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## Magnetic Silicon Nanoparticles

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# Magnetic Silicon Nanoparticles

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## Abstract

Prospects for diamond-structured magnetic Si are investigated experimentally, by model calculations, and numerically. Our theoretical analysis, using bond-orbital, Vienna *ab-initio* simulation package, and SIESTA calculations, suggest that some diamond-Si imperfection may carry a magnetic moment. In particular, for tetrahedral Si<sub>5</sub> clusters, we calculate a magnetic moment of 4  $\mu_B$  per cluster. These moments are more likely to be observed in nanoparticles, as compared with thin films, due to the larger surface-to-volume ratios of the former and to their more versatile atomic surface structure. Experimentally, we have prepared Si nanoparticles by cluster deposition and found a small magnetization of 2.9 emu/cm<sup>3</sup> at 10 K.

**Keywords:** exchange, impurity magnetism, local magnetic moments, magnetic nanoparticles

## I. Introduction

The occurrence of magnetism in nontransition-metal elements has been an intriguing research topic for more than a century, fueled by scientific curiosity and by potential applications in spin electronics. Conventional wisdom restricts magnetism to transition metals with partially filled inner shells, as indicated by the Stoner criterion. Recent research on oxides has revised this view,<sup>[1,2]</sup> leading to concepts such as *d*<sup>0</sup> magnetism, and molecular

oxygen,  $O_2$ , has been known to be paramagnetic for a long time. In such materials, magnetism arises from oxygen or cation vacancies.<sup>[3,4]</sup>

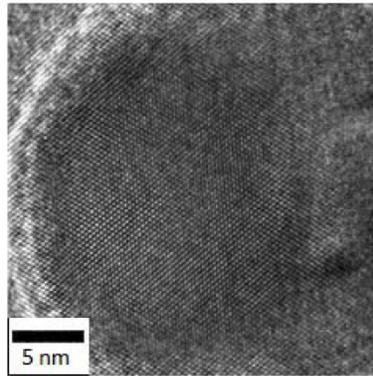
Our focus is on silicon, which is the most important material in present day electronics and where the situation is more complicated. Diamond-Si, as contrasted to graphitic silicon and silicene,<sup>[5]</sup> forms very stable crystals with tetrahedral coordination and a moderately large bandgap at the Fermi level  $E_F$ . More generally, among the elements of main group IV, the graphene structure becomes less favorable as the elements gets heavier. The ground state of the lightest of the elements, C, is graphite, with diamond carbon having a slightly higher energy, but starting with Si, the diamond structure is more favorable than the graphite structure.

The diamond-Si bandgap is adverse to magnetic-moment formation, because the Stoner criterion requires a high density of states (DOSs) at  $E_F$ . It is conceivable, however, that specific atomic configurations at surfaces support a magnetic moment, and there is experimental as well as theoretical research in this direction.<sup>[6,7]</sup> However, this paper focuses on Si nanoparticles, whose magnetism has not been investigated in the past. Going from thin films to nanoclusters is likely to enhance the density of moment-carrying defects, because the surface-to-volume ratio is large and because nanoparticles tend to exhibit a broader variety of crystalline imperfections.

Compared with bulk and thin-film Si, the magnetism of Si nanoparticle has not been investigated so far. In this paper, we produce Si nanoparticles by cluster deposition, study the structure and magnetism of the particles, and investigate the magnetic moment of Si by model calculations and numerically, using the Vienna *ab-initio* simulation package (VASP) and SIESTA codes.

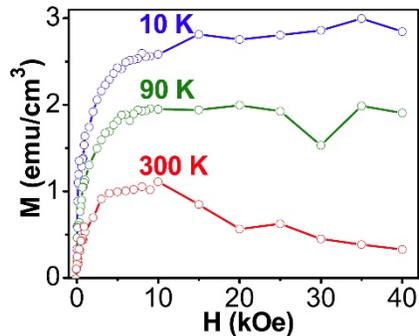
## II. Experimental Work

Our gas-phase cluster-deposition system<sup>[8,9]</sup> has been used to deposit Si nanoparticles on carbon-coated Cu grids and single crystalline Si (001) substrates for transmission electron microscope (TEM) and SQUID magnetometer measurements, respectively. Figure 1 shows a high-resolution TEM image of a typical Si nanoparticle; the average particle size estimated from a low-resolution TEM image is  $\sim 26$  nm (not shown here). The basic crystal structure is diamond-like, and this structure is nearly perfect in the middle of the particle, but the lattice is much less developed at the surface, with many imperfections.



**Figure 1.** Silicon nanoparticle. The crystal structure is diamond-cubic with  $a = 0.54$  nm. The nearly perfect lattice in the middle of the particle contrasts with the rugged structure near the surface.

Figure 2 shows the field-dependent magnetization curves for Si nanoparticles at different temperatures. The nanoparticles exhibit a small magnetic moment, corresponding to a saturation magnetization of 2.9 emu/cm<sup>3</sup> at 10 K. This is consistent with a small fraction of surface Si atoms carrying a magnetic moment, but it is not known at this stage whether this phantom magnetic signal involves non-Si elemental impurities.



**Figure 2.** Field dependence of the magnetization of diamond-Si nanoparticles, measured at different temperatures. Note that the magnetization curves are corrected with the strong diamagnetic slope of the Si (001) substrate.

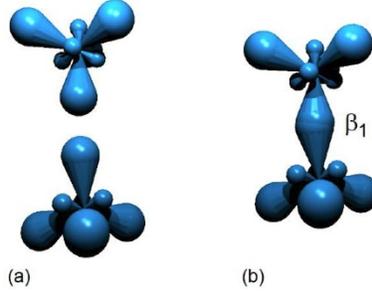
### III. Bond-Orbital Theory

The main structural feature of elemental Si is the diamond-like tetrahedral coordination of the atoms, which makes  $sp^3$  hybrids a natural basis for the analysis of the electronic structure. Figure 3(a) shows the relative orientation of the  $sp^3$  hybrids in the diamond structure. The main interaction between the hybrids on neighboring atoms is described by the hop-

ping parameter  $\beta_1$ ,  $\sim 4.28$  eV for Si.<sup>[10]</sup> This hopping integral describes hybrid orbitals directly pointing at each other, leading to an overlap of the large  $sp^3$  lobes, as shown in figure 3(b). In terms of fundamental Slater-Koster hopping integrals<sup>[11]</sup>

$$\beta_1 = \frac{1}{4}(V_{ss\sigma} - 2\sqrt{3}V_{sp\sigma} - 3V_{pp\sigma}) \quad (1)$$

The smaller hopping integrals  $\beta_2$ ,  $\beta_3$ , and  $\beta_4$  are characterized by the involvement of one or more of the smaller lobes of the  $sp^3$  hybrids.



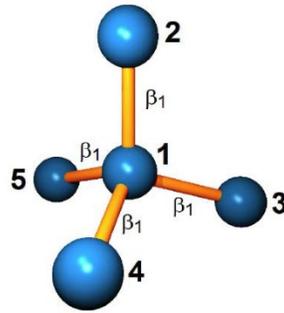
**Figure 3.** Hybrid orbitals in Si. (a) Unperturbed  $sp^3$  orbitals and (b) leading interaction between neighboring atoms.

A very simple theoretical explanation of possible Si moments is given by the bond-orbital model,<sup>[10,12]</sup> which provides a qualitatively correct explanation of the bandgap of Si. In the specific definition of [10], the model considers the leading hopping term  $\beta_1$  only but ignores the other hopping integrals and the promotion energy  $\varepsilon_p - \varepsilon_s$ , which determines the accuracy of the hybrid description.

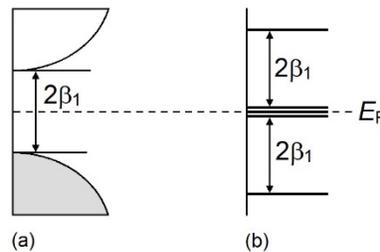
Figure 4 describes the bond-orbital picture for a hypothetical  $Si_5$  cluster where a central atom 1 is tetrahedrally coordinated by the four remaining atoms 2–5. The bond-orbital Hamiltonian

$$\mathcal{H} = \beta_1 \begin{pmatrix} 0 & 1 & 1 & 1 & 1 \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (2)$$

is easily diagonalized and yields a triplet at  $E = 0$  and two singlets at  $E = \pm 2\beta_1$ . Figure 5(a) and (b) compares the DOSs of bulk Si with those of the bond-orbital model of  $Si_5$ , respectively. The main difference is a finite DOS near the Fermi level, which is, in the Stoner picture, an indication for the formation of a magnetic moment. The analysis of the eigenfunctions of (2) shows that the triplet is formed from the ligand  $sp^3$  orbitals 2–5 exclusively, so that any magnetic moment resides at the ligands, and the spin density at the central Si atom 1 is zero.



**Figure 4.** Si cluster with tetrahedral coordination. The numbers labels the individual atoms: 1 is the central atom, whereas the ligands 2–5 form a coordinating tetrahedron.



**Figure 5.** Typical DOSs for half-filled bands in tetrahedrally bound (or diamond) carbon. (a) Bulk Si and (b) hypothetical  $\text{Si}_5$  molecule. In (b), the narrow level spacing clearly supports the formation of an atomic moment.

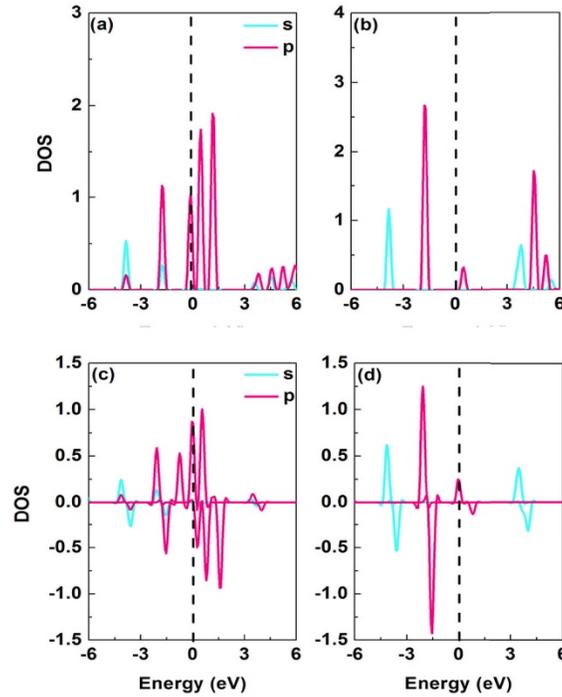
#### IV. First-Principle Calculations

To study the magnetism of the  $\text{Si}_5$  cluster from first principles, we have used the VASP and SIESTA codes. The VASP calculations<sup>[13]</sup> are performed using the frozen-core full-potential projected augmented wave method.<sup>[14]</sup> The electronic exchange and correlation effect are described within the generalized-gradient approximation, using the functional proposed in [15]. The energy cutoff of the plane wave basis set is taken as 450 eV, and energy convergence is set at  $10^{-6}$ . Calculations of this type are advanced standard for transition-metal magnets, for example, in permanent magnetism.<sup>[16,17]</sup> SIESTA is a self-consistent tight-binding code<sup>[18]</sup> widely used in chemistry. In all calculations, we have used the elemental bond length of Si, 2.35 Å.

Figure 6 shows the VASP results for the DOS in  $\text{Si}_5$ . These DOS confirm the main findings of Section III, namely that many eigenstates formed from the ligand atoms 2–5 are close to the Fermi level (a) and develop a magnetic moment due to the onsite Coulomb interaction (c). By contrast, the central atom 1 does not contribute to the moment (b) and (d).

The finite width of the peaks in figure 6 is a VASP artifact associated with treatment of the wave-vector space in the program. For the same reason, the VASP moments are non-integer for small magnetic clusters.<sup>[19,20]</sup> The DOSs (fig. 6) and corresponding spin density

distributions (not shown here) show that the main contribution to magnetic moment comes from the  $p_x$  and  $p_y$  orbitals of the ligand Si atoms. The SIESTA code, which is more accurate for small molecules, yields a magnetic moment of  $4 \mu_B$  per  $Si_5$ . In other words, each surface (ligand) atom in the  $Si_5$  cluster contributes  $\sim 1 \mu_B$  to the total magnetic moment, and thus this leads a total magnetic moment of  $\sim 4 \mu_B$  from four surface (ligand) atoms. Similar results have been predicted for stepped silicon surfaces with specific geometry.<sup>[7]</sup> By assuming only surface atoms contribute to magnetism in Si nanoparticles, the magnetic moment per surface atom is estimated to be  $\sim 0.12 \mu_B$ , and this trend is consistent with the theory. The experimental value is, however, an order of magnitude smaller than the maximally achievable theoretical magnetic moment ( $1 \mu_B$ /surface atom). Note that the Si nanoparticles (average particle size about 26 nm) are much larger than theoretically investigated smaller Si clusters having only five atoms, so that only a small fraction of surface sites may be magnetic. This fact along with possible interparticle interactions in the experimental sample may be responsible for the reduced magnetic moment of the surface atoms.



**Figure 6.** VASP DOSs in  $Si_5$ . (a) Paramagnetic DOSs the edge (tetrahedron) atoms 2–5, (b) paramagnetic DOSs for the central atom 1, (c) ferromagnetic DOSs for the edge atoms 2–5 in the tetrahedron, and (d) ferromagnetic DOSs for the central atom 1.

## V. Discussion and Conclusion

The simplicity of the bond-orbital approach can be seen from the overestimation of the bandgap due to the neglect of the s-p onsite or promotion energy  $\varepsilon_p - \varepsilon_s$ . In fact, the inclusion of the promotion energy would yield the Weaire-Thorpe model, which predicts a much more accurate bandgap.<sup>[10]</sup> However, the corresponding corrections go in the right direction because they narrow the bandgap. Our VASP and SIESTA calculations confirm the picture suggested by bond-orbital and show that exotic structural features with tetrahedral coordination completely remix the energy-level structure and may give rise to a magnetic moment. Note also that the moments of the Si<sub>5</sub> cluster reside at the surface of the cluster on the atoms that stick out.

However, the specific analysis of the surface morphology of the nanoparticles of figure 1 and the identification of structural features similar to figure 4 remains a challenge for future research. It is also possible that the magnetic signal in figure 2 involves impurities such as bridging oxygen atoms. The main aims of this paper have been: (1) to look for experimental magnetic moments in Si nanoclusters and (2) to explain how such moments may arise from an atomic viewpoint.

In summary, we have used several experimental and theoretical methods to investigate the magnetism of diamond-structured silicon nanoparticles. Our experiments reveal a clear magnetic signal, namely a saturation magnetization of  $\sim 2.9$  emu/cm<sup>3</sup> at 10 K, and our analytical and numerical calculations show that magnetic moments form due to specific morphological features. The example of Si<sub>5</sub> clusters shows how the quantum-mechanical mixture of sp<sup>3</sup> hybrids creates states near the Fermi level, which leads to moment formation. Future research is necessary to pinpoint the atomic origin of the observed magnetic moment.

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