Interplay of superexchange and orbital degeneracy in Cr-doped LaMnO$_3$

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We report on structural, magnetic, and electron spin resonance (ESR) investigations in the manganite system LaMn$_{1-x}$Cr$_x$O$_3$ ($x \leq 0.5$). Upon Cr-doping we observe a reduction of the Jahn-Teller distortion yielding less distorted orthorhombic structures. A transition from the Jahn-Teller distorted O$'$ to the pseudocubic O phase occurs between $0.3 < x < 0.4$. A clear connection between this transition and the doping dependence of the magnetic and ESR properties has been observed. The effective moments determined by ESR seem reduced with respect to the spin-only value of both Mn^{3+} and Cr^{3+} ions.

I. INTRODUCTION

It was recently shown that in La$_{1-x}$Sr$_x$MnO$_3$ the realization of an insulating and ferromagnetic ground state for $0.1 < x < 0.15$ results from a superexchange (SE) driven rearrangement of the high-temperature orbital order (OO) established by the Jahn-Teller (JT) distortion.[1,2] Upon Sr-doping the JT distortion in the parent compound gets suppressed and the degeneracy of the Mn^{3+} e_g electrons becomes almost restored. In this case the two-orbital model by Kugel and Khomskii becomes valid and ferromagnetic SE interactions between Mn^{3+} ions show up.[3] These drive the system into an orbitally ordered and ferromagnetic state. The exact nature of the OO is still unclear, although some proposals have been made by Khomskii recently,[4] based on the idea of the so called orbital polaron by Kilian and Khaliullin.[5] The realization of a ferromagnetic and insulating state has been recently addressed by Khomskii and Sawatzky[6] and also by Mizokawa *et al.*[7] For even higher Sr-doping levels ($x \geq 0.17$) the increasing double-exchange (DE) interactions become dominant and establish a ferromagnetic and metallic ground state.

Since the first studies of the series LaMn$_{1-x}$Cr$_x$O$_3$ in the 1950s,[8–10] it has been known that upon Cr-doping the antiferromagnetic Mott insulator LaMnO$_3$ develops a ferromagnetic component. Moreover, Taguchi *et al.* reported (for $T > 300$ K) that within the complete concentration range $0 \leq x \leq 1$ the samples show semiconducting behavior.[11] Sun *et al.* and Zhang *et al.* came to similar conclusions for the temperature range $T < 300$ K, recently.[12,13] Due to the ceramic nature of the samples a direct comparison of the resistivity values of these studies is vain, but both yield an increase in resistivity with increasing Cr concentration (at fixed temperatures) indicating the persistence of an insulating ground state throughout the whole concentration range. Hence, the LaMn$_{1-x}$Cr$_x$O$_3$ system is a promising candidate for studying the close relationship between JT distortion, SE interactions and orbital degeneracy, especially because in the simple ionic picture the Mn^{3+} ($3d^4$) ions are partially substituted by isoelectronic Cr^{3+} ions ($3d^3$), which have the same electronic configuration as Mn^{4+} (e.g., t_{2g}^3) in these compounds. Therefore no mobile charge carriers should be present in contrast to the Sr-doped case.

However, Sun *et al.* and Zhang *et al.* invoked the possibility of Mn^{3+}–O–Cr^{3+} double-exchange interactions in LaMn$_{1-x}$Cr$_x$O$_3$ in order to correlate their electronic transport data with the magnetic properties in their samples.[12,13] Magnetoresistance measurements ($T > 77$ K) have been reported by Gundakaram *et al.* in the system LnMn$_{1-x}$Cr$_x$O$_3$ (Ln $=$ La,Pr,Nd,Gd) indicating the absence of DE interactions.[14]

The influence of Cr-doping in mixed-valence manganites has been investigated by Cabeza *et al.* in the system La$_{0.7}$Ca$_{0.3}$Mn$_{1-x}$Cr$_x$O$_3$.[15] Their conclusion, namely that the Cr-ions do not contribute to the DE mechanism, is in accordance with the observations of Kimura *et al.* and Troyanchuk *et al.*, who investigated the influence of Cr-doping in Nd$_{0.5}$Ca$_{0.5}$Mn$_{1-x}$Cr$_x$O$_3$ and Nd$_{0.6}$Ca$_{0.4}$Mn$_{1-x}$Cr$_x$O$_3$, respectively.[16–18] In contrast, Sun *et al.* again found indications for the DE in La$_{0.67}$Ca$_{0.33}$Mn$_{1-x}$Cr$_x$O$_3$.[19]

In the present paper we try to shed some light on the controversial findings by comparing the influence of Cr-doping on the magnetic properties of LaMnO$_3$ with the intensively studied DE systems La$_{1-x}$(Ca,Sr)$_x$MnO$_{3+\delta}$.

II. EXPERIMENTAL DETAILS

The polycrystalline specimens were prepared using conventional ceramic techniques. Ultrapure oxide powders [La$_2$O$_3$ (4N), Mn$_2$O$_3$ (4N), and Cr$_2$O$_3$ (4N), Alpha] were dried, mixed in the appropriate amounts and carefully ball-milled to ensure homogeneous samples. The LaMn$_{1-x}$Cr$_x$O$_3$ ($0 \leq x \leq 0.5$) samples have been pressed into pellets and were prepared by heating in flowing pure nitrogen at 1400 °C for 120 h and then slowly cooled to room temperature. This procedure was repeated four times. Powder diffraction patterns were collected employing Cu-$K_{\alpha 1}$ radiation at room temperature. The magnetic susceptibility and magnetization were measured using a dc superconducting quantum interference device (SQUID) magnetometer (0–50 kOe, 1.5 K $\leq T \leq 400$ K).

ESR measurements were performed with a Bruker ELEXSYS E500 CW-spectrometer at X-band frequencies ($\nu \approx 9.35$ GHz) equipped with continuous gas-flow cryostats for He (Oxford Instruments) and N$_2$ (Bruker) in the temperature range between 4.2 K and 680 K. The polycrys-
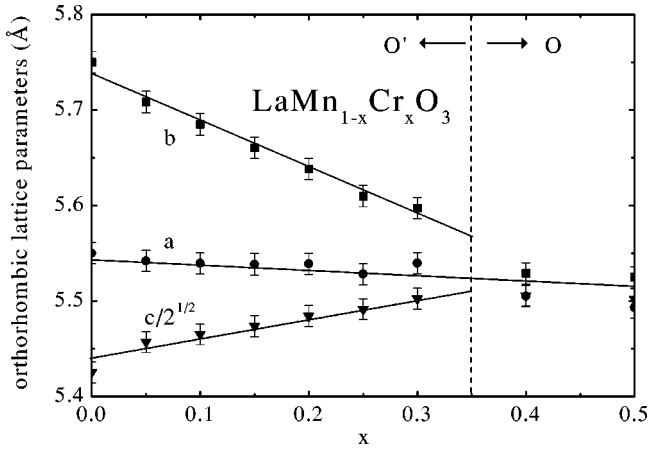
FIG. 1. Orthorhombic lattice parameters (a,b,c) as a function of Cr concentration x. A transition from the Jahn-Teller distorted O′-phase to the pseudocubic $(a \approx b \approx c/\sqrt{2})$ O-phase occurs between $0.3 < x < 0.4$. The lines are to guide the eyes.

talline samples were powdered and filled into quartz tubes and fixed with either paraffin (at low temperatures 4 K $\leq T \leq$ 300 K) or NaCl (at 300 K $\leq T \leq$ 680 K).

III. EXPERIMENTAL RESULTS

A. Structural properties

In Fig. 1 we show the orthorhombic lattice parameters (a,b,c) as a function of the Cr-concentration x. All parameters show a linear dependence on x up to 0.3. A transition from the Jahn-Teller distorted O′-phase to the pseudocubic $(a \approx b \approx c/\sqrt{2})$ O-phase occurs between $0.3 < x < 0.4$. In the Jahn-Teller distorted phase the Mn–O bond lengths in the MnO_6 octahedra are highly anisotropic and become isotropic in the pseudocubic O phase. Our findings are in agreement with the structural data of Gundakaram *et al.*[14] The authors also showed that the sample-preparation method described above ensures the absence of Mn^{4+} ions in these compounds confirmed by analysis of the samples via iodometric titration. Therefore we estimate the deviation from the ideal oxygen value to be $<1\%$. The persistence of the orthorhombic structure up to $x=0.5$ has also been reported by Nakazono *et al.*[20]

Sun *et al.* reported that a transition from rhombohedral to orthorhombic symmetry occurs around $x=0.2$.[12] Since no detailed analysis of the lattice parameters and information about the atmosphere used in the preparation procedure was provided, it is difficult to argue where this discrepancy results from: A closer look on the x-ray-diffraction spectra presented by Sun *et al.* might reveal the persistence of the orthorhombic distortion or a mixed phase up to $x=0.3$. The samples in the study by Zhang *et al.* ($x \leq 0.3$) reportedly were all found to exhibit rhombohedral symmetry,[13] whereas Taguchi *et al.* found rhombohedral symmetry for $x \geq 0.4$ and orthorhombic for $x \leq 0.4$ and a high Mn^{4+} content due to oxygen nonstoichiometry.[11]

It is known that if upon Sr-doping the percentage of Mn^{4+} in $LaMnO_3$ becomes larger than 20%, the room-temperature structure is rhombohedral.[21] The influence of
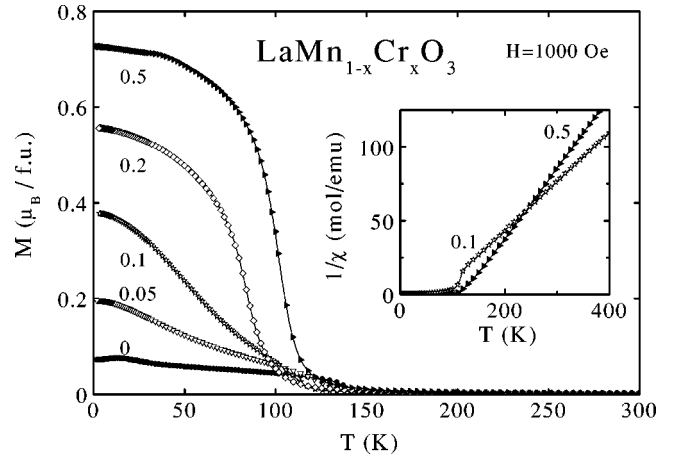

FIG. 2. Temperature dependence of the magnetization M with an applied field $H=1000$ Oe. In the inset the inverse susceptibility vs temperature is plotted for $x=0.1$ and $x=0.5$.

oxygen content on the structural properties has been intensively studied in $LaMnO_{3+\delta}$ by Prado *et al.*,[22] who found a rhombohedral structure at room temperature for an oxygen excess of $\delta > 0.09$, which corresponds to a Mn^{4+} content similar to a Sr concentration of $x=0.18$. Therefore, it is possible that oxidation (i.e., oxygen nonstoichiometry) of the samples holds for the differences in the structural, electronic, and magnetic properties.

Two main reasons account for the different behavior of Cr^{3+} and Mn^{4+} ions (both are not JT active): First, the ionic radius of the Cr^{3+} ion is larger than the corresponding one of the Mn^{4+} ion and hence the destabilization of the Mn^{3+} Jahn-Teller matrix is weaker than in the Sr-doped samples. Additionally, the mobile nature of the induced charge carriers (holes) in the case of Sr-doping allows for a dynamical change of the local electronic configuration and a homogenous distribution of the Mn^{4+} ions in the JT matrix, whereas the Cr^{3+} ions are fixed to the lattice sites at the time of sample preparation.

B. Magnetization

The magnetization M below the magnetic ordering temperatures increases upon increasing Cr content, as can be seen from the temperature dependence of the magnetization in Fig. 2. This is in agreement with the results of Sun *et al.* and Nakazono *et al.*,[12,20] who additionally observed a FC/ZFC splitting up to $x=0.5$ indicating a cluster-glasslike behavior. Since the magnetic transition temperatures cannot be unambiguously determined from the dc measurements, we restrict our discussion to the doping dependence of the Curie–Weiss (CW) temperature Θ. In the inset of Fig. 2 the inverse susceptibility vs temperature is plotted for $x=0.1$ and $x=0.5$. The susceptibilities for all samples follow a CW law $\sim (T-\Theta)^{-1}$ in the paramagnetic temperature regime. From this measurements we deduce the effective paramagnetic moments p_{eff} [Fig. 3(a)] and the paramagnetic CW temperature Θ [Fig. 3(b)]. From the doping dependence of p_{eff} it is noticeable that for x values smaller than 0.1 the measured values are slightly enhanced with respect to the simple ionic
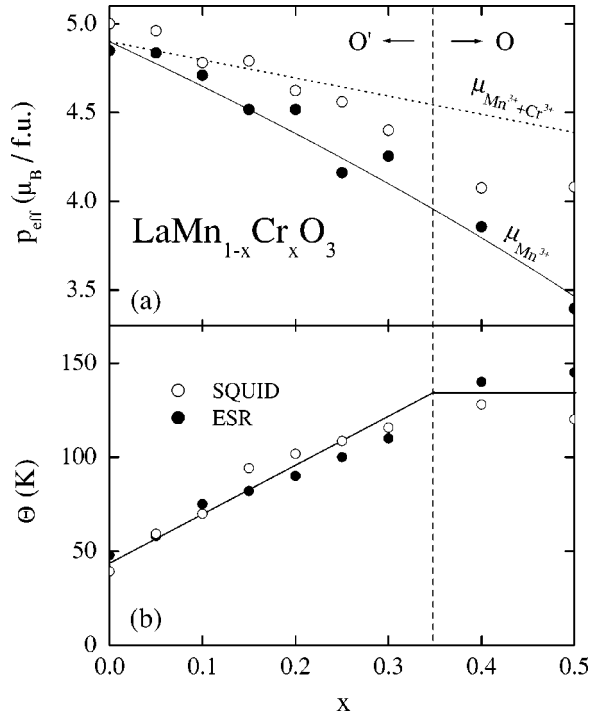
FIG. 3. Doping dependence of the effective paramagnetic moments p_{eff} (a) and the CW temperature Θ (b). The lines in (a) show the theoretical spin-only curve for the effective paramagnetic moment of $Mn^{3+}+Cr^{3+}$ (dotted) and Mn^{3+} (solid line), the lines in (b) are to guide the eyes.

spin-only values, while for $x \geq 0.2$ they lie well below the spin-only curve. Both parameters show a significantly different doping dependence in the O′ and O phases, respectively. While in the Jahn-Teller distorted regime (O′-phase) a linear dependence can be observed up to $x=0.3$, both p_{eff} and Θ become almost constant in the O phase.

In Fig. 4 hysteresis measurements up to 50 kOe at $T=5$ K are presented. The evolution of a ferromagnetic component upon increasing Cr-doping is clearly evident. Additionally, upon increasing Cr concentration the samples become magnetically softer, as indicated by the decreasing coercive fields in the hysteresis loops. As shown in the inset of Fig. 4, the spontaneous magnetization M_s (obtained by extrapolation from the data at the highest magnetic fields, see lower panel of Fig. 4) increases linearly with the concentration of Cr^{3+} and reaches a maximum at $x=0.3$. In the O-phase M_s shows a constant behavior, similar to p_{eff} and Θ.

In principle, the behavior of the magnetic parameters discussed above is in accordance with the early studies by Jonker and Bents.[8,9]

C. Electron spin resonance

Electron spin resonance detects the power P absorbed by the sample from the transverse magnetic microwave field as a function of the static magnetic field H. The signal to noise ratio of the spectra is improved by recording the derivative dP/dH with lock-in technique. ESR spectra, which are characteristic for the paramagnetic regime, are presented in Fig.
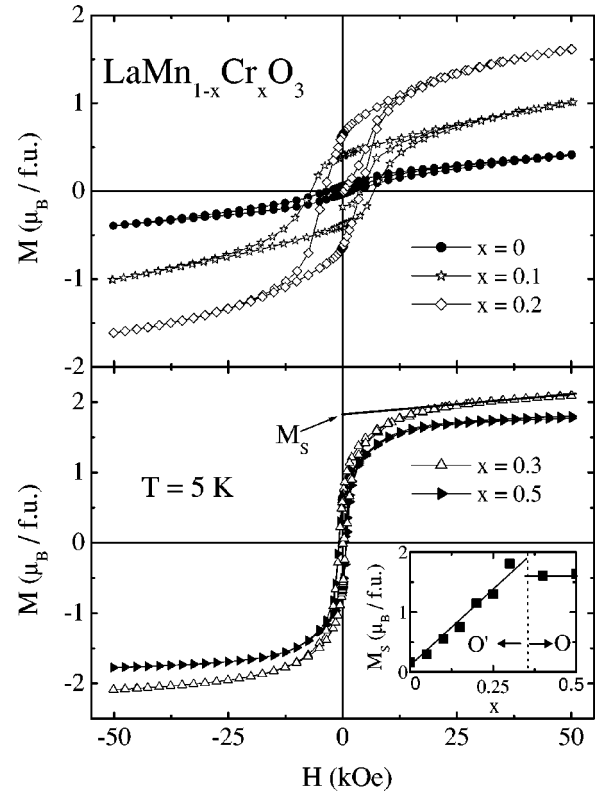

FIG. 4. Field dependence of the dc-magnetization M at $T=5$ K. Inset: spontaneous magnetization M_s as a function of Cr-doping.

5, illustrating their evolution with Cr concentration x (left column) and temperature T (right column). Within the whole paramagnetic regime the spectrum consists of a broad, exchange narrowed resonance line, which is well fitted by a Lorentzian line shape as described previously.[23]

The integrated intensity $I(T)$ of the resonance line measures the spin susceptibility χ_{ESR} of the ESR probe. For ferromagnetically coupled ions its temperature dependence usu-
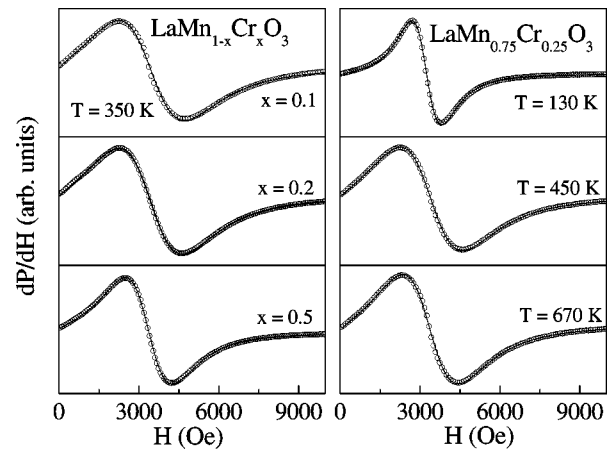

FIG. 5. ESR spectra of $LaMn_{1-x}Cr_xO_3$. Left column: various Sr concentrations x at $T=350$ K. Right column: temperature evolution of the ESR spectrum for $x=0.25$. Solid lines represent the fits using the Lorentzian line shape.
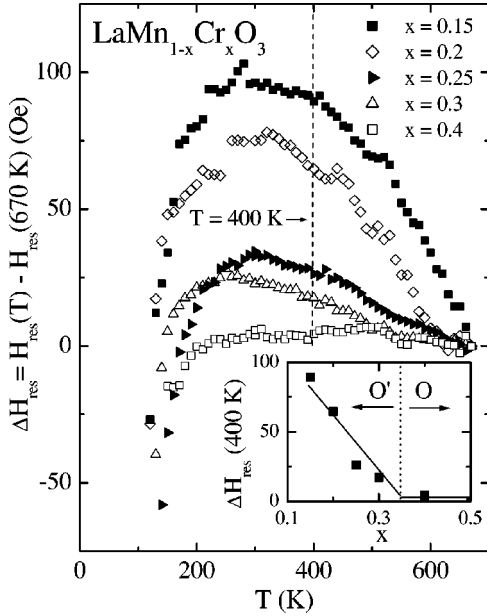
FIG. 6. Temperature dependence of the resonance shift ΔH_{res} for $LaMn_{1-x}Cr_xO_3$ ($x \geq 0.15$). Inset: Resonance shift at 400 K as a function of Cr-doping.

FIG. 7. Temperature dependence of the linewidth for $LaMn_{1-x}Cr_xO_3$. The solid lines represent the fits using Eq. (1). Inset: Linewidth at 450 K as a function of Cr-doping.

ally follows a CW law, where Θ is the CW temperature. Indeed, we observed a linear behavior of $1/I(T)$ in the paramagnetic regime within the whole concentration range. The CW temperatures as determined from the ESR experiments agree well with values obtained from susceptibility measurements [Fig. 3(b)]. By comparison with the intensity of the reference compound Gd_2BaCuO_5,[24] we obtained the effective moments, which are in good agreement with the magnetic susceptibility data except for $x = 0.5$.

In the non-JT distorted orthorhombic O phase ($x = 0.4$) the resonance field H_{res} yields an effective g value $g_{eff} \approx 1.99$ slightly below the free-electron value, which is characteristic for transition-metal ions with a less than half filled d-shell.[25] In Fig. 6 we show $\Delta H_{res} = H_{res}(T) - H_{res}(670 \text{ K})$ for concentrations $x \geq 0.15$. At 670 K the resonance fields for these samples reach values characteristic for the O phase $H_{res}(670 \text{ K}) \approx 3.34$ kOe. For $x < 0.15$ the resonance shift is even larger, but the structural phase transition seems to take place beyond our accessible temperature range. However, the resonance shift at $T = 400$ K for $x \geq 0.15$ (see inset of Fig. 6) clearly mirrors the structural phase transition as the shift decreases with increasing Cr concentration and drops to almost zero for $x \geq 0.4$.

Finally approaching the ordering temperature from above, the whole resonance becomes seriously distorted and is strongly shifted to lower fields due to the internal fields caused by the onset of magnetic order. A similar evolution of the resonance line has been reported by Sun *et al.* and interpreted as an indication for DE.[12] However, we restrict our discussion to the paramagnetic phase ($T > T_N$), because in order to characterize the magnetic order accurately one needs single-crystals of defined shape instead of randomly oriented powder which gives rise to the observed distortion of the line shape.
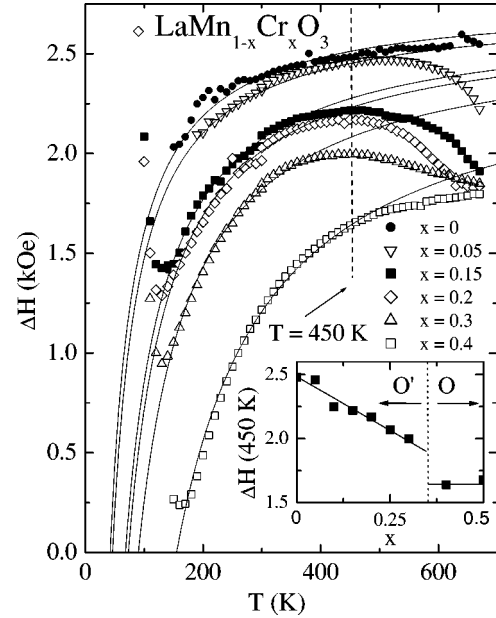
Figure 7 shows the characteristic temperature dependence of the ESR linewidth. All samples with $x \leq 0.3$ show a broad maximum in the JT distorted phase and a minimum above the critical broadening on approaching magnetic order. For the parent compound $LaMnO_3$ the maximum cannot be detected within the investigated temperature range, but has been reported by Causa *et al.*[26] For the highest temperatures under investigation the linewidth of all samples with $x > 0.05$ seem to converge indicating the range of the high-temperature limit. For $x > 0.3$ the maximum is not observable anymore and the linewidth shows a monotonous increase with increasing temperatures. The inset of Fig. 7 shows the dependence of the linewidth at 450 K on the Cr concentration. At this temperature the samples with $x \leq 0.3$ reveal the broad maximum, but have not yet reached the high-temperature limit. The obvious jump at the critical concentration reflects the transition from the O′- to the O-phase (Fig. 1) thus revealing a close correlation between spin relaxation and structural distortion.

IV. DISCUSSION

A. ESR linewidth and resonance field

The temperature dependence of the linewidth and the resonance field of $LaMn_{1-x}Cr_xO_3$ for $x \leq 0.3$ is very similar to the ones we observed in $La_{1-x}Sr_xMnO_3$ single crystals for $x \leq 0.15$.[23] Especially for a Sr concentration of 5% the features of linewidth and resonance field can be compared to the present system. $La_{0.95}Sr_{0.05}MnO_3$ is still an antiferromagnetic insulator ($T_N = 140$ K) dominated by $Mn^{3+} - O - Mn^{3+}$ SE interactions. The presence of the non-JT active Mn^{4+} ions, however, weakens the cooperative JT matrix resulting in a reduced JT transition temperature $T_{JT} = 600$ K. Below this

temperature both ΔH and H_{res} show an anisotropic behavior, which can be regarded as a characteristic feature of the O′ phase.[23,27]

If the external field is applied within the ferromagnetically coupled ab-plane, the linewidth reveals a broad maximum within the JT distorted O′ phase, whereas ΔH is nearly constant, if the external field is parallel to the antiferromagnetically coupled c-axis. We also investigated a powdered $La_{0.95}Sr_{0.05}MnO_3$ sample and found that the linewidth shows the same features as the single crystal for the external field applied within the ab-plane. Correspondingly, we observed a resonance shift to higher magnetic fields within the JT distorted O′ phase, when the external field is within the ab-plane, and a constant behavior along the c-axis. In our recent approach we presented a detailed analysis for the angular dependence of the linewidth and the resonance field in $La_{0.95}Sr_{0.05}MnO_3$ in the O′ phase by taking into account the crystal field (CF) and the Dzyaloshinsky-Moriya (DM) interaction,[28] which were shown to yield by far the largest contribution to the linewidth in manganites by Huber et al.[29] Due to the similarities in the temperature dependence of ΔH and H_{res} we assume that these two interactions also account for the ESR properties in Cr-doped $LaMnO_3$.

Unfortunately, in the case of polycrystalline samples such a detailed analysis is not possible due to the random orientation of the powder. However, a similar behavior of ΔH vs T has also been reported in polycrystalline $LaMnO_{3+\delta}$ by Tovar et al.,[30] who found a broad linewidth maximum in the O′ phase up to $\delta = 0.04$. The corresponding JT transition temperatures decrease from 700 K for $\delta = 0$ to 400 K for $\delta = 0.05$, and for $\delta > 0.05$ the cooperative JT distortion vanishes concomitantly with the broad maximum. The authors describe the temperature dependence of the exchange-narrowed linewidth by following Huber et al. as

$$\Delta H(T) = \frac{\chi_0(T)}{\chi(T)} \Delta H_\infty \tag{1}$$

with the free Curie susceptibility $\chi_0 \propto T^{-1}$ and the static susceptibility $\chi(T) \propto (T - \Theta)^{-1}$.[29] The high-temperature linewidth ΔH_∞ depends on the contributions of both the CF and the DM interaction. Thus, we fitted the linewidth data for all samples under investigation by using Eq. (1) (see Fig. 7), which can neither describe the critical broadening of the linewidth in the vicinity of a magnetic transition nor the structural transition at T_{JT}, but fits very nicely in between these transitions. The obtained parameters Θ and ΔH_∞ are shown in Fig. 8. Though the obtained CW temperatures are, in comparison with the values in Fig. 3(b), slightly lower for $x \leq 0.3$ (O′ phase) and enhanced for $x > 0.3$ (O phase), the overall tendency is the same. Moreover ΔH_∞ shows the same behavior as the linewidth values taken at 450 K (see inset of Fig. 7), confirming that the maximum linewidth is a good measure for the strength of the interactions.

The difference in ΔH_∞ observed between the O′ and the O-phase is due to the fact that concomitantly with the disappearance of the cooperative JT effect the contribution of the single-ion anisotropy of the CF vanishes at T_{JT} whereas the
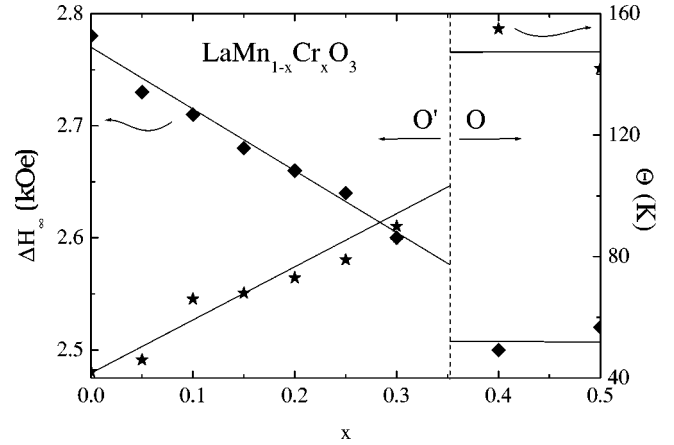

FIG. 8. Doping dependence of the CW temperature Θ and ΔH_∞ obtained by fitting with Eq. (1). The solid lines are to guide the eyes.

DM contribution is due to the tilting of the octahedra, which for $LaMnO_3$ has been shown to remain nearly unchanged through the transition.[31,32]

The obtained values in both phases are in agreement with those reported for $La_{1-x}Ca_xMnO_3$ and $LaMnO_{3+\delta}$ of $\Delta H_\infty \approx 2.7$ kOe for the O′-phase and $\Delta H_\infty \approx 2.2$ kOe for the O phase yielding values of the order of 1 K for both interactions.[29,30]

The influence of DE on the ESR linewidth in the paramagnetic regime is not fully understood and still the subject of a controversial discussion: Shengelaya et al. found that in $La_{0.8}Ca_{0.2}MnO_3$, where the cooperative JT distortion is already suppressed, the temperature dependence of the linewidth correlates with the conductivity and both parameters can be described by a small-polaron hopping model $\sim 1/T \exp(-E_a/k_B T)$ with similar activation energies E_a.[33] In contrast, in the optimally doped region $x = 0.33$ the linewidth has been described previously by Eq. (1) only.[34,35] Some authors argue that due to the different time scales the DE interaction, which manifests itself in the paramagnetic phase through the hopping of the JT polaron, cannot have any effect on the spin relaxation.[29,36] However, we want to emphasize that in our case the linewidth can be satisfactorily described without any additional relaxation process connected to polaron hopping.

B. Magnetic properties and ESR intensity

Though all observed parameters show a close correlation to the structural changes induced upon Cr-doping, the origin of the observed ferromagnetic component of the magnetization cannot easily be explained. From the values of the high-field magnetization (5 T) we deduce that the magnetic phase is not purely ferromagnetic, since the deviation from the theoretical values of $3 - 4 \mu_B$/f.u. for the full magnetic moment of all Mn^{3+} and Cr^{3+} spins cannot be attributed to temperature induced disorder, only. Therefore, we have to consider all exchange interactions between the Mn^{3+} and Cr^{3+} ions that could contribute to the magnetic state of the system.

In the parent compound $LaMnO_3$ the JT distortion lifts the degeneracy of the e_g orbitals and the

Mn^{3+}–O–Mn^{3+} SE interaction yields antiferromagnetic coupling along the *c*-axis and ferromagnetic coupling in the *ab*-plane. In the case of degenerated e_g orbitals, the Kanamori–Goodenough rules[37] do not apply and the two-orbital Kugel–Khomskii model yields a purely ferromagnetic Mn^{3+}–O–Mn^{3+} SE interaction.[3] Due to the weakening of the JT distortion upon Cr-doping, the degeneracy of the e_g orbitals can become almost restored (similar to the ferromagnetic insulating state of $La_{1-x}Sr_xMnO_3$) and favor ferromagnetism (FM). Taking into account the Kanamori–Goodenough rules[37] the Mn^{3+}–O–Cr^{3+} superexchange is ferromagnetic and therefore can also account for the increasing values of Θ in the O′-phase with increasing Cr-doping. Correspondingly, the antiferromagnetic Cr^{3+}–O–Cr^{3+} superexchange should contribute considerably with increased Cr content and could account for the stabilization of the magnetic state for $x > 0.3$, where the observed parameters become almost constant. Finally, a DE interaction between Mn^{3+}–O–Cr^{3+} ions has been proposed.[12,13]

Regarding the existence of DE, we can compare our data to observations of Prado *et al.*[22] in $LaMnO_{3+\delta}$, where one can clearly see the impact of Mn^{4+}–O–Mn^{3+} double exchange on the magnetic properties: Though the hysteresis loops show a similar behavior upon increasing oxygen surplus as upon Cr-doping, the magnetic phase transition from AFM to FM at $\delta \approx 0.04$ is characterized by the appearance of the full magnetic moment of $3-4\mu_B$/f.u. These features are also found upon doping with Sr.[2] How difficult it is to distinguish the involved interactions from the dc magnetization data only can be seen in comparison with the behavior of *M* vs *x* in electron doped $Ca_{1-x}La_xMnO_3$,[38] which looks very similar to our system. However, this behavior has been found to correlate with the electron mobility and attributed to the dynamical charge transfer due to DE interactions. As neither such correlations nor the appearance of the full magnetic moment has been observed in $LaMn_{1-x}Cr_xO_3$, we will consider the influence of DE in the following as negligible.

Due to the delicate interplay of the above SE interactions, Jonker favored the existence of a complex ferrimagnetism (FiM),[9] and Bents found in his neutron diffraction study that not only FM, but also A-type AFM (for $x \leq 0.15$) and G-type AFM (for $x > 0.3$) are present in the system.[8] A theoretical density-functional study by Yang *et al.* based on the data of these early publications supports the idea of FiM on account of positive Mn^{3+}–O–Mn^{3+} and negative Cr^{3+}–O–Cr^{3+} superexchange interactions. However, positive Mn^{3+}–O–Cr^{3+} interaction has not been found in the calculations.[39] Very recently, Ono *et al.* suggested another scenario based on their soft x-ray magnetic circular dichroism experiments.[40,41] They found that the Mn ions are aligned parallel to the direction of the magnetization, whereas the Cr magnetization seems to disappear. In order to simulate such a behavior by using the Monte Carlo method, they had to assume a negative Mn^{3+}–O–Cr^{3+} interaction in contrast to the Kanamori–Goodenough rules. Assuming antiferromagnetic Mn^{3+}–O–Cr^{3+} superexchange the latter authors explain the cluster-glasslike behavior of the system as a frustration of the spins due to the competing SE interaction.[20] Although the

reasons for the disappearance of the Cr magnetization are rather unclear, such a scenario is in accordance with the observed values of the spontanous magnetization M_S values (see inset of Fig. 4): The linear increase in the JT distorted O′ phase can be attributed to the partially restored degeneracy of the e_g orbitals,[3] weakening the antiferromagnetic Mn^{3+}–O–Mn^{3+} SE (along the *c*-axis) and finally yielding only ferromagnetic Mn^{3+}–O–Mn^{3+} interaction for $x > 0.3$. Thus, the theoretical values of $1.6-2\mu_B$/f.u. are in agreement with our data.

Astonishingly, we also observe that in contrast to Ca/Sr-doped $LaMnO_3$, where the ESR signal has been attributed to both Mn^{3+} and Mn^{4+} ions,[23,34] the ESR signal in the paramagnetic regime seems to be originated by the Mn^{3+} ions only (see Fig. 3): The effective moments determined by ESR follow the theoretical curve for Mn^{3+} up to $x = 0.5$ very nicely. The corresponding values from the magnetization measurements, however, are slightly enhanced in comparison to the ESR data, but the overall tendency is similar. In contrast to the SQUID measurements (see inset of Fig. 2), the ESR experiments were performed up to 670 K allowing a more reliable determination of the effective moments. Thus, the frustration of the Cr^{3+} ions even seems to influence the paramagnetic phase.

V. CONCLUSIONS

We presented a detailed magnetic analysis of the doping effect of Cr on $LaMnO_3$. The parent compound is an *A*-type AFM with orbital order induced by a strong JT effect due to the double degeneracy of the e_g-orbitals of the Mn^{3+} ions. Upon doping with Cr^{3+} ions, ferromagnetic interactions show up. The magnetically ordered state can be understood in terms of a competition of positive Mn^{3+}–O–Mn^{3+} and negative Mn^{3+}–O–Cr^{3+} and Cr^{3+}–O–Cr^{3+} SE interactions. Assuming the disappearance of the Cr magnetization the increasing ferromagnetic component can be ascribed to the Mn^{3+} ions the partial restoration of the double degeneracy of the e_g-orbitals due to the weakening of the JT matrix by non-JT active Cr^{3+}-ions. Additionally, the Jahn-Teller driven orbital order becomes weaker and finally disappears for doping levels between 0.3 and 0.4. All parameters, i.e., Θ, H_{res} and ΔH, reflect this transition in their doping dependence. Thus, the system can be considered as a ferromagnetic insulator with respect to Mn^{3+} in the sense of the two-orbital Kugel–Khomskii model, as the competing negative SE interactions seem to produce a disappearance of the Cr magnetization. The ESR properties can be naturally explained by the structural disorder induced upon Cr-doping and the effects of the CF and DM interactions. Moreover, the Cr^{3+} ions seem not to contribute to the ESR signal. From our experimental data we do not see any need to invoke the possibility of DE interaction between Cr and Mn ions. The questions about the origin of the disappearance of the Cr magnetization and why the Cr^{3+} ions seem to be ESR-silent remain unsolved problems and challenge further experimen-

tal and theoretical investigations.

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