Stern-Gerlach Experiments on $Mn@Sn_{12}$: Identification of a Paramagnetic Superatom and Vibrationally Induced Spin Orientation

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(Received 17 May 2013; published 24 September 2013)

Beam deflection experiments in inhomogeneous magnetic fields reveal a new limiting case of the magnetization distribution of isolated clusters. Endohedrally doped clusters are produced in a temperature controlled, cryogenically cooled laser ablation source. Temperature dependent experiments indicate a crucial contribution of molecular vibrations to the spin dynamics of $Mn@Sn_{12}$. In its vibrational ground state the cluster behaves magnetically like a paramagnetic atom, with quantized spin states. However, excited molecular vibrations induce spin orientation in the magnetic field.

DOI: 10.1103/PhysRevLett.111.133401 PACS numbers: 36.40.−c, 33.15.Bh, 75.20.−g

Spatial quantization of the electronic spin angular momenta of atoms is one of the earliest and most prominent experimental observations of the quantum nature of physics [1]. Since then, the experimental scheme, commonly referred to as the Stern-Gerlach experiment, has been employed to investigate the magnetic susceptibility of isolated atoms [2–4], molecules [5,6], and clusters [7–10]. If orbital angular momentum is zero, the inhomogeneous magnetic field causes the components of an atomic beam with total electronic spin quantum number S to split up, according to their magnetic spin quantum numbers $S_z = [-S, -S+1, \ldots, S]$. For atoms, S_z is a good quantum number and hence the projection of the spin magnetic moment in field direction is a constant of motion. The reduced symmetry of molecular environments, however, in general causes the additional rotational and vibrational degrees of freedom to couple with the spin angular momentum. Since a complete description of the coupling mechanisms is in general not available, the interpretation of Stern-Gerlach experiments on polyatomic species is still challenging. In the majority of such experiments regarding clusters, the beam is deflected in the direction of the field gradient. This is clearly a manifestation of net magnetization (i.e., spin orientation) of the clusters. Although the average deflection of the cluster beam can often be explained by employing the Brillouin function [11,12], the justification for this approach is not trivial.

Thermodynamic equilibrium of the spin with the continuous phonon spectrum is the very foundation of the Brillouin function to describe the magnetic susceptibility of paramagnetic solids. Isolated clusters, on the other hand, have discrete vibrational spectra and the spin cannot interact efficiently with the molecular vibrations. Thermal relaxation of the spin is also in conflict with conservation of angular momentum. Therefore, to rationalize the deflection of isolated paramagnetic clusters in a beam, an adiabatic mechanism for the magnetization of clusters was developed [10,13]. In contrast to atoms, clusters have low symmetry equilibrium structures, and in combination with spin-orbit coupling (we neglect spin-spin and hyperfine coupling here) this may produce zero field splitting (ZFS) of the spin microstates. This loss of spin microstate degeneracy couples spin and rotational degrees of freedom. Spin-rotation coupling then leads to avoided crossings among coupled states if the magnetic dipole moments of states with equal total angular momentum nearly cause accidental degeneracy in the magnetic field. Regardless of the initial rotational or spin state of the cluster, the large number of avoided crossings commonly encountered while passing the inhomogeneous magnetic field produces a similar average net magnetic moment of all clusters (of one species) in the beam. Moreover, the high-field and low-field limit of this adiabatic magnetization agree with the Brillouin function [10] and hence this mechanism gives an explanation for the observed shift of the beam profiles (BP, i.e., the spatial distribution) in such experiments. However, the influence of vibrational degrees of freedom during adiabatic magnetization remains unclear.

We have measured the response of the endohedrally doped clusters $Mn@Sn_{12}$ to inhomogeneous magnetic fields in order to investigate the influence of molecular vibrations in magnetic beam deflection experiments by varying the internal energy of the clusters. $Mn@Sn_{12}$ reflects the response of a paramagnetic atom in a sextet spin state, if no molecular vibrations are excited. To our best knowledge, we have experimentally identified the first (nanoalloyed) paramagnetic superatom. If the clusters are vibrationally excited, magnetization of the molecular beam is observed. This vibrationally induced spin orientation, however, is not caused by direct spin-vibration interaction. Instead, the reduced symmetry of the vibrationally excited state induces spin-rotation coupling, resulting in Brillouin-like response of the cluster, if the excited vibrational mode lifts the degeneracy of the spin orbitals.

We present an extensive study of the cluster $Mn@Sn_{12}$ by means of beam deflection experiments in inhomogeneous

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magnetic and electric fields and also by density functional theory (DFT). The electric deflection experiments, which will be discussed in more detail in a forthcoming article, are consistent with I_h symmetry of the cluster. This symmetry is also supported by DFT-based evolutionary inspired global optimization of the tin cage. As the system $Mn@Sn_{12}$ can be expected to show considerable charge transfer [14], only the dianionic cage of tin atoms is optimized by means of a genetic algorithm. We utilized the same code and a similar procedure as in Ref. [15]. The structures generated by the code are locally optimized and the local minimum energy is obtained from the GAUSSIAN 09 quantum chemistry program [16]. A manganese ion Mn^{2+} is formally introduced to the global minimum structure (I_h), which compensates the negative charges, and the resulting neutral bimetallic cluster $Mn@Sn_{12}$ is relaxed. The cluster of lowest energy is an icosahedral cage of tin atoms, encapsulating a manganese atom in its center [17,18]. While the electronic ground state of Sn_{12}^{2-} has zero spin, introducing Mn^{2+} results in a sextet electronic ground state.

The endohedrally doped nanoalloy cluster $Mn@Sn_{12}$ thus can be regarded as a paramagnetic Mn^{2+} ion encapsulated in the center of a diamagnetic, dianionic cage of tin atoms Sn_{12}^{2-} known as ''stannaspherene'' [14,19]. Formally, both 4s electrons of the manganese atom are transferred to the tin cage [20] and the magnitude of the magnetic dipole moment of the nanoalloy cluster is exclusively determined by the central Mn^{2+} ion [21]. In accordance to Hund's rules the valence electrons of Mn^{2+} in the 3d states produce a ground state electronic configuration with total electronic orbital angular momentum quantum number $L = 0$ and $S = 5/2$.

The DFT-based global optimization approach was initially carried out using Los Alamos National Laboratory (LANL) effective core potentials (ECPs) and LANL-2DZ basis sets. However, to obtain the final geometry, the charge distribution and the normal modes of vibration (harmonic approximation, see Table I), a local optimization was carried out utilizing the more accurate small core ECPs of the Stuttgart-Dresden-Bonn group and corresponding triple valence basis sets [22–24]. For all calculations we chose the B3P86 hybrid functional [25,26], because it performs well in reproducing the static polarizability of the tin atom [27], the tin dimer bond distance [27], and is a reasonable choice for transition metal compounds [28].

A detailed description of our experimental setup has been reported before [29]. Clusters were generated in a pulsed laser vaporization source from manganese doped tin rods (5 at. % Mn). The alloy clusters were subsequently expanded into high vacuum, after passing a 25 mm copper channel (2 mm diameter) at the end of the nozzle, which is cooled by a closed cycle helium cryostat. The dwell times in this channel were sufficient to produce isolated clusters with vibrational temperatures approximately equal to the nozzle temperature (T_{nozzle}) [30,31]. The BPs presented here were measured with a scanning slit in combination with photoionization time of flight mass spectrometry. At each position of the slit, 100 mass spectra were averaged at zero magnetic flux density B_z, then the same number were averaged at $B_z = 1.6$ T. During the measurement the positions were chosen randomly from a set of equally spaced coordinates, but every position was measured three times in total.

The deflection of an isolated cluster in an inhomogeneous magnetic field depends on the magnitude and orientation of the magnetic dipole moment $\boldsymbol{\mu}$, the mass m and longitudinal velocity v of the cluster, a geometrical parameter, and the gradient of magnetic flux density in the deflection magnet [29]. In the following, we present the results obtained from temperature dependent magnetic deflection studies of $Mn@Sn_{12}$ and discuss the observed effect. In an earlier work [29] magnetic beam deflection experiments on the same cluster species were conducted. The results were interpreted in the context of a spin magnetic moment strongly bound (i.e., locked) to the cluster's molecular structure. Improvements of our apparatus, regarding the possibility to achieve lower internal energies of the clusters [32] and better stability of the molecular beam intensity, now reveal a completely different cause of the anomalous magnetic response of $Mn@Sn_{12}$. The effect observed in the earlier work is in fact not a result of locked spin response, but a manifestation of the intermediate vibrational excitation of the cluster, as shown below.

Figure 1 shows the BPs of $Mn@Sn_{12}$ measured at $T_{\text{nozzle}} = 16$ K without and with an inhomogeneous magnetic field applied. The measured data points at zero magnetic field are approximated with a Gaussian function, fitted by least square procedure (blue line). The inhomogeneous magnetic field affects the spatial distribution of $Mn@Sn_{12}$ in the molecular beam drastically. The BP is almost symmetrically broadened and from left to right (low field to high field), six beam components are observed. The first two components of the molecular beam are well separated, while the remaining four beam components are not resolved. This is an issue of the experimental setup, however [33]. Without the experimental imperfections the molecular beam of this ''frozen superatom'' would be perfectly split into six components of equal magnitude and width.

According to our DFT results the electronic ground state of the cluster is $^6S_{5/2}$. Each spin component of the ensemble of clusters in the molecular beam is deflected by an amount proportional to S_z, due to the inhomogeneous magnetic field. The initial population of individual states is equal and therefore the six molecular beam components must have equal magnitude. Every cluster of the ensemble with certain S_z will be shifted by the same amount. Thus, the measured BP at 16 K with the magnetic field applied can be simulated as the sum of six Gaussian functions

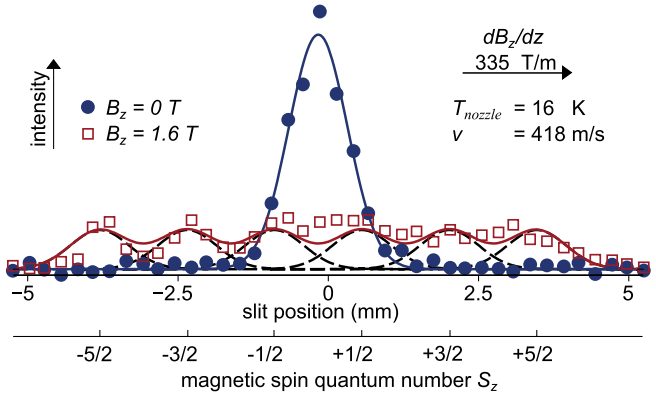

FIG. 1 (color online). Beam profiles of $Mn@Sn_{12}$ at $T_{nozzle} = 16$ K without (dots) and with (squares) a magnetic field applied. The simulated BP at 1.6 T (red line) is the sum of six individual beam components of equal magnitude (dashed black lines) shifted by an amount proportional to the quantized z component of the electronic spin angular momentum $S_z\hbar$, at velocity v of the cluster.

(black dashed line, Fig. 1). Each component has the same variance and 1/6 of the magnitude of the BP recorded without the magnetic field. To calculate the deflection for each magnetic state, we measured the velocity of the clusters using a mechanical chopper. The simulated BP of $Mn@Sn_{12}$ (solid red line, Fig. 1) with $\mu_z = g\mu_B S_z$ ($g = 2$, $\mu_B = 9.27 \times 10^{-24}$ J/T) is in very good agreement with the measured data, beside minor deviations in the central region of the BP. Therefore, it can be concluded that S_z is a good quantum number in the vibrational ground state (see Table I) of this highly symmetric cluster, in complete analogy to an isolated paramagnetic atom.

To investigate the influence of vibrational degrees of freedom on the magnetic response, the deflection experiment was conducted at various nozzle temperatures. Figure 2 shows BPs of $Mn@Sn_{12}$ produced at $T_{nozzle} = 30$ K, 50 K, and 70 K, without and with the magnetic field applied. The qualitative change in the BPs with rising temperatures can be summarized by a decreasing fraction of the clusters still showing response like the "frozen superatom" in the 16 K experiment and an increasing fraction which is deflected in the direction of the magnetic field gradient. The amount of this latter fraction is strongly correlated to T_{nozzle}.

The I_h symmetry of the cluster studied here and its electronic configuration do not produce any permanent ZFS [34]. Neglecting hyperfine coupling, interactions of the electron spin and the diamagnetic molecular environment result only from spin-orbit coupling. This effect is small for $L = 0$ but nonzero due to configuration interaction. The first excited state ^4G of isolated Mn^{2+} is 3.3 eV higher in energy [35], but contributes a small orbital angular momentum to the ground state. This interaction is very sensitive to the distortions of the molecular environment as known from studies of transition metal complexes

TABLE I. Wave numbers ω_i, label of the corresponding irreducible representation IR and degeneracy G of vibrational normal modes of $Mn@Sn_{12}$ obtained by DFT. $P_{0,i}(T_{nozzle})$ is the population of the vibrational ground state of the set of normal modes at T_{nozzle}, determined by Boltzmann distribution. The Jahn-Teller active modes are boldfaced.

			$P_{0,i}(T_{nozzle})$			
ω_i [cm^{-1}]	IR	G	16 K	30 K	50 K	70 K
65.1	H_u	5	0.986	0.799	0.435	0.219
84.1	**H_g**	**5**	**0.997**	**0.915**	**0.628**	**0.377**
93.4	**G_g**	**4**	**0.999**	**0.955**	**0.755**	**0.531**
102.7	T_{1u}	3	1.000	0.978	0.852	0.679
107.1	G_u	4	1.000	0.977	0.829	0.626
112.4	T_{2u}	3	1.000	0.986	0.887	0.731
122.4	**H_g**	**5**	**1.000**	**0.986**	**0.861**	**0.657**
131.5	A_g	1	1.000	0.998	0.977	0.933
193.0	T_{1u}	3	1.000	1.000	0.988	0.944

[36,37]. Therefore, the combined effect of spin-orbit coupling and distortions can give rise to ZFS in this highly symmetric cluster. Correlation of T_{nozzle} (i.e., vibrational excitation) and the observed influence of the magnetic field on the BP indicate that the magnetic response of the cluster is very sensitive to excitations of the vibrational modes. The d orbitals in the center of an icosahedron transform like the irreducible representation H_g in the icosahedral point group. According to the Jahn-Teller (JT) theorem, only normal modes that transform like the irreducible representations contained in the symmetric Kronecker product $H_g \otimes H_g = A_g \oplus G_g \oplus 2H_g$ cause first order interactions with these orbital states [38,39].

In order to explain the microscopic origin of the vibrationally induced spin orientation, all excited JT active modes are assumed to have the same effect. The vibrating clusters are influenced by a fluctuating (i.e., transient) ZFS, which couples the spin and rotational degrees of freedom, leading to avoided crossings. Accordingly, the thermally excited clusters show a deflection behavior which can be described by the Brillouin function, taking the vibrational temperature of the clusters into account. The experimentally observed BP then is obtained as the sum of two components given by the superatom model and the avoided crossing model (dotted and dashed black lines in Fig. 2, respectively). The fraction of clusters with thermally excited vibrations is determined by a Boltzmann distribution taking the wave numbers ω_i and degeneracies G of the vibrational modes into account (obtained from DFT calculations of the global minimum structure, see Table I).

The avoided crossing model is applied only to clusters excited in those normal modes which split the orbital degeneracy of the d states (boldfaced in Table I). The total fraction of clusters which are in the vibrational ground state according to those normal modes is the product of the individual ground state population of each JT active

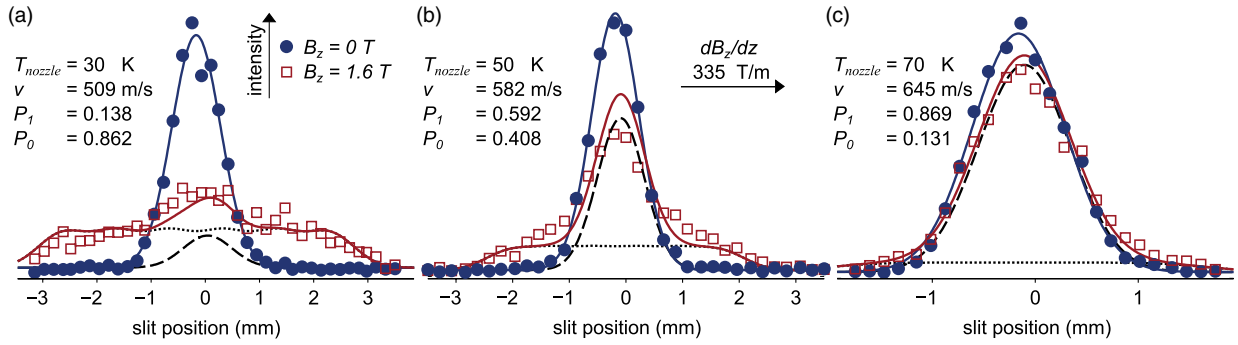

FIG. 2 (color online). Beam profile of $Mn@Sn_{12}$ at $T_{nozzle} = 30$ K (a), 50 K (b), and 70 K (c) without (dots) and with (squares) a magnetic field applied. The simulated BP at 1.6 T (red line) is obtained as the sum of a contribution from the superatomic model (dotted line, P_0) and a contribution showing Brillouin-like response (dashed line, P_1). The contribution P_0 is given by the product of individual ground state populations of Jahn-Teller active modes $P_{0,i}(T_{nozzle})$ (see Table I) and $P_1 = 1 - P_0$. The range of slit positions is adjusted to the decreasing effect of the magnetic field at higher velocities v.

mode (the fully symmetric A_g mode leaves the orbital states degenerated and is therefore neglected). The sum of both fractions is the simulated BP plotted in solid red in Fig. 2. All simulated BPs are obtained with the assumption $T_{vib} \approx T_{nozzle}$ and with the magnitude of the magnetic dipole moment $\mu_0 = \sqrt{S(S+1)}\mu_B = 5.9\mu_B$. The simulated BPs are in very good agreement with the limiting superatomic response at low temperature and the nearly pure Brillouin type response at high nozzle temperatures. At 50 K [Fig. 2(b)], where neither of the two fractions dominates, experimental data and the two component model are not in full agreement. This discrepancy might well be related to the equivalent treatment of all JT active modes. Spin orientation can be expected to depend also on the type of distortion (i.e., rhombic and axial components of the transient ZFS).

Our interpretation of the experimental observations crucially depends on the assumption $T_{vib} \approx T_{nozzle}$. With typical source conditions and He as the carrier gas, the vibrational energy of the clusters in the molecular beam is hardly influenced by the supersonic expansion [30,31]. Therefore, if carrier gas and nozzle reach equilibrium, the vibrational temperature of the clusters after expansion is approximately equal to the nozzle temperature. The maximum Mach speed of He then is $v_{He} = \sqrt{5k_B T_{He}/m_{He}}$ [40] with the Boltzmann constant k_B, the mass of the He atom m_{He}, and the He temperature $T_{He} = T_{nozzle}$. Except at 16 K, the velocity of the clusters is below v_{He} and accordingly for all measurements in Fig. 2 it seems reasonable to use $T_{vib} \approx T_{nozzle}$. Because of velocity slip [40] v measured is in general smaller than v_{He} (this effect increases with the terminal Mach speed). At 16 K, however, the velocity v of the clusters is slightly higher than v_{He}, indicating insufficient cooling and indeed this explains the deviations in the central region of Fig. 1, caused by a small amount of clusters which are not in the vibrational ground state.

In conclusion, we have shown experimentally that the isolated cluster $Mn@Sn_{12}$ in its vibrational ground state can be understood as a true paramagnetic superatom. We have demonstrated the tremendous sensitivity of the field-induced response to the vibrational state of the cluster. It is concluded that the vibrationally induced distortion of the clusters equilibrium structure causes a coupling between spin and rotational degrees of freedom. Therefore, clusters which are vibrationally excited show a response according to the Brillouin function. The results presented here contribute experimental evidence for spin-lattice interactions mediated by solely internal molecular vibrations.

We acknowledge financial support by the *Deutsche Foschungsgesellschaft* through Grant No. SCHA 885/10-1. We thank Professor Peter Schwerdtfeger and the *Centre for Theoretical Chemistry and Physics* at Massey University, New Zealand for the hospitality and computer resources provided. We are also indebted to Dr. Behnam Assadollahzadeh and members from our work group for proofreading the manuscript. U. R. gratefully thanks the *Deutscher Akademischer Austauschdienst* for a traveling stipend and Professor Robert Berger for helpful discussions.

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