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Magnetization curves of Dy_N clusters

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Abstract. Magnetic properties of isolated Dy_N clusters are studied in a molecular beam performing Stern-Gerlach experiments. The magnetizations μ_z of Dy_N are measured in dependence of the magnetic field strength $B = 0$–1.6 T and at nozzle temperatures $T_n = 18$ K and $T_n = 300$ K. At room temperature the magnetization augments linear with the field following a simple paramagnetic model. At $T_n = 18$ K the magnetization curves saturate at field strengths $B \geq 0.8$ T. To explain the magnetization process at low temperatures two models are discussed: A model for adiabatic magnetization based on cluster rotation effects and a modified van-Vleck model.

PACS. 39.10.+j Atomic and molecular beam sources and techniques – 36.40.Cg Electronic and magnetic properties of clusters – 75.50.Cc Other ferromagnetic metals and alloys

1 Introduction

Throughout the last years many studies have been performed on the magnetic properties of small isolated d- and f-metal clusters like Co_N [1], Ni_N [2] and Gd_N [3]. Most of the results were obtained by the use of Stern-Gerlach deflection experiments [4] on isolated clusters in molecular beams. In all experiments deflections of the clusters to the strong field side of the gradient field were observed in contrast to the well known deflection patterns of atoms and small molecules [5,6]. This effect was explained within the frame of the classical Langevin model for superparamagnetic particles [7,8] using statistical mechanics. The Langevin model can be applied, if the following conditions are fulfilled: First, the heat bath provided by the clusters' vibrational degrees of freedom is large enough to guarantee an isothermal magnetization process. Second, the thermal energy is smaller than the coupling energy between the magnetic moments of the atoms $\boldsymbol{\mu}_i$ giving rise to one large magnetic moment $\boldsymbol{\mu}_0 = \sum_i \boldsymbol{\mu}_i$. If this is not the case paramagnetic behaviour is expected instead of superparamagnetic behaviour. Third, the coupling of the magnetic moment $\boldsymbol{\mu}_0$ of the cluster to the cluster lattice is smaller than the thermal energy, *i.e.* the magnetic moment is able to rotate freely. Since most of the experiments have been performed on clusters with relatively small anisotropy energies at nozzle temperatures which were smaller than the Curie temperature, but high enough to give rise to an isothermal heat bath, the application of the Langevin model was possible. Assuming that the temperature of the clusters T_c is approximately equal to the nozzle temperature T_n and using the fact that in most cases the thermal energy k_BT_c was much larger than the magnetic energy $\mu_0 B$, the weak field approximation of the Langevin model

$$\mu_z = \frac{1}{3}\frac{\mu_0 B}{k_B T_n}\mu_0 \tag{1}$$

could be used to obtain information about the magnetic moment of the cluster μ_0. The results obtained for the magnetic moments per atom μ_0/N of large Co_N [1], Fe_N [9] and Ni_N [2] clusters with $N \geq 2500$ were consistent with macroscopic magnetic properties of Fe, Co and Ni. However, for cold clusters with large anisotropy energies the Langevin model is likely to break down.

Bertsch *et al.* proposed an adiabatic model, which can explain magnetization processes for clusters without vibrational heat bath and high anisotropy energies, using rotation effects [10]. In the strong field regime ($k_BT_R \ll \mu_0 B$) with T_R being the rotational temperature of the cluster, the expression

$$\mu_z = \mu_0\left(1 - \sqrt{\frac{32}{9\pi}}\sqrt{\frac{k_BT_R}{\mu_0 B}}\right) \tag{2}$$

was obtained, while in the weak field regime the equation

$$\mu_z = \frac{2}{9}\frac{\mu_0 B}{k_B T_R}\mu_0 \tag{3}$$

holds. Bloomfield *et al.* studied rare earth cluster with large anisotropy energies at moderate nozzle temperatures between 73 K and 303 K. The authors find clusters which seem to show deflection profiles consistent with

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the adiabatic model, while others follow the superparamagnetic Langevin behaviour [11]. This might indicate that these studies were performed under conditions where both isothermal magnetization and adiabatic magnetization can take place. Recently saturation magnetization curves of Dy_N particles (N = 17-55) were measured at very small nozzle temperatures $T_n \leq 18$ K, which could be explained by applying the adiabatic model (Equation (2)) in the strong field regime $k_B T_R \ll \mu_0 B$ [12]. However, the magnetizations measured in the weak field regime, could not be explained very well by using Equation (3). The rotational temperatures obtained were in the range of 0.5-2 K, while the magnetic moments per atom μ_0/N of the Dy_N clusters were found to be in the range of 0.3-0.6 μ_B, which is much smaller than the bulk value ($\mu_{\mathrm{Dy}} = 10.6\mu_B$). This was attributed to the modified spin-spin coupling (RKKY interaction [13]) of the magnetic moments of the atoms due to size effects leading to nearly antiferromagnetic coupling even well below the Curie temperature of 86 K.

In this paper we want to discuss an alternative model to explain the shape of the saturation magnetization curves of Dy_N clusters and their reduced magnetic moments at low temperature. Then we analyse the magnetic properties of these clusters at high temperatures.

2 Experimental

For the generation of Dy_N clusters we use a pulsed laser evaporation cluster source incorporated in a Stern-Gerlach molecular beam apparatus. The experimental setup is described elsewhere [14]. 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 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. A more detailed description of the expansion conditions is given in [12]. 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 [14].

3 Results and discussion

Examples for the saturation magnetization curves of Dy_N clusters ($N = 17-29$) obtained at T_n = 18 K and of Dy_N clusters ($N = 10-19$) generated T_n = 300 K are displayed in Fig. 1 and in Fig. 2. For T_n = 300 K linear dependence of the magnetization μ_z on the field can be seen, while at T_n = 18 K saturation of the magnetization is observed. As pointed out in [12] these magnetization curves can be fitted in the strong field range using Equation (2), but the weak field range is not reproduced very

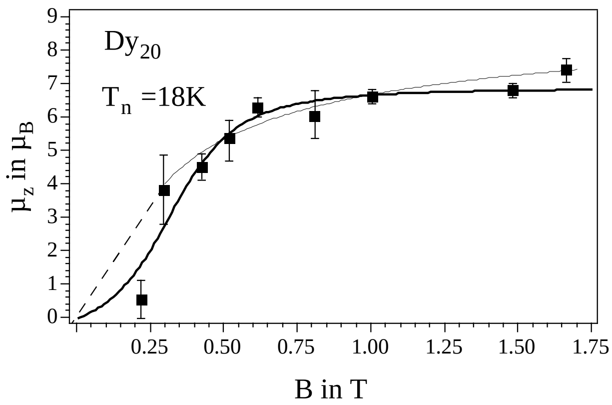

Fig. 1. The magnetization curve of Dy_{20} is shown. The thin line is the fitting function according to the adiabatic model by Bertsch *et al.* in the strong field limit, the dotted line in the weak field limit, while the thick line corresponds to the fitting function according to the modified van-Vleck model.

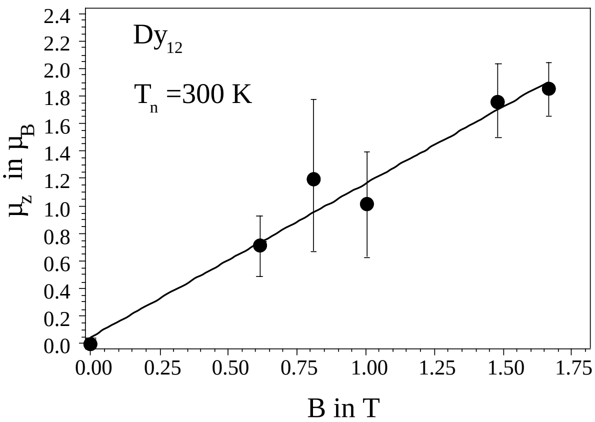

Fig. 2. Magnetization curve at T_n = 300 K. The solid line represents the fitting function applying the paramagnetic model.

well (Fig. 1). The main result obtained by applying this model was that the coupling between the f^9 total angular momenta $\boldsymbol{j}_i$ of the Dy cores in cold clusters is nearly antiferromagnetic. In the present paper we want to present an alternative approach to understand the shape of the magnetization curves especially at weak fields which has some similarity to the well known van-Vleck-Model [15]. We assume that the unperturbed ground state $|0\rangle$ of the Dy_N clusters exhibits a completely antiferromagnetic ordering, where the total angular momentum of the cluster $\boldsymbol{J}(B=0) = \sum_i \boldsymbol{j}_i = 0$ vanishes with $\boldsymbol{j}_i$ denoting the total angular momenta of the Dy atoms in the cluster. However, magnetization of the clusters is still possible, if an excited electronic state $|\epsilon\rangle$ with the energy ϵ and the magnetic moment $\mu_\epsilon \neq 0$ is incorporated in the model. Since the unperturbed ground state is not magnetic, the transition matrix elements $\langle 0|H|\epsilon\rangle$ between $|0\rangle$ and $|\epsilon\rangle$ must vanish for $B = 0$, *i.e.* they are of the form $\langle 0|H|\epsilon\rangle = b \cdot B$, with b being a constant and neglecting higher order terms in B. Then the perturbed ground state $\epsilon_0(B)$ for $B \neq 0$ is

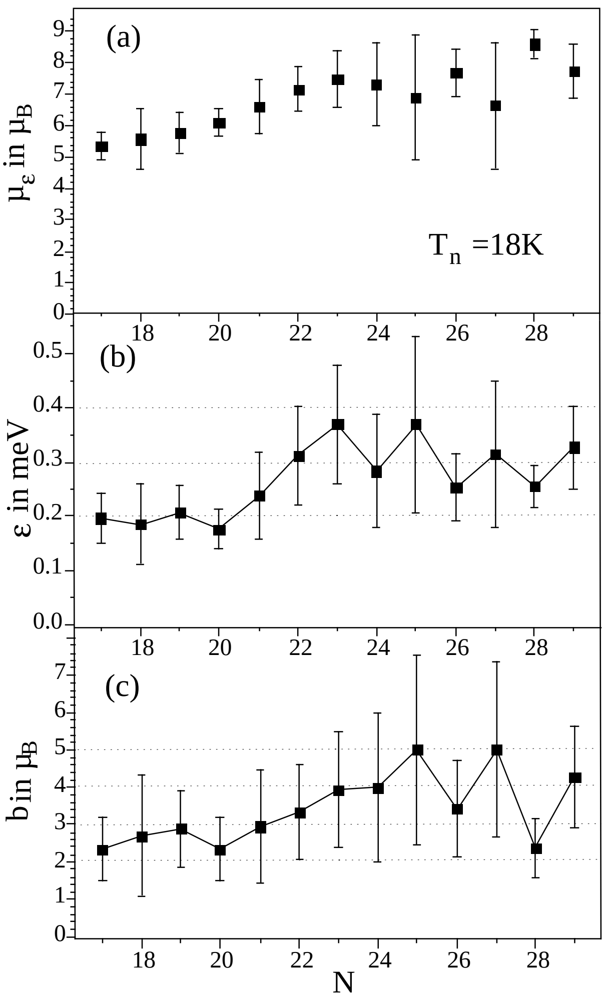

Fig. 3. In (a) the magnetic moments μ_ϵ of Dy_N are plotted against N, in (b) the energy ϵ and in (c) the coupling constant b.

found by diagonalizing the Hamiltonian matrix

$$H = \begin{pmatrix} 0 & b \cdot B \\ b \cdot B & \epsilon - \mu_\epsilon \cdot B \end{pmatrix}. \tag{4}$$

The derivative of the new ground state energy eigenvalue $\epsilon_0(B)$ with respect to the field B gives an expression for the magnetization curve

$$\mu_z(B) = \frac{\partial \epsilon_0(B)}{\partial B} = \frac{1}{2}\mu_\epsilon + \frac{1}{2}\frac{\mu_\epsilon^2 B - \mu_\epsilon \epsilon + 4b^2 B}{\sqrt{\epsilon^2 - 2\mu_\epsilon B\epsilon + \mu_\epsilon^2 B^2 + 4b^2 B^2}}. \tag{5}$$

This calculated magnetization curve yields a good description of the overall shape of the experimental curves, as shown in Fig. 1. Fitting the experimental data measured at $T_n = 18$ K, we obtain μ_ϵ, b and ϵ, as displayed in Fig. 3.

The magnetic moment per atom of the excited state $\mu_\epsilon/N \approx 0.3\mu_B$ in Dy_N clusters is smaller than the ground state magnetic moment calculated from the adiabatic model (Equation (2)) with $\mu_0/N \approx 0.5\mu_B$ in average. In the modified van Vleck model the magnetic moment of the excited state becomes larger with the growing cluster size, but the magnetic moment per atom μ_ϵ/N stays rather constant. The same behaviour was observed using the adiabatic model [12]. Further it must be mentioned that b and ϵ do not show any systematic dependence on N in the size range investigated. The coupling constant b ranges from $2\mu_B$ to $5\mu_B$, while the energy level distance between ground state and excited state corresponds to $\epsilon \approx 0.3$ meV $= 3$ K $\cdot\, k_B$. This indicates that the cluster temperature lies well below 3 K, since at higher temperatures the thermal population of the excited energy level would destroy the bending shape of the magnetization curve at weak fields.

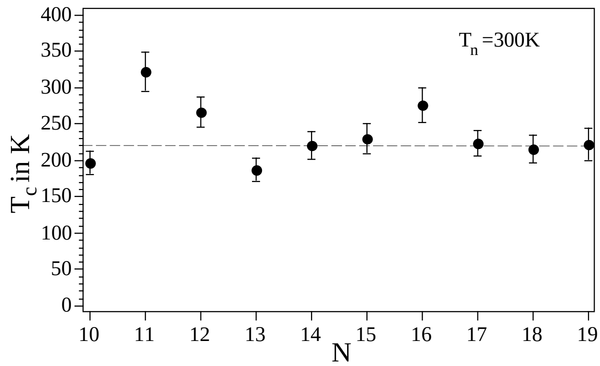

Fig. 4. Cluster temperatures T_c obtained by applying the paramagnetic model.

Now we want to turn to the magnetic properties of Dy_N clusters ($N = 10-19$) generated at nozzle temperature $T_n = 300$ K. Since the cluster size range observed at $T_n = 300$ K is shifted to smaller N compared to the size range of clusters generated at $T_n = 18$ K, there is unfortunately no overlap in size. In Fig. 2 the magnetization curve for Dy_{12} is displayed. In contrast to the magnetization curves measured for $T_n = 18$ K no saturation effects were observed and the dependence of the magnetization on the field seems to be purely linear. This is not very surprising, taking into account bulk magnetic properties of Dy. Since the nozzle temperature $T_n = 300$ K is well above the Curie temperature, *i.e.* 86 K, and the Néel temperature of Dy, *i.e.* 176 K, we expect that the magnetic moments of the Dy atoms $\mu_{\rm Dy} = 10.6\mu_B$ in the cluster are not coupled any longer. This means a paramagnetic behaviour

$$\mu_z = \frac{1}{3}\frac{\mu_{\rm Dy}B}{k_B T_c} N\mu_{\rm Dy} \tag{6}$$

of the Dy_N clusters at $T_n = 300$ K. Assuming that this model is correct, we can calculate the cluster temperatures T_c, which are displayed in Fig. 4. The obtained temperatures scatter statistically around a mean temperature of 220 K. The fact that the mean cluster temperature is a bit lower than the nozzle temperature can be explained very well with the cooling of rotational and vibrational degrees of freedom [16] by the adiabatic expansion, taking place behind the source nozzle. The absence of dependence of T_n on N in Fig. 4 is another important piece of information. The difference between superparamagnetic and paramagnetic behaviour becomes obvious by replacing μ_0 in Equation (1) by $N\mu_{\mathrm{Dy}}$. Then the dependence of μ_z or T_c on N is linear in the paramagnetic case and proportional to N^2 in the superparamagnetic case. Since we do not observe any additional linear dependence of the determined T_c on N, superparamagnetic behaviour of Dy_N clusters at $T_n = 300$ K can be ruled out. This confirms our assumption that the magnetic moments $\boldsymbol{\mu}_i$ in the cluster are uncoupled.

4 Conclusion

We have shown that the magnetization curves of Dy_N clusters at low temperatures ($T_c \leq 18$ K) can be described with a modified van-Vleck model, assuming a non magnetic unperturbed ground state, while clusters at $T_c \approx 220$ K are easily understood assuming paramagnetism.

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References

1. I.M.L. Billas, A. Chatelain, W.A. de Heer, Science **264**, 1682 (1994).
2. S.E. Apsel, J.W. Emmert, J. Deng, L.A. Bloomfield, Phys. Rev. Lett. **76**, 1441 (1996).
3. D.C. Douglas, J.P. Bucher, L.A. Bloomfield, Phys. Rev. Lett. **68**, 1774 (1992).
4. O. Stern, Phys. Z. **13**, 3052 (1922).
5. A. Gedanken, N.A. Kuebler, M.B. Robin, J. Chem. Phys. **90**, 3981 (1989).
6. N.A. Kuebler, M.B. Robin, J.J. Yang, A. Gedanken, Phys. Rev. A **38**, 737 (1988).
7. C.P. Bean, J.D. Livingston, J. Appl. Phys. **30**, 120S (1959).
8. S.N. Khanna, S. Linderoth, Phys. Rev. Lett. **67**, 1441 (1991).
9. I.M.L. Billas, J.A. Becker, A. Chatelain, W.A. de Heer, Phys. Rev. Lett. **71**, 4067 (1993).
10. G. Bertsch, N. Onishi, K. Yabana, Z. Phys. D **34**, 213 (1995).
11. L.A. Bloomfield, J. Deng, A.J. Cox, J.W. Emmert, H. Zhang, D.B. Haynes, J.G. Louderback, D.C. Douglass, J.P. Bucher, A.M. Spencer, M. Donath, P.A. Dowben, W. Nolting, *Magnetism and Electronic Correlations in Local-Moment Systems: Rare-Earth Elements and Compounds* (World Scientific, Singapore, 1998), p. 153.
12. S. Pokrant, Phys. Rev. A **62**, 1 (2000).
13. J. Kondo, Solid State Phys. **23**, 184 (1969).
14. T. Hihara, S. Pokrant, J.A. Becker, Chem. Phys. Lett. **294**, 357 (1998).
15. C. Kittel, *Einführung in die Festkörperphysik* (Oldenbourg, München 1996), p. 471.
16. D.R. Miller, G. Scoles, *Atomic and Molecular Beam Methods* (Oxford, New York, 1988), Vol. 1, pp. 14-16.