

The Stability of Orthorhombic and Monoclinic-Layered LiMnO₂

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LiMnO₂ is one of only a few ternary oxides which are known to form in the orthorhombic *Pmmn* structure. The layered α -NaFeO₂ structure, favored for application as a Li-insertion electrode, is found in many other alkali transition metal oxides. We find that the strong antiferromagnetic interactions between Mn³⁺ ions contribute to the stabilization of the orthorhombic structure. Using first-principles pseudopotential calculations, we find that doping with Al, Co, Cr, V, Ti, Mo, Mg, Nb, Zn, and Pd helps stabilize the layered structure over the orthorhombic structure.

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Lithiated manganese oxides are important for application in rechargeable Li batteries due to their reasonable performance and low cost.¹ One significant drawback of the manganese compounds is that they are difficult to synthesize in the layered α -NaFeO₂ structure which is common to LiCoO₂ and LiNiO₂. When synthesized under equilibrium conditions, LiMnO₂ forms an orthorhombic structure with space group *Pmmn*.²⁻⁴ A tetragonal structure can also be formed by synthesizing an LiMn₂O₄ spinel and further lithiating it up to composition Li₂Mn₂O₄.⁵ Recently, metastable layered LiMnO₂ with space group *C2/m* has been made through ion exchange processes starting from the layered α -NaMnO₂ precursor.^{6,7} In addition, partial substitution of Mn by Cr⁸ and Al⁹ have been shown to stabilize the layered structure. The orthorhombic form of LiMnO₂ is particularly intriguing. It is found only for LiMnO₂,³ β -NaMnO₂,³ and a metastable form of LiFeO₂.^{10,11} Most other LiMO₂ compounds with M close to Mn (except for Fe) in the periodic table form the layered α -NaFeO₂ structure. Besides its scientific interest, understanding the uncommon stability of the orthorhombic structure may be of practical interest in designing layered lithium-manganese oxides which form in different structures. In this paper we discuss the physical mechanism that stabilizes orthorhombic LiMnO₂ over layered LiMnO₂ and discuss how the latter may be stabilized by a judicious choice of dopants.

It is well understood^{4,12} that in alkali transition metal oxides the layered structure is stabilized by the size difference between the alkali and transition metal ion. When the alkali-oxygen and transition metal-oxygen bond lengths are similar, the α -LiFeO₂ structure is stable as it has a lower electrostatic energy than the layered cation arrangement. When the bond lengths are more different, the relaxation contribution to the electrostatic energy becomes more important and other structures can become stable. One of these structures is the layered α -NaFeO₂ which allows for independent relaxation of the alkali-oxygen and transition metal-oxygen bond lengths and is therefore favored in systems where these bond lengths are very different. It has been found that the layered structure is stable when the ratio of transition metal ionic radius to alkali radius is less than 0.9.¹²

LiMnO₂ is a notable exception to this rule. The ionic size of Mn³⁺ (~0.64 Å¹³) places it within the stability region of the layered structure, though the orthorhombic structure is the actual ground state. A recent study from our group¹² indicated that there is little reason to believe the orthorhombic structure can be stabilized on the basis of size or electrostatic effects. Another reason for the stability of this structure in LiMnO₂ therefore must be sought.

Mn³⁺ ions introduce two particular features which may distinguish LiMnO₂ from other lithium-metal oxides. In its high-spin configuration, Mn³⁺ has four unpaired electrons with parallel spin, giving the ion a large magnetic moment. Magnetic interactions in manganese oxides can, therefore, be an important factor in deciding the energy difference between different structures. In addition to the strong magnetic interaction between Mn³⁺ ions, a strong electron lattice coupling exists due to the single occupancy of a nearly degenerate e_g level which leads to a Jahn-Teller (J-T) distortion. This J-T distortion reduces the symme-

try of the layered form from rhombohedral $R\bar{3}m$ to monoclinic *C2/m*. Magnetism can couple to the Jahn-Teller effect as the orbital splitting induced by the distortion can lead to enhanced magnetic interactions along the distortion axis.

Method and Model

To investigate the relative stability of orthorhombic and layered LiMnO₂ we use the first-principles ultrasoft-pseudopotential method.¹⁴ The exchange correlation correction was applied in the generalized gradient approximation as parameterized by Perdew and Wang.¹⁵ In a detailed study of various lithiated manganese oxide structures, we found that the more common local density approximation was not accurate enough to capture the subtle effects of the J-T distortion in this material.¹⁶ Computational details are the same as in Ref. 16. First-principles methods have been used successfully to predict insertion potentials,¹⁷⁻¹⁹ phase diagrams,²⁰⁻²² and structural properties of materials.²³

An advantage of a first-principles calculation is that physical effects (such as magnetism) can be turned on or off, thereby lending direct insight into the contribution these effects make to the relative stability of a given structure. Hence, we calculated the crystal geometry and energy for LiMnO₂ in the nonmagnetic, ferromagnetic, and antiferromagnetic state. The latter is often neglected by researchers as the antiferromagnetic spin ordering can lead to a unit cell that is several times the size of the conventional crystallographic cell.

For the antiferromagnetic ordering of the orthorhombic structure we used the low-temperature spin configuration measured by Greedan *et al.*²⁴ using neutron diffraction. In this configuration antiferromagnetic chains run along the direction of shortest Mn-Mn bonds (*a* axis). The coupling between different chains is antiferromagnetic and ferromagnetic in equal proportion so that this effect on the energy cancels out. These chains are coupled antiferromagnetically along the third dimension although this coupling is expected to be weak as the puckered Mn layers are separated by Li planes. For the monoclinic layered structure we used the configuration determined theoretically by Singh²⁵ (configuration *AF3* in Ref. 25). This structure is reasonable as it has antiferromagnetic chains running along the shortest Mn-Mn bonds (for which the antiferromagnetic interaction is expected to be strongest). The coupling between the chains consists of an equal number of ferro and antiferro bonds. This structure therefore has analogous features to that experimentally determined for the orthorhombic phase (antiferromagnetic along short Mn-Mn bonds and cancelling contributions along other directions). To further investigate its relative stability we performed fully relaxed energy calculations on three other magnetic configurations (those of Singh²⁵) and found them to be higher in energy (in agreement with Singh's nonrelaxed calculations). We are not aware of any experimental determination of the spin ordering in monoclinic layered LiMnO₂, although some recent results by Jang *et al.*²⁶ indicate possible spin-glass behavior at low temperature.

Results

Table I shows the energies and bond lengths of monoclinic layered (*C2/m*) and orthorhombic (*Pmmn*) structures with no spin polarization (low-spin Mn³⁺), ferromagnetic spin polarization, and antiferromag-

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Table I. Energies and bond lengths of the monoclinic layered ($C2/m$) and the orthorhombic ($Pmnn$) structures for nonmagnetic, ferromagnetic, and antiferromagnetic structures. In parenthesis after the bond length is the number of bonds with this length. The magnitude of the J-T distortion as defined in the text is also indicated.

		E (meV)	$d_{\text{Mn-O}}$	$d_{\text{Mn-Mn}}$	J-T distortion (%)
Nonmagnetic	$C2/m$	0	1.93 (6)	2.72 (6)	0
	$Pmnn$	241	1.91(2), 1.98(2), 2.02(2)	2.75(2), 2.95(4)	5.6
Ferromagnetic	$C2/m$	-888	1.92 (2), 2.34(4)	2.82(2), 3.11(4)	19
	$Pmnn$	-881	1.91(2), 1.95(2), 2.32(2)	2.80(2), 3.19(4)	20
Antiferromagnetic	$C2/m$	-1015	1.92(2), 1.93(2), 2.39(2)	2.79(2), 3.09(2), 3.12(2)	22.5
	$Pmnn$	-1047	1.92(2), 1.95(2), 2.35(2)	2.78(2), 3.10(2), 3.12(2)	21

netic spin arrangements. The zero of energy has been taken as the energy of the nonmagnetic layered structure. The magnitude of the J-T distortion is measured as the difference between the longest and shortest Mn-O distance divided by the average Mn-O distance.

Several important conclusions can be inferred from Table I. Clearly, when magnetic effects are turned off, layered LiMnO_2 is stable as would be expected from ionic size considerations.¹² No stable J-T distortion could be obtained in this case. The small difference in bond lengths in the orthorhombic structure is due to the less-than-octahedral symmetry around the Mn ion. The absence of a J-T distortion is to be expected as the Mn^{3+} is low spin under these conditions, giving it no reason to J-T distort. Allowing a magnetic moment to form on Mn^{3+} , but restricting the moments to be aligned ferromagnetically brings the energy of orthorhombic and monoclinic layered closer together, but with the latter remaining lowest. We find J-T distortions around 20% which is in good agreement with experiments. Only when antiferromagnetic spin ordering is allowed does the orthorhombic structure become stable.

Antiferromagnetism is to be expected in these structures through direct Mn-Mn interaction and 90° superexchange. The fact that we find it lower in energy than the ferromagnetic or nonmagnetic state is therefore not surprising. But it is not directly obvious why antiferromagnetism favors the orthorhombic structure. Both structures have similar bond lengths and spin configurations. In both cases, antiferromagnetic chains run along the direction of shortest Mn-Mn distances. Along these short Mn-Mn bonds the antiferromagnetic interaction is expected to be strongest. For both structures, the coupling between the chains cancels out as it contains an equal amount of ferromagnetic and antiferromagnetically aligned spin pairs. The only significant difference between the two structures is a $170^\circ e_g\text{-p}_{\text{oxygen}}\text{-}e_g$ superexchange interaction in the orthorhombic structure along the direction of J-T distortion. This interaction couples second-neighbor chains. Stronger antiferromagnetism in the orthorhombic structure compared to the monoclinic one is however consistent with the reported Néel temperatures for these phases (-1056 K ²⁴ and -790 K ²⁷, respectively).

Long-range antiferromagnetic spin ordering is unlikely to be the direct physical cause for the stability of orthorhombic LiMnO_2 . These oxides are typically fired at elevated temperatures at which long-range magnetic order is absent. Even under those conditions orthorhombic LiMnO_2 is obtained. Direct calculations on a paramagnetic state are difficult as they require large supercell calculations and nonscalar magnetic approaches. However, interpolating between the ferro and antiferromagnetic state to estimate the energy of both structures in the paramagnetic state indicates that in paramagnetic conditions the orthorhombic structure is still lowest in energy. Therefore, our results indicate that even at high temperatures, at which the system is paramagnetic orthorhombic LiMnO_2 is formed. In addition, the high Néel temperature of orthorhombic LiMnO_2 indicates that even at elevated temperature, significant antiferromagnetic correlation may be present. Another possibility is that the difference between the ferromagnetic and antiferromagnetic result introduces the effect of electron localization as a factor in stabilizing LiMnO_2 in the orthorhombic structure. Electron hopping between Mn ions depends strongly on the magnetic

Table II. Energy difference between monoclinic layered and orthorhombic structures for doped lithium manganese oxides. The magnitude of the J-T distortion as defined in the text is also indicated.

Composition	$E_{\text{MLA}} - E_{\text{ORTHO}}$ (meV)	J-T distortion (%)	
		MLA	ORTHO
$\text{Li}(\text{Al}_{0.25}\text{Mn}_{0.75})\text{O}_2$	-38	17	19
$\text{Li}(\text{Co}_{0.25}\text{Mn}_{0.75})\text{O}_2$	-20	13	18
$\text{Li}(\text{Ni}_{0.25}\text{Mn}_{0.75})\text{O}_2$	+66	21	20
$\text{Li}(\text{Cr}_{0.25}\text{Mn}_{0.75})\text{O}_2$	-45	16	16
$\text{Li}(\text{V}_{0.25}\text{Mn}_{0.75})\text{O}_2$	-35	16	14
$\text{Li}(\text{Fe}_{0.25}\text{Mn}_{0.75})\text{O}_2$	+35	20	20
$\text{Li}(\text{Ti}_{0.25}\text{Mn}_{0.75})\text{O}_2$	-67	15	14
$\text{Li}(\text{Mo}_{0.25}\text{Mn}_{0.75})\text{O}_2$	-64	18	13
$\text{Li}(\text{Mg}_{0.25}\text{Mn}_{0.75})\text{O}_2$	-24	13	15
$\text{Li}(\text{Nb}_{0.25}\text{Mn}_{0.75})\text{O}_2$	-16	12	11
$\text{Li}(\text{Zn}_{0.25}\text{Mn}_{0.75})\text{O}_2$	-47	18	15
$\text{Li}(\text{Pd}_{0.25}\text{Mn}_{0.75})\text{O}_2$	-41	15	18

spin configuration of the two ions. For ferromagnetic alignment, an electron from one Mn ion can hop to the other ion (transferring its spin) without an intraionic exchange energy penalty. In the antiferromagnetic state (and to a large extent in the paramagnetic one), an electron that jumps to another Mn ion will violate Hund's rule there. The intraionic exchange interaction which forces electron spins to be parallel in ions that are less than half-filled will make this excited configuration high in energy. Antiferromagnetism therefore tends to reduce the bandwidth of the electron states and localize them. It is possible that the reduced electron mobility in the antiferromagnetic state (which likely persists in the paramagnetic state) stabilizes the orthorhombic structure. However, exactly how electron localization favors the orthorhombic structure is not clear at this time. While antiferromagnetism clearly favors the orthorhombic structure, other effects may also contribute in stabilizing on structure over the other. Such effects may be more easily identified in a transition metal oxide with a smaller magnetic moment, where the effect of antiferromagnetism would be reduced.

Engineering Structural Stability

The realization that antiferromagnetic interactions are a factor in the stability of the orthorhombic structure raises the possibility of engineering the relative stability of layered LiMnO_2 by chemical substitutions. Either nonmagnetic ions or ions with valence other than +3 should be particularly useful to make the layered form as they will perturb the magnetic Mn-Mn interaction and/or the electronic charge on the Mn ion.

We tested this hypothesis by calculating the energies of the two structures with several ions substituting for Mn at the 25% level [*i.e.*, composition $\text{Li}(\text{M}_{0.25}\text{Mn}_{0.75})\text{O}_2$]. All structures were fully relaxed and the magnetic configurations used were the same as in the unsubstituted

phases (monoclinic or orthorhombic). The results are shown in Table II. The chemical modifications we investigated fall into three categories.

1. Small ions M which form layered LiMO_2 when undiluted by Mn. In this category we tested Al, Cr, Co, Ni, and V. Not surprisingly, most of these stabilized the layered structure. Replacement of Mn by Ni however does not give a layered structure, even though LiNiO_2 itself is layered. In all cases the structure remains J-T distorted. When comparing these results with experimental data, one should keep in mind that the calculations are performed at 0 K and the effect of temperature can disorder a J-T distortion to the stage where it is no longer cooperative.²⁸

2. Larger transition metal ions (Mo, Fe, Ti, Nb, and Pd). Of these, only LiMoO_2 forms the layered structure. All substitutions, except for Fe, enhance the stability of the monoclinic layered structure over the orthorhombic one. As in category 1, all substituted materials remain J-T distorted.

3. Large nontransition metals ions (Mg, Zn). Both Mg and Zn favor the monoclinic layered structure, with the effect for Zn being the largest.

Discussion

Remarkably, the large majority of dopants stabilizes the monoclinic layered structure over the orthorhombic one. Fe has no effect on the energy difference between these two structures and Ni enhances the stability of the orthorhombic structure. Several conclusions can be drawn from the results.

1. Ionic size is not a discriminating factor in the stability of the monoclinic structure in Mn-based compounds. While smaller ions, which themselves form in the layered structure enhance the stability of this polymorph, several large ions do just as well or better. Ti, one of the largest 3d transition metals, produces the largest stabilization energy between the monoclinic layered and orthorhombic structure. Zn and Pd are larger or as large as the Li^+ ion, but clearly favor the layered arrangement. In contrast, Ni, one of the smallest ions, actually decreases the relative stability of the layered structure.

2. For the larger ions, electronic effects seem to determine the stability of the layered structure. The lower-valence cations, such as Zn and Mg introduce holes in the Mn valence bands, creating effectively Mn^{4+} ions. These Mn^{4+} ions perturb the antiferromagnetic spin arrangement, hence they enhance the monoclinic layered structure. The very high stabilization energy for Ti may be evidence for the role of electron localization in the stability of the orthorhombic phase. As an early transition metal, Ti has wide d orbitals which will overlap significantly with the d states on Mn, leading to enhanced delocalization.

3. The J-T effect does not seem to be a conclusive factor in the stability of orthorhombic LiMnO_2 . It is present in both monoclinic layered and orthorhombic phases, with and without doping, and no correlation between stability and magnitude of the J-T distortion is evident from the results. This idea is further confirmed by the occurrence of metastable orthorhombic LiFeO_2 ¹⁰ in which no J-T distortion likely occurs. The J-T effect may however assist in the localization of the e_g electron and stronger antiferromagnetic interactions. In addition, the different connectivity of the MnO_6 octahedra in both structures may produce different strain contributions to the energy from the J-T distortion. According to Goodenough²⁹ the J-T strain is expected to favor the orthorhombic structure.

The results above indicate that several alloying elements can be substituted for Mn in order to make the layered structure stable. Whether these materials can actually be synthesized depends on several factors. Only two structures were compared in this study and it cannot be excluded that other structures exist with lower energy. One particular structure that occurs relatively frequently in alkali transition metals^{4,12,30} is the structure of $\alpha\text{-LiFeO}_2$. We calculated the energy of this structure for LiMnO_2 , $\text{Li}(\text{Fe}_{0.25}\text{Mn}_{0.75})\text{O}_2$, $\text{Li}(\text{Co}_{0.25}\text{Mn}_{0.75})\text{O}_2$, and $\text{Li}(\text{Mg}_{0.25}\text{Mn}_{0.75})\text{O}_2$ and found it to be 77, 143, 139, and 192 meV higher in energy than the monoclinic structure, respectively.

Another factor to be considered is the miscibility of the dopant into LiMnO_2 . For Al, Cr, and Ti doping we calculated the mixing enthalpy starting from either layered or orthorhombic LiMnO_2 and layered

LiAlO_2 , LiCrO_2 , and LiTiO_2 (although the latter is not known to exist). For $\text{Li}(\text{Al}_{0.25}\text{Mn}_{0.75})\text{O}_2$, $\text{Li}(\text{Ti}_{0.25}\text{Mn}_{0.75})\text{O}_2$, and $\text{Li}(\text{Cr}_{0.25}\text{Mn}_{0.75})\text{O}_2$ we find mixing enthalpies of, respectively, 76, -54, and 48 meV. Negative values indicate energy lowering upon mixing. However even the positive value for $\text{Li}(\text{Al}_{0.25}\text{Mn}_{0.75})\text{O}_2$ is likely to be overcome when sintering at sufficiently high temperature. Dopants such as Ti^{3+} may require extreme reducing conditions to be incorporated.

Both Al and Cr doping have been shown experimentally to lead to stabilization of the monoclinic layered structure.^{8,9} $\text{Li}(\text{Co}_{0.1}\text{Mn}_{0.9})\text{O}_2$ has been synthesized in the layered structure by ion-exchange from the corresponding Na compound.³¹ Since this is a metastable reaction path it is not possible to conclude from this that 10% Co substitution leads to an equilibrium layered structure, although our results would indicate that Co has a beneficial effect on the stability of the layered structure.

Because antiferromagnetic interaction between Mn^{3+} ions help stabilize the orthorhombic structure in LiMnO_2 , substitutions that lead to charge compensation on Mn are all expected to favor the layered structure. Although we demonstrated how this can be achieved with cation modifications, it is conceivable to arrive at the same result by substitution of the anion. Lower valence anions such as F, Cl, or Br will create Mn^{2+} whereas N and P may lead to Mn^{4+} . In each case we expect perturbations of the magnetic interactions and/or enhancement of electron hopping, hence increased stability of the layered structure over the orthorhombic one.

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References

1. M. M. Thackeray, *Prog. Solid State Chem.*, **25**, 1 (1997).
2. G. Ditrch, *Z. Anorg. Allg. Chem.*, **368**, 262 (1969).
3. R. Hoppe, G. Brachtel, and M. Jansen, *Z. Anorg. Allg. Chem.*, **417**, 1 (1975).
4. T. A. Hewston and B. L. Chamberland, *J. Phys. Chem. Solids*, **48**, 97 (1987).
5. M. M. Thackeray, W. I. F. David, P. G. Bruce, and J. B. Goodenough, *Mater. Res. Bull.*, **18**, 461 (1983).
6. F. Capitaine, P. Gravereau, and C. Delmas, *Solid State Ionics*, **89**, 197 (1996).
7. A. R. Armstrong and P. G. Bruce, *Nature*, **381**, 499 (1996).
8. I. J. Davidson, R. S. McMillan, H. Sleg, B. Luan, I. Kargina, J. J. Murray, and I. P. Swainson, *J. Power Sources*, Submitted (1998).
9. Y.-I. Jang, B. Huang, Y.-M. Chiang, and D. R. Sadoway, *Electrochem. Solid-State Lett.*, **1**, 13 (1998).
10. R. Kanno, T. Shirane, Y. Kawamoto, Y. Takeda, M. Takano, M. Ohashi, and Y. Yamaguchi, *J. Electrochem. Soc.*, **143**, 2435 (1996).
11. Y. Sakurai, H. Arai, S. Okada, and J. Yamaki, *J. Power Sources*, **68**, 711 (1997).
12. E. J. Wu, P. D. Tepeesch, and G. Ceder, *Philos. Mag. B*, **77**, 1039 (1998).
13. R. Shannon, *Acta Crystallogr. A*, **32**, 751 (1976).
14. G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, **6**, 15 (1996).
15. J. P. Perdew and Y. Wang, *Phys. Rev. B: Condens. Matter*, **33**, 8800 (1986).
16. S. K. Mishra and G. Ceder, *Phys. Rev. B*, **59**, 6120 (1999).
17. M. K. Aydinol, A. F. Kohan, G. Ceder, K. Cho, and J. Joannopoulos, *Phys. Rev. B*, **56**, 1354 (1997).
18. G. Ceder, M. K. Aydinol, and A. F. Kohan, *Comput. Mater. Sci.*, **8**, 161 (1997).
19. G. Ceder, Y.-M. Chiang, D. R. Sadoway, M. K. Aydinol, Y.-I. Jang, and B. Huang, *Nature*, **392**, 694 (1998).
20. A. Van der Ven, M. K. Aydinol, G. Ceder, G. Kresse, and J. Hafner, *Phys. Rev. B*, **58**, 2975 (1998).
21. A. Van der Ven and G. Ceder, *Phys. Rev. B*, **59**, 742 (1999).
22. C. Wolverton and A. Zunger, *Phys. Rev. Lett.*, **81**, 606 (1998).
23. R. Benedek, M. M. Thackeray, and L. H. Yang, *Phys. Rev. B*, **56**, 10707 (1997).
24. J. E. Greedan, N. P. Raju, and I. J. Davidson, *J. Solid State Chem.*, **128**, 209 (1997).
25. D. J. Singh, *Phys. Rev. B*, **55**, 309 (1997).
26. Y. I. Jang, F. C. Chou, and Y.-M. Chiang, Personal communication.
27. M. Tabuchi, K. Ado, H. Kobayashi, H. Kageyama, C. Masquelier, A. Kondo, and R. Kanno, *J. Electrochem. Soc.*, **145**, L29 (1998).
28. H. Yamaguchi, A. Yamada, and H. Uwe, *Phys. Rev. B*, **58**, 8(1998).
29. J. B. Goodenough, *Le Journal de Physique et le Radium*, **20**, 155 (1959).
30. E. Posnjak and T. Barth, *Phys. Rev. B*, **38**, 2234 (1931).
31. A. R. Armstrong, R. Gitzendanner, A. D. Robertson, and P. G. Bruce, *Chem. Commun.*, 1833 (1998).