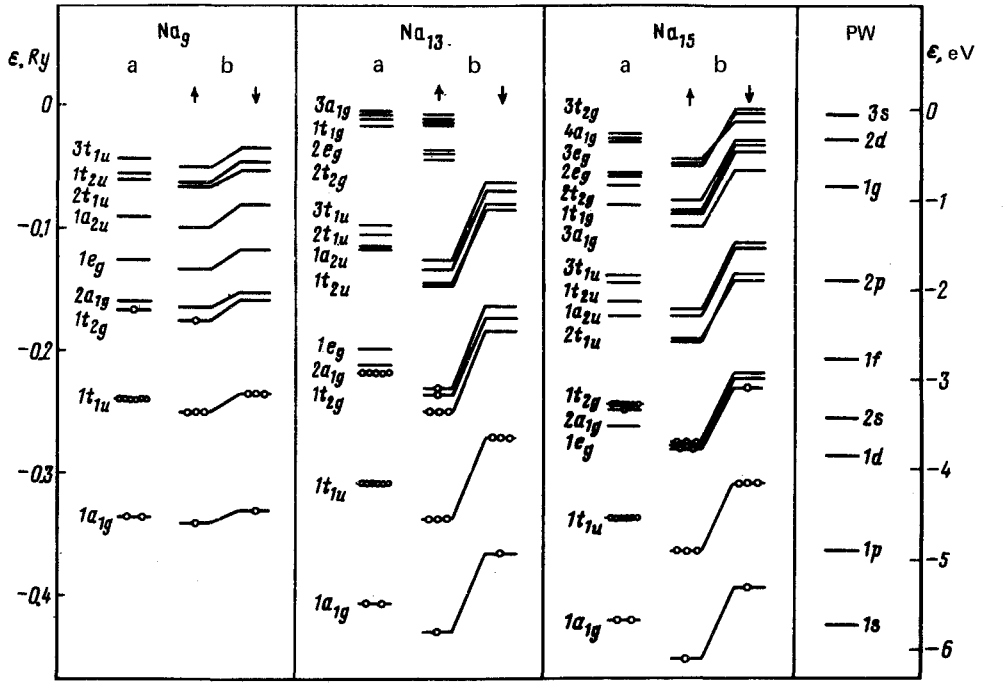

FIG. 1. (a) Single-particle energies ϵ of SNP and (b) of the SP ground states of Na_9, Na_{13}, and Na_{15} clusters. The circles represent the number of electrons in single-particle levels. The PW energy spectrum ($R = 11.62$ at. units and $V_0 = 6.39$ eV) is shown at the right.

12 atoms had the (110) configuration, and that of 6 atoms had the (200) configuration. Each cluster was surrounded by a Watson sphere with a radius R_W (10.53 at. units for Na_9 and Na_{13} and 11.62 at. units for Na_{15}). The exchange parameter α was equal to 0.73115.

Figure 1 shows the results of a calculation of the single-particle energies ϵ, which were measured from the vacuum zero for the spin-nonpolarized (SNP) and SP ground states of each cluster. We can see that the $1t_{2g}$, $2a_{1g}$, and $1e_g$ levels are not completely filled by electrons and that they are separated from the adjacent levels by a gap. The $t_{2g}-e_g$ decreases with increasing coordination number. For comparison, the spectrum of a PW, which has a radius of 11.62 at. units and a depth of 6.39 eV (the depth is determined by a fitting requiring that it approximate the spectrum of the Na_{15} cluster), is shown on the right-hand side of Fig. 1.

The total energy of the clusters, which was calculated by us using the SCA $X\alpha$ method,[4] shows that the SNP states of the clusters are stable for the chosen interatomic spacing. The binding energy is 0.59, 0.71, and 0.59 eV/atom for Na_9, Na_{13}, and Na_{15}, respectively. We note that the experimental value for the bulk metal is 1.13 eV/atom.[5] Spin polarization leads to an additional reduction of the total energy. Let us assume that $\mu = q_\uparrow - q_\downarrow$ is the spin excess, which is equal to the difference in the number of electrons having upward and downward spins. It follows from the calculations, therefore, that the ground state of Na_9 is an SP state with $\mu = 1$, while

those of Na_{13} and Na_{15} are the SP states with $\mu = 5$. In this case the reduction in the total energy of the ground state of Na_{13} and Na_{15}, compared with the SNP state, is appreciable: 0.68 and 1.12 eV, respectively. A variation in the total energy can also be accurately estimated ($\lesssim 5\%$ relative error) directly from the single-electron spectra in the transition state.

It also follows from the calculations that the total energy is determined primarily by the value of μ, and for a given μ it depends to some extent on the filled levels within a given group and on those that are not filled. As μ increases, the total energy initially decreases, reaches a minimum at a certain μ, and then begins to increase. Thus, the dependence of the total energy on the projection of the spin moment $M_s = \mu/2$ obeys an analog of the Hund law for a field that differs slightly from a spherical field.

The causes leading to a spin polarization are not characteristic of valence $3s$ orbitals of Na, and a similar behavior should be expected for clusters of other simple metals. A comparison with the PW model makes it possible to predict that the projections of the spin moments can amount to 5 or $7\mu_B$ for high-symmetry clusters containing 13 or 27 valence electrons, respectively. In particular, the electron configuration of Hg_{13} must be "created" by the $1s^2 1p^6 1d^{10} 2s^2 1f^6$ PW configuration; consequently, it is more sensible to compare the magnetic properties of such clusters with the properties of Sm^{2+} ions, rather than those of Fe, as suggested in Ref. 1.

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