PHYSICAL REVIEW B **67**, 224427 (2003)

Tunneling magnetoresistance between Co clusters coated with CO molecules

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(Received 31 January 2003; published 19 June 2003)

Films made of in-beam prepared Co clusters (mean diameter ≈4.5 nm) coated with CO molecules show an unusual large tunneling magnetoresistance (TMR) of about 50% at $T=1.7$ K. Using a model for the T-dependence of the TMR which includes T-dependent spin disorder at the cluster surface and higher-order tunneling processes below 4 K we obtain a spin polarization P of the tunneling electrons of $|P|=0.80(3)$. Such a high $|P|$ value can be explained by an interaction between the Co cluster surface atoms and the CO molecules which leads to preferred d-electron tunneling. An increased spin polarization of the d-electrons due to a charge transfer process from the CO molecule to the Co atom may be an additional reason for the unusual large TMR.

DOI: 10.1103/PhysRevB.67.224427 PACS number(s): 75.47.−m, 73.40.Gk, 73.40.Rw, 61.46.+w

I. INTRODUCTION

Granular systems nowadays can be produced in a rather well-defined way by using the co-deposition technique of in-beam prepared metallic clusters together with matrix gas atoms or molecules onto a cold substrate.[1,2] Using this technique one can study the tunneling magnetoresistance (TMR) of granular films made from transition metal clusters embedded in any insulating molecular matrix. Foregoing studies using the insulating matrices Kr(Xe), CH_4, C_2H_4, and CO_2 seem to indicate that the TMR increases with increasing interaction between the Co clusters and the matrix molecules.[3–6] The interaction between the Co clusters and the matrix molecules in all the above mentioned systems, however, is not strong enough to chemically bind the molecules to the clusters. This is quite evident, for example, from the experimental fact that heating the Co/C_2H_4 and Co/CO_2 films above $T\approx 70$ K and 80 K, respectively, results in an evaporation of the matrix molecules.

In order to find a granular system wherein the TMR eventually might be even larger than that found for or Co/C_2H_4 Co/CO_2, respectively, we decided to study the TMR in granular systems wherein the interaction between the Co clusters and the matrix molecules is even stronger than in those systems we had studied before. Such systems are granular films made from Co clusters coated with CO molecules. It is well known that CO molecules strongly interact with transition metal atoms (T) forming different carbonyls $T_m(CO)_n$. For that reason coating of Co clusters with CO molecules can be accomplished by depositing in-beam prepared Co clusters on a cooled substrate together with CO gas molecules present in the deposition chamber. A similar technique has been used by Fedrigo, Haslett, and Moskowits[7] to study the interaction of very small Co clusters Co_n ($n\leqslant 3$) with CO.

II. EXPERIMENTAL SET-UP

A detailed description of the experimental set-up for sample preparation and magnetoresistance measurements already has been given elsewhere.[8] The Co clusters are prepared in-beam with the help of a so-called inert-gas (Ar) aggregation cluster source.[9] Coating of Co clusters with CO was obtained by depositing the in-beam prepared Co clusters (mean cluster diameter ≈4.5 nm) in the presence of CO gas molecules onto a sapphire substrate hold at $T\approx 35$ K. This temperature is high enough to ensure that CO molecules do not condense at the substrate if they are not bound to a Co cluster [$p_{CO}(35\text{ K})\approx 10^{-3}$ mbar$\gg p_{\text{vacuum chamber}}\approx 10^{-7}$ mbar]. Cluster deposition rate was controlled by quartz balances. The cluster size distribution was determined *ex situ* by transition electron microscopy (TEM) of a thin carbon foil which was brought for a short time into the cluster beam. Analysis of the TEM pictures[10] give a cluster size distribution around a mean value of $L\approx 4.5$ nm with a variation ΔL (FWHM) in L of $\Delta L/L\approx 0.3$. The CO gas was introduced in the deposition chamber through an adjustable needle valve. The chosen CO gas inlet rates resulted in pressures in the deposition chamber during cluster deposition lying in the range 10^{-5}–10^{-6} mbar. The sapphire substrate on which the CO coated Co clusters were deposited is mounted onto the coldfinger of a variable temperature ^{4}He cryostat. Ag electrodes for resistance measurements have been evaporated on the sapphire substrate before cluster-film deposition. Distances between the Ag electrodes varied between 25 μm and 1.5 mm. Typical film dimensions were: 70 nm thickness, 3 mm width. Resistance were measured by a dc technique using an electrometer. Resistances up to about 5 GΩ could be measured with our set-up. The ^{4}He cryostat contains a split-coil superconducting magnet ($B\leqslant 1.2$ T) allowing *in-situ* magnetotransport measurements on the evaporated films. Due to hysteresis of the magnetoresistance these measurements were made with a sweeping magnetic field.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Tunneling resistance

Different samples have been prepared in the way described above. All samples showed high resistances which are lying in the range of about 1–10 kΩ at $T=35$ K and which are strongly increasing with decreasing temperature. This clearly shows that the Co clusters indeed are coated by an insulating CO layer. In order to check the stability of this coating some of the samples have been heated up to room temperature. No drastic drop of the sample resistance was

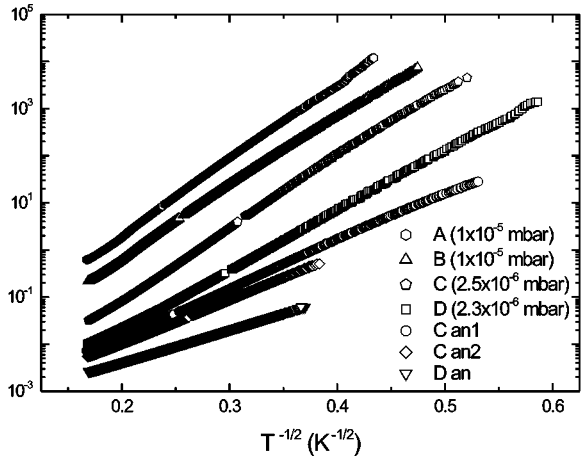

FIG. 1. Resistivity vs temperature for different TMR samples. The linear behavior corresponds to the expected $\rho \propto \exp(\sqrt{T_0/T})$-law. The CO pressure p during Co cluster deposition for different as-prepared samples is given.

observed during this heating which would have been a sign for desorption of CO. This fact indicates that the CO molecules are strongly bound to the Co cluster surface atoms. Our finding essentially is in agreement with the studies of Hill *et al.*[23] who observed CO desorption from Co clusters around $T \geqslant 300$ K. Since our He-cryostat does not allow to heat the samples above 300 K we can not perform similar desorption studies on our samples. In Fig. 1 we have plotted the resistivity ρ on a logarithmic scale versus $T^{-1/2}$ for all samples. The CO pressure p in the deposition chamber during cluster deposition decreases going from sample A to sample D. In addition, we have annealed samples C and D in order to reduce ρ. Sample C has been annealed in two steps. The maximum annealing temperature was 150 K. Decreasing CO pressure p during Co cluster deposition leads to reduced sample resistivity ρ (see Fig. 1). A change from $p = 1 \times 10^{-5}$ mbar (sample A) to $p = 2.3 \times 10^{-6}$ mbar (sample D) results in a decrease of ρ of about two orders of magnitude. However, the change of the slope m of the straight lines is only very small going from sample A to sample D. As we will explain below, this finding means that the tunneling barrier width essentially is independent of the CO gas inlet rate and it is only the density of the tunneling percolation network which differs for the different samples, resulting in different values for ρ. In this respect the Co/CO system is quite different from the noninteracting Co/(Kr,Xe) system: The latter is a percolating system wherein the tunneling barrier width strongly depends on the CO/Kr(Xe)-ratio and a change of this ratio results in a change of *both*, ρ and m.[4]

The fact that we observe straight lines in Fig. 1 indicates that $\ln \rho \propto T^{-1/2}$. In the following we want to discuss in more detail why the resistivities of our samples show such a behavior. The tunneling resistance ρ of granular samples made of clusters having the same size and a well-defined tunneling barrier with s, i.e., which have a homogeneous Coulomb barrier, should show an $\exp(AT^{-1})$-behavior. This indeed was observed in the work of Peng *et al.*,[11] where the TMR of CoO coated Co clusters has been studied. The $\exp(AT^{-1})$ is expected to change to a $\exp(AT^{-1/2})$-behavior if one goes from granular samples with a homogeneous Coulomb barrier to samples wherein the tunneling occurs between clusters with varying Coulomb barrier (“variable range tunneling”). If we suppose that the Co cluster are coated with one monolayer of CO (see below) we have rather a well-defined tunneling barrier width s corresponding to 2 layers of CO, but a somewhat varying cluster size (see Sec. II). Almost all ($\simeq 90\%$) clusters have a size lying in the range $L \pm \Delta L$, i.e., are in the regime 3 nm$\lesssim L \lesssim$6 nm. There may be an additional variation in cluster size due to the “short cuts” between those Co clusters which are not completely covered with CO. This can lead to the formation of some cluster aggregates (see below). Calculations by Sheng and Klafter[12] using the critical path method have shown that for a cluster size distribution where the maximum cluster size is only about a factor 2.5 times the minimum cluster size the $\exp(AT^{-1/2})$ temperature dependence of ρ already holdes over a wide temperature range. Our observation of $\ln \rho \propto T^{-1/2}$ confirms these calculations.

According to theory the tunneling resistivity for “variable range tunneling” is given by $\rho = \rho_0 \exp[(T_0/T)^{-1/2}]$ with $T_0 = 8\kappa s E_c/k_B$.[13,14] Here κ is the wave vector of the tunneling electron, s is the mean tunneling barrier width, and E_c is the mean Coulomb energy involved in the tunneling process. ρ_0 or $\rho(T \to 0)$ is a measure of the density of the tunneling percolation network. The observed decreasing ρ_0 going from sample A to D therefore means that the number of tunneling percolation channels is increasing. Changes in the slope $m \propto T_0^{1/2}$ reflect changes in either s and/or E_c. In the spherical capacitor model[13] the Coulomb energy $E_c \propto s$, i.e., $T_0 \propto s^2$. The observed rather small change in the value of T_0 from 1400 K to 1250 K going from sample A to sample C therefore means that s decreases by only about 5%, despite the fact that the CO gas pressure for sample preparation decreased by a factor of 4. This is another confirmation that in all samples we essentially have monolayer of chemically bound CO covering the Co cluster surface, resulting in a rather homogeneous and fixed tunneling barrier width corresponding to two layers of CO. The lower value of T_0 for sample D ($T_0 = 800$ K) and the further reduction of T_0 for the annealed samples C and D ($T_0 = 250$ K for annealed sample D) can be explained in the following way: either too low CO pressure during cluster deposition or annealing at a temperature of about 150 K results either in a incomplete or partially destroyed CO monolayer covering the Co cluster surface and as a consequence in the occurrence of some “short cuts” between neighboring Co clusters. Such “short cuts” will lead to an increase in the average cluster size and therefore in a decrease in $E_c \propto C^{-1}$ due to an increase in the capacitance C. The formation of such aggregates can also be seen in the increased TMR of sample D and annealed samples C and D at very low temperature (see Sec. II C) as well as in the coercive field H_c (see Sec. II C). The annealed samples show a small coercive field well above the blocking temperature of the isolated single domain clusters which can be explained by the formation of multidomain aggregates.

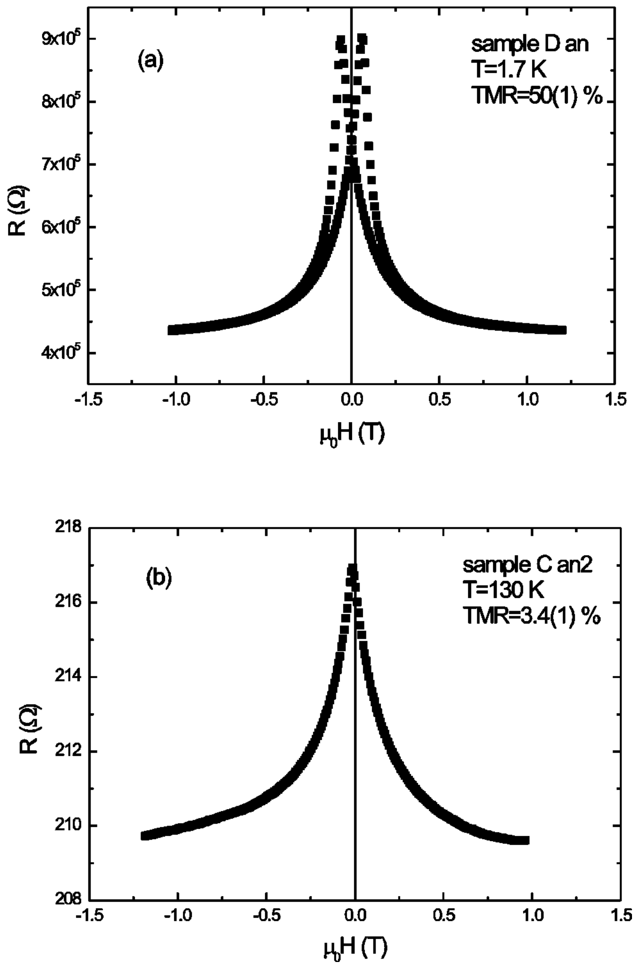

FIG. 2. Resistivity as a function of magnetic field $\mu_0 H$ (a) for sample D at $T = 1.7$ K and (b) for sample C at $T = 130$ K.

B. Tunneling magnetoresistance

The change of the tunneling resistance R with external magnetic field H has been measured for the as-prepared samples in the temperature region $3 \leqslant T \leqslant 35$ K. For the annealed samples $R(H)$ has been measured up to 130 K. $R(H)$ of the annealed sample D could be measured down to 1.7 K since this sample had the lowest resistivity. In Figs. 2(a) and 2(b) we show two examples of our $R(H)$-measurements: (a) sample D (annealed) at $T = 1.7$ K, (b) sample C (annealed 2) at 130 K. We define the tunneling magnetoresistance TMR as $\mathrm{TMR} = [R(H_c)\text{-}R(H_s)]/R(H_c)$ with H_c and H_s being the coercive and saturation field, respectively. A value of TMR $= 50(1)\%$ at $T = 1.7$ K is obtained for the annealed sample D. This the largest TMR-value reported so far for a granular Co-based system. A comparison of Figs. 2(a) and 2(b) shows the strong decrease of the TMR and of H_c with increasing temperature. The temperature dependences of TMR and H_c, as obtained from such $R(H)$-measurements of all samples, are shown in Figs. 3 and 4, respectively. It is important to emphasize that both, TMR- and H_c-data, are completely *sample independent*. In the following we want to discuss in detail these data.

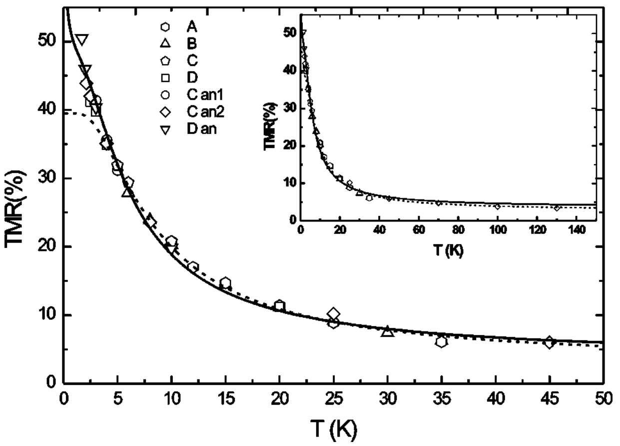

FIG. 3. TMR(T) for all Co/CO samples studied. The dashed line is a fit using the model given by formula (1) (see text). The solide line is a fit using a combination of formulas (1) and (2) (see text). The insert shows TMR(T) up to 130 K.

Figure 3 shows the temperature dependence of the TMR for all Co/CO samples studied. In order to understand this temperature dependence we have started with the same model we already have used for explaining TMR(T) of the other granular systems we have studied in the past.[4–6,20] In this model, which assumes the occurrence of increasing spin disorder at the Co cluster surface with increasing temperature (similar to that observed for Fe clusters),[15] the TMR(T) is given by

$$\mathrm{TMR}(T) = \frac{[1-4f(1-f)]\mathrm{TMR}(0)}{1-4f(1-f)\mathrm{TMR}(0)} \tag{1}$$

with $f(T) = A\mathrm{e}^{-E/k_BT}/(1 + A\mathrm{e}^{-E/k_BT})$. E is the energy needed to misalign a magnetic moment at the cluster surface; the parameter A gives the ratio of the number of misaligned moments to that of the aligned ones at the cluster surface for $k_BT \gg E$. The dashed line in Fig. 3 is a least-squares fit to the data points with the parameters $E = 10(1)$ K, $A = 0.66(2)$, and $\mathrm{TMR}(0) = 39(1)\%$. The fit to the data points is excellent for $T \geqslant 4$ K. However, as it is quite evident, the TMR date for $T < 4$ K can *not* be fitted with this model. All data points

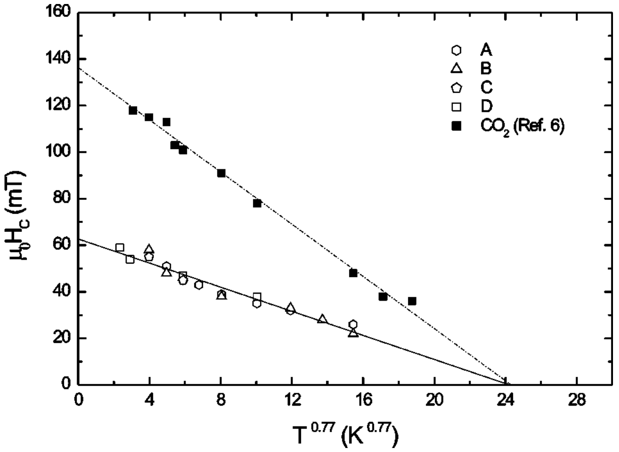

FIG. 4. Temperature dependence of the coercive field H_c. The solid line through the data points is a least-squares fit. $H_c(T)$ of Co/CO$_2$ is shown (dashed–dotted line) for comparison.

below 4 K are from low-resistivity samples (sample D, and annealed samples C and D) since only this samples have a low enough resistance to allow accurate measurements of $R(H)$ at such low temperature. These samples probably contain some aggregates of Co clusters due to "short cuts" between some clusters which occur either due to too low CO pressure (sample D) or during annealing at high temperature (see above). It is therefore quite reasonable to allow higher-order tunneling processes occurring in this annealed samples at very low temperatures: as proposed by Mitani *et al.*,[16] higher-order tunneling processes become important at low temperatures in such granular systems which have a broad distribution of cluster size. In such systems Coulomb blockade prevents tunneling through small clusters but allows higher-order tunneling processes, which means that an electron is transferred from a charged large cluster to another neutral large cluster via small clusters sitting between the two large clusters. Due to this so-called co-tunneling processes the temperature independent TMR changes to a temperature dependent

$$\mathrm{TMR}^*(T) = 1 - (1 + m^2 P^2)^{-(n^*+1)} \tag{2}$$

with $n^*(T) \approx (E_c/8\kappa s k_B T)^{1/2}$ and P being the spin polarization of the tunneling electrons. The magnetization m in Eq. (2) can be set to $m=1$ since co-tunneling is important only at very low T. Using $T_0 = 8\kappa s E_c/k_B$ (see above), n^* can be transformed to $n^*(T) \approx (1/8\kappa s)(T_0/T)^{1/2}$. One can interpret (n^*+1) as being the average number of electrons involved in the tunneling processes. For $n^* \rightarrow 0$, i.e., if co-tunneling processes are absent, one obtains a temperature independent $\mathrm{TMR} = P^2/(1+P^2)$ which is in accordance with Jullière's value for the TMR in granular systems with a random orientation of the cluster magnetic moments.[17] Since these higher-order tunneling processes are important only at very low temperatures where the change of the TMR due to spin disorder is negligible we can combine these two effects by a simple modification of formula (1): the temperature independent TMR(0) in formula (1) is substituted by the temperature dependent $\mathrm{TMR}^*(T)$ given in formula (2). In order to fit the experimental data points with this modified formula (1) we have estimated n^* for the annealed sample D in the following way: T_0 is obtained from Fig. 1 to be 250 K; the tunneling barrier width s corresponding to two layers of CO is $s \approx 0.44$ nm; the tunneling electron wave vector κ is given as $\kappa = [2m(V_B\text{-}E_F)/\hbar^2]^{1/2}$ with V_B being the band gap of the insulating barrier (CO) and E_F the Fermi energy of the tunneling electron. Making the usual assumption that E_F is pinned in the middle of the gap, i.e., $V_B\text{-}E_F \approx 1/2\mathrm{V}_B$, and taking the ionization energy[18] $E_{\mathrm{ion}} \simeq 14$ eV as a crude estimate of V_B we obtain $\kappa \approx 13.5\ \mathrm{nm}^{-1}$ and finally $n^*(T) \approx 0.33T^{-1/2}$ (with T in K). The solid line in Fig. 3 is a least-squares fit to *all* data points with $n^*(T)$ as estimated above and using P^2, E, and A as free fitting parameters. It is quite clear that this new fit now is excellent in the whole temperature regime despite the fact that the number of fitting parameters is the *same* as that for the dashed line in Fig. 3. The obtained fitting parameters are: $P^2 = 0.67(2)$, $E = 8(1)$ K, and $A = 0.63$ (2). While the parameter E and A are slightly different for the two different fits (dashed and solid line, respectively), the most important parameter, namely P^2, is the same for both fits: the dashed line corresponds to $\mathrm{TMR}(0) = 0.39(1)$ or $P^2 = 0.64(2)$ while the solid line gives $P^2 = 0.67(2)$. This fact clearly shows that in our samples higher-order tunneling processes are negligible for $T \geqslant 4$ K. The obtained value of P^2 corresponds to $|P| = 0.82(3)$ which is a factor of 2 larger than that observed, for example, in granular Co/Kr(Xe) or planar Co/$\mathrm{Al_2O_3}$/Co.[4,19] It is higher than the value observed for the granular Co/$\mathrm{CO_2}$ $[|P| = 0.68(2)]$ and even slightly higher than that found in granular Co/$\mathrm{MgF_2}$ $[|P| = 0.76(2)]$.[6,20] Since the spin polarization of the Co-4s electrons is $P(4s) \approx 0.42$ while that for Co-3d electrons is $P(3d) \approx$ -0.80,[25] dominant Co-3d electron tunneling, caused by the hybridization of Co-3d with the matrix (O,F) 2p-electrons, has been proposed to occur in granular Co/$\mathrm{CO_2}$ and Co/$\mathrm{MgF_2}$.[6,20]

C. Spin polarization

In the following we want to discuss possible reasons for the large $|P|$ value we obtain for Co/CO using the model for the T-dependence of the TMR as described above. Our values for P^2 or $|P|$ are based on the assumption that the Co cluster magnetic moments have a random distribution, i.e., that there exists no short-range magnetic correlations between the Co clusters. We have shown that such correlations do not exist, for example, in Co/$\mathrm{CO_2}$ or in Co/$\mathrm{MgF_2}$.[6,20] This information results from the analysis of the hysteresis loops, calculated from the measured $R(H)$-curves. The temperature dependence of the coercive field $H_c(T)$ is directly obtained from the $R(H)$-curves for Co/CO, measured at different temperatures [two examples are given in Figs. 2(a) and 2(b)]. The result is shown in Fig. 4 for the as-prepared samples A–D together with that for Co/$\mathrm{CO_2}$.[6] Here we have plotted $H_c(T)$ vs $T^{0.77}$ since according to theory $H_c(T) \propto T^{0.77}$ for a random assemble of noninteracting magnetic particles.[21] The solid line through the data points is a least-squares fit giving the same blocking temperature T_B $[T_B = T(H_c = 0)]$ as that obtained for Co/$\mathrm{CO_2}$, namely, $T_B \approx 65$ K. We should mention at this point that the $R(H)$-curves taken for the *annealed* sample C at the temperature well above T_B still show some hysteresis, i.e., indicate that the blocking temperature of this *annealed* sample is higher than 130 K. The reason for this finding certainly is an cluster aggregation which takes place during annealing (see above), resulting in the formation of multidomain aggregates having a larger blocking temperature than the isolated single domain clusters. It is quite evident from Fig. 4 that there is a reduction of $H_c(0)$ for Co/CO by about a factor of 2 compared to the $H_c(0)$ value found for Co/$\mathrm{CO_2}$. Since $H_c(0)$ for Co/$\mathrm{CO_2}$ corresponds to an anisotropy constant K which is in perfect agreement with that found for *free* Co clusters of similar size[22] we can interpret the reduction in $H_C(0)$ found for Co/CO as a reduction of K by a factor of 2 compared to that of free Co clusters. The reason for such a strong reduction has to be the interaction of the CO molecules with the Co cluster surface atoms. In the following we want to discuss in more detail what already is known about this interaction.

The influence of CO adsorption on the ferromagnetic resonance (FMR) of small Co particles deposited on Al_2O_3 has been studied by Hill *et al.*[23] These experiments reveal a strong reduction of the magnetic moments μ_{Co} of the Co surface atoms. Even a complete quenching of μ_{Co} at the cluster surface, similar to that found for CO coated Ni clusters,[23] cannot be excluded. Our TMR results clearly rule out such a complete quenching of μ_{Co} at the cluster surface. However, a reduction of μ_{Co} at the cluster surface has not to be in contradiction with our results for the following reason: TMR measurements give the spin polarization $|P|$ of the tunneling electrons, i.e., the difference in the density of states at the Fermi energy E_F between spin-up and spin-down electrons of those electrons which are tunneling. The magnetic moment, on the oder hand, is given by the difference in the occupation of the spin-up und spin-down bands, respectively. Spin dependent density of states calculations by Moodera *et al.*[19] for bulk Co show that an increase in E_F will lead to a decrease in μ_{Co} but an increase in $|P(3d)|$. These calculations also show that the Ni magnetic moment μ_{Ni} will be much more sensitive to such a shift in E_F, i.e., only a small increase in E_F will result in a complete quenching of the Ni magnetic moment μ_{Ni}. An electron transfer from CO to Co, therefore, can explain both the reduced μ_{Co} observed in FMR and the increased $|P(3d)|$ found in the TMR, providing that we have a preferred Co$(3d)$-electron tunneling. Tunneling of Co(4s) electrons, on the other hand, can *not* explain both results since the spin polarization of the Co$(4s)$ electrons is $P \approx 0.4$ for a *free* Co cluster surface and will be reduced if μ_{Co} is decreased.

We now come bake to the observed reduction of H_C for Co/CO (see Fig. 4). If the reduction of μ_{Co} at the Co cluster surface due to Co–CO interaction is accompanied by a decrease in the anisotropy constant K, we could explain this result. Short range antiferromagnetic interaction between neighboring Co clusters, on the other hand, could also be the reason for the observed reduction of H_c. In order to get more information about such an interaction we have analyzed the hysteresis loops as calculated from the measured $R(H)$-curves.[5] The remanent magnetization m_r obtained from these loops has a value of $(m_r)_{\mathrm{exp}}=0.47(1)$, i.e., is only slightly smaller than the value $(m_r)_{\mathrm{th}}=0.5$ theoretically expected for noninteracting, single domain particles with a random orientation of their magnetic moments.[24] Antiferromagnetic interactions between the Co clusters will reduce m_r. We do not believe that the observed small reduction in $(m_r)_{\mathrm{exp}}$ compared to $(m_r)_{\mathrm{th}}$ can be taken as an indication for such an antiferromagnetic interaction being present in our Co/CO samples.

D. Conclusion

Granular samples of CO coated Co clusters have been successfully prepared. Annealing of these samples showed that the CO coating is stable up to temperatures of about 300 K, indicating a strong binding of the CO molecules to the Co cluster surface. The TMR is very much enhanced if compared, for example, with granular Co/Kr(Xe).[4] It reaches a value of about 50% at 1.7 K which is the largest TMR value reported so far for any granular Co system. The complete quenching of the Co magnetic moment at the Co cluster surface, similar to that observed for CO coated Ni clusters, therefore can be excluded. We explain the large TMR value as follows: (i) tunneling essentially occurs by 3d-electrons (spin polariation $P \approx$ -0.8),[25] and (ii) the TMR is further enhanced at temperatures $T < 4$ K due to higher-order tunneling processes. The spin polariation of the Co(3d)-electrons may be enhanced due to an electron transfer from CO to Co. Such a transfer would explain both, the reduced μ_{Co} found in the FMR experiments[23] and the increased TMR, if the latter is caused by $3d$-electron tunneling. The system of CO coated Co clusters could be a model system for theoretical studies of the TMR in systems where there is a strong interaction between the surface atoms of the ferromagnetic electrodes and the insulating molecules sitting between these electrodes.

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