A correlation between the spin wave stiffness constant and the cation size disorder in the perovskite manganites

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Abstract

We investigated the temperature dependence of magnetization in the ferromagnetic phase of La\(_{0.67-2x}\)Nd\(_{2x}\)Ca\(_{0.33-2x}\)Sr\(_x\)MnO\(_3\) \((x = 0, 0.1, 0.02\) and 0.33\) manganites in terms of the spin wave theory. A relation between the spin wave stiffness constant \((D)\) and the cation size mismatch was obtained. By means of this relation we could reproduce the values of \(D\) determined by different techniques reported in the literature for some samples. These findings may have important implications on the spin dynamics and the metallic electrical resistivity at low temperatures.

Keywords: A. Magnetically ordered materials; D. Order–disorder effects and spin dynamics

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1. Introduction

It has been demonstrated that the stress and the disorder created by cations of various ionic radii affect the magnetoresistive properties of the so-called colossal magnetoresistive (CMR) manganites AMnO\(_3\) \((A = \{\text{Ln,Me}\}; \text{Ln} = \text{La, Nd… etc. and Me} = \text{Ca, Sr, Ba… etc.})\) \([1,2]\). It was shown in a series of manganites Ln\(_{0.7}\)Me\(_{0.3}\)MnO\(_3\) that with a constant A-site radius \(\langle r_A \rangle\) \(T_C\) varies linearly with the variance of the cation radius in the A-site \([3]\). This effect was attributed to the displacements of the oxygen atoms due to the A-site disorder. One of the main interests of this revived subject is to investigate the effect this disorder has on the spin dynamics of these materials at low temperatures. Using the one-parameter scaling theory Sheng et al. \([4]\) have shown that the standard spin wave theory remains applicable in the presence of spin and cation size disorder in these manganites. However the spin wave stiffness constant may be affected by one of the factors, viz. (i) the average ionic radius of the A-site \(\langle r_A \rangle\); (ii) The number of the Mn\(^{4+}\) ions as they facilitate the double exchange interaction; (iii) the magnetic moment of the rare earth ions present at the A-site that may couple to the Mn ions; and (iv) the cation size mismatch \(\sigma^2\). A number of neutron inelastic scattering (INS) and muon spin resonance (\(\mu^+\)SR) experiments have been dedicated to study the spin dynamics \([5,6]\). P. Dai et al.\([7]\) have observed by INS that there is a damping of magnons at large wave vectors due to strong magnon–phonon coupling at low temperatures. They have shown the magnon damping at the zone boundary to become more prominent when \(\langle r_A \rangle\) is decreased. The spin wave dispersion relation in Ln\(_{0.7}\)Me\(_{0.3}\)MnO\(_3\) remains unchanged by substituting of Ln by La, Pr or Nd, and Ca by Sr implying thereby that the spin wave stiffness constant \(D\) is only marginally affected by the changes in \(\langle r_A \rangle\). Analyzing the resistivity of La\(_{1-x}\)Sr\(_x\)MnO\(_3\) below 30 K in terms of one magnon scattering, Furukawa \([8,9]\) has found \(D\) to be proportional to the number of the Mn\(^{4+}\) ions present in the ferromagnetic state. In this material, however the cation size mismatch is small and \(\langle r_A \rangle\) is large. For this report we have studied the effect of cation size mismatch on the value of the stiffness constant. We have chosen the 3-dimensional manganites \((\text{La,Nd})_{0.67}(\text{Ca, Sr})_{0.33}\)MnO\(_3\) and have measured their magnetization from 5 to 350 K in fields up to 5 T. By appropriate substitutions, simultaneously of La by Nd and Ca by Sr, the fraction Mn\(^{3+}/\text{Mn}\(^{4+}\) has been maintained constant. As the
Nd ions carry small magnetic moment, they will have negligible effect on the Mn$^{3+}$–Mn$^{3+}$ exchange interaction and therefore the stiffness constant ($D$) will remain essentially unaffected by it. We find the measured values of $D$ to be essentially governed by the ionic size mismatch.

2. Experimental

Polycrystalline samples of La$_{0.67-x}$Nd$_x$Ca$_{0.33}$Sr$_x$MnO$_3$ were prepared by the conventional solid state reaction by mixing the two oxides La$_2$O$_3$ and Nd$_2$O$_3$ (dried at 1023 K for 24 h) of purity not less than 99.99% and the two carbonates SrCO$_3$ and CaCO$_3$ of purity not less than 99.9%. The powders were thoroughly ground with acetone, dried and calcinated at 1223 K for 24 h. The resulted black powders were ground and heated at 1273 K for 48 h with two intermittent grindings and then pressed into pellets and fired at 1623 K. Data for X-ray powder diffraction (XRD) were collected for 2$\theta$ from 20 to 80$\theta$ with step scan 0.01 using Cu-K$_\alpha$ radiation. The phase purity and the lattice parameters were determined by means of FULLPROF program [10] utilizing the standard Rietveld refinement method. Magnetization data were collected by means of a SQUID magnetometer. Isothermal magnetization studies [11] in La$_{1-x}$Ca$_x$MnO$_3$ (0.2 ≤ $x$ < 0.5) showed that whereas the $Pnma$ symmetry was preserved the lattice parameters as well as the Mn–O–Mn bond angle and length varied with temperature, nevertheless. In the ferromagnetic ground state the spins remain under strain depending on the degree of the cation size mismatch. Upon heating from 0 K the samples with large mismatch are easily affected by the thermal excitations, hence their magnetization decreases relatively faster than of those with smaller mismatch. Appearance of ferromagnetism and metallic conductivity in the perovskite manganites has been ascribed to the mechanism of double exchange interaction (DEX) [12]. The temperature dependence of magnetization in these mixed valence manganites does not fully conform to the conventional Brillouin function [13]. Our magnetization data for these samples measured at 0.01, 1 and 5 T is shown in Fig. 1. All the samples show saturation at the lowest temperatures for fields in excess of 1 T. Below 150 K the magnetization data at 1 and 5 T coincide with each other and start separating from each other above it. A similar behavior was seen in La$_{0.815}$Sr$_{0.185}$MnO$_3$ by X. Xiong et al. [14]. Isothermal magnetization measured at 5 K shown in Fig. 1 also shows the curves leveling off at fields greater than ~ 1 T for the samples La$_{0.67-x}$Nd$_x$Ca$_{0.33}$Sr$_x$MnO$_3$ (called SC1) and La$_{0.47}$Nd$_{0.37}$Ca$_{0.12}$Sr$_{0.15}$MnO$_3$ (called SC2) whereas it increases with field for La$_{0.37}$Nd$_{0.75}$Ca$_{0.25}$Sr$_{0.2}$MnO$_3$ (called SC3) and Nd$_{0.67}$Ca$_{0.33}$MnO$_3$ (called SC4). As the substitution at the La site (by Nd) as well as the Ca site (by Sr) are isovalent, the average valence of the Mn ion remains unchanged (3.33) by these substitutions. Electron paramagnetic resonance (EPR) measurements on these samples, give $g \approx 2.01$ for all the concentrations [15]. This gives 3.67 $\mu_B$/Mn-ion as the spin only saturation magnetization. The magnetization measured at 5 K coincides with this value for the samples SC1 and SC2 but for the other two samples the saturation value is slightly higher. The saturation magnetization (Ms) measured here are given in Table 1 for all the samples. This extra magnetic moment appears to be contributed by the Nd ions as it is seen to increase with the content of Nd ions in samples. Nd ions were reported to order ferromagnetically in Nd$_{0.75}$Ba$_{0.25}$MnO$_3$ at a field greater than 1.5 T below 10 K [16]. If the measured magnetization is corrected for this contribution (~0.27 $\mu_B$/Nd), then the saturation appears to set in at fields starting below 1 T for all the samples.

We attempted to fit the magnetization at temperatures below 100 K to the equation

$$M = M_0 \left(1 - B \left(\frac{T}{T_C}\right)^n\right)$$

(1)

$M_0$, $B$ and $n$ were considered as adjustable parameters. The value of $n$ that best agreed with the data was found to be ~ 1.5, which is consistent with the spin wave exponent 3/2. The values of $M_0$ obtained were also found to agree well down to the lowest temperatures. Low temperature neutron powder diffraction studies [11] in La$_{1-x}$Ca$_x$MnO$_3$ (0.2 ≤ $x$ < 0.5) showed that whereas the $Pnma$ symmetry was preserved the lattice parameters as well as the Mn–O–Mn bond angle and length varied with temperature, nevertheless.

![Fig. 1. The magnetization data measured at 0.01, 1 and 5 T for the samples SC1, SC2, SC3 and SC4. The solid curve is the result of fitting Eq. (2).](image-url)
with the theoretical (spin only) values. It is to be noted that the ferromagnetic ordering temperatures obtained from this equation fall in the range 250–270 K and agree with those obtained from the $dM/dT-T$ plots. The analysis was then extended to higher temperatures using the full spin wave expression [17]

$$M(T) = M_0(1 - B[(f(x)/\zeta(x)]T^{3/2} - C[f(x)/\zeta(x)]T^{5/2})$$

(2)

where $x = k_BT/\mu_B H$, $f$ is the Bose–Einstein function, $\zeta(x) = 2.612$ and $\zeta(x) = 1.341$ are the Riemann zeta functions. The coefficient $B$ in Eq. (1) is related to the spin wave stiffness constant by

$$D = ak_BT_C \left(\frac{0.06}{5\pi aB}\right)^{2/3}$$

(3)

where $S$ is the average spin of the Mn ions, $a$ the lattice constant, and $\alpha = 1$ for the perovskite cubic lattice [18]. The values of $D$ obtained from Eq. (3) for all the samples are given in Table 2. The value 147 meV Å$^2$ obtained here for the sample SC1 is in good agreement with the value 155 meV Å$^2$ determined from $\mu^+\text{SR}$ experiment [6]. As the magnetization data measured below 150 K at the fields 1 and 5 T have the same values (Fig. 2), the coefficient $B$ in Eq. (2) also remains unaltered in fields larger than 1 T, but the coefficient $C$ depends on the magnetic field. The values of $B$ and $C$ are given in Table 2. $C$ appears to decrease at

![Fig. 2. Isothermal magnetization measured at 5 K for the samples SC1, SC2, SC3 and SC4.](image)

Table 1
<table>
<thead>
<tr>
<th>Sample</th>
<th>$\langle s \rangle$ (Å)</th>
<th>$B$</th>
<th>$T_C$ (K)</th>
<th>$M_0$</th>
<th>$M_s (\mu_B/Mn)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC1</td>
<td>1.2054</td>
<td>0.1329</td>
<td>269</td>
<td>270*</td>
<td>3.66</td>
</tr>
<tr>
<td>SC2</td>
<td>1.2075</td>
<td>0.3087</td>
<td>267</td>
<td>265*</td>
<td>3.64</td>
</tr>
<tr>
<td>SC3</td>
<td>1.2095</td>
<td>0.3802</td>
<td>258</td>
<td>255*</td>
<td>3.64</td>
</tr>
<tr>
<td>SC4</td>
<td>1.2115</td>
<td>0.4310</td>
<td>261</td>
<td>265*</td>
<td>3.67</td>
</tr>
</tbody>
</table>

* These values were determined from the $dM/dT$ plots.
Table 2
The values of the stiffness constant determined from Eq. (3)

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\langle r_a \rangle (\text{Å}))</th>
<th>(\sigma^2)</th>
<th>(D) (meV Å(^2))</th>
<th>(B) (1 T)</th>
<th>(B) (5 T)</th>
<th>(C) (1 T)</th>
<th>(C) (5 T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC1</td>
<td>1.2054</td>
<td>0.00032</td>
<td>147</td>
<td>0.1329</td>
<td>0.1391</td>
<td>1.20</td>
<td>1.09</td>
</tr>
<tr>
<td>SC2</td>
<td>1.2075</td>
<td>0.00246</td>
<td>83</td>
<td>0.3070</td>
<td>0.3031</td>
<td>1.44</td>
<td>1.16</td>
</tr>
<tr>
<td>SC3</td>
<td>1.2095</td>
<td>0.00318</td>
<td>69</td>
<td>0.3803</td>
<td>–</td>
<td>1.57</td>
<td>–</td>
</tr>
<tr>
<td>SC4</td>
<td>1.2115</td>
<td>0.00478</td>
<td>64</td>
<td>0.4310</td>
<td>0.4307</td>
<td>1.29</td>
<td>0.82</td>
</tr>
</tbody>
</table>

Table 3
Comparison between the values of the spin wave stiffness constant determined experimentally and those calculated from Eq. (5)

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\sigma^2)</th>
<th>(D_{\text{cal}}) (meV Å(^2))</th>
<th>(D_{\text{exp}}) (meV Å(^2))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(<em>{0.67})Ba(</em>{0.33})MnO(_3)</td>
<td>0.01404</td>
<td>44</td>
<td>47</td>
<td>[20]</td>
</tr>
<tr>
<td>La(<em>{0.62})Y(</em>{0.07})Ca(_{0.33})MnO(_3)</td>
<td>0.0014</td>
<td>90</td>
<td>87</td>
<td>[21]</td>
</tr>
<tr>
<td>La(<em>{0.62})Y(</em>{0.15})Ca(_{0.33})MnO(_3)</td>
<td>0.00239</td>
<td>77</td>
<td>50</td>
<td>[21]</td>
</tr>
<tr>
<td>La(<em>{0.52})Ca(</em>{0.47})MnO(_3)</td>
<td>0.00036</td>
<td>137</td>
<td>135</td>
<td>[5]</td>
</tr>
<tr>
<td>La(<em>{0.67})Sr(</em>{0.33})MnO(_3)</td>
<td>0.00135</td>
<td>183</td>
<td>167</td>
<td>[6]</td>
</tr>
<tr>
<td>La(<em>{0.67})Sr(</em>{0.33})MnO(_3)</td>
<td>0.00177</td>
<td>168</td>
<td>176</td>
<td>[6]</td>
</tr>
</tbody>
</table>

Fig. 3. The variation of the spin wave stiffness constant as a function of variance of size of the A-site cations. Solid circles are for the present data, solid squares are the values of \(D\) taken from literature and the solid curve has been calculated by Eq. (5).
higher fields in all the samples. It is worth noting that the temperature region within which the coefficient $C$ is effective in reducing the magnetization is also the region where the magnetoresistance becomes colossal.

From Table 1 we find the saturation magnetization of these samples to be independent of $\langle r_\alpha \rangle$. However, we find that $D$ decreases as we go down Table 2, where $\langle r_\alpha \rangle$ increases. As pointed out above $D$ does not vary with $\langle r_\alpha \rangle$. To correlate $D$ with the disorder in the lattice that arises due to the mismatch in the radius of the various ions at the A-site, we plotted the values of $D$ against the variance of the ionic radii $r_i$ about the mean radius of the A-site ion $\langle r_\alpha \rangle$ defined as in [3]

$$\sigma^2 = \sum y_i r_i^4 - \langle r_\alpha \rangle^2$$

(4)

where $y_i$ is the fractional occupation of a cation in the A-site and $r_i$ is the ionic radius (from Shannon’s standard ionic radii tables [19]) of a cation partially occupying the A-site. Fig. 3 shows the relation between $D$ and $\sigma^2$, which excellently follows the power law defined by

$$D = A (\sigma^2)^{\nu}$$

(5)

with $A \approx 11.902$ and $\nu \approx 0.31 \sim 0.001$.

This power law appears to be applicable extensively. We have checked its validity by estimating the values of the spin wave stiffness constant $D$ for some samples whose $D$ values have been reported in literature. These $D$ values have been determined by many different techniques. Our estimations are in good agreement with those reported by S. Lofland et al. [20] for La$_{0.67}$Bi$_{0.33}$MnO$_3$, where $D$ was measured by means of spin wave resonance in thin films, with B. Martinez et al., in (La$_{1-x}$Y$_x$)$_{2/3}$Ca$_{1/3}$MnO$_3$ ($x$ = 0.07 and 0.15) [21], where it was determined from magnetization in polycrystalline samples, and J. Rhyne et al., for La$_{0.53}$Ca$_{0.47}$MnO$_3$ [5] where inelastic neutron scattering was used. The series La$_{1-x}$Sr$_x$MnO$_3$ studied by L. Vasiliu-Doloc et al. [22] and La$_{0.3}$Pb$_{0.7}$MnO$_3$ studied by T. Pering et al. [23] both have rhombohedral structure. These structures can be described by a cubic unit cell having half the volume of the rhombohedral cell (the crystal structure of the La$_{1-x}$Sr$_x$MnO$_3$ was described by such a cubic cell with a equal to 7.75 Å [24]). $\alpha$ in Eq. (3) then equals 2 for such structures [18]. With this value of $\alpha$, the values of $D$ predicted by Eq. (4) are shown in Table 3, along with its measured values. The agreement is excellent.

4. Conclusion

In conclusion the magnetization of a series of samples with a nominal composition La$_{0.67-2}$Nd$_3$Ca$_{0.33}$Sr$_2$MnO$_3$ were studied under different magnetic fields. The variation of the value of the spin wave stiffness constant ($D$) obtained from the magnetization data were discussed in terms of different structural and magnetic factors. A relation between the spin wave stiffness constant and the magnitude of the cation size mismatch was obtained. By means of this relation we could reproduce the values of spin wave constant determined in different experiments reported in the literature. The strain on the spins imposed by the cation size mismatch is suggested to be the key parameter that controls $D$. These findings may have important implications on the spin dynamics and electrical resistivity at low temperatures.

References