Interplay between magnetism and lattice distortions in LaMn$_{1-x}$Ga$_x$O$_3$

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Abstract. A theoretical investigation of the structure, magnetism and thermal conductivity of LaMn$_{1-x}$Ga$_x$O$_3$ has been made. A local, cluster model is introduced. It is proposed that gallium substitution may cause neighbouring Mn$^{3+}$ $(3x^2 - r^2)/(3y^2 - r^2)$ orbitals to transform into the $3z^2 - r^2$ state. This unique idea is the basis of a successful description of the structure and magnetism of LaMn$_{1-x}$Ga$_x$O$_3$. The evolution of the crystal lattice parameters has been simulated; agreement with experimental data is excellent; changes in orthorhombic strain and cell volume are also well predicted. The behaviour of the magnetization has been successfully described by a spin-flipping model: over the entire range of doping, good qualitative consistency between simulation predictions and experimental data is observed. Ultimately, the aforementioned results indicate that lattice distortions alone may be responsible for the observed magnetic order in these manganites. Additionally, the thermal conductivity of LaMn$_{1-x}$Ga$_x$O$_3$ has been analysed. The results are fitted with a kinetic model. It appears that thermal currents in LaMn$_{1-x}$Ga$_x$O$_3$ may be limited by scattering of phonons from the structural changes near the Ga ions.
1. Introduction

Since the discovery of colossal magnetoresistance in La–Ca–Mn–O films [1], mixed-valence manganites of composition R$_{1-x}$A$_x$MnO$_3$ (R and A represent rare- and alkaline-earth ions respectively) have been studied extensively [2]–[4]. They have very rich phase diagrams because of the interplay between Jahn–Teller effects, charge ordering and conductivity, giving rise to a variety of structural and magnetic phases that exist as a function of doping with the divalent element A. In this case, the dopant introduces mobile carriers which suppress the Jahn–Teller effects. Many phases show significant magnetoresistance effects close to the magnetic-ordering temperature.

The parent compound, LaMnO$_3$, has unpaired electrons in $e_g$ states that are strongly Jahn–Teller active, which leads to an orthorhombic ground state with an orbital order [5]–[9]. The orbital order results in magnetic exchange interactions that favour an A-type antiferromagnetic structure [10, 11].

In order to ascertain the relative importance of removing a Jahn–Teller active ion and doping with mobile carriers, both of which occur in R$_{1-x}$A$_x$MnO$_3$, the parent compound LaMnO$_3$ diluted with non-magnetic non-Jahn–Teller active ions [12]–[18] such as Ga$^{3+}$, Sc$^{3+}$ or Al$^{3+}$ were studied previously. These elements preserve the valence of the Mn at 3+ and all the compounds are insulating. There is least lattice distortion for gallium and also the maximum amount of experimental information is available. So this is the substitution that we consider in detail. As $x$ increases, both the crystallographic distortions disappear and the A-type antiferromagnetism is rapidly suppressed as the material becomes a spin glass or ferromagnet. The effects are significant. For example, at low temperatures and in a moderate magnetic field of 5.5 T, the magnetic moment of LaMn$_{1-x}$Ga$_x$O$_3$ varies linearly with $x$ for 0 < $x$ < 0.08 with a slope that indicates that the introduction of each Ga$^{3+}$ ion increases the magnetic moment per Mn ion by $\sim 16 \mu_B$. This is a significant effect to occur for a non-magnetic ion and, as a result, the LaMn$_{1-x}$Ga$_x$O$_3$ system has generated considerable interest; detailed measurements have been made of the crystal structure, bond lengths, magnetization and thermal conductivity [12]–[17]. We describe a model that gives a satisfactory understanding of these measurements with a minimum number of assumptions and no adjustable parameters.

One of the characteristics of the insulating manganites is that the interactions are short ranged. The Jahn–Teller distortions around a manganese ion depend on the local coordinates.
of the neighbouring oxygen ions, each of which is shared with another Mn ion in the parent structure. We use a localized, real-space model to study the mixed compound. This is actually a refinement of the early theory [12]. In this communication, we show that all the structural and magnetic data for LaMn$_{1-x}$Ga$_x$O$_3$ may be fitted at least qualitatively from the assumption that the size of the Ga$^{3+}$ ion disturbs the orbital order of some of its neighbours. The change in the orbital order, in turn, disturbs the magnetic order. No adjustable parameters are needed; the model uses the measured bond lengths and measured exchange interactions. We also discuss a fit to the thermal conductivity data on the basis of this model. Our analysis has consequences for the understanding of other manganites because it is a case study of a scenario where the local distortion drives the orbital order and the orbital order drives the magnetism. This question is actively debated in other materials where the lattice contribution has been measured directly [9], although it is known that the electronic energies alone could cause the orbital order [19].

2. Orbital and spin order in LaMnO$_3$

The Jahn–Teller interaction of the $e_g$ states in LaMnO$_3$ causes the Mn ions to have two long, 2.18 Å, and two short bonds, 1.90 Å, to neighbouring oxygen ions in the $x$–$y$ plane. These are arranged such that each oxygen in the $x$–$y$ plane is farther from one Mn$^{3+}$ and closer to the other. In the $x$–$y$ plane, each line of ions Mn–O–Mn has one long Mn–O bond and one short bond. This is an antiferrodistortive orbital arrangement in the plane. The orbits are stacked parallel up the $z$-axis and the bond lengths are undistorted, 1.96 Å, although the bond angles differ from 180$^\circ$.

At the structural transition at 750 K, the long-range orbital order disappears and a nearly cubic high-temperature phase exists where the orbits have become disordered but the local distortions around the manganese ions remain. The relative strength of the interactions that cause the ordering of the Jahn–Teller sites and the magnetic interactions that cause the antiferromagnetism may be deduced from the transition temperatures, 750 K for the structural transition and 120 K for the antiferromagnetism.

In table 1, we give the different energies for the relative orientations of the long bonds corresponding to the Jahn–Teller orbits and the different exchange energies. The configurations (1) and (2) occur in LaMnO$_3$. The magnitudes of the interactions between different orbital arrangements have been calculated by Khomskii and Kugel [20]; long-range effects actually favour configuration (2) over configuration (3) [21].

We note that the orbital arrangement determines the magnitude and sign of the magnetic exchange as may be predicted from the Goodenough–Kanamori–Anderson rules [10]. The magnetic exchange parameters for configurations (1) and (2) are taken from experiment [22]. The value of the exchange for configuration (3) was deduced following [5] from the fact that the Slater–Koster hopping parameter is lower by a factor of 2 for this configuration compared with configuration (1) and this would predict a value of the exchange that is lower than that for configuration (1) by a factor of 1/4. Similar arguments suggest that the antiferromagnetic interaction for configuration (4) is 16 times that for configuration (2). We note that there is a large energy penalty for orbit configuration (4) ‘head-to-head’, so this configuration is very unlikely to occur. The orbits in LaMnO$_3$ are arranged in configurations (1) and (2) as shown in figures 1 and 2.
Table 1. The magnetic exchange energies and the orbital energies for pairs of nearest-neighbour Mn ions.

| Orbital configuration | Magnetic exchange integral | Elastic energy [20] |
|-----------------------|---------------------------|--------------------|
| 1                     | Ferromagnetic 9.6 K [22]  | $-\frac{\lambda}{2}$ |
| 2                     | Antiferromagnetic $-6.7$ K [22] | $\frac{\lambda}{4}$ |
| 3                     | Ferromagnetic $9.6/4 = 2.4$ K | $\frac{\lambda}{4}$ |
| 4                     | Strongly antiferromagnetic $\sim 16 \times (-6.7)$ K $\sim -107$ K | $\lambda$ |

Figure 1. The $e_g$ orbital arrangement in the $x$–$y$ plane near a single Ga$^{3+}$ in LaMnO$_3$. Flipping of the orbits marked $\alpha$ in the $x$–$y$ plane is forbidden because it would produce a configuration (4).

3. Structure of LaMn$_{1-x}$Ga$_x$O$_3$

We now consider how an isolated Ga ion will perturb the orbital order. The Ga$^{3+}$ ion is slightly smaller than Mn$^{3+}$, by 0.62 Å compared with 0.64 Å [16]. The Ga–O distance is 1.97 Å, which is closer to a Mn–O short bond, 1.90 Å. This suggests that it is favourable for the Ga ion to be in the configuration Ga–O–Mn where Mn has a long bond to the oxygen. In the orbital structure in the $x$–$y$ plane for LaMnO$_3$ shown in figure 1, we see that the Ga ion already has two long orbits pointing towards the Ga site. It is very unfavourable for the other orbits to flip around because this would give two long orbits pointing towards each other as in configuration (4) in table 1. Thus we assume that there is no disturbance of the orbital ordering in the $x$–$y$ plane containing an isolated Ga ion. However, in the LaMnO$_3$ structure, the orbits stack parallel up the $z$-axis as shown in figure 2. In this case, the manganese orbitals above and below the Ga can flip to lying up the $z$-axis without incurring penalty. In this paper, we assume that this flip occurs. In LaMnO$_3$, the Mn–O–Mn bonds in the $x$–$y$ plane are highly strained because the short Mn–O
Figure 2. The $e_g$ orbital arrangement in (a) LaMnO$_3$ and (b) near a Ga$^{3+}$ dopant (shaded circle) in LaMnO$_3$. The ‘diagonal’ orbitals extend into the page. The presence of the Ga ion has changed the orbital configuration on the Ga neighbours in the $z$-direction.

bond is compressed into 1.90 Å rather than 1.96 Å. In the $z$-direction, the bonds are not strained: so in LaMnO$_3$, each Mn has four strained bonds and two non-strained bonds with neighbouring Mn. Upon including a gallium, the orbits on the Mn above (and below) the Ga flip to $3z^2-r^2$. From figure 2(b), we see that Mn with the flipped orbit has only two strained bonds in plane and one strained bond in the $z$-direction. Because Ga is a non-Jahn–Teller ion, the Mn–O–Ga bond is not strained but Ga is pushed away from Mn (as is evident from the measured increase along the $c$-axis for large values of $x$). Therefore, after Ga is included, only three rather than four of the bonds of Mn with the flipped orbit are strained. Because the short-range strain energy is the dominant one, the orbital-flipping model is plausible.

This assumption, together with the measured bond lengths, accounts for the structural properties of the mixed compound LaMn$_{1-x}$Ga$_x$O$_3$ over the whole concentration range.

The evolution of the crystal structure of LMGO was simulated by considering a simple cubic lattice ($L = 10$) of Mn orbitals with periodic boundary conditions implemented. Firstly, the orbital order of LaMnO$_3$ (figure 2(a)) was initialized on the lattice. For each value of $x (= 0, 0.05, \ldots, 1)$, 1000 random lattice sites were chosen and the anisotropic Mn orbital on each of these sites was replaced by a Ga ion. The $(3x^2-r^2)/(3y^2-r^2)/$Mn orbitals directly above and below (along the $z$-axis) each of the Ga were then flipped into the $3z^2-r^2$ state.

If a site above/below any Ga already contained a $3z^2-r^2$ orbital or a Ga ion, orbital flipping is not necessary. Additionally, because ‘head-to-head’ orbital configurations (configuration (4) in table 1) are energetically unfavourable, flipping of a $(3x^2-r^2)/(3y^2-r^2)/$Mn orbitals was forbidden if the neighbouring site along the $z$-axis contained a $3z^2-r^2$ orbital. The lengths of the Jahn–Teller-distorted Mn–O bonds were assumed to be 1.90 and 2.18 Å (identical to those in LaMnO$_3$); a Ga–O bond length of 1.97 Å (as measured by neutron diffraction [16]) was also incorporated into the simulations. The measurements of Blasco et al [16] indicate that, generally, the low-temperature thermal expansion of LaMn$_{1-x}$Ga$_x$O$_3$ is negligible: with respect to simulation of the lattice parameters, effects of temperature were therefore not considered in the theoretical model.
In each of the three spatial directions, a sum of the sizes of all bonds (using the experimental bond-length measurements) was made; the corresponding lattice parameter was the average of this sum. For each $x$, the orbital flipping and bond counting was repeated 1000 times for different, randomly chosen lattice configurations; the results of simulation presented in figure 3 correspond to an average of these 1000 configurations.

At $x = 1$, each of the simulated lattice parameters should have converged to a single value; the spread of the $x = 1$ data therefore corresponds to the maximum systematic error in the simulation process. The statistical errors in the structure simulation were negligible.

In LaMnO$_3$, the cooperative, orthorhombic Jahn–Teller distortion is such that $b > a > c/\sqrt{2}$. As the Mn$^{3+}$ are randomly replaced by Ga$^{3+}$, the cooperative distortion is suppressed and, consequently, a structural transition into a pseudocubic phase ($a \approx b \approx c/\sqrt{2}$) occurs at $x \approx 0.55$. Over the entire range of doping, the results of simulation are consistent with the neutron diffraction measurements of Blasco et al [16] ($T = 2$ K) as shown in figure 3. The orthorhombic strain, $s = 2(b - a)/(b + a)$, and cell volume, $V = abc$ of LaMn$_{1-x}$Ga$_x$O$_3$, may also be calculated. The simulated evolution of $s$ and $V$ are compared with experimental data [15] in figures 4(a) and (b) respectively. Overall, agreement between these theoretical predictions and experimental measurements (made at $T = 5$ K) is excellent. The orbital-flipping hypothesis therefore successfully predicts the evolution of the crystal structure of LaMn$_{1-x}$Ga$_x$O$_3$ as the gallium proportion is varied.

There were no adjustable parameters in these theoretical estimates. They were based on the measured Mn–O and Ga–O distances in LaMnO$_3$ and LaGaO$_3$ alone. This model also predicts
that the local variation in the lattice parameters that would give rise to an increase in the Debye–Waller factor [17], varies linearly with $x$ up to $x \sim 0.5$. The status of the model is less secure as the fraction of Ga passes 0.4. The size of the Jahn–Teller distortion, as measured by XANES, decreases slightly for $0 < x \leq 0.4$ and then decreases to zero for $x = 0.6$, where there is a large Debye–Waller factor [17] that indicates a distribution of bond lengths. In view of this, the good agreement between the model and the crystallographic data for large values of $x$ is surprising.

We note that the average number of Ga neighbours increases rapidly as $x$ increases. It appears that it is critical to the development of a Jahn–Teller distortion that the average number of Ga neighbours of the Mn site does not exceed three. The fraction of Mn sites with three or more Ga neighbours is 0.46, 0.66 and 0.83 for $x = 0.4$, 0.5 and 0.6, respectively.

4. Magnetic properties of LaMn$_{1-x}$Ga$_x$O$_3$

The proposed model agrees with the observed structural data, so we now examine how the change in the orbits will affect the magnetic order through the change in the superexchange [10] as shown in table 1. In ordered LaMnO$_3$, the spin on each Mn ion is connected to four neighbours in the $x$–$y$ plane in configuration (1) with ferromagnetic interaction $J_1$ and to two neighbours along the $z$-direction in configuration (2) with antiferromagnetic interaction $J_2$. The site where the orbital has flipped now has two neighbours in the $x$–$y$ plane in configuration (3) with ferromagnetic interaction $J_3 \sim J_1/4$ and the other two still in configuration (1). In the $z$-direction, the flipped orbital has one neighbour in the Ga ion and the other is oriented in configuration (1), so that the exchange has become ferromagnetic.

The $z$-axis is contracted in LaMnO$_3$ and we assume that the ferromagnetic coupling induced along the $z$-axis is increased sufficiently to align the spin on the site of the reoriented orbit. This is our second assumption. In figure 5, we show the configurations that would be adopted in a magnetic field of 5.5 T, as has been used experimentally [15]. In this model, it is assumed that the enhanced exchange comes from reorientations of the orbit. Zhou et al

Figure 5. (a) A schematic illustration of the spin flipping (the flipped spins are shaded) that results from doping with LaMnO$_3$ with Ga$^{3+}$ (shaded circle). Additional strong ferromagnetic bonds are shown as dotted lines. (b) The configuration adopted in a large magnetic field if the Ga ion was placed on the ‘down’ sublattice. Additional strong ferromagnetic bonds are shown as dotted lines.
Figure 6. Comparison of the simulated variation in magnetization per Mn\(^{3+}\) in LaMn\(_{1-x}\)Ga\(_x\)O\(_3\) with experimental data from [15]; \(T = 5\) K, \(B = 5.5\) T. At small values of \(x\), the additional line corresponds to increases in magnetization of 15\(\mu_B\).

[13] considered an enhanced ferromagnetic vibronic exchange that drove the system towards a ferromagnetic phase. The main difference between these models is that we assume an additional strong ferromagnetic exchange only between bonds in the \(z\)-direction, whereas the vibronic superexchange is isotropic. In the \(A\)-type antiferromagnetic structure, the spins are parallel in planes and the antiferromagnetic interaction is between planes. Thus a new strong ferromagnetic interaction between spins in neighbouring planes is very effective in destroying the long-range antiferromagnetism and driving the system to a ferromagnetic phase when there is a percolating cluster of Ga ions.

The magnetic exchange between two Mn ions depends on the relative orientation of the orbits as given in table 1. Monte Carlo simulations have been performed for the spins on Mn ions with the orbital configurations found from the earlier calculation. The change in magnetization of LaMn\(_{1-x}\)Ga\(_x\)O\(_3\) as a consequence of the orbital flipping that gave the correct structure may be calculated. All the exchange parameters were taken from experiments as in table 1, except for the proposed ferromagnetic exchange for the flipped orbits shown in figure 5. A nearest-neighbour Ising model was simulated; this ruled out the possibility of canting; it also meant that the model failed to account for the contribution from the perpendicular susceptibility that is present in a polycrystalline sample. The angular momentum was assumed to be quenched such that each Mn\(^{3+}\) has a spin-only moment \(\mu\) of 3.7\(\mu_B\) as it was observed in [15]. Simulations for \(T = 5\) K and \(B = 5.5\) T for the average moment per Mn ion are compared with experiments of [15] in figure 6. The calculations were performed for \(10^5\) Monte Carlo steps for each doping level. The overall agreement is most satisfactory.

We can understand the results for the very low doping regime from figures 5(a) and (b). We note that, in both configurations, the two spins connected with a dotted line are parallel. The effect of the magnetic field is to move the flipped spin onto the unfavourable sublattice so that the net magnetization increases for both positions of the Ga ion. The net magnetization of the clusters arises both because the Ga ion is non-magnetic and because of the spin flips. The moments for the clusters shown in figures 5(a) and (b) correspond to three and five Mn magnetic moments, respectively. Assuming the moment to be 3.7\(\mu_B\) as is found for \(x \approx 0.5\), we find a moment of \(\sim 15\mu_B\) per Ga ion introduced at low Ga. We see that the experimental magnetization increases linearly with Ga content for \(x < 0.05\) and that the slope is as predicted from this cluster model.
For $0.05 < x < 0.25$, the clusters begin to overlap and the number of Mn in the cluster decreases and so the behaviour is complicated. Nevertheless, our simulations work well. The offset is due to the fact that we have not included the perpendicular susceptibility of the antiferromagnetic phase.

Experimentally, the antiferromagnetic order parameter is perpendicular to the magnetic field and the ferromagnetic moment is parallel to the field [16]. We can understand the directions of the moments from the following qualitative argument. We see that the pair of magnetic moments above and below the Ga sites are either parallel or antiparallel to all their neighbours in the plane. Thus the net effect of the neighbours in plane cancels for the two sites together. This means that the exchange energy would be the same if the ferromagnetic moments were aligned perpendicular to the underlying lattice. This is favoured by the magnetic field which aligns the antiferromagnetic order parameter perpendicular to the field and the ferromagnetic component along the field.

The clusters are large and either three or five sites are involved. The simple estimate of the percolation concentration ($p_c \sim 1/z_{\text{eff}}$, where $z_{\text{eff}}$ is the number of sites where the clusters would be neighbours or overlap) leads to $p_c \sim 1/15 \sim 0.07$ for these clusters. It is interesting that the isolated limit actually works for such a small region of the phase diagram. The two essential features predicted by this model are that, firstly, the Ga ion generates a small ferromagnetic cluster and, secondly, this cluster can reorient in a field as small as $5 \, \text{T}$.

The simulations also predict that the breakdown of the linear regime occurs close to $x \sim 0.3$, although the simulations do not predict the magnitude of the jump very well. For $0.3 \leq x \leq 0.7$, both the Ga and Mn ions form percolating lattices. This is the ferromagnetic regime and is reproduced in our simulations.

For $x > 0.7$, the Mn$^{3+}$ ions will be in finite clusters. The spins in the clusters are likely to be parallel because the ferromagnetic exchange is the largest one for favourable orbits as is shown in table 1. The Zeeman energy for a cluster with $n$ Mn spins will be $3.7 n \mu_B B$. At $T = 5 \, \text{K}$ and $B = 5.5 \, \text{T}$, we have $3.7 \mu_B B/k_B T = 2.73$ so an isolated Mn$^{3+}$ ($n = 1$) is predicted to have a moment of $\sim 3.2 \mu_B$. Any larger cluster, with $n > 1$, will be fully aligned. The model predicts that the moment per Mn ion will be $3.2 \mu_B$ with probability $x^6$ and fully aligned with moment $3.7 \mu_B$ with probability $1 - x^6$. This gives the points in figure 6.

We note that this is a local picture. Experimentally, it would be hard to distinguish the region at low $x$ from the canted antiferromagnetic structure that has been assumed previously [16]. In both cases, there will be a net moment in a field and also a net staggered moment that would be seen in a scattering experiment.

5. Thermal conductivity of LaMn$_{1-x}$Ga$_x$O$_3$

The addition of Ga has a profound effect on the thermal conductivity. In this section, we discuss how this might be understood using the same orbital model. The thermal conductivity $\kappa$ was measured [13, 23] for single crystals of LaMn$_{1-x}$Ga$_x$O$_3$ for $0 < x < 0.5$, and a crossover from static, coherent to local, dynamic Jahn–Teller distortions was proposed as the reason for the overall reduction in $\kappa$ as $x$ is increased. As an alternative to this dynamic Jahn–Teller scenario, we suggest using a simple kinetic model and Mattheissen’s rule, $\kappa(x, T) = AC(T) \lambda(x, T)$ where

$$\frac{1}{\lambda(x, T)} = \frac{1}{\lambda(0, T)} + \frac{1}{\lambda_x}.$$
Figure 7. The variation of \((\kappa(0,T)/\kappa(x,T)) - 1\)^{-1} with temperature in LaMn\(_{1-x}\)Ga\(_x\)O\(_3\) for \(x = 0.15, 0.25, 0.35\) and 0.5 [13, 23].

In this relation \(\lambda(0, T)\) is the mean free path for undoped LaMnO\(_3\) and \(\lambda_x^{-1}\) is due to the scattering from the gallium and the orbital distortions induced around it. If this relationship holds then the ratio of the thermal conductivities for concentration \(x\) and for \(x = 0\) is given by,

\[
\frac{\kappa(0,T)}{\kappa(x, T)} = \frac{\lambda(0, T)}{\lambda(x, T)} = 1 + \frac{\lambda(0, T)}{\lambda_x}.
\]

Hence the ratio

\[
\frac{\lambda_x}{\lambda(0, T)}
\]

may be obtained from the thermal conductivity data. Figure 7 shows a plot of

\[
\left[\frac{\kappa(0,T)}{\kappa(x, T)} - 1\right]^{-1} = \frac{\lambda_x}{\lambda(0, T)}
\]

as a function of temperature for various values of \(x\) obtained from the data of Zhou and Goodenough [23]. The similarity of the curves shows that, at least below 125K the curves may be collapsed on to a universal curve with a temperature independent coefficient. This shows that the dominant temperature effect is coming from the temperature dependence of the mean free path in the pure material \(\lambda(0, T)\).

For \(T < 125\) K, the linearity of the data implies that \(\lambda_x/\lambda(0, T) = TC(x)\), where \(C(x)\) is the gradient of each line. On the basis of the four different values of \(x\), the scattering rate \(C(x^{-1})\) is found to be proportional to \(x^{1.45}\), whereas the localized model would predict a dependence of \(x\) (as is found experimentally for the Debye–Waller factor). This may be due to the fact that the phonon scattering at these temperatures is particularly sensitive to the size of the distortions. If \(\lambda_x\) is temperature-independent, it would imply that \(\lambda_x(0, T) \propto 1/T\). The thermal conductivity of LaMnO\(_3\) varies linearly with inverse temperature in this range [13] and hence the assumption that \(\lambda_x\) is independent of \(T\) leads to the unphysical result that the specific heat capacity is a constant. Rather, the \(1/T\) dependence of \(\kappa_0(T)\) may be attributed to phonon scattering from point defects [24], and our results indicate that the mean free path due to the defects around the Ga ions varies with one higher power of \(T\), consistent with the strain induced by the Ga being extended over several lattice sites.

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6. Conclusions

As an alternative to Ga$^{3+}$, trivalent scandium and aluminium are also appropriate dopant ions [18]. Either of them is a more disruptive dopant as the volume changes indicate [18]. An Sc$^{3+}$ ion is larger than Mn$^{3+}$ and Al$^{3+}$ is considerably smaller. The magnetization of the scandium-doped compound is very reminiscent of the gallium-doped material. It is possible that a localized model producing a ferromagnetic cluster that can be reoriented in a small field similar to that considered here will work for this compound too. Goodenough et al [18] attributed the behaviour at low doping to a canted phase. The aluminium compound shows a very different behaviour. The magnetization varies quadratically with doping rather than the linear behaviour discussed above, which implies that the single-defect model of a ferromagnetic cluster that can be aligned in a small field as discussed here is certainly inappropriate for this case.

In conclusion, it has been shown that a local model with a single hypothesis—namely ‘orbital flipping’—may successfully describe the evolution of the crystal structure in LaMn$_{1-x}$Ga$_x$O$_3$. One strong ferromagnetic bond is assumed to be generated between the flipped orbit and its neighbours and, with this assumption alone, the change in magnetization is predicted over the whole range of concentrations. A notable point is that the increase of magnetization at low Ga concentration, $(\partial M/\partial x)|_{T=5K,B=5.5T} \approx 16 \mu_B$, is an immediate consequence of the cluster model. Analysis of thermal conductivity data indicates that the local, static Jahn–Teller scenario that is the basis of this work may also explain the thermal conductivity. Ultimately, this theoretical study has shown that, in these manganites, lattice distortions may be responsible for the behaviour of the $d$-electron magnetism; additional electronic effects are relatively insignificant.

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