Parameters controlling magnetic interactions in perovskite manganites

B Dabrowski, J Mais, S Kolesnik and O Chmaissem
Department of Physics, Northern Illinois University, DeKalb, IL, USA
E-mail: dabrowski@anl.gov

Abstract. Magnetic superexchange interactions in single-valent perovskites (R,A)MO$_3$ (R,A = Rare and Alkaline Earth's, M = transition metal) are known to dependent on the M-O-M bond angle $\theta$ and the interatomic distances \(<M-O>\) through the band-width relation $W \sim \cos \theta / \langle M-O \rangle^n$ ($n \sim 3.5$). It was observed previously that $T_N \sim W^2 \sim \cos^2 \theta$ for RMO$_3$ with M = Cr$^{3+}$ ($t^3$), Fe$^{3+}$ ($t^{3e_2}$), and Ni$^{3+}$ ($t^{6e_1}$) when \(<M-O>\) are constant. We have observed similar dependence for Mn$^{3+}$ ($t^{3e_1}$). When the \(<M-O>\) bonds were stretched beyond their equilibrium values in mixed-valent La$_{0.5}$Sr$_{0.5-x}$Ba$_x$Mn$^{3.5+}$O$_3$, a strong suppression of magnetic interactions was observed. In addition, size disorder on the A-site suppressed $T_N$ for Sr$_{1-x}$Ca$_x$Mn$^{4+}$O$_3$ because of a local variance of bond angles $\Delta \theta$. By removing the effects of stretched \(<M-O>\) bonds and size disorder we have increased Curie temperatures of the layer ordered manganites $R_{1-y}Ba_yMnO_3$. Frequently interesting compounds with $\theta \sim 180$ deg are not possible to obtain due to the limited range of sizes and charges of the A and R ions. Recently, in an attempt to increase the bond angle $\theta$ in compounds, which are not possible to obtain through simple A-site substitutions, we have studied the double substituted R- and Mn-site perovskites. Properties of these compounds depend mostly on dilution of the magnetic Mn-O lattice in addition to the previously discussed parameters.

1. Introduction
Perovskites ABO$_3$ have been studied comprehensively for years because of intriguing magnetic, electronic and other properties resulting from competing charge, exchange, and phonon interactions [1]. The properties can be tuned over a wide range through the choice of the sizes and charges of the large size 12-coordinated A cations, which control the degree of structural distortions (bandwidth, W) and the formal valence (band filling, x) of the smaller size 6-coordinated B ions, here the B-site ions of interest are Mn. The relatively rigid MnO$_6$ octahedra sharing corners and forming Mn–O–Mn bond-angles $\theta$ are mostly responsible for electronic and magnetic properties. Based on systematic study of the relationship between structural and magnetic properties of perovskite manganites we have developed phenomenological correlation between magnetic transition temperature and structural parameters for compounds with fixed valence of Mn: $T_M \sim W^2 \sim \{\cos \theta / \langle Mn-O \rangle^n\}^2 - ps^2$ ($n \sim 3.5$), where \(<Mn-O>\) is bond length and $s^2$ is variance of the A-site sizes causing local variance of bond angles $\Delta \theta$. Understanding this correlation enabled the preparation of improved materials and predicting new exciting compounds. However, many of them were not possible to obtain through
simple A-site substitutions due to the limited range of sizes and charges of available ions. To synthesize interesting compounds with $\theta \sim 180^\circ$ we have studied the double substituted R- and Mn-site perovskites and found that magnetic properties of these compounds depend mostly on dilution of the magnetic Mn-O lattice in addition to the previously discussed parameters.

2. Magnetic transitions and structural features for single-valent systems

Our description of magnetism and spin-transport in manganites is based on concepts of local sites of individual magnetic ions and crystal-field theory, which grasp most of essential physics. This approach is justified by the inability of current band structure calculations to capture all aspects of the strong coupling among electrons, spins, and phonons as well as to describe strong correlations of the 3d electrons in distorted crystal fields [2]. The description uses internal structural parameters of the Mn-O-Mn bond angles and the A-O and Mn-O bond lengths that are obtained from neutron diffraction measurements. These structural measurements are combined with detailed magnetic measurements that are performed over a wide temperature range to provide accurate composition-structure-property phase diagrams.

![Figure 1](image)

**Figure 1.** Magnetic transition temperatures versus $<\cos^2 \theta>$ for RMn$^{3+}$O$_3$ perovskites.

The range of the Mn oxidation states considered here spans from Mn$^{3+}$ to Mn$^{4+}$. In the cubic crystal field, which is characteristic for perovskites, these oxidation states of Mn display well-defined ionic ground states of $t^1\!e^1$ and $t^1\!e^0$ for Mn$^{3+}$ and Mn$^{4+}$, respectively. These single-valent states can be achieved by using rare earth's (R = La, Pr, Nd, ...) and alkaline earth's (Ca, Sr, and Ba) on the A-sites. The filling of atomic electronic d-orbitals, $t_{2g}$ and $e_p$, with electrons that is consistent with the Hund's and crystal-field splitting rules has been described in several textbooks. Because the spin-orbit coupling is quenched for perovskite manganites [2], the antiferromagnetic (AF) and ferromagnetic (FM) superexchange describe very well the coupling between magnetic moments for the single-valent states. The Goodenough-Kanamori rules of superexchange interactions predict the sign of the interaction for straight Mn-O-Mn bond angles [3]. When the Mn-O-Mn bonds are not straight, the interactions can be described as a superposition of 180 and 90 deg bonds [4]. The correlation of antiferromagnetic transition temperatures to the Mn–O–Mn bond-angle $\theta$, $T_N \approx T_{N_{\text{max}}} - T_s(1 - <\cos^2 \theta>)$, has been clearly established for single valent RBO$_3$ systems with B = Fe$^{3+}$ ($t^1\!e^2$) and Cr$^{3+}$ ($t^3$) when there is only one kind of Rare Earth on the A–site and the <$B$-$O$> bonds lengths are constant [4,5]. We have recently shown that similar relationship between the Mn–O–Mn bond-angle and $T_N$ holds for the RMnO$_3$ perovskites with a single valent Mn$^{3+}$ ($t^1\!e^1$) while for the solid solution system Sr$_{1-x}$Ca$_x$MnO$_3$ with Mn$^{4+}$ ($t^4$), the structural disorder on the A-site introduces a measurable
Figure 2. Dependence of $T_N$ on $<\cos^2\theta>$ for the solid solution system $\text{Sr}_{1-x}\text{Ca}_x\text{Mn}^{4+}\text{O}_3$.

deviation from this relationship [6,7]. Figure 1 shows magnetic transition temperatures versus $<\cos^2\theta>$ for RMnO$_3$ perovskites. The complex AF $A$-type magnetic structure of these compounds is a result of the Jahn-Teller distortion and the orbital order present below temperatures, $T_{JT}$ [8]. Figure 2 shows that the linear dependence of $T_N$ on $<\cos^2\theta>$ observed for $\text{RMn}^{3+}\text{O}_3$ is less regular for the solid solution system $\text{Sr}_{1-x}\text{Ca}_x\text{Mn}^{4+}\text{O}_3$. The size difference between interatomic distances of the Sr-O and Ca-O introduces local variance of the bond angles $\Delta\theta$ that suppresses $T_N$ by $\sim 20$ K at $x = 0.5$ where the variance of sizes is the largest [9].

Figure 3. Neutron powder diffraction measured bond lengths [Mn$^{3.5+}$-O] and bond angles $\theta$ as a function of Ba content for the $\text{La}^{3+}_{0.5}\text{Sr}^{2+}_{0.5}\text{Ba}^{2+}_{x}\text{Mn}^{3+}\text{O}_3$ system at room temperature.
3. Magnetic transitions and structural features for mixed-valent systems

Decreasing Curie temperatures have been observed for several mixed-valent manganites as a function of increased substitution of the large-size Ba, and interpreted in terms of increasing variance of the A-site sizes $s^2$. Recently, by using highly accurate interatomic distances we have shown that the explanation of $T_c$ behavior only in terms of bond angle and size variance is not sufficient, especially in the regime where structural distortions from the cubic structure are very small [10].

Figure 3 shows measured bond lengths [Mn$^{3.5+}$-O] and bond angles $\theta$ as a function of Ba content for the La$^{3+}$$_{0.5}$Sr$^{2+}$$_{0.5}$Ba$^{2+}$$_x$Mn$^{3.5+}$O$_3$ system at room temperature. Compositions $x = 0$ – 0.2 and 0.3 – 0.5 are tetragonal (slightly distorted) and cubic, respectively. Bond lengths [Mn$^{3.5+}$-O] exhibit small increase already in non-cubic phase and more rapid increase imposed by requirement of matching bond lengths [A-O] and $\sqrt{2}$[Mn$^{3.5+}$-O] in cubic phase. Figure 4 shows $T_c$’s and the variance of sizes $s^2$ as a function of the bond length [A-O] for several (La$_{0.5}$A$_{0.5}$)MnO$_3$ compounds (A=Ca, Sr, Ba). We observe that $T_c$ decreases for both tetragonal and cubic phases despite increasing bond angle and decreasing variance of sizes. Thus, the explanation of the observed $T_c$ reduction in terms of increasing ionic size variance cannot be employed. Additional cause is required when the crystal structure is cubic or nearly cubic. Such a cause can arise from presence of the [Mn-O] bonds that are stretched beyond their equilibrium values. Fraction of such bonds would be present because the equilibrium $\sqrt{2}$[Mn-O] bonds are smaller than the longest [A-O] bonds (i.e., the [Ba-O] bonds) even if the average structure is non-cubic, i.e., when the average $\theta \neq 180$ deg. As the formula for the band-width $W$ shows, elongation of these bonds would cause very strong and non-linear decrease of $T_c \approx [\text{Mn-O}]^{-7}$ that is not modeled by the variance of sizes. As the materials become cubic considerable internal strains develop that stretch the [Mn$^{3.5+}$-O] bonds, thus, lowering $T_c$ by narrowing the bandwidth $W$.

![Figure 4](image)

**Figure 4.** $T_c$’s and the variance of sizes $s^2$ as a function of the bond length [A-O] for several (La$_{0.5}$A$_{0.5}$)MnO$_3$ compounds.

We have used derived formula for $W$ to increase $T_c$ of La$_{1-x}$Ba$_x$MnO$_3$ compounds that can be obtained in two forms: randomly mixed perovskite and layered-ordered LaBaMn$_2$O$_6.6$ phase [7,9].
Comparison of layered-ordered and randomly substituted compounds with the same charge doping $x$ revealed much greater effects of structural disorder on the ferromagnetic transition temperature for mixed valent perovskite manganites than was observed for the $T_N$ of single-valent Sr$_{1-x}$Ca$_x$MnO$_3$ system [9,11]. Because the measured variance of size is small $s^2 = 0.009\,\text{Å}$ at $x=0.5$, the effects of structural disorder are anticipated to be small. Nonetheless, we have observed a large, $\sim 80\,\text{K}$, difference of ferromagnetic $T_C$ between the two structural forms. We attribute the different properties of the randomly substituted and layered-ordered phases to the local A-site charge disordering that disturb the coherent electronic states of the Mn-O bonds. The layer-ordered phase with composition $x = 0.42$ shows the second highest $T_C$ of 365 K ever observed for the perovskite manganites. Similar effects of local structural/charge order no doubt have profound effects on the properties of other complex oxides and can be used to optimize their useful functionalities.

4. Magnetic transitions and structural features of double substituted perovskites

Frequently interesting compounds with $\theta \sim 180$ deg are not possible to obtain due to the limited range of sizes and charges of the available A and R ions. Recently, in an attempt to increase the bond angle $\theta$ in RMnO$_3$ compounds, which show significantly distorted orthorhombic structure even for the largest $R = \text{La}$, we have studied the double substituted R- and Mn-site perovskites. Figure 5 shows an example of the measured $T_N$ for isoelectronically substituted on the Mn site perovskites by $B^{3+} = \text{Al}, \text{Ga}, \text{Sc},$ and In ions with increasing ionic size. Despite achieved increase of $\theta$ that should increase Neel temperature a rapid decrease of $T_N$ is observed. Similar effects were observed for a double substituted La$_{1.33}$Ba$_{0.67}$Mn$_{1.3}$Mo$_3$O$_{12}$, however due to much large increase of $<\cos^2\theta>$ for small $x$, an increase of $T_N$ and transition to ferromagnetic phase have been observed for the first time with Mn$^{3+}$. Our results show that the effects of bond angle $<\cos^2\theta>$ and variance of sizes, $s^2$ on $T_N$ are clearly observable; however the most dominant effect is dilution of the magnetic network by the non-magnetic impurities [12].

Figure 5. $T_N$ for isoelectronically substituted on the Mn site perovskites with $B^{3+} = \text{Al}, \text{Ga}, \text{Sc},$ and In ions.
5. Conclusions
Bond angles Mn-O-Mn and bond lengths [A-O] have been used to describe T_N of the single-valent manganites through the relation to the band-width. Maximum T_N’s were found for straight bonds [cos(\theta) = 1] and minimal variance of sizes (s^2 = 0). Study of the correlations between chemical, structural, and physical properties for mixed-valent manganites show that T_C and T_N depend strongly on the bond angle, charge doping, structural and charge disorder, and bond lengths through the relation T_M \sim W^2 \sim \{cos(\theta '-')_n^2 - p^2\}. Properties of double substituted R- and Mn-site perovskites depend mostly on dilution of the magnetic Mn-O lattice in addition to the previously discussed parameters. Understanding of similar effects of local structural/charge order can be used to optimize magnetic, electronic, thermoelectric, and other properties of several perovskites.

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