APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 12, 387–391 (1998)

Antiferromagnetism of Colloidal $[Mn^0 \cdot 0.3THF]_x$

Joachim Sinzig,[1] L. Jos de Jongh,[1] Helmut Bönnemann,[2]* Werner Brijoux[2] and Rainer Köppler[2]
[1]Kamerlingh Onnes Laboratory, Leiden University, PO Box 9506, NL 2300 RA Leiden, The Netherlands
[2]Max-Planck-Institut für Kohlenforschung, Postfach 101353, D-45466 Mülheim an der Ruhr, Germany

The reduction of $MnBr_2 \cdot 2THF$ (THF = tetrahydrofuran) using $K[BEt_3H]$ yields the organosol $[Mn \cdot 0.3THF]_x$. According to the UV/Vis, ESR (electron spin resonance spectroscopy), HRTEM (high-resolution transmission electron microscopy), XPS (X-ray photoelectron spectroscopy) and XAS (X-ray absorption spectroscopy) data, this nanosized metal colloid consists of small THF-stabilized Mn^0 particles which show, in susceptibility investigations, a diminished magnetic coupling as deduced from the Weiss temperature, $\Theta = 96$ K. The Neél temperature T_N is likewise strongly reduced in comparison with the bulk value (95 K). The THF-stabilized Mn^0 particles exhibit superparamagnetism below 20 K, with a partial blocking at 10 K, and to our knowledge represent the first colloid consisting of particles of an elemental antiferromagnetic metal.

Appl. Organometal. Chem. **12**, 387–391 (1998)

Keywords: colloidal manganese; ESR; susceptibility; antiferromagnetism; superparamagnetism

Received 16 January 1998; accepted 6 February 1998

INTRODUCTION

Because of the possibility of studying the size dependence of the magnetic transition temperature, the Neél temperature T_N, antiferromagnetic particles have often been investigated in recent years. In contrast to normal ferromagnets, the T_N values of some antiferromagnets lie below RT (room temperature) and can therefore be studied in commercial magnetometers.[1] Early results were published by Richardson and Milligan;[2] they reported a dramatic decrease in T_N from 523 K for bulk NiO to 95 K for NiO particles with an average diameter of 8 nm. Similar results were recently obtained on MnO particles by measuring the ESR (electron spin resonance spectroscopy) line width.[3] In manganese the situation is more complicated because of the complex magnetic structure. The magnetism in bulk manganese can be described in terms of localized magnetic moments, which generally allows the analysis of the susceptibility data in terms of a Curie–Weiss law.

Colloidal dispersions of manganese may be synthesized via chemical reduction of the manganese halides in THF (tetrahydrofuran) suspension. The synthesis (Eqn [1]), and an XPS (X-ray photoelectron spectroscopy) and XAS (X-ray absorption spectroscopy) study of the organosol $[Mn \cdot 0.3THF]_x$, have been reported recently.[4] As the starting material for the salt reduction, $MnBr_2 \cdot 2THF$ was used with $K[BEt_3]H$ in THF as the reducing agent. A subsequent cooling step to -78 °C allowed more than 95% of the insoluble by-product KBr to be separated from the manganese sol (Eq. 1). *In vacuo* (0.1 Pa), H_2 and BEt_3 may be completely removed together with the solvent.[4]

$$MnBr_2 \cdot 2THF + 2K[BEt_3H] \xrightarrow{THF}$$

$$[Mn \cdot 0.3THF]_x + 2\ BEt_3 + 2\ KBr \downarrow + H_2 \uparrow \quad [1]$$

The isolated $[Mn \cdot 0.3THF]_x$ particles are extremely oxophilic, very soluble in THF, but insoluble in hydrocarbons. Electronic and geometric structure investigations of the colloidal manganese using XPS and XAS showed that it consists of zero-valent manganese particles surrounded by intact THF molecules.[4] By HRTEM (high-resolution transmission electron microscopy) colloidal manganese particles with a mean particle size of 1–2.5 nm were detected.[4]

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* Correspondence to: Professor Dr Helmut Bönnemann., Max-Planck Institut für Kohlenforschung, Postfach 101353, D-45466 Mülheim an der Ruhr, Germany.
E-mail: boennemann@mpi-muelheim.mpg.de

CCC 0268–2605/98/050387–05 $17.50

EXPERIMENTAL

Preparation of [Mn·0.3THF]$_x$

A solution of K[BEt$_3$H] (50 ml, 0.226 M) in THF was added at RT over 3 h to a stirred suspension of MnBr$_2$·2THF (1.7 g, 5.12 mmol) in THF. During the reduction approximately 5 mmol of H$_2$ was released. The reaction mixture was stirred for another 16 h at RT. The precipitated KBr was removed by filtration. BEt$_3$ and THF were removed from the brown filtrate *in vacuo* (0.1 Pa). The product was dried *in vacuo* for 16 h. Elemental analysis: Found: Mn, 60.5; K, 4.2; Br, 8.6; B, 0.5; C, 16.6; H, 2.9%.

All manipulations were carried out under an argon atmosphere using Schlenk techniques. The solvents were dried and distilled under argon.

ESR investigations of [Mn·0.3THF]$_x$

The apparatus used for the measurements was a JES-RE2X spectrometer. The frequency of the microwave source was ≈9.4 GHz for RT measurements and ≈8.9 GHz for samples cooled with liquid nitrogen. The difference was due to the distinction between the cavities used for the two temperatures. The magnetic field could be swept from 0 to 0.8 T. For the calibration of the spectrum, the free radical DPPH (diphenylpicrylhydrazyl) was used as a marker, so all g values were taken with respect to DPPH ($g = 2.0036$). Samples were prepared in a glove box (O$_2$, H$_2$O < 1 ppm), and sealed Suprasil tubes were used as sample holders.

Susceptibility measurements on [Mn·0.3THF]$_x$

Measurements of the magnetic susceptibility χ and the magnetization M were performed in two different set-ups: (1) with a commercial SQUID magnetometer (SQUID, superconducting quantum interference device) type S600c in a ^{4}He cryostat for temperatures between 1.6 K and RT and in fields up to 5 T; and (2) with a home-built SQUID susceptometer for even lower temperatures down to 60 mK.[5] To average out any noise and the drift of the magnetic field, several scans were taken moving upwards and downwards and only the averaged curve was used to determine the M value of the sample. The transfer of the samples into special holders for susceptibility measurements was carried out in a glove box (O$_2$, H$_2$O < 1 ppm).

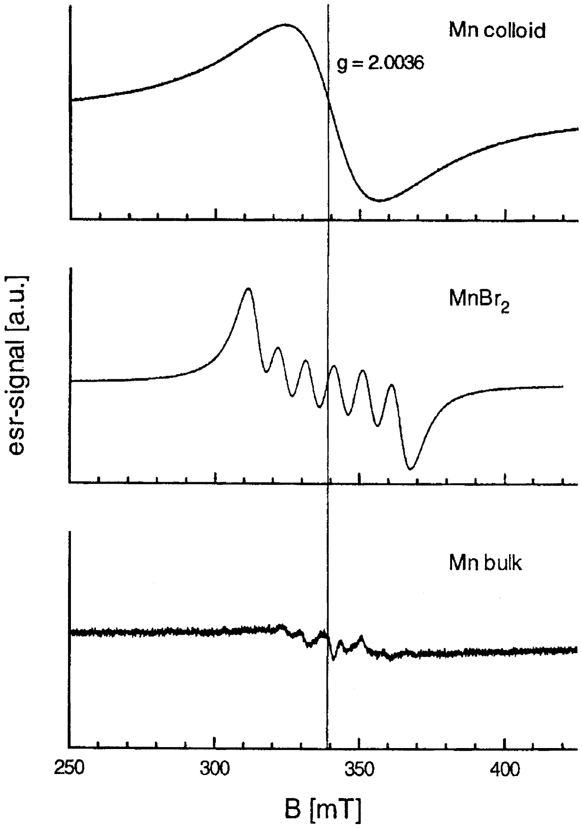

Figure 1 ESR spectra of the Manganese colloid, MnBr$_2$ and a bulk sample. (The scale on the x-axis is the same for all three spectra.)

RESULTS AND DISCUSSION

ESR

The manganese colloid, bulk manganese, and MnBr$_2$ were investigated by ESR to check the quality of the sample. The spectra measured at RT are shown in Fig. 1. The MnBr$_2$ sample exhibits the six-line splitting of the resonance curve due to the $s = 5/2$ spin state of the Mn^{2+} ions. The intensity of the bulk manganese spectrum is very weak because of the usual broadening of ESR signals in metals. The six weak lines in the spectrum most probably originate from surface oxidation. By contrast, the manganese colloid sample shows a pronounced broad resonance centred at the g value of the free electron ($g = 2.0023$). A broad resonance line was also published for the ESR spectra of other small metal particles and appears to be a common feature (see Ref. 6). The six-line splitting of MnBr$_2$ is

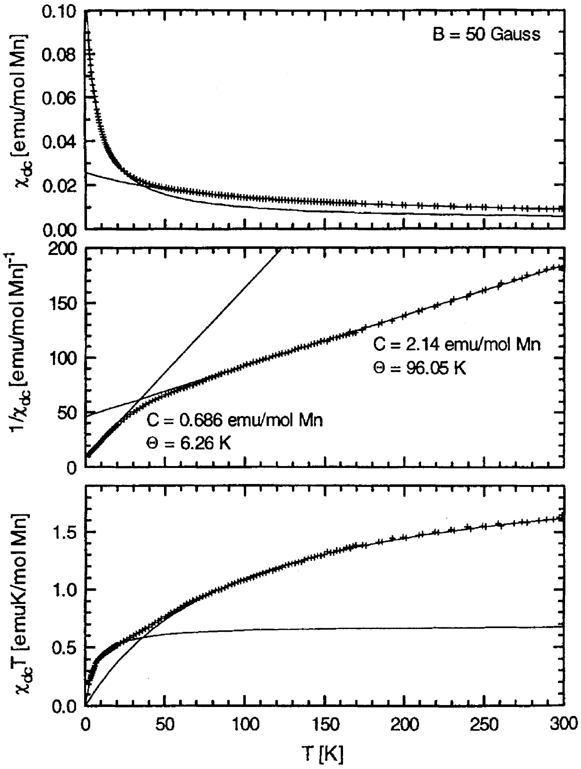

Figure 2 Dc susceptibility of the Manganese colloid measured in a field of 5×10^{-3} T. The plots are χ_{dc}, $[1/\chi_{dc}]$, and $[\chi^{dc} \cdot T]$ vs temperature. The solid lines are fits to the data with the same parameters for all plots.

absent here, indicating that there is no oxidized Mn in the colloid sample. Because the XPS and XAS results[4] show independently that the manganese colloid consists of zero-valent manganese particles, it may be concluded that manganese is in the metallic state in $[\mathrm{Mn}\cdot 0.3\mathrm{THF}]_x$.

Susceptibility measurements

In the dc-susceptibility (χ_{dc}) plot of $[\mathrm{Mn}\cdot 0.3\mathrm{THF}]_x$ shown in Fig. 2 at higher temperatures a Curie-law-like behaviour is observed, but at lower temperatures no clear transition to a magnetically ordered phase is to be seen. However, a careful fit of the data set exhibits a transition between 30 and 50 K to a different Curie characteristic with changed parameters (see also $[1/\chi_{dc}]$ and $[\chi_{dc}\cdot\mathrm{T}]$ plots in Fig. 2).

As can be observed in the figure, the curve may be divided into two temperature regions. Above 50 K, χ_{dc} can be described by a Curie–Weiss law (Eqn. [2]) with the Curie constant $C = 2.14$ emu (mol Mn)$^{-1}$ and the Weiss temperature $\Theta = 96$ K.

$$\chi_{dc} = C/(T + \Theta) \qquad [2]$$

For comparison, the dc susceptibility χ_{dc} measured for a bulk manganese sample, shown in Fig. 3, has a cusp and decreases at lower temperatures. Magnetic impurities, e. g. iron atoms, in the bulk sample lead to the somewhat higher Neél temperature $T_N \approx 100$ K compared with pure manganese ($T_N = 95$ K) and the increase in χ_{dc} below 60 K.[7,8] According to mean field theory, a condition for a stable antiferromagnetic state is $1 \leq \Theta/T_N \leq 3$ (see Ref.[9,] pp. 454 –457), but the upper limit has to be extended to $\Theta/T_N \leq 5$ in more complex structures like MnO. The magnetic structure in antiferromagnetically ordered α-manganese (the only stable form of manganese below RT) is rather complicated. The magnetic unit cell of manganese consists of 58 atoms with four different sites for the Mn atoms.[7,8,10] The magnetic moments per atom corresponding to the four sites in the magnetic unit cell are 1.9 (two atoms), 1.7 (eight), 0.6 (24) and 0.25 μ_B/atom (24). Therefore the Weiss temperature for bulk manganese was estimated to be $\Theta = 475$ K ($\Theta/T_N = 5$, as in MnO), which is much higher than the value deduced here for the colloid ($\Theta = 96$ K) in the range above 50 K.

From this we conclude that the antiferromagnetic coupling in the Mn particles (1–2.5 nm) is much weaker than in the bulk metal. The much lower magnetic ordering temperature is similar to the results for NiO and MnO particles.[2,3] The expected bulk sample ratio $\Theta/T_N = 5$ leads for the colloid to a

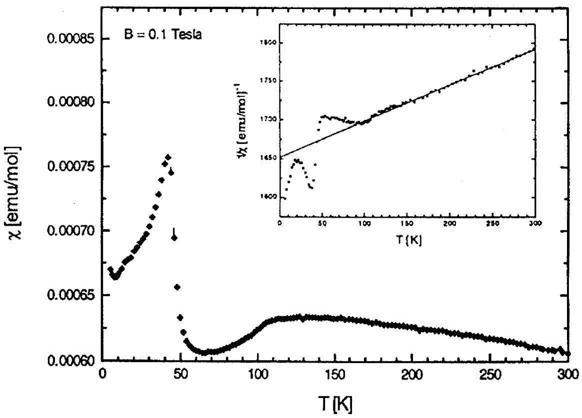

Figure 3 Dc susceptibility of bulk manganese. The insert shows $1/\chi_{dc}$ plotted vs temperature.

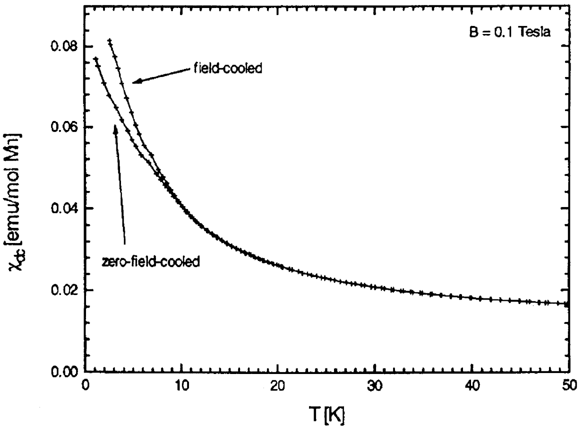

Figure 4 Dc susceptibility of zero-field-cooled and field-cooled samples of the Manganese colloid in a field of 0.1 T.

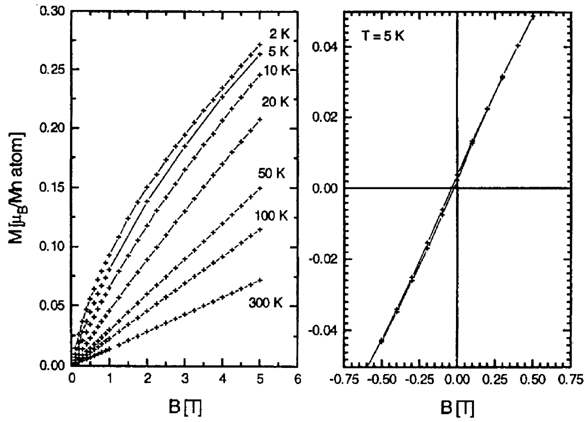

Figure 5 Magnetization M vs magnetic field for the manganese colloid, and a hysteresis loop measured at 5 K.

Neél temperature $T_N \approx 19.2$ K. This may be related to the observed difference in Curie behaviour at temperatures below 20 K, as shown in Fig. 2. The Curie constant, $C = 0.686$ emu (mol Mn)$^{-1}$, is much lower than the high-temperature value ($C = 2.14$ emu mol)$^{-1}$. Again, it has to be emphasized that the χ_{dc} curve cannot be described by a superposition of two Curie–Weiss laws over the whole temperature range, but that χ_{dc} shows a transition from the behaviour above 50 K to the low-temperature behaviour. Moreover, below 20 K the [Mn·0.3THF]$_x$ particles exhibit superparamagnetism which is not likely to originate from iron impurities. Due to the starting materials of the manganese colloid synthesis, there should be far fewer impurity atoms included in the colloidal sample than in the bulk material. The results shown could be reproduced in three separately prepared samples. Figure 4 shows the temperature dependence of the zero-field-cooled and field-cooled dc susceptibility χ_{dc} in a field of 0.1 T. Both values increase with decreasing temperatures, but split at 10 K.

The hysteresis loop taken at 5 K and the magnetization (M) curves at various temperatures are shown in Fig. 5. The hysteresis is very small (the loop is already closed at 0.5 T), which is not expected for a manganese material with iron inclusions. The $M(B)$ data also show linear field dependence above 20 K, which is unlikely for iron impurities. The magnetization M is not yet saturated at 5 T, even at the lowest temperatures, a behaviour which is expected for an antiferromagnetic particle, in which the net magnetic moment originates from uncompensated surface spins, as was pointed out by, for example, Pankhurst and Pollard.[11] The average magnetic moment per Mn atom lies still below 0.3 μ_B/atom at 5 T. Because of the unsaturated magnetization curves (Fig. 5) the determinination of a precise value is very difficult. In bulk manganese the average magnetic moment is 0.63 μ_B/atom, when averaged with respect to the occupation of the four sites in the bulk. Compared with this value, the observed magnetization of 0.3 μ_B/atom at 5 T for the [Mn·0.3THF]$_x$ particles (with *ca* 500 Mn atoms per particle) appears to be reasonable.

Relaxation of the magnetization M is a typical superparamagnetic feature for blocked particles. Therefore the time dependence of the magnetiza-

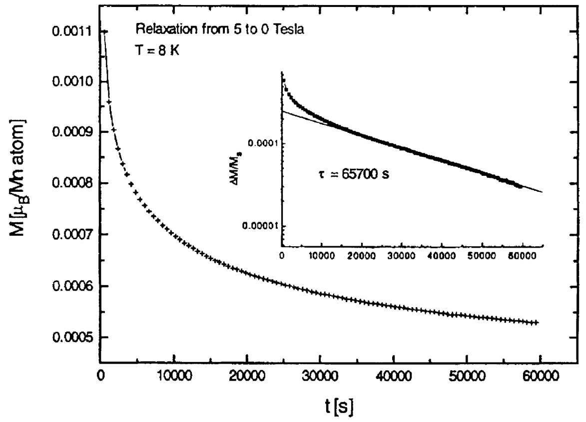

Figure 6 Relaxation measurement on the manganese colloid. In the insert the fit with an exponential decay is shown in a semi-logarithmic plot.

tion M of the $[\mathrm{Mn}\cdot 0.3\mathrm{THF}]_x$ particles was investigated. After the sample had been cooled to 8 K in a field of 5 T, the field was reduced to zero and the magnetization M was determined at certain time intervals. The curve obtained, shown in Fig. 6, could be fitted with an exponential time dependence after a non-exponential start, which is probably due to the particle size distribution.

Therefore, the manganese colloid, at temperatures below 20 K, exhibits all the features expected for a superparamagnetic sample, with partly blocked particles below 10 K, and no evidence for a clear magnetic ordering transition. Furthermore, a much lower value of the antiferromagnetic exchange is found in comparison with bulk manganese, in agreement with other investigations on antiferromagnetic particles. The magnetic behaviour observed below 20 K should be ascribed to a combination of anisotropy and interparticle magnetic interactions.

Acknowledgment The authors are thankful to Professor Reedijk and his group at the Gorlaeus Laboratory in Leiden for the ESR measurements.

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