Evidence for Adiabatic Magnetization of cold Dy\textsubscript{N} Clusters

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this purpose we study cold Dy$_N$ clusters ($T_n = 13\text{K}$) with a large bulk anisotropy energy ($10^4\text{erg/cm}^3$ at 0K [1]).

For the generation of Dy$_N$ clusters ($17 \leq N \leq 55$) we used a pulsed laser evaporation cluster source incorporated in a Stern-Gerlach molecular beam apparatus. The experimental setup is described elsewhere [2]. The source has been modified to produce clusters with very small temperatures. Now it is possible to cool the nozzle down to temperatures of $T_n=13\text{K}$ using liquid He. Additionally, the source is constructed such that the dwell time of the clusters in the cold nozzle channel should be sufficient to establish thermal equilibrium between clusters, He and nozzle. Therefore it can be expected that the cluster temperature before the adiabatic expansion equals the nozzle temperature. To favor a strong adiabatic expansion through the nozzle into the high vacuum of the flight tubes, which leads to further cooling of the clusters, a large He pressure of about 100mbar in the nozzle channel is applied. In fact the velocity of the clusters measured behind the nozzle confirms the existence of strong adiabatic expansion and thermal equilibrium between nozzle and clusters: Using the equation $V_{He} = \sqrt{5RT_{He}/m_{He}}$ [3], where $m_{He}$ denotes the molecular weight, $R$ the gas constant and $T_{He}$ the He temperature, we can calculate the He terminal speed $V_{He}$, if we replace $T_{He}$ by $T_n$ assuming thermal equilibrium between nozzle and He. At small nozzle temperatures ($13\text{K} \leq T_n \leq 40\text{K}$) the calculated He terminal speed $V_{He}$ agrees very well with the measured velocity of the clusters $V_C$, while for higher temperatures a growing velocity slip is observed. For example, at $T_n=13\text{K}$ we find $V_C = 396\text{m/s} \pm 30\text{m/s}$ and $V_{He} = 368\text{m/s} \approx V_C$ versus $V_C = 1200\text{m/s} \pm 40\text{m/s}$ and $V_{He} = 1765\text{m/s}$ at $T_n=300\text{K}$. The fact that no slip between the calculated He velocity and the velocity of the clusters is observed for $T_n \leq 40\text{K}$ indicates a strong adiabatic expansion and a thermal equilibrium between nozzle and clusters [3].

After being collimated the cluster beam passes the Stern-Gerlach magnet. The deflection is detected size selectively by a time of flight mass spectrometer in combination with an ionization laser beam. The magnet and the detection unit are described in [2].

For Dy$_N$ clusters generated at nozzle temperatures $T_n=13\text{K}$ and $T_n=18\text{K}$, we observe a shift of the Stern-Gerlach profile in the direction of the increasing magnetic field. This indicates that relaxation processes are involved. Studying the field dependence of the magnetization, we obtain magnetization curves which show saturation at large field strengths as displayed in Figure 1.

To make sure that the observed saturation of the magnetization is not an effect of the relaxation time scales involved, we repeat the deflection experiments on Dy$_N$ clusters with a Stern-Gerlach magnet of half of the length. We obtained half of the deflection and therefore the same magnetization. This shows that the measurement of the magnetization takes place under stationary conditions. Hence, within our resolution, there are no relaxation processes involved with relaxation times in the order of magnitude of the experimental time scale of typically 200$\mu$s which is the time Dy$_N$ clusters need to traverse the Stern-Gerlach magnet.

Now we turn to the question whether we expect isothermal or adiabatic magnetization under the experimental conditions described above. To understand the nature of the relaxation process it is important to consider which degrees of freedom are accessible in the cluster. As pointed out above, the clusters are in thermal equilibrium with the nozzle before the adiabatic expansion. After the adiabatic expansion the clusters exhibit a vibrational temperature $T_{vib}$ which is close to the nozzle temperature ($T_{vib} \approx T_n \leq 18\text{K}$). However, the rotational temperature $T_R$ is smaller, because the adiabatic cooling is more effective for rotations than for vibrations [3], since the coupling of the rotations on the translational modes is stronger. To estimate the number of vibrational states, which are thermally accessible in Dy$_N$ clusters, we calculate the vibrational partition sum and the occupation number of the vibrational ground state of the dimer Dy$_2$. As an eigen frequency we use the Einstein frequency of bulk Dy. We find that the ground state is occupied with a probability of 99.9% at $T_{vib} = 18\text{K}$. Although it is very likely that in Dy$_N$ clusters vibrational states with smaller frequencies than the Einstein frequency are available, this example demonstrates that only very few of the vibrational levels will be thermally accessible. To estimate the number of thermally accessible rotational states, we calculate the rotational occupation numbers of Dy$_{20}$. We approximate the complicated cluster structure by a sphere with the density of bulk Dy and the mass of Dy$_{20}$. For $T_R = 1\text{K}$ we obtain an occupation maximum at the rotational level $J_R = 27$ (2.2%), where $J_R$ denotes the rotational quantum number. Taking into account that large quantum numbers like $J_R=80$ are still populated (0.15%), the rotation of the clusters can be described in good approximation by the model of the classical rotor.

In the next step we want to address the problem, whether isothermal magnetization is possible, when the contribution of the vibrations to the heat bath necessary for the isothermal Langevin process is negligible, i.e. when the heat bath consists exclusively of rotational degrees of freedom. This question can be answered by considering the entropy transfer between the spin and the rotational system employing the Second Law of Thermodynamics. According to Boltzmann the entropy $S$ can be written as $S = -\sum_i k_B \omega_i \ln \omega_i$, where $\omega_i$ denotes the occupation probability of the state $i$ [14]. The entropy loss $\Delta S_J$ provoked by the magnetization process is due to fixing the orientation of the total angular momentum $J$ of the clusters in the magnetic field direction $z$ at large field strengths. This corresponds to the saturation of the magnetization. Without field the cluster has $2J+1$ possibilities of equal probability $\omega_i$ to orientate the total angular momentum versus the z-axis. Since we observe experimentally the saturation of
the magnetization (see Fig. 1), the order of magnitude of the magnetic moment $\mu_0 = g_J \sqrt{J(J+1)} \mu_B$, where $g_J$ denotes the $g$-factor of the cluster, can be estimated by taking into account that the saturation magnetization $\mu_S$ is approximately equal to the magnetic moment $\mu_0$. Assuming that the $g$-factor of the clusters is in the order of magnitude of the $g$-factor of the ground state of the Dy atom $g_J = 1.33 \approx g_J$, one obtains for Dy$_{20}$ with $\mu_S \approx \mu_0 \approx 9 \mu_B$ a total angular momentum of $J \approx 6$ and hence an entropy loss $\Delta S_J = \sum_{i=1}^{13} \ln(1/13) k_B / 13 = -k_B \ln 13$. According to the Second Law of Thermodynamics the rotational entropy $\Delta S_R \geq -\Delta S_J$ has to augment at least by the same amount. This entropy gain changes the rotational temperature $T_R$ according to the equation $\Delta S_R = c_{VR} \Delta T_R / T_0$, where $c_{VR}$ is the heat capacity and $T_0$ denotes the temperature of the clusters, before the field was applied. We have shown above that many rotational levels with large quantum numbers are occupied in Dy$_{20}$. Therefore we approximate $c_{VR}$ by the high temperature value $c_{VR} = 3 k_B / 2$. Hence the temperature change due to the magnetization process is given by the expression $\Delta T_R / T_0 \geq \ln(2J + 1) / 3$. For clusters with an initial rotational temperature $T_0 \approx 1$K the temperature rises during the magnetization process by $\Delta T_R \approx 1.7$K. This significant change of the rotational temperature shows, that in case it is not suitable to use the isothermal magnetization model.

Now let us turn to the question, whether adiabatic magnetization is possible. For the magnetization process the time $t_s \approx 10^{-7}$s needed by the clusters to move from a zero field region into the magnet with the full field applied, is important, because adiabatic magnetization is only possible when the magnetization takes place at much larger time scales than the relaxation process. Since the typical time scale for cluster rotations is $10^{-9}$s, the magnetization can take place adiabatically. Hence, we consider whether the adiabatic model proposed by Bertsch et al. can be applied to evaluate our experimental data.

The assumptions made in this model (classical rotation, classical spin and locked spin) reflect our experimental conditions. It has been discussed above that the rotations can be treated classically. In first approximation the spin of the cluster can be treated classically as well, because the saturation magnetization of the clusters indicates the existence of large total angular momenta (see Dy$_{20}$). The locked spin model is justified, since the thermal energy of the clusters ($T_c \leq 18$K) is much smaller than the magnetic anisotropy energy. Using the anisotropy energy of bulk rare earths ($\approx 10^4$erg/cm$^3$ at 0K [10]), we estimate for Dy$_{20}$ an anisotropy energy which corresponds to a temperature of about 500K. Therefore we use the adiabatic model proposed by Bertsch et al. to fit the magnetization curves of Dy$_N$ clusters, recorded for $N=17-29$ at $T_n=18$K and for $N=32-55$ at $T_n=13$K. Since most of the data measured at $T_n=18$K and at $T_n=13$K belong to the strong field regime (see Fig. 1), we use Equation 1 to fit our magnetization curves. After plotting the magnetizations versus $1/\sqrt{B}$, the magnetic moments and the rotational temperatures $T_R$ of the Dy$_N$ clusters are determined by linear regression, as shown in Fig. 2a. In average Equation 2 gives a good fit for the clusters generated at $T_n=18$K and at $T_n=13$K. Only magnetizations measured at very small field strengths, i.e. $B=0.22$T for $T_n=18$K do not fit the expected behavior, because they do not belong to the strong field regime. $T_R$ is calculated from the slope of the line fit and depends on the prefactors imposed by the structural assumptions and the assumptions about the distribution of the rotational energy. Hence the temperature scale depends on the geometrical details of the clusters, while the magnetic moment is independent.

Figure 2a shows the magnetic moments per Dy atom $\mu_0 / N$ of Dy$_N$ clusters with $N=17-55$ and their rotational temperatures $T_R$ obtained by applying the adiabatic model as described above. In average the magnetic moments per atom range between 0.3 to 0.6 $\mu_B$. In comparison to the magnetic moment of Dy $\mu_{Dy} = 10.6 \mu_B$ in
the ferromagnetic bulk phase the magnetic moments of the clusters are smaller by a factor of 20. This suggests that the magnetic ordering in the clusters is rather antiferromagnetic than ferromagnetic \((J = \sum_{i,j} j_{i} j_{j} \approx 0, \text{ with } j \text{ being the total angular momentum of the cluster and } j_{i} \text{ being the total angular momentum of the Dy atom})\), although the rotational cluster temperatures are well below the Curie temperature of the bulk \(T_{c}(\text{Dy})=86K\). Keeping in mind that the ferromagnetic ordering in rare earth metals is determined by indirect coupling through the valence electrons (RKKY interaction \([3]\)), this result is not very surprising and similar behaviour has been observed for other rare earth clusters \([10]\). Since the structure of small clusters differs strongly from the bulk lattice to compensate surface effects, the wave functions of non localized electrons like valence electrons change in response to the change of the long range structural ordering. As a result the coupling between the 4f⁹ cores of the Dy atoms in the clusters differs from the coupling in the bulk, since electrons in irregularly shaped cluster orbitals are polarized instead of electrons in orbitals described by regularly oscillating Bloch functions. The theoretical study performed by Pappas et al. on Gd₁₃ illustrates the effect of the modified exchange coupling on the magnetic structure of small rare earth particles very well \([7]\). In Figure 3a the rotational temperatures \(T_{R}\) of the clusters are shown. Since the rotational temperatures (0.2-2.0K) are much smaller than the nozzle temperatures \((T_{n}=13K\) and 18K), we conclude that the adiabatic cooling of the rotational degrees of freedom after the expansion takes place very efficiently, as it is suggested in \([3]\).

Although the adiabatic model developed by Bertsch et al. fits the recorded magnetizations very well in the strong field limit, the overall shape of the magnetization curve does not match the theoretical prediction in Ref. \([9]\) for a spherical cluster. The theoretically predicted adiabatic magnetization curve shows a linear dependence of the magnetization at small fields (Equation 2) like the isothermal magnetization, whereas the experimental data (Fig.3) suggest the existence of higher order terms. Since it cannot be assumed that all Dyₙ clusters in a size range of \(N=16-55\) are spherical, the breaking of the spherical symmetry could probably account for the differing curve shapes at small fields, as it was shown by quanummechanical calculations \([10]\).

In summary, the magnetization of Dyₙ clusters generated at low nozzle temperatures can be understood by assuming adiabatic magnetization, while an isothermal process is not consistent with the experiment. By measuring the saturation of the magnetization, the magnetic moment and the temperature of the clusters can be determined at the same time independently. The rotational temperatures obtained suggest a strong adiabatic cooling. The Dyₙ clusters exhibit a nearly antiferromagnetic spin order, although bulk Dy is ferromagnetic in the temperature range studied. This can be understood in the frame of the RKKY theory. The complicated size dependence of temperature and magnetic moment of the clusters remains an open question.

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\[\text{FIG. 3. In (a) the magnetic moments per Dy atom } \mu_{0}/N \text{ of Dy}_{N} \text{ clusters are plotted versus } N, \text{ in (b) the rotational temperatures } T_{R}. \text{ Filled squares denote Dy}_{N} \text{ clusters generated at } T_{n}=18K, \text{ empty squares denote Dy}_{N} \text{ clusters generated at } T_{n}=13K.\]
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