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Electronic transfer in Sr_2FeMoO_6 perovskites

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Abstract. The magnetic properties of Sr_2FeMoO_6 oxides are investigated over a broad temperature range extending from 10 K to 800 K. It is found that the magnetization fully saturates at low temperatures at a value of 3.75 μ_B. In the paramagnetic regime, above the Curie temperature ($T_C \approx 420$ K), the magnetic susceptibility can be well described by a Curie–Weiss law. It is found that the experimental effective moment μ^*_{eff} is gradually reduced under a field, an effect that can be attributed to some non-intrinsic behaviour. By means of detailed data analysis, it is shown that the paramagnetic effective moment μ_{eff} is close to that expected for a $3d^6$:$4d^0$ atomic configuration. This result is interpreted as due to some electronic charge transfer from the itinerant $4d^0$(Mo) towards the $3d^5$(Fe) orbitals in the paramagnetic phase. We have also observed that the paramagnetic Curie temperature θ_P is positive and that $\theta_P \approx T_C$, thus suggesting that the nearest-neighbour magnetic interactions are ferromagnetic in nature. These observations strongly support a double-exchange picture for the ferromagnetic coupling in these oxides.

In spite of the intensive research effort that double perovskites of the Sr_2FeMoO_6 type have triggered in the last few years, their magnetic structure and properties remain largely unknown. The driving interest in the investigation of these materials derives from the fact that they appear to be promising candidates for application as magnetoresistive materials and in devices, owing to their half-metallic ferromagnetic nature and high Curie temperature [1].

The metallic behaviour of these oxides is essentially due to carrier motion within the conduction band which is of minority-spin $4d^{x,\beta}$(Mo) and $3d^{(1-x),\beta}$(Fe) parentage and which is above the filled majority-spin-up $3d^{5,\alpha}$(Fe) subband [1, 2]. The saturation magnetization (M_S) values suggest an antiferromagnetic coupling between the Fe and Mo sublattices giving rise to some sort of ferrimagnetic structure [3]. Accordingly, $M_S = 4\ \mu_B$ is predicted for antiferromagnetic coupling of $3d^5$(Fe):$4d^1$(Mo) ions. However, experiments commonly find a reduced saturation magnetization that is believed to be caused by antisite defects arising from misoccupancy of Fe sites by Mo species and vice versa [1, 4, 5]. Therefore magnetization measurements have not so far been able to provide conclusive evidence of antiferromagnetic coupling of the Fe and Mo sublattices and still less the ionic character of this bonding. Neutron diffraction measurements at low temperature have led to a variety of results that go from an almost null moment at Mo sites [6, 7] to about $-0.42\ \mu_B$ [8]. Interestingly, magnetic measurements on the paramagnetic phase should in principle be insensitive to the existence of antisite effects. Indeed, the effective moment μ_{eff} measured above T_C should reflect the spin

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configurations in the system, irrespective of atomic-scale defects, and thus it may provide new information on the electronic and spin states of the Fe and Mo species.

In this paper we report a magnetic study of Sr_2FeMoO_6 ceramics over the temperature range from 10 K to about 800 K, i.e. well above the Curie temperature T_C of these oxides ($T_C \approx 420$ K). We will show that the magnetic susceptibility above T_C can be well described by a Curie–Weiss law over a very substantial temperature range, but remarkably, the effective moment μ^*_{eff} is found to be distinct from that expected from the observed values of the saturation magnetization irrespectively of whether ionic Fe^{3+}/Mo^{5+} or Fe^{2+}/Mo^{6+} configurations are assumed. Of even more relevance is the observation that for the paramagnetic state, μ^*_{eff} is found to be magnetic field dependent: a decreasing function of field. These remarkable results are discussed in terms of a field-promoted charge transfer from $4d^1$(Mo) to $3d^5$(Fe) atomic states. It is also argued that the observation of a positive paramagnetic Curie temperature closely coincident with T_C strongly militates against a superexchange mechanism for ferromagnetic coupling.

Ceramic Sr_2FeMoO_6 samples were prepared as described in [5]. In short, using appropriate solid-state reaction at high temperatures ($T_S = 1200\,^\circ$C) under a H_2/Ar stream, samples having a controlled concentration of antisite defects were obtained. X-ray diffraction powder patterns were collected using a Rigaku Ru-200B diffractometer. No traces of impurities could be detected in the x-ray pattern, thus setting a rough upper limit of about 2% for any crystalline impurity present. The (101) superstructure spots, which reflect the ordering of Fe/Mo ions at sites of the structure, were clearly visible. Satisfactory fits of the x-ray diffraction profile could be achieved by using the $P4/mmm$ space group (figure 1). It has recently been suggested that the monoclinic group $P4_2/m$ provides a better refinement of the neutron diffraction patterns

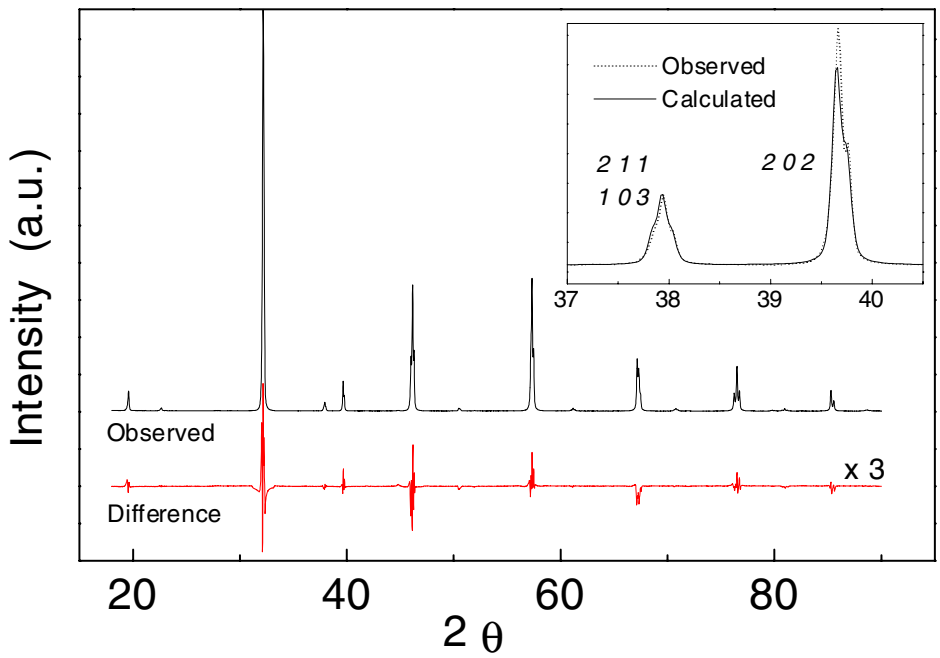

Figure 1. X-ray diffraction patterns for a Sr_2FeMoO_6 ceramic sample. The difference (refined − experimental) pattern spectrum is indicated. Inset: detail of the profile refinement in the high-angle region.

and a better description of the structure [8]. However, attempts to refine our data using this monoclinic space group do not lead to any significant improvement of the refinement of the x-ray data. In addition, in this monoclinic group there is a unique Wyckoff Fe site whereas in the tetragonal $P4/mmm$ group there are two inequivalent Wyckoff Fe sites equally populated. Mössbauer spectra of these samples revealed the presence of two distinguishable Fe sites with comparable occupancies [5]. These results naturally fit within the $P4/mmm$ group but not within the $P4_2/m$ group. However, as shown in the inset of figure 1, detailed inspection of the x-ray data reveals that at high angles some systematic discrepancies still exist among the experimental and calculated spectra, thus indicating that further refinements are still required to definitively establish the room-temperature space group for Sr_2FeMoO_6. Rietveld refinement of the patterns using the $P4/mmm$ space group indicates that any Fe/Mo antisite disorder cannot be larger that 2%.

The magnetization of the samples has been measured by using the Quantum Design SQUID magnetometer up to 5.5 T and in the 10 K–800 K temperature range.

The magnetization versus field curves $M(H)$ recorded at 10 K for the Sr_2FeMoO_6 ceramic shown in figure 2(a) indicate that the magnetization rapidly saturates to a value of about $M_S \approx 3.75\ \mu_B$. This M_S-value is smaller than the ideal ($\sim 4\ \mu_B$) one, thus probably reflecting the presence of some marginal antisite disorder [5]. In figure 2(b) we present the temperature-dependent magnetization measured up to high temperature under various magnetic fields. A Curie temperature of about 420 K can be clearly identified by the sharp onset of magnetization at the lowest measuring field (5 kOe).

The magnetic behaviour in the paramagnetic region above T_C can be better inspected in figure 3(a) where we plot the reciprocal susceptibility (χ_{exp}^{-1}) versus temperature for some of the measured fields. Over a broad temperature range extending more than 300 K ($\sim 1.8\ T_C$) above 1.1 T_C, the magnetic susceptibility can be well described by using a Curie–Weiss law ($\chi = C/(T - \theta_P)$). The solid lines through the data illustrate the results of the fits. The Curie constant C allows one to extract an effective paramagnetic moment μ_{eff}^*. Inspection of the data immediately reveals a systematic dependence of the measured μ_{eff}^* on H. This is clearly unexpected for a paramagnet. The data in figure 3(a) show that μ_{eff}^* is reduced under a field. In figure 3(b) we collect the extracted μ_{eff}^*-values for each field. The gradual decreasing of μ_{eff} is apparent: it lowers from $\mu_{eff}^* \approx 5.9\ \mu_B$ for $H = 100$ Oe to $\mu_{eff}^* \approx 4.5\ \mu_B$ for 55 kOe. Above the $H \geqslant 40$ kOe field range, some sort of saturation in $\mu_{eff}^*(H)$ is observed.

The effective paramagnetic moment μ_{eff} is related to the spins (S_{Fe} and S_{Mo}) of the atomic species via

$$\mu_{eff}^{cal} = g_J \mu_B \sqrt{(S_{Fe}(S_{Fe}+1) + S_{Mo}(S_{Mo}+1)}$$

where $g_J \approx 2$ is the gyromagnetic ratio. The dashed lines in figure 3(b) indicate the values of μ_{eff}^{cal} expected for $3d^5$(Fe):$4d^1$(Mo) and $3d^6$(Fe):$4d^0$(Mo) atomic configurations. These atomic configurations represent the limiting states for Fe and Mo ions in a stoichiometric sample. In fact we know from Mössbauer experiments—performed at room temperature and below—that $Fe^{3+/2+}$ ions are in a mixed-valence state $3d^{5/6}$ [5, 9]. The data in figure 3(b) reveal that upon increasing the field, μ_{eff}^* evolves from a value similar to that expected for a localized $3d^5$(Fe):$4d^1$(Mo) atomic configuration towards that expected for $3d^6$(Fe):$4d^0$(Mo).

This remarkable result might suggest that under a field there is a progressive charge transfer from the partially occupied upper-lying spin-down $4d^1$(Mo) states towards neighbouring $3d^5$(Fe) empty states.

Although this interpretation might appear at first sight appealing, other more *prosaic* effects may also lead to similar behaviour. Among them we would like to mention that the presence of ferromagnetic impurities in the samples may produce a field-dependent μ_{eff}^* similar

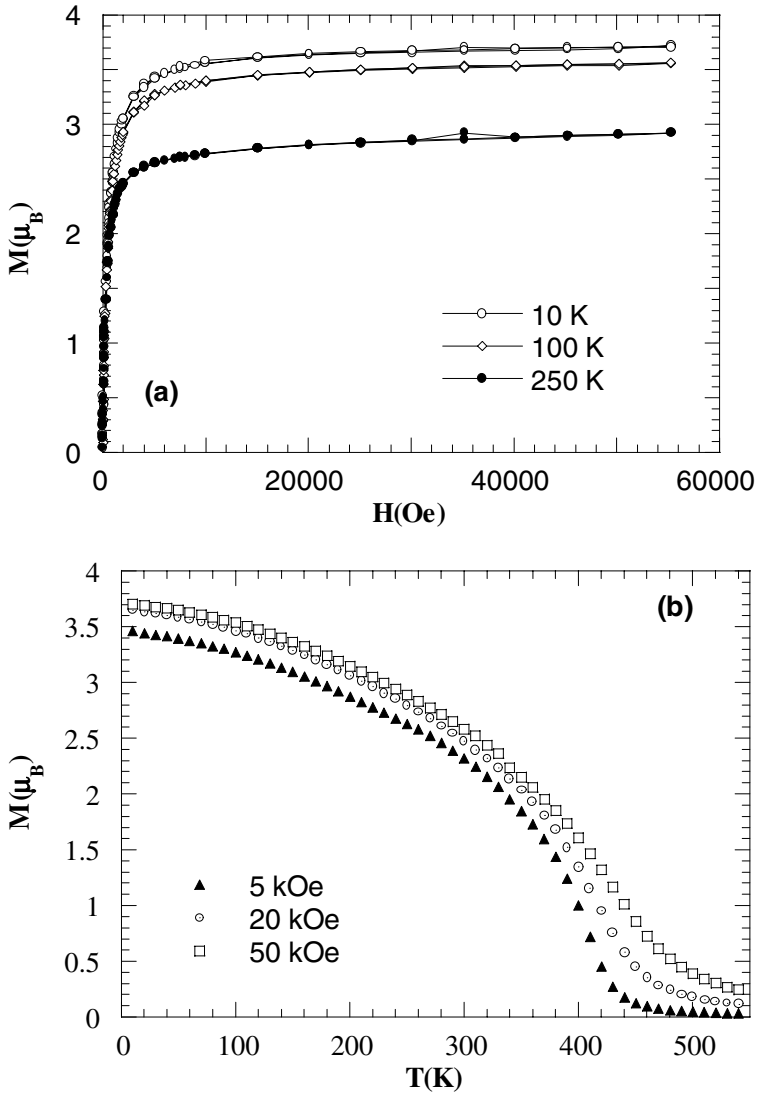

Figure 2. (a) Magnetization versus magnetic field H at 10 K for the Sr_2FeMoO_6 sample. (b) Magnetization versus temperature curves at various magnetic fields.

to that observed in the present experiments. Indeed, it can be shown that when a small fraction x of a ferromagnetic impurity is present, the experimental susceptibility $\chi_{\rm exp}$ should display a field dependence given by $\chi_{\rm exp} = (1-x)\chi + xM_{\rm S}^0/H$ where χ is the actual susceptibility of the material and $M_{\rm S}^0$ is the saturation magnetization of the ferromagnetic impurity. Accordingly, at any temperature, $\chi_{\rm exp}$ should be linear in $1/H$ with slope $xM_{\rm S}^0$ and intercept the $1/H = 0$ axis at $\chi_{\rm exp} \approx \chi$ (because $1 - x$ should not be very different to $\approx$1). In figure 4 (inset) we show that it is indeed the case that $\chi_{\rm exp}(T) \approx 1/H$. The linear fit of these $\chi_{\rm exp}(1/H)$ data at each temperature allows us to extract χ and $xM_{\rm S}^0$. In figure 4 the $\chi(T)$ values obtained are plotted versus $1/T$. The Curie–Weiss law is recovered but now with a field-independent effective paramagnetic moment $\mu_{\rm eff} \approx 4.2\ \mu_{\rm B}$. Before going further, we would like to point

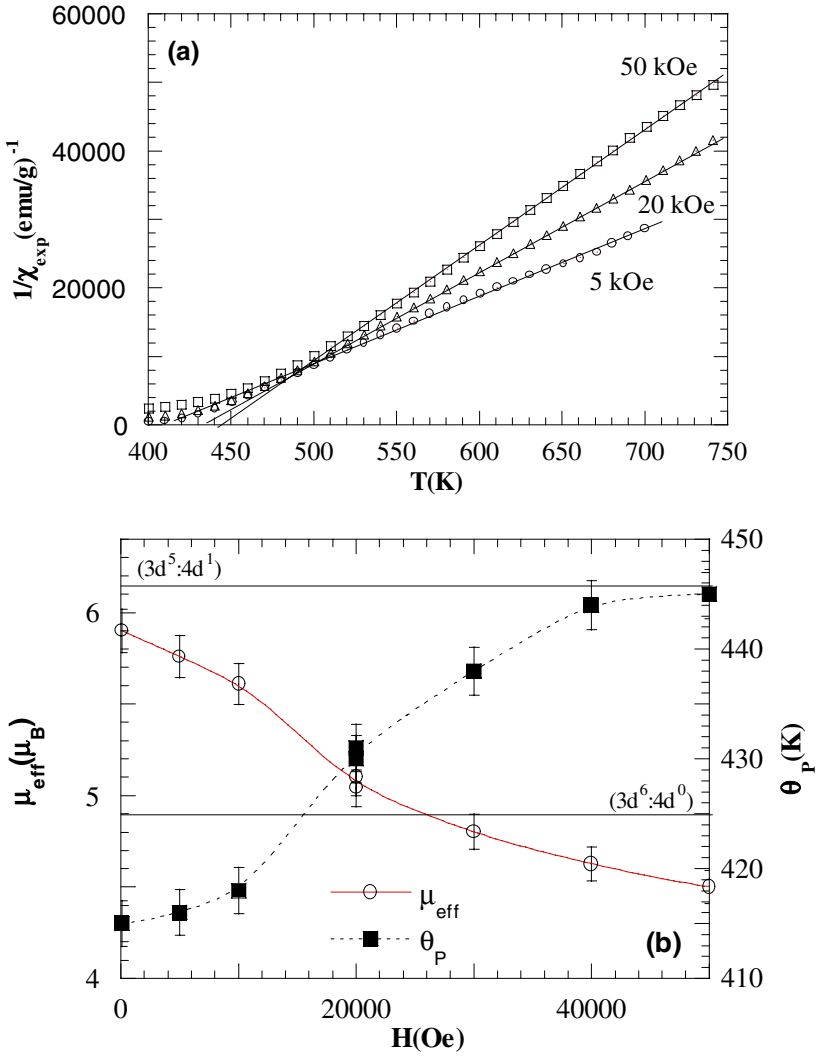

Figure 3. (a) Inverse experimental susceptibility χ_{exp} versus temperature measured under various magnetic fields. The solid lines through the data are the results of the fits of the experimental data to the Curie–Weiss law. (b) *Left-hand axis*: dependence of the effective magnetic moment μ^*_{eff} extracted from (a) on the magnetic field. The dashed lines represent the μ^{cal}_{eff}-values expected for Fe^{3+}/Mo^{5+} and Fe^{2+}/Mo^{6+} couples as described in the text. *Right-hand axis*: extrapolated paramagnetic Curie temperature θ_P versus applied magnetic field.

out that the slope of $\chi_{exp}(1/H)$ is found to be $xM^0_S \approx 0.1$ emu g^{-1}. This value would allow us to obtain an estimate of the fraction x if M^0_S was known. If one assumes that tiny amounts of metallic Fe could be present in the sample, then $M^0_S \approx 220$ emu g^{-1} and thus $x \approx 0.1\%$. Obviously this level of Fe impurity cannot be observed with the analytical techniques used and thus the possibility of its existence cannot be excluded. As a consequence, the observed dependence of μ^*_{eff} on the field plausibly does not have an intrinsic origin.

We would like to stress, however, that our data analysis has led to the conclusion that $\mu_{eff} \approx 4.2\ \mu_B$, a value that is close to (although about 10% smaller than) that expected

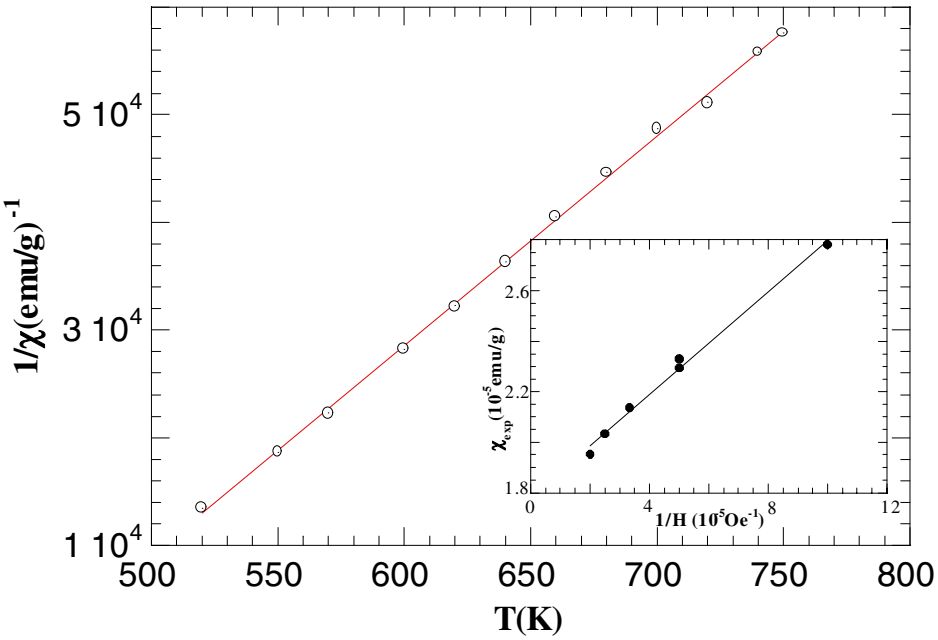

Figure 4. Main panel: the temperature dependence of the corrected magnetic susceptibility. Inset: the isothermal (T = constant) field dependence of the measured magnetic susceptibility $\chi_{\rm exp}$.

for a $3d^6$:$4d^0$ atomic configuration as can be appreciated in figure 3(b). This means that in the paramagnetic phase, a charge transfer from the mixed $4d^{1/0}$(Mo):$3d^{5/6}$(Fe) configuration as observed in the Mössbauer spectra [5, 9] to a $4d^0$(Mo):$3d^6$(Fe) configuration has indeed taken place.

On the other hand, it can be observed in figure 3(a) that the paramagnetic Curie temperature $\theta_{\rm P}$ is obviously positive ($\theta_{\rm P} \approx 420$ K) and almost coinciding with the Curie temperature $T_{\rm C}$ as determined from the $M(T)$ curves shown in figure 2(b). The data analysis procedure that we have used allows the extracting of a $\theta_{\rm P}$-value that is not affected by the eventual presence of ferromagnetic impurities. In figure 3(b) a small dependence of the observed $\theta_{\rm P}$ on field is depicted. This behaviour is expected for a system where ferromagnetic interactions are prevalent and thus it indicates that the most intense magnetic interactions ($J_{\rm F}$) have a ferromagnetic $J_{\rm F} > 0$ character. We note that within a superexchange scenario for magnetic coupling, the ferromagnetic ordering of the Fe magnetic moments arises from the antiferromagnetic nature of the Fe:$3d^5$–Mo:d^1 nearest-neighbour interactions. Accordingly, one should expect to observe a negative $\theta_{\rm P}$ as commonly observed for the spinel ferrites, which are prototypical ferrimagnetic systems [10]. Clearly this is not the case, as $\theta_{\rm P} \approx T_{\rm C} > 0$ as for most common ferromagnets. This observation raises serious questions as regards the picture of a superexchange-mediated ferrimagnetic ordering of the magnetic structure used. In fact, it strongly favours a double-exchange picture where the parallel alignment of the spin-down moments is promoted by the itinerant carriers in the conduction band, and thus the localized subband of $3d^5$ is a spin-up band.

In summary, we have shown that the paramagnetic susceptibility of Sr_2FeMoO_6 displays a number of features of the highest relevance for the understanding of the magnetic properties and the electronic structure of these double perovskites. We have shown that superexchange does

not appear to be the mechanism of the ferrimagnetic ordering in these materials. In addition, the effective moment in the paramagnetic phase suggests that there is a charge transfer from $4d^x$(Mo) to $3d^{6-x}$(Fe) orbitals. Notice that under these circumstances the Sr_2FeMoO_6 oxides would appear to have rather subtle properties, where the carrier occupancy in the conduction band can be tailored using the temperature. Under these circumstances, the magnetoresistance could not be limited to temperatures close to or below T_C but would also occur above T_C. This unique behaviour might broaden the temperature range of the magnetoresistance in these oxides and thus enlarge the range for practical applications.

Acknowledgments

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Note added in proof. After submission of this paper, Niebieskikwiat *et al* [11] reported a high-temperature study of the magnetic susceptibility of a Sr_2FeMoO_6 ceramic. It was also found there that in the paramagnetic region the susceptibility displays a non-conventional Curie–Weiss behaviour. In their case, the saturation magnetization of the sample is only of 2.7 μ_B, i.e. much lower than that of the sample used in the present study. These authors suggested that at high temperature, carriers become gradually delocalized. Although certainly suggestive, the proposed model is not backed by solid experimental evidence. We have shown that our data, obtained for a sample that has a moment of 3.752.7 μ_B, i.e. closer to the optimal value, can be quantitatively understood using a simpler model.

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