Quenching of Magnetic Moments by Ligand-Metal Interactions in Nanosized Magnetic Metal Clusters

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Local density functional calculations and experimental magnetization studies on giant nickel carbonyl clusters are presented. The results show convincingly that the effect of the carbonyl ligation is to quench completely the magnetic moments of the nickel atoms at the surface of the clusters, leaving the inner-core metal atoms relatively unaffected. The relation with surface coating of magnetic particles for recording media is pointed out.

The study of ligand-metal interactions in the chemisorption of molecules on metal surfaces is of interest for fundamental surface science, as well as for applications involving, e.g., the catalytic or magnetic properties of small metal particles [1–4]. Metal cluster compounds are chemical compounds of well-defined stoichiometry, which constitute attractive model systems to study such problems [5–7]. They are composed of metal cluster molecules, which essentially are small metal particles (10 to 10^3 atoms), each particle being coordinated by a shell of ligand molecules (CO, PPh_3, etc.). In a given compound, only one type of metal cluster occurs so that the materials are ideally monodisperse. The ligand-metal bonds are quite similar to those occurring in the chemisorption of the same molecules on macroscopic metal surfaces. However, due to the very large surface-to-volume ratio (30%–90%) of the metal atoms in the clusters, the effects of the ligand-metal bonding can become predominant, instead of being a minor disturbance as in surface chemisorption. In this Letter we present local density functional calculations and experimental magnetization studies on giant nickel carbonyl clusters, which show convincingly that the effect of CO ligation is to quench completely the magnetic moments of the surface Ni atoms. Indications for an analogous quenching effect have earlier been reported from photoelectron spectroscopic studies of CO chemisorption on Ni [8]. Our results are also of relevance for understanding the large magnetic anisotropy observed in coated magnetic particles, e.g., of interest for magnetic recording [2,4].

The magnetization of a series of Ni carbonyl clusters was measured as a function of field (up to 6 T) and temperature (1.7–300 K), using a commercial SQUID magnetometer. In contrast to earlier studies on powders [9,10], single-crystal samples, weighing 16 mg or less,

were available for the present experiments. Besides the compound $[Ni_{38}Pt_6(CO)_{48}H]^{5-}[AsPh_4^+]_2[NBu_4^+]_3$, that contains the high-nuclearity $Ni_{38}Pt_6$ clusters, three low-nuclearity clusters were studied, namely $[Ni_9(CO)_{18}]^{2-}[N(CH_3)_4^+]_2$, $[Ni_{10}(CO)_{16}C_2]^{2-}[PPN]_2^+$, and $[Ni_{12}(CO)_{21}H_2]^{2-}[N(CH_3)_3CH_2Ph^+]_2$. All samples are air-sensitive, so that special care had to be taken in handling them. The $Ni_{38}Pt_6$ cluster core (cf. Fig. 1) is composed of an inner octahedron of six Pt atoms, enclosed in an outer octahedron of 38 Ni atoms. The 48 CO ligands are bonded to the Ni atoms. The structures of the Ni_9, Ni_{10}, and Ni_{12} clusters are not shown, but in all cases all Ni atoms are at the surface of the cluster (no inner-core Ni atoms present).
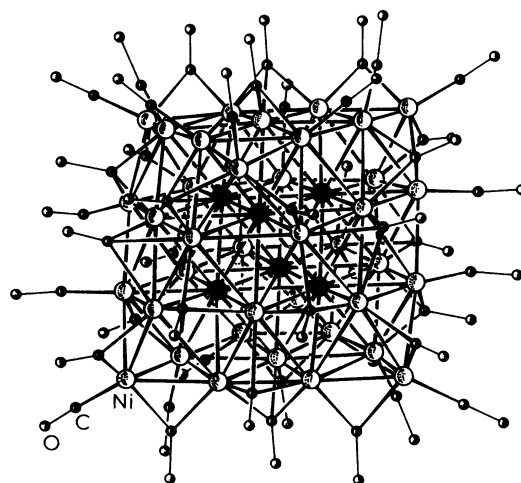

FIG. 1. Structure of the $Ni_{38}Pt_6$ core in the largest molecular cluster studied (filled circles denote Pt atoms). The 48 CO ligands are seen to form a "shell" around the metal cluster.

From the earlier studies [9,10], it was already inferred that the moment per atom in the Ni carbonyl clusters was strongly reduced with respect to the bulk value of about $0.6\mu_B$/atom. The effective magnetic moments were found to be one to a few μ_B/cluster, implying a moment per atom of only 10%–20% of the bulk value. By contrast, in studies of *bare* transition metal clusters in atomic beams, it is usually found that the moment per atom is comparable to the bulk [11]. Accordingly, the observed reductions were tentatively attributed to the bonding of the CO ligands. These ligation effects are now firmly corroborated by the theoretical calculations and the single-crystal studies presented in this Letter. In Fig. 2 we show representative results for the susceptibility ($\chi = \partial M/\partial B$) in low fields as a function of temperature (data corrected for the estimated diamagnetic contribution of the ligand molecules). Apart from a weak, temperature-independent term, ascribed to a combination of orbital diamagnetic and Van Vleck contributions [12], only a very small spin contribution in the form of a Curie tail at the lowest temperatures can be discerned. The effective moment corresponding to this Curie term ($\chi \propto C/T$, with $C = N_A \mu_{eff}^2/3k_B$) amounts to only 0.001–0.01 μ_B/atom for the low-nuclearity clusters, and to about $0.03\mu_B$/atom for the $Ni_{38}Pt_6$ cluster. Similar low values are deduced from the behavior of the magnetization as a function of field, as shown for the $Ni_{38}Pt_6$ single crystal in Fig. 3. For this sample, an induced magnetic moment as small as $0.01\mu_B$/atom is measured at $T = 1.7$ K in a field of 3 T. For the Ni_9, Ni_{10}, and Ni_{12} samples the induced moment/atom is again an order of magnitude smaller.

It is difficult to envisage such small magnetic moments to be an intrinsic property of the metal clusters themselves. In this respect, the present data on single crystals are very important, since they show systematically much lower magnetic moments than the earlier measurements on powders. We mention that, after grinding a few crystallites of the Ni_9 compound into a powder, the measured susceptibility shows a Curie constant C twice as

FIG. 3. Experimental magnetization curves for the $Ni_{38}Pt_6$ single-crystal sample. Numbers indicate the temperature in K.

large (cf. Fig. 2). This suggests that contamination at the sample surface (due to oxidation or reduction) may play a role. Another source for the small magnetic moments, however, could be deviations from exact stoichiometry in a small fraction of the clusters, for instance in the ratio of Ni to Pt, or in the precise number of H atoms in the cluster. Also a positional interchange of a Pt and Ni atom could be a reason, as will be further outlined below. The fraction of such cluster isomers in the sample could also differ for single crystals and powders.

We conclude therefore, that the *intrinsic* magnetic moment is to all probability zero also for the $Ni_{38}Pt_6$ cluster, and that the small moments yet observed have to be ascribed to imperfections. If a moment is present on a random fraction of the clusters, these moments will interact (very) weakly by exchange interactions through overlap of wave functions in the ionic cluster crystal. To arrive at the above value of an effective moment of $0.005\mu_B$/Ni-atom, one may assume, for instance, one out of five $Ni_{38}Pt_6$ cores to carry a spin of $1\mu_B$. The observed behavior of the magnetization is, at least qualitatively, in agreement with such a scenario. In fact, it cannot be modeled by a simple Brillouin curve, but instead mimicks the behavior previously observed in *random* magnetic systems, like spin glasses [13], or diluted antiferromagnets [14]. Note in particular the nonlinear behavior of M down to low fields, which is typical for such random systems. Since the $Ni_{38}Pt_6$ clusters are on the sites of a regular crystal lattice, and since we found the magnetization to be independent of the direction of the applied field, we have done Monte Carlo calculations for the diluted Heisenberg (isotropic) antiferromagnet in a magnetic field, to mimick the observed behavior. A fraction (we took $p = 0.20$) of spins were randomly distributed over the sites of a $40 \times 40 \times 40$ cubic lattice (with periodic boundary conditions). Spins on nearest-neighboring sites were allowed to interact via: $\mathcal{H} = J\mathbf{S}_i \cdot \mathbf{S}_j$ ($J > 0$). Thermodynamic quantities, such as the magnetization shown in Fig. 4, were calculated using the "Metropolis" algorithm [15]. The curve shown is the average of ten different spin configurations, and
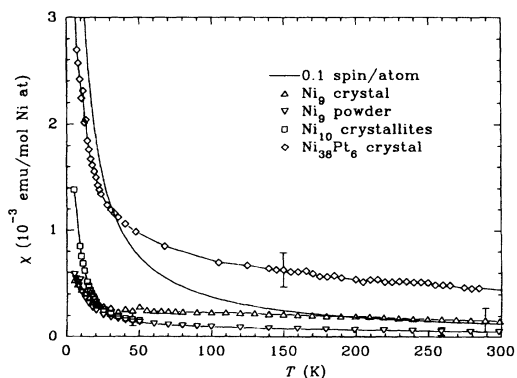

FIG. 2. Susceptibility χ versus temperature T for the clusters studied (here χ is the derivative of the magnetization curve at low fields). Solid curve is the theoretical Curie susceptibility $\chi = C/T$, assuming an effective moment of $0.1\mu_B$/atom.
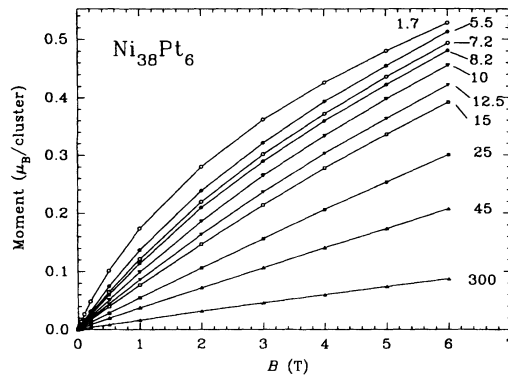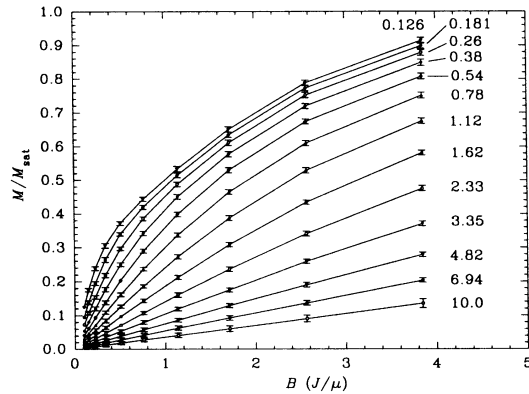
FIG. 4. Magnetization curves for the site-diluted Heisenberg antiferromagnet calculated with the Monte Carlo method. M_{sat} denotes the saturation value, μ the classical moment, and J the exchange constant. Numbers indicate temperature in units J/k_B.

TABLE I. Average distribution of unpaired electrons between surface (s) and core (c) atoms in free and carbonylated Ni_nPt_m clusters from LDF calculations.

Cluster	n_s/atom				n_s
	Ni^s	Ni^c	Pt^s	Pt^c	Tot.
$Ni_{38}^s Ni_6^c$ [a]	0.75	0.72	···	···	32.7
$Ni_{38}^s Pt_6^c$	0.76	···	···	0.22	29.9
$Ni_{32}^s Pt_6^s Ni_6^c$	0.85	0.82	0.36	···	34.0
$[Ni_{38}^s Ni_6^c (CO)_{48}]^{6-}$ [a]	0.00	0.59	···	···	3.6
$[Ni_{38}^s Pt_6^c (CO)_{48}]^{6-}$	0.00	···	···	0.00	0.0
$[Ni_{32}^s Pt_6^s Ni_6^c (CO)_{48}]^{6-}$	0.01	0.58	-0.01	···	4.1

[a]From Refs. [16,17].

is for a temperature $T = 0.1J/k_B$. The good, qualitative agreement with experiment corroborates the scenario outlined in the above (typical value of J/k_B is ~10 K).

The conclusion that the surface Ni atoms have their moments completely quenched by the CO ligands (and that the Pt atoms in the interior of the $Ni_{38}Pt_6$ cluster are nonmagnetic) is strikingly confirmed by recent, state-of-the-art quantum theoretical calculations on very large, bare (Ni_{44}), and carbonylated $Ni_{44}(CO)_{48}$ clusters [16,17]. The structure of the Ni_{44} core considered is essentially the same as in Fig. 1, but with the six Pt atoms replaced by Ni. For the naked Ni_{44} cluster, a moment per atom of about $0.7\mu_B$ was found for all Ni sites (cf. Table I). For the carbonylated version, the moments of the surface atoms are completely quenched, whereas the six inner-core Ni atoms still carry a moment of about $0.6\mu_B$/atom [16,17]. This finding demonstrates, in fact, that the influence of the ligand-metal bonding is mainly restricted to the outer surface metal atoms, in agreement with a recent Mössbauer study on $Pt_{309}Phen_{36}{}^*O_{30}$ [18].

In order to confirm the absence of magnetic moments on the Pt atoms in the interior of the $Ni_{38}Pt_6$ cluster, the calculations in Refs. [16,17] were extended to the actual $Ni_{38}Pt_6$ "alloy" cluster, as we shall now discuss. The calculations are done within the local density functional (LDF) approach, using a scalar relativistic version of the LCGTO (linear combination of Gaussian-type orbitals) method [19]. All electron, spin-polarized calculations have been performed. The fractional occupation number technique was used to determine the occupancies [16,17,19]; according to this procedure each one-electron level is broadened by a Gaussian and the resulting density of state is filled by the appropriate number of electrons. The cluster Fermi energy is thus determined self-consistently. In this work we used a broadening of 0.3 eV, but similar results have been obtained with smaller broadenings [20]. Experience has shown that, al-

though the absolute values of the magnetic moments may change by about ±10% as a function of the broadening, the general conclusions about the magnetic or diamagnetic character of the cluster do not depend on this parameter.

In the ground state, the naked $Ni_{38}Pt_6$ cluster is highly magnetic too, with a total of $n_s = n_\uparrow - n_\downarrow = 29.9$ unpaired electrons. The unpaired spins are localized in the $3d$ shell of the Ni atoms, with an average net moment of $0.76\mu_B$/atom (Table I). The six Pt atoms in the cluster "core" also carry a small moment of $0.22\mu_B$/atom. Since bulk Pt is a nonmagnetic metal, this moment is probably induced by the exchange interaction with the Ni atoms, and should be absent as soon as the latter would become nonmagnetic. The addition of the ligand shell, $[Ni_{38}Pt_6(CO)_{48}]^{6-}$, indeed results in complete quenching of all magnetic moments (cf. Table I). The cluster ground state is thus predicted to be diamagnetic, as for carbonylated Ni clusters of small nuclearity. The complete quenching of the magnetic moment for the surface Ni atoms is just as found previously [16,17] in $[Ni_{38}^s Ni_6^c(CO)_{48}]^{6-}$. Here the superscripts "s" and "c" indicate surface and core atoms of the cluster, respectively. The moments of the latter cluster are entirely located at the inner-core Ni atoms, see Table I. This suggests that substitution of a Pt in the core of the $Ni_{38}^s Pt_6^c$ cluster by a Ni atom could result in a small magnetic moment per cluster. To further verify this hypothesis, we have considered a cluster isomer of $[Ni_{38}^s Pt_6^c(CO)_{48}]^{6-}$, in which the six Pt atoms are placed at the vortices of the outer octahedron, and are replaced by six Ni atoms in the inner core. We denote this cluster by $[Ni_{32}^s Pt_6^s Ni_6^c(CO)_{48}]^{6-}$. For the naked $Ni_{32}^s Pt_6^s Ni_6^c$ cluster, all atoms are found to be magnetic, yielding a total magnetic moment of $34\mu_B$, which is higher than that of $Ni_{38}Pt_6^c$ (Table I). Adding the ligand shell leads again to complete quenching of the moments of all (Ni and Pt) surface atoms, while each core Ni atom retains a magnetic moment of $0.58\mu_B$/atom. A positional interchange of Ni and Pt in a fraction of the clusters thus could indeed explain the small, effective magnetic moment per cluster found experimentally.

Summarizing, both experiment and theory lead to the conclusion that CO ligation results in complete quenching of the surface Ni moments, leaving eventual

inner Ni atoms magnetic, in excellent agreement with experimental findings of the effects of CO chemisorption on bulk Ni surface [8]. In the bare metal clusters the electronic configuration of Ni is close to $3d^9 4s^1$. The coordination by CO favors intra-atomic redistribution of the Ni configuration from $3d^{9+x} 4s^{1-x}$ to $3d^{10}$, mainly due to the repulsive interaction between the CO 5σ charge density and the Ni $4s$ electrons [16,17]. By the ensuing destabilization of $4s$-derived orbitals well above the highest occupied molecular orbital of the bare cluster, $4s \rightarrow 3d$ transfer takes place, the local $3d$ shell becomes filled, and the Fermi level shifts *above* the $3d$ band. Effectively, the Ni configuration thus becomes similar to Cu, and the density of states at the Fermi energy is reduced considerably. We mention that we have observed similar surface-quenching effects in a recent study of size-dependent magnetization of (giant) Pd clusters and Pd colloids [21]. It also follows that different magnetic effects might be expected for, e.g., ligated Co or Fe clusters.

Finally, we point out that the destabilization of the sp-derived orbitals, with the accompanying change in magnetic moment, can be seen as the (macro) molecular analog of the high-spin/low-spin transition, familiar in transition metal complexes (e.g., of Mn and Fe ions) [9,10,16]. The chemical bonding of ligands to a (single) metal atom in such complexes may be described as a ligand field. In ligand-field theory, a low-spin complex results when the crystal field splitting of the d orbitals is large enough to overcome Hund's rule. The latter favors distribution of electrons with parallel spin in different orbitals, thereby minimizing the Coulomb energy. But for large enough orbital splitting the highest level is destabilized, which may result in either moment quenching, or in highly anisotropic values for the resulting moments. Thus, this ligand-field analogy may help in understanding the unexpectedly large surface magnetic anisotropies in magnetic particles of α-Fe [4], and of γFe$_2$O$_3$, Fe$_3$O$_4$, NiFe$_2$O$_4$, CoFe$_2$O$_4$, coated with surfactants like oleic acid or sodium phosphate [2,22,23]. The bonding of surfactant molecules should be equivalent to a strong ligand field acting on the surface atoms. Such a ligand field may cause a very strong pinning of the magnetic moments of Ni^{2+} or Fe^{2+} ions in the surface layer, which pinning is then transferred well into the interior of the particle via the magnetic exchange interactions [2,4,22,23]. For nonspherical particles, this should indeed lead to strong anisotropy, explaining the observed slow rise to saturation of the high-field magnetization [23].

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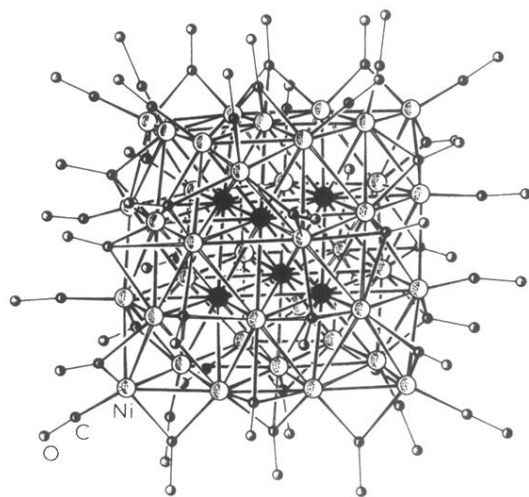FIG. 1. Structure of the $Ni_{38}Pt_6$ core in the largest molecular cluster studied (filled circles denote Pt atoms). The 48 CO ligands are seen to form a "shell" around the metal cluster.