

## Surface-Enhanced Magnetism in Nickel Clusters

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We have used the Stern-Gerlach deflection technique to study magnetism in nickel clusters containing 5 to 740 atoms. These superparamagnetic particles are highly magnetic, with magnetic moments per atom that decrease toward the bulk value as their size increases. This approach toward the bulk is not monotonic; we observe magnetization minima for clusters with closed geometrical shells and maxima for relatively open clusters. This result is consistent with enhanced magnetization of the cluster surface. We also observe a decrease in magnetization with increasing cluster vibrational temperature. The implications of various cluster geometries are discussed in conjunction with existing chemical probe studies and theoretical calculations.

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Recent studies of magnetism in small nickel clusters have found them to be highly magnetic, with moments per atom  $\mu$  that exceed the bulk value of  $0.61\mu_B$  per atom [1,2]. These observations support theoretical predictions of enhanced magnetization in systems with decreased coordination between atoms, increased symmetry, and reduced dimensionality [3,4]. This effect extends throughout the transition metals. Cobalt and iron clusters are also more magnetic than the bulk [2,5,6], and clusters of rhodium, a nonmagnetic  $4d$  transition metal, exhibit giant magnetic moments [7,8].

But while the surfaces of both solids and clusters are expected to show enhanced magnetizations, such surface effects have proven difficult to observe directly. In solids, surface magnetism is hard to separate from bulk magnetism, although some measurements of surface magnetism have been performed [9]. Even deposited monolayers are complicated by epitaxial effects. Since clusters are almost entirely surface, they would seem to be ideal systems in which to look for surface magnetism. However, previous cluster studies were not able to show a direct relationship between the number of atoms at a cluster's surface and its magnetic moment per atom.

In this Letter, we report measurements of magnetism in nickel clusters containing 5 to 740 atoms. These measurements are precise enough to resolve subtle differences in the magnetizations of nearby cluster sizes. The size-dependent magnetizations (magnetic moments *per atom*) that we observe demonstrate the importance of surface magnetism in enhancing a cluster's overall magnetic moment. Clusters with relatively little surface are substantially less magnetic than those with more surface. The very smallest clusters, which have no internal atoms at all, are extremely magnetic, in agreement with theoretical predictions by Reuse and Khanna [10].

We study the nickel clusters using the Stern-Gerlach magnetic deflection technique [5,6,11]. The nickel clusters are grown in a helium-filled source chamber from metal vapor produced when a pulsed laser beam strikes

a nickel disk. The clusters gradually stop growing, cool, and come into thermal equilibrium with the source, a process that takes about 1 to 2 ms [5,6,11]. During this time, the helium-cluster mixture bleeds out of the source chamber through a conical nozzle as a supersonic molecular beam.

While the free-jet expansion that forms the beam cools the translational and rotational temperatures of the clusters, it has little or no effect on their vibrational temperatures. Collings *et al.* have used delayed thermionic emission to study the temperatures of small niobium clusters emerging from helium supersonic expansions and have observed negligible vibrational cooling [12]. We have performed a similar thermionic emission study with our source and have shown that clusters in our beam are never colder than the source itself [13].

By restricting our studies to clusters that have reached thermal equilibrium with the source chamber, we are able to establish the clusters' vibrational temperatures to within a few K. The source chamber is attached to a closed-cycle helium refrigerator and electrical heater, so that its temperature can be controlled between 60 and 350 K. A mechanical chopper near the source passes only a brief pulse of these equilibrated clusters and also serves as a reference event for calculating the cluster beam velocity.

The cluster beam is collimated by two slits, 0.4 mm wide by 2.5 mm high, and then passes through a 250 mm long gradient field magnet. The clusters accelerate in this gradient field in proportion to the projections of their magnetic moments onto the field axis. They deflect in a 1183 mm drift tube before entering the ionization region of a time-of-flight mass spectrometer. There the clusters are ionized by a narrow ultraviolet beam from an ArF excimer laser (193 nm), directed antiparallel to the cluster beam. This laser beam scans slowly back and forth, mapping out the profile of deflected clusters.

Once ionized, the nickel clusters are dispersed and detected in the mass spectrometer. By analyzing the spectra of clusters obtained at many positions of the excimer laser

beam, we are able to determine cluster deflections as functions of cluster size, vibrational temperature, and magnetic field. We can measure the deflections of individual cluster sizes up to 200 atoms, but the limited resolution of our mass spectrometer forces us to average over several cluster sizes above that point.

Over the temperature range of this study, the nickel clusters behave superparamagnetically [14]. Although each nickel cluster exhibits ferromagnetic order and has a giant magnetic moment, the orientation of that moment fluctuates on the nanosecond time scale. The moment is only weakly attached to the cluster's atomic lattice, and thermal agitation from the vibrational modes causes the moment to explore all possible orientations during the several hundred microseconds the cluster spends in the gradient field magnet.

This fluctuating giant moment responds paramagnetically to an applied magnetic field, yielding a smaller time-averaged magnetic moment aligned with that field. The applied field modifies the Boltzmann factors weighting the moment's possible orientations, so that the cluster exhibits an effective moment per atom  $\mu_{\text{eff}}$  that is reduced from its full internal moment per atom  $\mu$  by the Langevin function  $\mathcal{L}$ ,

$$\mu_{\text{eff}} = \mu \mathcal{L} \left( \frac{N\mu B}{kT} \right) = \mu \left[ \coth \left( \frac{N\mu B}{kT} \right) - \frac{kT}{N\mu B} \right], \quad (1)$$

where  $N$  is the number of atoms in the cluster,  $B$  is the magnitude of the applied field,  $k$  is Boltzmann's constant, and  $T$  is the cluster's vibrational temperature. Since our deflection measurement yields a value for  $\mu_{\text{eff}}$ , we invert this relationship to obtain  $\mu$ , the cluster's internal magnetic moment per atom [5,15].

To maximize their ferromagnetic ordering, we studied clusters of 5 through 200 atoms at 198 K and below. At these low temperatures, we obtained  $\mu$ 's ranging from  $0.85\mu_B$  to  $1.81\mu_B$  (Fig. 1). We had to study the larger clusters (210 through 740 atoms) at 303 K because moment-lattice coupling effects perturb superparamagnetism in large clusters at low temperatures [13]. In these larger, warmer clusters, we obtained  $\mu$ 's ranging from  $0.68\mu_B$  to  $0.78\mu_B$  (Fig. 2).

The smallest clusters are by far the most magnetic, in agreement with recent predictions by Reuse and Khanna [10].  $\mu$  then generally decreases with increasing cluster size toward the bulk value of  $0.61\mu_B$ . However, this decrease is not monotonic for the smaller clusters. Instead,  $\mu$  depends strongly on cluster size, exhibiting maxima for clusters with relatively large surfaces and minima for clusters that are highly compact. The contribution of surface atoms is particularly important for clusters with fewer than 100 atoms, where shifting even one atom from the interior to the exterior of a cluster can have a significant impact on the average moment of the entire cluster.

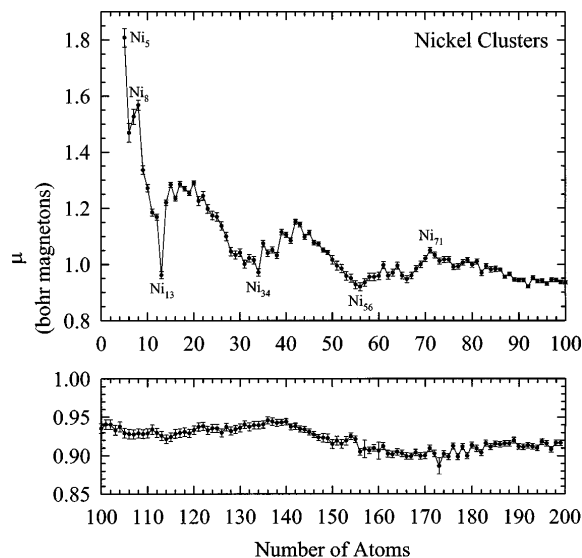


FIG. 1. Nickel cluster magnetic moment per atom ( $\mu$ ) as a function of cluster size, at temperatures between 73 and 198 K. The error bars reflect statistical uncertainty (1 s.d.). The systematic uncertainty in these measurements is  $\pm 0.05\mu_B$ .

This size dependence in  $\mu$  provides structural information about the nickel clusters. At the smallest sizes, our magnetic measurements support the calculations of Reuse and Khanna [10], who predicted strong magnetization in  $\text{Ni}_5$  and  $\text{Ni}_6$  and less magnetization in  $\text{Ni}_{13}$ . Our measurements also fit well with the adsorption studies of Parks *et al.* [16], providing considerable insight into how the structures of nickel clusters develop with increasing size.

$\text{Ni}_5$ , with a  $\mu$  of  $1.81\mu_B$ , is thought to be a trigonal bipyramid [10,16]. The low coordination of its atoms allows them to retain almost their full atomic spin moments ( $2\mu_B$ ).  $\text{Ni}_6$  is a more tightly bound octahedron [10,16], with a smaller  $\mu$  of  $1.47\mu_B$ . The next several atoms first increase the surface area of the cluster and then begin to fill it in, leading to a rise in  $\mu$  toward  $\text{Ni}_8$  and then a decrease toward  $\text{Ni}_{13}$ . The large value of  $\mu$  for

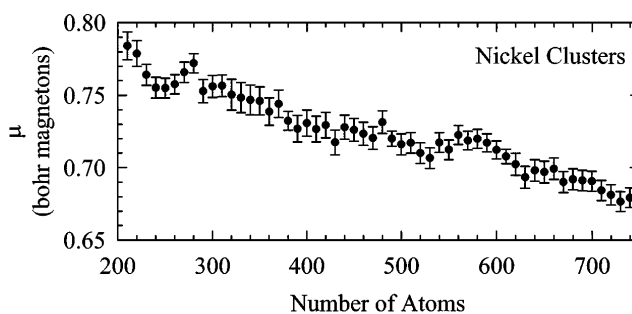


FIG. 2. Nickel cluster magnetic moment per atom ( $\mu$ ) as a function of cluster size. Values for  $\mu$  are averages over 10 cluster sizes, made at 303 K. The error bars reflect statistical uncertainty (1 s.d.). The systematic uncertainty in these measurements is  $\pm 0.04\mu_B$ .

Ni<sub>7</sub> is consistent with studies showing that a single atom added to an octahedron is weakly bound [17].

Ni<sub>13</sub> is a closed-shell icosahedron [10,16], the first cluster with an interior atom. Its compact structure explains its anomalously small  $\mu$  of  $0.96\mu_B$ . Ni<sub>14</sub>, with a  $\mu$  of  $1.22\mu_B$ , is much more magnetic and evidently has a very open structure. Parks *et al.* have suggested a bicapped hexagonal antiprism [16].

With the further addition of atoms, the clusters develop as a growing assembly of interpenetrating icosahedra [16]. The double icosahedron occurs at Ni<sub>19</sub> and the triple icosahedron at Ni<sub>23</sub>.  $\mu$  remains fairly steady in this size range, though it decreases whenever adding an atom completes an icosahedron.

Parks *et al.* have not predicted structures for Ni<sub>27</sub> through Ni<sub>48</sub>. From the gradual decrease in  $\mu$ , it appears that the clusters continue to add interpenetrating icosahedra up until Ni<sub>34</sub>. Above that size, the clusters become more open toward Ni<sub>42</sub>, and then begin to fill in toward the next shell closing at Ni<sub>55</sub>.

Like Ni<sub>13</sub>, Ni<sub>55</sub> is a very compact structure. It has 13 interior atoms and a  $\mu$  of only  $0.93\mu_B$ . However, Ni<sub>55</sub> shares the local minimum in magnetization with Ni<sub>56</sub>. Though Parks *et al.* suggest that Ni<sub>56</sub> is just Ni<sub>55</sub> with a single atom on one of its faces [16], its low magnetization suggests that Ni<sub>56</sub> has undergone substantial surface reconstruction to reduce the strain of its icosahedral structure. By using the extra atom to relax its surface, Ni<sub>56</sub> has kept its magnetization small [18].

Beyond Ni<sub>56</sub>, Parks *et al.* predict that three-atom caps develop on adjacent faces of the Ni<sub>55</sub> icosahedron [16]. Ni<sub>61</sub> and Ni<sub>64</sub> have two and three such caps, respectively. These two clusters are more magnetic than their neighbors because when three atoms are not available to form a complete cap, the extra atoms act to relax surface strain in the cluster and reduce its magnetization. By Ni<sub>70</sub>, five caps have formed around a single apex atom of the underlying Ni<sub>55</sub> icosahedron. The next atom sits between the five caps [16], creating the highly magnetic Ni<sub>71</sub>.

Beyond Ni<sub>71</sub>,  $\mu$  generally declines toward the third icosahedral shell closing at Ni<sub>147</sub>, and the contributions of individual atoms become harder to observe. That  $\mu$  decreases even somewhat beyond Ni<sub>147</sub> probably reflects the surface strain present in the complete icosahedron and the relaxation that occurs when additional atoms are available.

Beyond 200 atoms, we could not study the nickel clusters at low temperatures because couplings between their lattices and their magnetic moments were strong enough to impede the thermal fluctuations that produce superparamagnetism. We had to continue our studies at higher temperatures, even though this change decreases the clusters' magnetic ordering slightly.

To determine the effects of temperature on magnetic order in nickel clusters, we studied  $\mu$  as a function of temperature for Ni<sub>156</sub> to Ni<sub>200</sub>. Between 98 and 353 K,

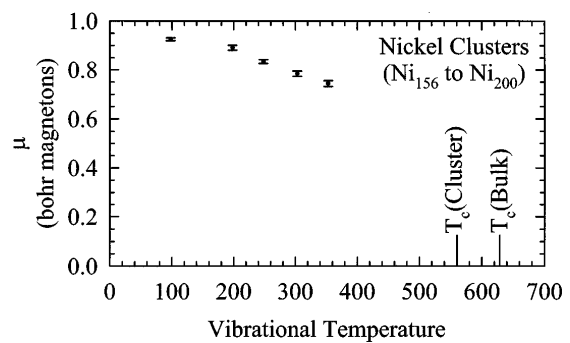


FIG. 3. The average magnetic moment per atom ( $\mu$ ) for clusters Ni<sub>156</sub> to Ni<sub>200</sub>, taken at several different vibrational temperatures. The decrease in  $\mu$  with temperature suggests a loss of ferromagnetic order.

we observe a reduction of  $\mu$  with increasing temperature (Fig. 3), but we could not go above 353 K to observe the complete loss of ferromagnetic order. In bulk nickel, this Curie temperature is 627 K, while in clusters of this size it has been predicted to be about 560 K [19].

At 303 K,  $\mu$  gradually declines from Ni<sub>210</sub> to Ni<sub>740</sub>, reaching  $0.68\mu_B$  for Ni<sub>740</sub> (Fig. 2). This value is still above the bulk  $\mu$  of  $0.61\mu_B$ , despite the warm cluster temperatures. Evidently, the approach to bulk magnetism is extremely slow and requires that the internal atoms greatly outnumber those on the surface. It may also require a transition from the icosahedral structure of the smaller clusters to the fcc structure of bulk nickel.

We have shown that most nickel clusters up to and perhaps beyond 150 atoms have an underlying icosahedral symmetry. We find a strong surface enhancement of magnetization in relatively open clusters and reduced magnetization in clusters with minimal surfaces. This enhanced magnetization extends to the largest clusters studied, indicating that the effects of surface are still extremely important in clusters with hundreds of atoms.

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