Spin Relaxation in Small Free Iron Clusters

Walt A. de Heer, Paolo Milani, and A. Châtelain
Institut de Physique Expérimentale, Ecole Polytechnique Fédérale de Lausanne, CH 1015, Lausanne, Switzerland
(Received 16 April 1990)

Stern-Gerlach deflections of cold iron clusters in a molecular beam, with from 15 to 650 atoms per cluster, have been measured. It is found that the clusters deflect uniquely in the direction of the increasing field, indicating spin relaxation within the isolated clusters. The measured average magnetic moments increase with increasing cluster temperature and with increasing field, and in all cases they are found to be below the bulk value.

PACS numbers: 75.50.Bb, 36.40.+d

Investigations of magnetic properties of small magnetic particles is an active field of research,[1-4] both because of its importance for fundamental physics as well as for applications such as high-density magnetic memory devices. Nevertheless, to our knowledge, only one other experiment has been performed on free iron clusters.[3]

We have observed the deflections of small iron clusters by an inhomogeneous magnetic field in a collision-free molecular beam. For all clusters studied, the deflections are uniquely towards the high field, as for macroscopic iron particles. We also find that the measured magnetic moments increase with increasing cluster temperature. The deflections indicate a relaxation process within the isolated clusters which provides for the first time an example of intramolecular spin relaxation, giving rise to nonzero average magnetic moments.

The effects we describe below have been observed for all clusters studied, i.e., for $N=15$ to 650, where N is the number of atoms per cluster. In this Letter we concentrate on the magnetic properties in three size ranges of clusters: $N=56$–72, 120–140, and 225–256.

The experimental apparatus has been described previously[5] and a brief description follows, including relevant modifications. The clusters are produced in a laser-vaporization source designed to produce cold and stable cluster beams.[6] The hot iron metal plasma, produced by irradiating an iron rod with light from a pulsed Nd-doped yttrium aluminum garnet laser (50–75 mJ/pulse, 10 Hz), is quenched in a short pulse of He gas in a chamber with a volume of about 1 cm^3, after which the He gas-metal vapor mixture passes through a 3-mm-diam, 15-mm-long tube which terminates in a 1.5-mm-diam cylindrical nozzle with a tapered entrance and 1-mm channel length. The tube and nozzle are thermally insulated from the source body and can be cooled to liquid-nitrogen temperatures. The beam is collimated by means of two slits (0.8 mm×4 mm), 100 cm apart, and then passes between the pole faces of a Stern-Gerlach magnet,[7] of which the length of the deflecting field is 12.5 cm.

The collimated beam then enters a time-of-flight mass spectrometer[5] which is oriented perpendicular to the beam axis. The mass spectrometer is located 240 cm from the source, and 100 cm from the magnet. The clusters are then ionized with light from an excimer laser (ArF, 193 nm), which is synchronized with the vaporization laser. Deflections of the particles may be measured either by position-sensitive time-of-flight mass spectrometry[5] or by scanning the collimated ionizing light (0.5 mm×10 mm), across the beam. The latter method is used exclusively in the measurements presented here. The former is used to measure deflections of individual clusters species and we will comment on some of the results below. The measurements here are performed by gating the time-of-flight signals so that only the clusters with masses corresponding with the time window are counted. Prior to a run, detailed mass spectrum are recorded to verify that the oxide contamination is low, i.e., that less than 5% of the clusters ($N<100$) contain an oxygen atom. The mass spectrometer resolution is better than 1/1000, and no contaminants other than oxygen are observed.

Figure 1 shows Stern-Gerlach profiles of clusters with 120–140 atoms per cluster, for several values of the deflecting field. Note that the peak moves towards the

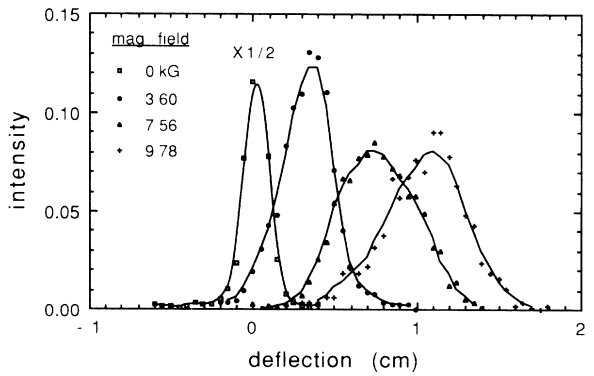

FIG. 1. Representative Stern-Gerlach deflection profiles for $N=120$–140 atom clusters, for several magnetic-field strengths. Note that the deflections are uniquely in the direction of increasing field. The zero-field profile is normalized to $\frac{1}{2}$, whereas the others are normalized to 1.

right with increasing field, and that there is no significant intensity to the left of the zero-field profile. Analysis of the deflection profiles shows that the underlying magnetic-moment distributions extend up to about $1\mu B$ and that the average magnetic moment increases with increasing field.

The average measured magnetic moments are determined from the average deflections d and the measured velocities v, using the relation[7] $\mu = Kdmv^2/B$, where m is the mass, B is the field, and K is a geometrical constant which is experimentally determined from the Stern-Gerlach deflections of aluminum atoms. This procedure gives the average magnetic moment, which is related to the degree of alignment of the intrinsic magnetic moment with respect to the applied field. It is important to stress that the measured magnetic moment is a lower bound for the magnitude of the intrinsic magnetic moment of the cluster.

The measured magnetic moments per atom for three cluster size ranges in various fields are shown in Fig. 2. For low fields the moment rises approximately linearly with field. The smaller cluster ranges show structure with significant changes in the slope. In no cases have we found clear evidence for saturation of the moment and the measured moments are well below the bulk value of $2.2\mu B$ per atom. The largest moment measured is for clusters near $N=500$, with about $1.4\mu B$ per atom. The shapes of these curves may be compared with the related magnetization curves of bulk ferromagnetic, and for bulk paramagnetic samples,[8] which are quite smooth. The observed reproducible fine structure (see Fig. 2 and Fig. 4 below) has no counterpart in bulk magnetization curves.

Temperature effects were investigated in the following experiments. Figure 3(a) gives the measured moments for $N=120$–140 with $B=11$ kG for several cluster velocities, and for two nozzle temperatures: 300 and 77 K. In this experiment the excimer laser was fired at the indicated times t so that clusters with well defined velocities are selected.[5] The time t corresponds to the time interval between the firing of the vaporization and photoionization lasers and the selected velocity is approximately equal to L/t, where L is the source to spectrometer distance. As will be shown below, the cluster temperatures are related to t. For both nozzle temperatures the magnetic moments of the clusters depend sensitively on t, and the lowest moments measured with the nozzle at 300 K are at least 3 times as large as those with the 77-K nozzle [Fig. 3(a)]. This preliminary observation gives a first indication that the measured magnetic moment increases with increasing temperature.

Further evidence for this temperature effect is as follows. The times t, which correspond with the minimal moments for a given nozzle temperature, also correspond with the maxima in the cluster intensities [Fig. 3(b)], and with cluster velocities most closely equal to that of the carrier gas. This is significant since those clusters which arrive at later times (i.e., larger t) will be slower and are therefore subject to velocity slips with the carrier gas. This velocity slip will cause heating[9] of the rotational and vibrational degrees of freedom. By the same mechanism, clusters which are faster than the carrier gas

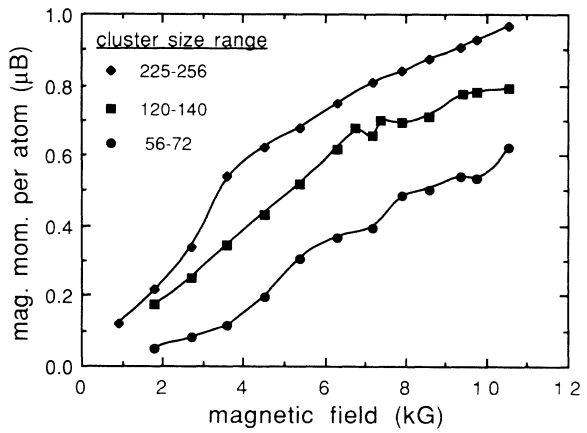

FIG. 2. Measured magnetic moments as a function of cluster size, for three size ranges as indicated. The solid squares correspond with the data presented in Fig. 1. Absolute error bars are estimated to be on the order of 10%, whereas the relative error bars within a set of data are estimated on the order of 5%.

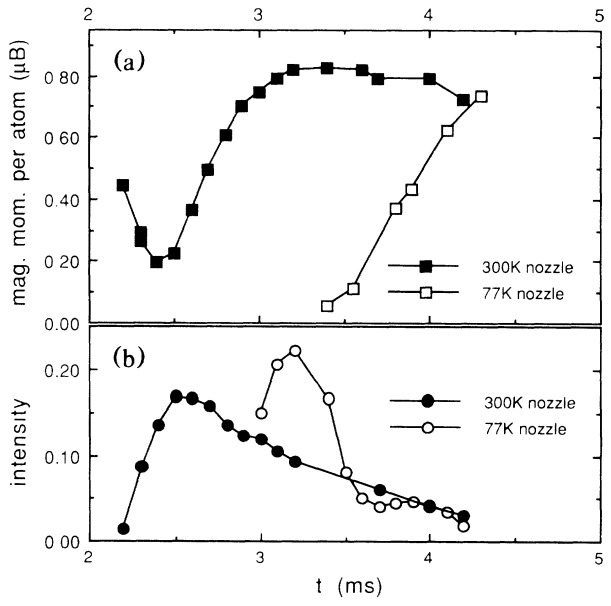

FIG. 3. (a) Average magnetic moments for $N=120$–140 atom clusters for clusters produced with a 77-K nozzle and with a 300-K nozzle, as a function of the time of ionization (see text). (b) Measured cluster-beam intensities corresponding with the measurements in (a). Note the pronounced minima in the magnetic moments which occur at the maximum of the beam intensity and that for the cold nozzle the minimum is much below that of the room-temperature nozzle.

should also be expected to be hotter. From these observations and the data presented in Fig. 3 we conclude that, in general, *the measured magnetic moments increase with increasing cluster temperature.*

To further illustrate the temperature effect related to the velocity slip, Fig. 4 shows the magnetic moments as a function of the field strength for several velocities (the nozzle is at 300 K). Note that clusters with large velocity slips have larger slopes and more structure than those with small velocity slip. This shows that not only the magnitude, but also the fine structure of the measured magnetic moments as a function of field are temperature dependent.

We crudely estimate the relevant temperatures as follows. Since the clusters undergo on the order of 10^5–10^6 collisions with the carrier gas in the nozzle tube, we may assume that they equilibrate with it. They are therefore at least as cold as the nozzle and are then cooled further in the expansion processes to their terminal beam temperatures. The expansion gives rise to translational temperatures of about[10] 15 and 4 K, for nozzle temperatures of 300 and 77 K, respectively. The clusters, however, have temperatures which are greater than this,[10] and taking velocity slip effects into account, under the conditions of Fig. 4, the rotational temperatures are estimated[9] to range from about 75 to 225 K. As explained below, we expect that the rotations are particularly important in the relaxation process.

Possible effects caused by the changing field strength experienced by the clusters as they enter the magnetic field have been investigated as follows. The entrance into the deflecting field of the magnet is provided with "ears," i.e., a tapered section to reduce dB_z/dx (Ref. 7) (i.e., the field gradient along the the beam direction), whereas the exit has no such provision and dB_z/dx is much larger. No change in the measured moments is observed when the magnet is reversed (i.e., the entrance and exit are interchanged) so that dB_z/dx is not expected to be important in the relaxation process.[7]

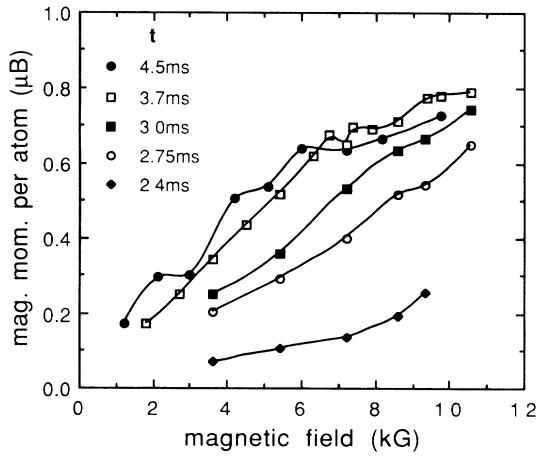

FIG. 4. Magnetic moments of 120–140 atom clusters as a function of field strength for several t, showing the increase in the measured magnetic moment as a function of temperature. Note that the high-temperature data (i.e., those with large t) show a tendency towards saturation at high fields.

Although we cannot fully explain the observed effects, several general statements based on the conservation of angular momentum can be made. Regardless of the processes involved, the component of the total angular momentum of the cluster along the field axis must be conserved[11] so that the relaxation effects most likely involve a coupling of rotational and spin angular momenta. Such a coupling may result from a preferred direction of the total spin in the atomic framework of the cluster (i.e., analogous to the magnetic anisotropy[8] in the bulk). This couples the spin to the rotations,[11] providing a mechanism for the spin and rotation to exchange angular momentum. Preliminary numerical calculations along these lines are underway and are able to simulate some of the relaxation effects observed;[12] however, the results are not yet conclusive. We do not believe that the vibrational modes are very important for two reasons: These modes do not have angular moment, and furthermore, even the lowest vibrational frequencies (estimated from the bulk speed of sound and the cluster diameters) are much larger than the magnetic energies involved.

In conclusion, these experiments provide striking evidence for spin relaxation in free iron clusters, not anticipated[13] in the previous investigations of Ref. 3. Although the relaxation is clearly a complex phenomenon, involving the cluster size, the applied field, and the temperature, general trends can be identified as we have shown here.

Extensive investigations of the magnetic properties of size-selected iron clusters are underway, and preliminary measurements of clusters from 15 to 50 atoms per cluster show effects qualitatively similar to those observed for the larger clusters.

We are very grateful to Dr. Pietro Ballone for many helpful suggestions and discussions throughout the course of these experiments. Discussions with Dr. W. A. Saunders and Professor L. Falicov are gratefully acknowledged. This work was supported by the Swiss National Foundation for Scientific Research.

[1] *Magnetic Properties of Low-Dimensional Systems,* edited by L. M. Falicov and J. L. Moran-Lopez (Springer-Verlag, Heidelberg, 1986); *Magnetic Properties of Low-Dimensional Systems II,* edited by L. M. Falicov, F. Mejia-Lira, and J. L. Moran-Lopez (Springer-Verlag, Heidelberg, 1989).

[2] G. M. Pastor, J. Dorantes-Davila, and K. H. Benneman, Phys. Rev. B **40**, 7642 (1989); C. Y. Yang, K. H. Johnson, D. R. Salahub, J. Kaspar, and R. P. Messmer, Phys. Rev. B **24**, 5673 (1981).

[3] D. M. Cox, D. J. Trevor, R. L. Whetten, E. A. Rohlfing, and A. Kaldor, Phys. Rev. B **32**, 7290 (1985).

[4] F. Schmidt, U. Stapel, and H. Walther, Ber. Bunsenges.

Phys. Chem. **88**, 310 (1984).

[5]W. A. de Heer, P. Milani, and A. Châtelain, Phys. Rev. Lett. **63**, 2834 (1989).

[6]P. Milani and W. A. de Heer (to be published).

[7]N. F. Ramsey, *Molecular Beams* (Clarendon, Oxford, 1956).

[8]C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1986).

[9]E. Kolodney and A. Amirav, Chem. Phys. **82**, 269 (1983).

[10]J. B. Anderson and J. B. Fenn, Phys. Fluids **8**, 780 (1965).

[11]C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill, New York, 1955).

[12]W. A. de Heer, P. Milani, and P. Ballone (to be published).

[13]Note that in those experiments only the on-axis depletion factor as a function of the magnetic-field gradient was measured, compared with the full deflection profiles in this work. The magnetic-moment distributions were then inferred, rather than measured, from an incomplete set of data.