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Measurement of magnetic moments of free Bi_NMn_M clusters

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Magnetic properties of free Bi_NMn_M clusters ($N=2-20$, $M=0-7$) are determined from Stern-Gerlach deflections at low temperature (46.5 K). Pure bismuth clusters with odd number of atoms exhibit paramagnetic deflections. The addition of manganese atoms produces a ferromagnetic response which is strongly size dependent. Certain combinations have very large magnetic moments such as Bi_5Mn_3, Bi_9Mn_4, $Bi_{10}Mn_5$, and $Bi_{12}Mn_6$.

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INTRODUCTION

The study of free magnetic clusters in molecular beams is not only important for the fundamental understanding of ferromagnetism but also for potential applications as it can uncover properties of materials in the nanoscopic size range. For example, Stern-Gerlach (SG) deflection experiments with cluster beams have shown that nickel, iron, and cobalt clusters are ferromagnetic and their magnetic moments per atom are enhanced compared to the bulk.[1] It has also revealed that small rhodium clusters are ferromagnetic with magnetic moments per atom of as much as 0.8 Bohr magnetons (μ_B),[2] while bulk rhodium is paramagnetic. Manganese clusters were found to be ferromagnetic or ferrimagnetically ordered in the size range from Mn_5 to Mn_{99},[3,4] with magnetic moments per atom in the range $0.3-1\mu_B$.

Time-of-flight mass-spectrometry (TOFMS) methods allow clusters with different compositions to be measured simultaneously, so that their magnetic properties can be determined with essentially perfect mass resolution, which eliminates uncertain effects due to contaminations or interactions with substrates.

Recently, the SG deflection method has also been applied to study magnetism in alloy clusters.[5–7] For example, experiments on Bi_NCo_M clusters[5] show that the cobalt atoms are responsible for most of the magnetic properties and bismuth merely produces a reduction in the Co magnetic moment.

The binary alloy cluster system studied here, Bi_MMn_N is inspired by the important properties of the bulk $Bi_{0.5}Mn_{0.5}$ alloy, known as bismanol, which is ferromagnetic with one of the largest known coercivities.[8] Manganese is an important magnetic element in molecular magnets and in ferromagnetic semiconductors,[9–12] which underscores the importance of this element as a component in magnetic materials.

EXPERIMENT

The bismuth manganese alloy clusters are produced by laser ablation of a 2 mm diameter rod of the alloy $Bi_{0.5}Mn_{0.5}$. The sample was prepared by co-melting Bi needles and Mn flakes in an electric arc furnace in an argon atmosphere using a home-built copper crucible with a cylindrical mold. The cluster beam machine has been described previously.[13] Briefly, the helium carried cluster beam is produced in a cryogenically cooled pulsed laser vaporization source. The source temperature is maintained at $T=46.5$ K using a closed cycle cryogenic refrigerator (Sumitomo, SRDK) and a feedback controlled heating system on the source. The cluster beam is skimmed and collimated (to a width of about 0.3 mm) before entering the inhomogeneous magnetic field produced by the Stern-Gerlach magnet ($B=0.91$ T and $dB/dz=345$ T/m). The clusters are photoionized using an ArF excimer laser (193 nm wavelength) and detected in a position-sensitive time-of-flight mass spectrometer (PSTOFMS).[14] This spectrometer allows simultaneous detection of both the masses and the positions of the clusters in the beam.

The time of flight is approximated by

$$\mathrm{TOF} = (C_1 + C_2 x)\sqrt{m}, \tag{1}$$

where C_1 and C_2 are constants, m is the mass of the cluster, and x is the initial position. In the PSTOF method mass resolution is traded for position sensitivity (using appropriately tuned electric fields) hence it is most effective when the masses of the clusters are well separated. In the present case both manganese and bismuth have a single isotope and the cluster masses never coincide in the size range where we study them. Two typical position sensitive mass peaks are shown in Fig. 1. The masses are separated by 11 amu. When the magnetic field is applied the peaks are shifted towards the right-hand side due to their spatial deflections.

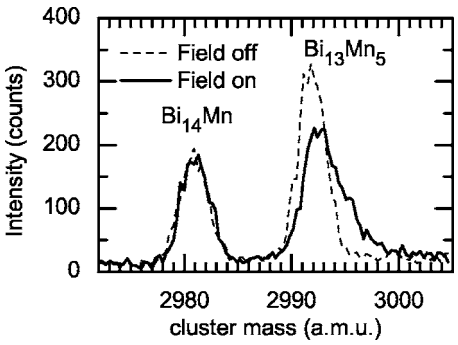

FIG. 1. Position-sensitive time-of-flight spectrum of two adjacent peaks in the mass spectrum, $Bi_{14}Mn$ (2981 amu) and $Bi_{13}Mn_5$ (2992 amu). The dashed thin line is without magnetic field applied ($B=0$) and the solid line is with $B=0.91$ T. The shift in the mass peaks with the magnet on is due to the deflections. In this case, the $Bi_{14}Mn$ is shifted by 0.04 mm and $Bi_{13}Mn_5$. is shifted by 0.56 mm.

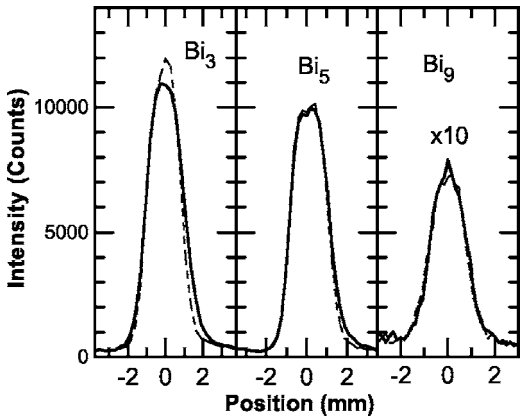

FIG. 2. Deflection profiles of pure bismuth clusters Bi_N, $N=3$, 5, and 9. The thin dashed line is without magnetic field ($B=0$) and the solid line is with $B=0.91$ T. Notice that the trimer deflects both towards high field (the right in the figure) and lower field (left), but the pentamer deflection is single sided. For the latter, the deflection is given by the Langevin equation.

RESULTS

Since the bismuth atom has an odd number of electrons, all Bi_N cluster with odd-N have at least one unpaired spin and hence they are paramagnetic. It is known that coupling of the spin to the rotations causes spin-relaxation-like effects so that deflections are reduced and only towards high fields (that explains why earlier experiments on Bi clusters failed to detect deflections[15,5]). The average beam deflection follows the Langevin equation even for very small cold clusters,[16] as they do for warmer large clusters.[17]

We do see deflections in small odd-N clusters of pure Bi_N clusters (see Fig. 2). Odd-N clusters with $N \geqslant 5$ show single sided deflections, that is, they deflect uniquely in the direction of increasing field. Even-N clusters show no response. The magnetic moment μ_N and the magnetization M_N (the projection of μ_N along the field directions) are related by the Langevin equation [Eq. (2)] (for a detailed discussion, see Ref. 16, we further note that this result can be contrasted with the symmetric deflections that we observed in niobium clusters, which indicates that the spin is not coupled to the cluster[13]).

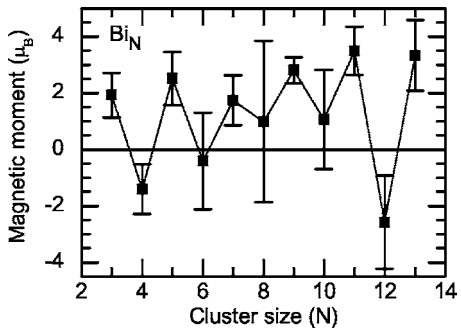

FIG. 3. Magnetic moments of pure bismuth clusters determined from their magnetization ($B=0.91$ T, $T=46.5$ K).

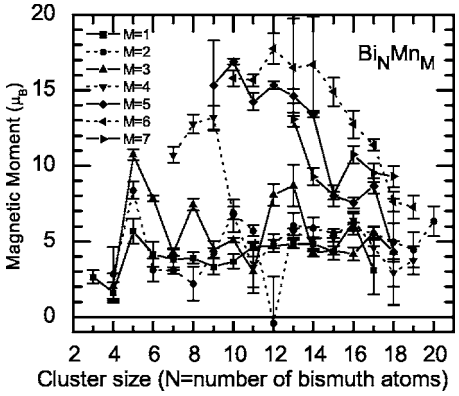

FIG. 4. Magnetic moments of Bi_NMn_M. Note the particularly large moments of Bi_5Mn_3, Bi_9Mn_4, $Bi_{10}Mn_5$, and $Bi_{12}Mn_6$.

$$M_N = \mu_N \left[\coth\left(\frac{\mu_N B}{k_B T}\right) - \frac{k_B T}{\mu_N B} \right], \tag{2}$$

where B is the magnetic field, k_B is Boltzmann constant, and T is the temperature; μ_N is experimentally determined from the deflections. Note that in the limit of $\mu_N B / k_B T \ll 1$,

$$M_N \approx \frac{{\mu_N}^2 B}{3 k_B T}. \tag{3}$$

Figure 3 shows μ_N as a function of N; the odd-even alternation is clear. The total magnetic moments of pure Bi clusters are less than $3\mu_B$.

Adding manganese to these clusters generally enhances the magnetic response. The magnetic moments are presented in Fig. 4. Several clusters stand out with particularly large moments, for example, Bi_5Mn_3, Bi_9Mn_4, $Bi_{10}Mn_5$, and $Bi_{12}Mn_6$. The data are graphically represented in Fig. 5 which also shows the magnetic moments of pure manganese clusters.[4]

Note in particular the total magnetic moment is very sensitive to the number of Bi atoms in the cluster. For example, the total magnetic moment of Bi_NMn_3 clusters varies from $3\mu_B$ to $11\mu_B$ in the range $2 < N < 20$. This can be contrasted with the Bi_NCo_M system,[5] where not much size dependence

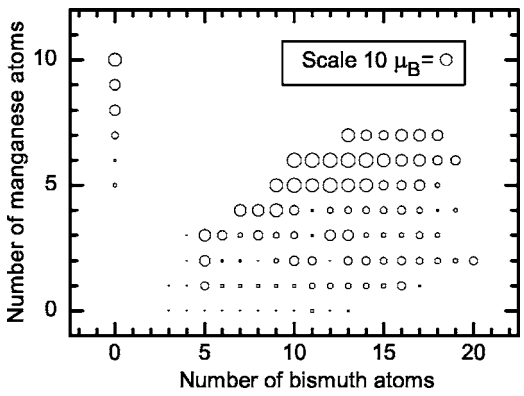

FIG. 5. Magnetic moments of Bi_NMn_M as a function of N and M. The diameters of the circles are proportional to the total moments of the clusters. The data for pure manganese clusters are from Ref. 4.

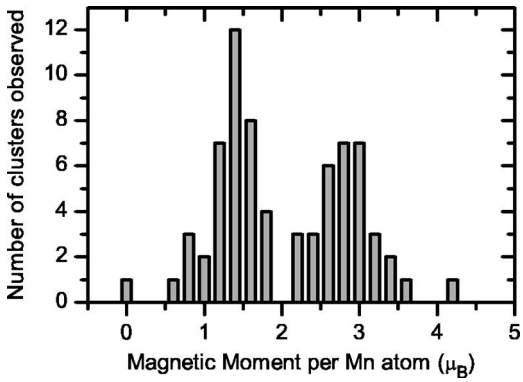

FIG. 6. Histogram of the magnetic moments per Mn atom for clusters Bi_NMn_M observed in these experiments with more than two Mn atoms. The distribution is bimodal. The peak at $3\mu_B$ is identified with ferromagnetic coupling between Mn moments; the peak at $1.3\mu_B$ is identified with ferrimagnetic coupling.

was found for $M>2$ and the magnetic moment is essentially exclusively determined by the value of M in that case. In this context note that Bi/Co is an immiscible system so that a Bi_NCo_M cluster is probably segregated and hence the total magnetic moment is mainly due to the Co component. In contrast, Bi/Mn forms an alloy, so that it is likely that in a Bi_NMn_M cluster is also an alloy. Note that the magnetic order of a Mn cluster is expected to be sensitive to its structure. For example, Mn_n clusters are expected to be ferromagnetic for $n<4$ and ferrimagnetic for $n\geq 5$ (Refs. 18 and 19) which is consistent with the experimental result for $n>4$.[20] Hence, one can speculate that the effect of the Bi in the alloy clusters is to modify the exchange interactions between the manganese atoms, which affects both the local moments on the atoms as well as the magnetic order.

A histogram of the magnetic moment per Mn atom for $M>1$ (Fig. 6) sheds some light on the magnetic order. Two peaks are observed in the distribution, one is at $\sim 3\mu_B$ and the other around $1.3\mu_B$. It can be argued that the clusters that show $\sim 3\mu_B$ per Mn atom are ferromagnetically ordered (all spins are mutually aligned) and the others have ferrimagnetic order (some of the spins are antialigned). The magnetic moment of $\sim 3\mu_B$ of a Mn atom in Bi_NMn_M clusters is considerably smaller than the $5\mu_B$ local moment suggested by Khanna[21] for Manganese clusters. This reduction can be understood as due to the Mn—Bi covalent interaction in these clusters.[22] For example, there are two phases for the manganese bismuth alloy, $Mn_{0.5}Bi_{0.5}$ and $Mn_{0.52}Bi_{0.48}$. Their saturation magnetizations are $3.8\mu_B$ and $3.1\mu_B$ per Mn atom, respectively. The magnetic moment per Mn atom we find in clusters is closer to that of the less symmetric phase $Mn_{0.52}Bi_{0.48}$.

Our data further indicates that ferromagnetic order usually occurs when Bi to Mn ratio is close to 2 (cf. Bi_5Mn_2, Bi_5Mn_3, Bi_9Mn_4, $Bi_{10}Mn_5$, and $Bi_{12}Mn_6$), which suggests for this composition the separation between manganese atoms is optimal for ferromagnetic coupling.

CONCLUSIONS

Low temperature Stern-Gerlach magnetic deflection experiments have been performed on Bi_NMn_M alloy clusters and pure Bi clusters. Pure Bi_N clusters are paramagnetic and exhibit an even-odd alternation; there is no evidence for ferromagnetism. Nevertheless, the magnetic moments of the alloy clusters are very sensitive to the number of Bi atoms in them, the maximum moments occur approximately for $N:M=2:1$. This composition dependence suggests that the bismuth affects the coupling (and hence the magnetic order) of the manganese magnetic moments. The local magnetic moments of Mn atoms in these clusters are inferred to be about $3\mu_B$. Hence we surmise that the Bi atoms affect the magnetism in Bi_NMn_M clusters is two ways, (1) they bond with Mn atoms covalently and change their local magnetic moment; (2) they affect the interatomic distances between the Mn atoms which in turn affects the magnetic order.

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