02026. The funds for the purchase of the mass spectrometer used in the research were supplied by the Atomic Energy Commission under Contract At(11-1)-92. We are grateful to Mr. Robert A. Silverman for help with some of the experiments.

CHICAGO 37, ILLINOIS

[CONTRIBUTION FROM WESTINGHOUSE RESEARCH LABORATORIES]

A Study of the $Li_xMn_{(1-x)}O$ System[1]

BY W. D. JOHNSTON AND R. R. HEIKES

RECEIVED JANUARY 17, 1956

Compositions in the previously unreported system $Li_xMn_{(1-x)}O$ have been prepared by sintering Li_2O_2 and MnO at elevated temperatures. A study of the products of this reaction by X-ray diffraction has permitted a partial phase diagram to be constructed. Throughout a large range of composition single phase products having a sodium chloride structure may be obtained. At higher lithium compositions the compound $LiMnO_2$ is formed. It has been found to have orthorhombic symmetry with two formula weights per unit cell. The products having the sodium chloride structure have been studied magnetically. These data are discussed in terms of a double exchange interaction.

Introduction

Certain theoretical predictions can be made as to the electrical and magnetic properties of the system $Li_xMn_{(1-x)}O$. These predictions are based primarily on the interpretation by Zener[2] of the magnetic and electrical properties of the manganese perovskites. The manganese perovskites $(La_{(1-x)}A_x)MnO_3$ where A = Ca, Sr or Ba were found by Jonker and Van Santen[3] to be ferromagnetic where $0.2 < x < 0.4$. Further, in this composition range the compounds proved to be good electrical conductors. Zener explained this behavior on the basis of a ferromagnetic coupling of the 3d shell electrons of manganese by the double exchange mechanism. This mechanism is based on the degeneracy caused by the presence of manganese ions of two different valences in equivalent crystallographic sites. It involves an electron transfer from Mn^{+3} to an adjacent Mn^{+4} through an intermediate $O^{=}$. Such a transfer favors a parallel alignment of the manganese spin vectors which results in the observed ferromagnetism. The transfer of electrical charge in this exchange mechanism gives rise to the relatively high electrical conductivity found in these compounds.

In addition to the double exchange interaction expected in the $Li_xMn_{(1-x)}O$ system, super-exchange will also be present. This interaction, which arises from the deviation of the ground state from pure ionic character, can produce either a ferromagnetic or an antiferromagnetic spin alignment, depending on the number of electrons in the d shell. With less than five electrons in the d shell the simple theory of super-exchange predicts ferromagnetism, while with five or more d electrons antiferromagnetism is predicted. In terms of perturbation theory, the super-exchange is a higher order interaction than the double exchange. It would therefore be expected to be a weaker interaction than double exchange under similar conditions.

By writing a more complete formula for $Li_xMn_{(1-x)}O$ on the basis of lithium and oxygen having their usual valences of +1 and −2, respectively, *i.e.*, $Li_x^{+1}(Mn^{+2}_{(1-2x)}Mn_x^{+3})O^{-2}$, it can be seen that both Mn^{+2} and Mn^{+3} should be present in this system. If single phase structures are possible in which the Mn^{+2} and Mn^{+3} are randomly distributed over equivalent crystallographic sites, the requirements for double exchange are fulfilled. On this basis one might expect certain compositions of $Li_xMn_{(1-x)}O$ to be both ferromagnetic and good electrical conductors. The assumption that lithium has a plus one valence is easily justified by a consideration of the ionization potentials of the elements involved. Alternative possibilities exist, however, in the case of the valence of oxygen. If this system proved to consist of either manganese oxygen covalences or mononegative oxygen ions the double exchange requirements would not be satisfied and ferromagnetism would not result.

Verwey[4] and others[5-7] have prepared similar systems such as $Li_xNi_{(1-x)}O$, $Li_xCo_{(1-x)}O$ and $Li_xCu_{(1-x)}O$. In these systems the presence of lithium in normal cation sites of the crystal lattice causes the transition metal ions which also occupy normal cation sites, to take on both di- and trivalent oxidation states in the same way as was described for $Li_xMn_{(1-x)}O$. Lithium was chosen by these workers since it has nearly the same size as the transition metal and thus should be easily accommodated in the crystal lattice. It further has a fixed valence which differs from that of the transition metal in the parent oxide, *e.g.*, NiO, and hence requires the transition metal ion to exist in two valence states in compounds such as $Li_xNi_{(1-x)}O$. These compounds have been found to have much lower resistivities than the pure oxide (*i.e.*, 1 ohm cm. for $Li_{0.1}Ni_{0.9}O$ *vs.* 10^8 to 10^{12} ohm cm. for NiO) where the transition metal exists essentially in the divalent state. This behavior is in agreement with the present theories of double exchange. Unfortunately, however, no magnetic data are available on these compounds.

---

[1] Work supported in part by Wright Air Development Center, U. S. Air Force.

[2] C. Zener, *Phys. Rev.*, **82**, 403 (1951).

[3] G. H. Jonker and J. H. Van Santen, *Physica*, **16**, 337 (1950).

[4] E. J. W. Verwey, P. W. Haayman, F. C. Romeijn and G. W. van Oosterhout, *Philips Res. Rpt.*, **5**, 173 (1950).

[5] P. J. Fensham, THIS JOURNAL, **76**, 969 (1954).

[6] (a) K. Hauffe and J. Block, *Z. physik. Chem.*, **196**, 438 (1951); (b) K. Hauffe and A. L. Vierke, *ibid.*, **196**, 160 (1950).

[7] H. Hauffe and H. Grunewald, *ibid.*, **198**, 248 (1951).

TABLE I

Original compn.	Final compn.	Apparent pressed density	Apparent sintered density	(Sintered density)/(X-ray density)
$Li_{0.05}Mn_{0.95}O$	$Li_{0.046}Mn_{0.954}O$	4.34	4.32	0.822
$Li_{0.10}Mn_{0.90}O$	$Li_{0.094}Mn_{0.906}O$	4.25	3.96	.769
$Li_{0.15}Mn_{0.85}O$	$Li_{0.143}Mn_{0.857}O$	4.08	3.77	.750
$Li_{0.20}Mn_{0.80}O$	$Li_{0.195}Mn_{0.805}O$	4.00	3.58	.728
$Li_{0.25}Mn_{0.75}O$	$Li_{0.247}Mn_{0.753}O$	3.83	3.40	.706
$Li_{0.30}Mn_{0.70}O$	$Li_{0.296}Mn_{0.704}O$	3.84	3.30	.702
$Li_{0.35}Mn_{0.65}O$	$Li_{0.347}Mn_{0.653}O$	3.62	2.89	.629
$Li_{0.40}Mn_{0.60}O$	$Li_{0.397}Mn_{0.603}O$	3.69	2.94	
$Li_{0.45}Mn_{0.55}O$	$Li_{0.444}Mn_{0.556}O$	3.41	2.55	
$Li_{0.50}Mn_{0.50}O$	$Li_{0.494}Mn_{0.506}O$	3.28	...	

Discussion

Preparation.—The preparation of the system $Li_xMn_{(1-x)}O$ by conventional methods presented certain difficulties which were ultimately resolved by adopting a completely new preparational method. Probably the most commonly used preparational method for compounds of this type is that used by Verwey[4] and others[5-6] in the case of $Li_xNi_{(1-x)}O$ and $Li_xCo_{(1-x)}O$ and Hauffe and Grunewald[7] in the case of $Li_xCu_{(1-x)}O$. This method involves sintering mixtures of Li_2O and the divalent transition metal oxides in air at high temperatures. Part of the oxygen required for this type of reaction is supplied by the air as shown in the equation

$$\frac{x}{2}\,Li_2O + (1-x)MO + \frac{x}{4}\,O_2\,(air) \longrightarrow Li_xMn_{(1-x)}O$$

(M is Ni, Co, or Cu)

Air oxidation would be clearly unsuitable for the preparation of the $Li_xMn_{(1-x)}O$ system since higher oxides of manganese would be formed.

Another method which has been used to prepare a system similar to that of $Li_xMn_{(1-x)}O$ is that of Collongues and Chaudron[8] who prepared Li_x-$Fe_{(1-\ )}O$ by sintering mixtures of $LiFeO_2$ and FeO at 850° in an inert atmosphere. This method was also unsuitable for the preparation of $Li_xMn_{(1-x)}O$ since there was no manganese analog to $LiFeO_2$ reported in the literature.

The method adopted for the preparation of the $Li_xMn_{(1-x)}O$ system can be best described by the reaction

$$x/2Li_2O_2 + (1-x)MnO \longrightarrow Li_xMn_{(1-x)}O$$

The reaction product is obtained by sintering pressed pellets of the intimately mixed reactants at an appropriate elevated temperature and quenching. The important difference between the above reaction and the method of Verwey[4] is the substitution of Li_2O_2 for Li_2O. In this way the oxygen necessary to give the proper composition is found in the solid reactants and oxidation by the air is not required. In order to conserve this oxygen the sintering reaction is performed in a sealed inert container of small volume. This also has the effect of protecting easily oxidizable substances such as MnO from being transformed to higher oxides by heating in air. It should be noted that this method is generally applicable to the preparation of similar systems. Two such systems, $Li_xNi_{(1-x)}O$ and $Li_xCu_{(1-x)}O$, have been prepared by this method and have been tested in this Laboratory. These will be reported in a separate communication.

By sintering the composition $Li_{0.33}Mn_{0.67}O$ at various temperatures for 24 hr. and then quenching to room temperature, it was found that 900° was a sufficient temperature to obtain a single phase product as determined by X-ray diffraction studies. Samples prepared at lower temperatures were multiple phase, one phase of which was a sodium chloride structure with varying lattice parameter. As will be seen later, this low temperature region did not represent an incomplete reaction but was actually an equilibrium two-phase region.

It is interesting to note from Table I that the apparent density after sintering is actually less than the apparent density of the pressed compact. Further, from a consideration of the variation of this decrease in density as well as the variation of the ratio (sintered density/X-ray density) given in Table I, it can be seen that this decrease in density upon sintering increases with lithium content. This suggests a gas phase reaction which is probably due to lithium peroxide decomposing to lithium oxide and oxygen prior to the actual sintering reaction.

X-Ray Studies.—X-Ray diffraction studies have shown that compounds prepared in this manner are single phase in the range $0 < x < 0.35$. They exhibit the NaCl structure. Throughout this composition range the X-ray lattice parameter decreases monotonically with increased lithium content, as is shown in Table II. This system also shows positive deviation from Vegard's law. A decrease in lattice spacing with increased lithium content also has been noted in the $Li_xNi_{(1-x)}O$ system.[4,9]

TABLE II

Composition	X-Ray lattice parameter	Composition	X-Ray lattice parameter
MnO	4.4450	$Li_{0.195}Mn_{0.805}O$	4.3646
$Li_{0.046}Mn_{0.954}O$	4.4280	$Li_{0.247}Mn_{0.753}O$	4.3350
$Li_{0.094}Mn_{0.906}O$	4.4075	$Li_{0.296}Mn_{0.704}O$	4.3098
$Li_{0.143}Mn_{0.857}O$	4.3897	$Li_{0.347}Mn_{0.653}O$	4.2827

The sample having composition $Li_{0.5}Mn_{0.5}O$ gave a completely new X-ray pattern. Samples $Li_{0.4}Mn_{0.6}O$ and $Li_{0.45}Mn_{0.55}O$ also show this pattern as well as several other lines which are as yet unidentified. This pattern, in combination with

---

(8) R. Collongues and G. Chaudron, *Compt. rend.*, **231**, 143 (1950).

(9) L. D. Brownlee and E. W. J. Mitchell, *Proc. Phys. Soc.* (*London*), **65B**, 710 (1952).

NaCl phase lines exhibiting various lattice parameters, was also found in the X-ray pictures of low temperature preparations of $Li_{0.33}Mn_{0.67}O$.

It was thus considered important to index this pattern in order to find if it were single phase and if so to determine the composition. It was considered unlikely that a single crystal of this material could be readily obtained so attempts were made to index the powder pattern. All lines of the $Li_{0.5}Mn_{0.5}O$ material were finally indexed on an orthorhombic unit cell. Pycnometric density measurements indicate that two formula weights of $LiMnO_2$ (four formula weights of $Li_{0.5}Mn_{0.5}O$) are in each unit cell. Data are given in Table III. The determination of atomic parameters and crystal class have not been successfully completed.

TABLE III

X-RAY DATA FOR $LiMnO_2$

$a = 2.811_7$	Density experimental	4.23
$b = 5.763_4$	Density calcd. for	
$c = 4.579_6$	2LiMnO$_2$	4.20

The following data either measured directly as Fe Kα or converted from Fe Kα_1 and Fe Kα_2 to Fe Kα radiation $\lambda = 1.93728$ Å.

	hkl	$\sin^2\theta$ exp.	$\sin^2\theta$ calcd.	$\sin^2\theta$ calcd. cor. for absorption
VS	010	0.0286	0.0282	0.0284
VS	011	.0734	.0730	.0733
W	100	.1194	.1187	.1191
M	110	.1476	.1469	.1474
W	021	.1583	.1577	.1582
W	101	.1641	.1634	.1639
S	002	.1796	.1790	.1794
M	111	.1923	.1917	.1921
M	012	.2077	.2072	.2077
S	120	.2322	.2317	.2321
VW	030	.2548	.2542	.2547
VW	031	.2994	.2990	.2994
M	112	.3262	.3259	.3263
W	130	.3731	.3730	.3734
S	122	.4110	.4106	.4111
M	131	.4182	.4176	.4181
W diffuse	013 032	.4322	.4309 .4332	.4314 .4336
M	040	.4523	.4520	.4524
M	200	.4753	.4747	.4752
VW	210	.5032	.5030	.5034
VW	023	.5163	.5156	.5161
VW	103	.5220	.5213	.5218
W	113	.5500	.5496	.5500
W	141	.6159	.6154	.6157
M	042	.6310	.6309	.6313
W	202	.6541	.6537	.6540
W	212	.6822	.6819	.6823
M	004	.7160	.7158	.7162
VVW	014	.7438	.7440	.7444
Mα_1 Wα_2	051	.7512 .7511	.7509	.7512
Mα_1 Wα_2	133	.7757 .7759	.7755	.7758
W	114	.8629	.8627	.8629
VW	052	.8854	.8851	.8853
W	213	.9063	.9056	.9058
W	240	.9272	.9267	.9268
Sα_1 Mα_2	124	.9478 .9477	.9475	.9475
W	143	.9738	.9733	.9733

Phase Diagram.—By indexing the X-ray pattern of $LiMnO_2$ it became possible to construct a partial phase diagram of the $Li_xMn_{(1-x)}O$ system. X-Ray pictures of low temperature preparations of $Li_{0.33}Mn_{0.67}O$ indicated that a two-phase low temperature region was probable in this composition range, the phases being $LiMnO_2$ and the previously discussed rock salt structure having $Li_xMn_{(1-x)}O$ composition. In order to substantiate this contention and to accurately determine a phase boundary, several samples were prepared in such a manner that equilibrium was approached from two directions. Since the data obtained by these two approaches are in substantial agreement, as shown in Fig. 1 and Table IV, it can be assumed that the phase boundary shown describes the actual equilibrium situation.

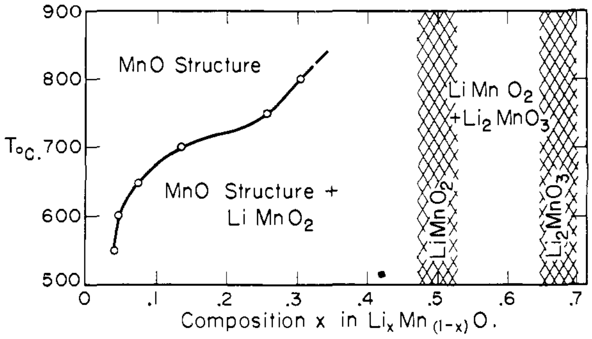

Fig. 1.—Phase diagram for $Li_xMn_{(1-x)}O$.

TABLE IV

X-RAY DATA FOR PHASE DIAGRAM

Original sample compn.	Sample heat treatment, °C.	Lattice parameter of MnO phase	Compn. of MnO phase
$Li_{0.33}Mn_{0.67}O$	Prep. at 600	4.426_4	$Li_{0.046}Mn_{0.954}O$
$Li_{0.33}Mn_{0.67}O$	Prep. at 700	4.392_3	$Li_{0.135}Mn_{0.865}O$
$Li_{0.33}Mn_{0.67}O$	Prep. at 800	4.303_3	$Li_{0.308}Mn_{0.692}O$
$Li_{0.20}Mn_{0.80}O$	Prep. 900 Anneal 650	4.416	$Li_{0.074}Mn_{0.926}O$
$Li_{0.35}Mn_{0.65}O$	Prep. 900 Anneal 750	4.331_2	$Li_{0.257}Mn_{0.743}O$
$Li_{0.20}Mn_{0.80}O$	Prep. 900 Anneal 750	4.361_5	$Li_{0.20}Mn_{0.80}O$ (Single Phase)
$Li_{0.20}Mn_{0.80}O$	Prep. 900 Anneal 550	4.427_9	$Li_{0.042}Mn_{0.958}O$

A preparation of $Li_{0.6}Mn_{0.4}O$ shows two phases to be present. One phase is $LiMnO_2$, while the other has been shown to be Li_2MnO_3. This latter compound has been previously described.[10] From the relatively slight changes in the position of the (124) line of the $LiMnO_2$ phase in either two-phase region, it is estimated that the region of solid solution in the $LiMnO_2$ phase is rather small. This region of solid solution is qualitatively indicated by a shaded area in Fig. 1. The Li_2MnO_3 phase also appears to have a small region of solid solution.

---

[10] R. B. Ellestad, R. M. Steward and B. R. Babbitt, U. S. Pat. 2,562,705 (1951).

The situation at 900° and compositions $Li_{0.4}Mn_{0.6}O$ and $Li_{0.45}Mn_{0.55}O$ is not clearly understood. The X-ray patterns for these materials show both the $LiMnO_2$ lines and four lines of an unidentified phase; d = 2.4460, 2.0564, 1.5278, 1.2280. Since these compositions are near the phase boundary it is possible that these lines represent an intermediate phase resulting from disproportionation.

At this point it should be emphasized that the transformation from the single phase high temperature NaCl structure to the two-phase low temperature region is sufficiently sluggish that it is possible to retain essentially all of the high temperature phase by quenching. This is evidenced by the absence of any lines of the $LiMnO_2$ phase on the X-ray patterns of the quenched high temperature phases where $0 < x < 0.35$. It should be further pointed out that the magnetic tests reported in this paper were made at such temperatures that decomposition into the two-phase region did not occur. In certain preliminary testing where disproportionation did occur this was immediately obvious by both sudden departures from the expected behavior and a lack of reproducibility. These materials, disproportionated at 450°, were very poorly crystallized according to their X-ray patterns and had compositions between $Li_{0.05}Mn_{0.95}O$ and MnO in accordance with the phase diagram. The $LiMnO_2$ phase did not appear, presumably due to insufficient thermal activation for formation or crystallization.

Magnetic Studies.—In Fig. 2 the susceptibility is plotted against temperature for several compositions of this system. As the lithium content is increased the susceptibility curve changes in character from that of a typical antiferromagnetic material to one resembling a paramagnetic material. These curves are qualitatively similar to those by Bizette[11] on $Mg_xMn_{(1-x)}O$ and by Elliot[12] on $Mg_xCo_{(1-x)}O$. The similarity below the Curie point, 116°K. for stoichiometric MnO, can be understood most simply on the basis of the dilution of the magnetic ion. The theory of antiferromagnetism gives the result that the susceptibility is inversely proportional to the average number of nearest neighbor magnetic ions which surround each magnetic ion. Thus as lithium is added substitutionally, χ is expected to increase. The introduction of magnesium should give a similar behavior.

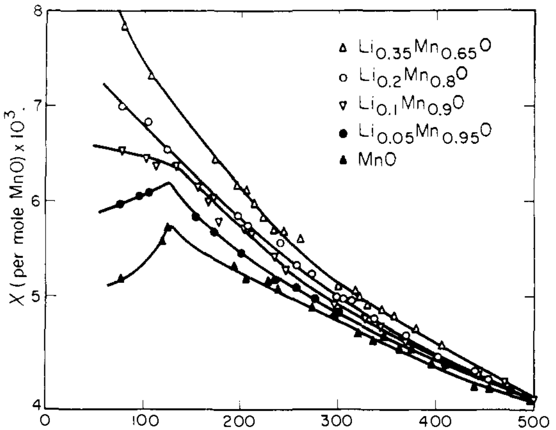

Fig. 2.—X (per mole MnO) for $Li_xMn_{(1-x)}O$ *vs.* temperature °K.

A detailed analysis of the region above the Curie point, however, shows rather striking differences in the cases of magnesium and lithium substitution. The data in all cases obey the Curie–Weiss law

$$\chi = C/(T - \theta)$$

where χ is the susceptibility per mole of magnetic ion, C the Curie constant per mole of magnetic ion, and θ is the temperature at which χ becomes infinite. In the case of a ferromagnetic substance, θ is positive and is approximately equal to the ferromagnetic Curie temperature. In the case of an antiferromagnetic substance, θ is negative and represents an extrapolated temperature at which χ would become infinite. The Curie constant is found theoretically to be equal to $N\mu_B^2g^2J(J+1)/3k$. N is Avogadro's number, μ_B is the Bohr magneton, g is the Landé factor, J is the total angular momentum quantum number and k is the Boltzmann constant. In the $Mg_xMn_{(1-x)}O$ and $Mg_xCo_{(1-x)}O$ the Curie constant per mole of magnetic ion (Mn or Co) is independent of composition. This is to be expected as the magnesium does not alter the valence of the component ions. The effect therefore is again one of dilution. For the same reason θ goes to zero linearly with composition in both cases of magnesium substitution. Figures 3 and 4 show that the dependence of C and θ on lithium content in the present system is quite different. For comparison the behavior for magnesium substitution in MnO is also shown.

If one assumes that lithium and oxygen are present in the +1 and −2 valence states, respectively, the Curie constant per mole of manganese ion may be calculated on the basis of the formula

$$Li_{x/(1-x)}Mn^{+2}{}_{(1-2x)/(1-x)}Mn^{+3}{}_{x/(1-x)}O^{=}{}_{1/(1-x)}$$

A molecular field treatment of magnetic materials always gives the first-order result that the Curie constant is simply the sum of the Curie constants of the component ions. In the present case

$$C_x = \frac{1-2x}{1-x}(C_{Mn^{+2}}) + \frac{x}{1-x}(C_{Mn^{+3}})$$

If the usual assumption is made that $g = 2$ (orbital moment completely quenched), the Mn^{+2} has a moment of five Bohr magnetons ($J = 5/2$) and the Mn^{+3} has a moment of four Bohr magnetons ($J = 2$). A curve of C *vs.* χ calculated on the basis of this assumption is shown in Fig. 3. This is clearly a bad fit. Instead it appears from the experimental data that the Mn^{+3} ions behave as if they had zero moment. This condition can arise if $g = 1$. The orbital momentum would then give its full contribution. The moment of the Mn^{+2} would remain unchanged since there is no orbital moment present. As is seen from the figure, the Curie constant calculated on the basis of this assumption agrees well in the initial region.

Above 10–15% lithium the experimental curve and the plot for $g = 1$ diverge. At the same time

---

(11) H. Bizette, *J. phys. radium*, **12**, 161 (1951).

(12) N. Elliot, *J. Chem. Phys.*, **22**, 1924 (1954).

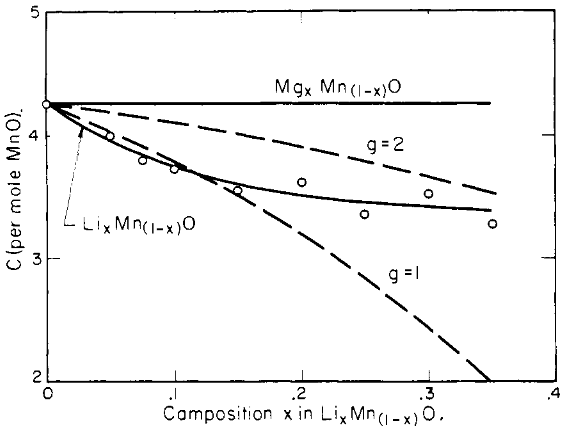

Fig. 3.—Curie constant *vs.* composition.

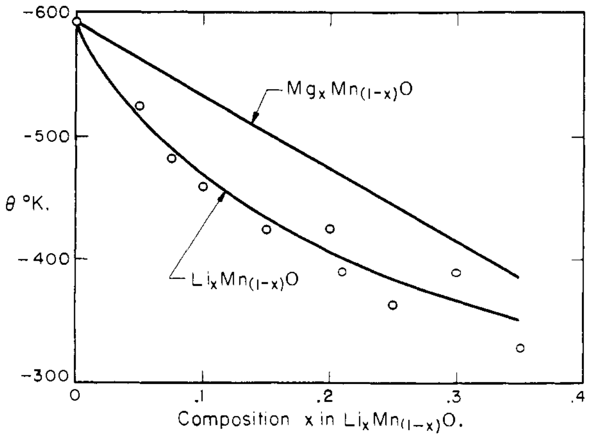

Fig. 4.—θ °K. *vs.* composition.

the slope of the experimental curve becomes much less steep. Very naively this could be understood on the assumption that at high lithium contents the addition of a lithium atom does not appreciably change the valence of manganese due to the formation of a covalent Mn–O bond with considerable O^- character. The possibility of the O^- valence was pointed out by Verwey[4] in the case of $Li_xNi_{(1-x)}O$. The same behavior is also inferred from the measurements of electrical resistivity for $Li_xMn_{(1-x)}O$ which will be published in a separate communication. The resistivity, found to have a minimum in the neighborhood of 8–10% lithium, is interpreted as meaning that the introduction of additional lithium (above 10%) does not add more carriers; in other words, Mn^{+3} ions are not formed.

From the plot of θ *vs.* % Li found in Fig. 4, it is seen that θ remains negative. This means that the antiferromagnetic interaction is dominant in all compounds measured. The absence of ferromagnetism is consistent with the assumption that no additional Mn^{+3} ions are formed when the lithium content exceeds 10–15%. This prevents the attainment of the maximum number of ionic Mn^{+3}–O–Mn^{+2} linear linkages which would be expected at a concentration $x = 0.25$. Thus the optimum conditions for double exchange are never attained and ferromagnetism does not result.

Experimental

Preparation.—Lithium peroxide was prepared by treating lithium hydroxide with hydrogen peroxide in aqueous solution and subsequently removing all water by distilling with *n*-propanol.[13] This purity can be compared with the

Anal. of Li_2O_2	Calcd.	Found
% O (active)	34.9	34.1
% Li_2O	65.1	64.2
Total	100	98.3

Spec (in p.p.m.) Al 10–500, B 10–500, Ca present, Co n.d.,[a] Cu 0.1–10, Fe 8–500, Mg 0.07–3 Ni n.d., Si 5–300, Na 20–500, Sn 30–1000.

[a] Not detected.

34.8% active oxygen reported by Winternitz[13] and the 98.5% total purity obtained by Cohen[14] who prepared Li_2O_2 by a different method.

Manganous oxide was prepared by dissolving electrolytic manganese in concentrated nitric acid, decomposing this solution by heating to form MnO_2 and finally reducing the MnO_2 to MnO with dry hydrogen at 900°.[15] This material analyzed as 100.3% pure on the basis of manganese content. The manganese was determined by oxidation with sodium bismuthate followed by reaction with standard ferrous sulfate solution and titration with $KMnO_4$. This material was also analyzed spectroscopically.

Spec. (in p.p.m.) Si > 100, Fe < 50, Co < 10, Cr < 10, Ti < 10, V < 10, Cu < 5, Ni n.d.

A sample of Li_2MnO_3 was prepared by heating Li_2CO_3 + $MnCO_3$ in air at 1000°.[10]

Compositions in the system $Li_xMn_{(1-x)}O$ were prepared by grinding weighed quantities of MnO and Li_2O_2 in a mullite morter under an atmosphere at argon or nitrogen. The material was then pressed in a 1/4″ diameter steel die at 50,000 p.s.i. without allowing the ground powder to come in contact with the air. The pellets so obtained were placed in small platinum containers in which platinum wires were placed such that the contact between platinum and the pellet was minimized.

Microscopic examinations have shown that Li_2O_2 from the pellet made a very slight solid phase attack on the platinum at these contacts. No vapor phase attack was observed. Spectroscopic analysis shows that in most cases the presence of platinum is questionable in the product (<10 p.p.m.). In samples containing large amounts of lithium, platinum was reported as present (10–50 p.p.m.). Considerable attack was observed in the preparation of $Li_{0.6}Mn_{0.4}O$.

The pellet in its platinum container was finally placed in a Vycor bulb (1″ dia. × 5″ long) and sealed off under 1/3 atmosphere of argon. Argon was used to suppress vaporization of Li_2O from the sample. Generally the samples were heated for 2 hr. at 300°, 2 hr. at 450° and 20 hr. at 900° and then quenched by quickly immersing the Vycor bulb in water. This has been shown to give single phase material over much of the composition range. For the phase diagram work two types of heating programs were followed. The first involves following the steps enumerated in the general heating schedule and at the end of the 20 hr. at 900° annealing for 6–24 hr. at a lower temperature and then quenching. The other involves the usual preliminary heating for 2 hr. at 300° and 2 hr. at 450° and then heating for 20 hr. at some temperature lower than 900° and quenching. These two schedules have the effect of approaching equilibrium from two directions.

The materials obtained in all cases are black in color, in contrast to MnO which is green, and are mechanically strong. Apparent densities were measured before and after sintering by measuring the pellet dimensions with a micrometer and weighing. These data are found in Table I.

In most cases the vycor container was somewhat attacked by Li_2O or Li_2O_2 which volatilizes slightly from the reaction mixture at high temperatures. The amount of lithium lost in this manner is not large and for most purposes could be

---

(13) P. F. Winternitz, U. S. Pat. 2,488,485 (1949).

(14) A. J. Cohen, THIS JOURNAL, **74**, 3762 (1952).

(15) S. S. Todd and K. R. Bonnickson, *ibid.*, **73**, 3894 (1951).

TABLE V

Composition	Lithium, % Calcd.	Lithium, % Found	Mn^{+3}, % Calcd.	Mn^{+3}, % Found	Mn Total, % Calcd.	Mn Total, % Found	At.% Li^+/ At. Mn^{+3}
$Li_{0.046}Mn_{0.954}O$	0.46	0.48	3.7	3.9	76.2	76.8	0.98
$Li_{0.094}Mn_{0.906}O$	0.99	1.02	7.8	8.0	75.1	75.3	1.01
$Li_{0.143}Mn_{0.857}O$	1.52	1.50	12.3	11.9	73.4	73.2	1.00
$Li_{0.195}Mn_{0.805}O$	2.19	2.17	17.4	17.4	71.7	71.5	0.98
$Li_{0.247}Mn_{0.753}O$	2.89	2.84	23.0	22.3	69.9	70.1	1.01
$Li_{0.296}Mn_{0.704}O$	3.62	3.52	28.7	28.4	68.0	67.3	0.98
$Li_{0.347}Mn_{0.653}O$	4.42	4.31	35.0	34.2	65.9	65.1	1.00
$Li_{0.397}Mn_{0.603}O$	5.29	5.23	42.0	41.5	63.7	62.7	1.00
$Li_{0.444}Mn_{0.556}O$	6.18	5.82	49.2	49.8	61.3	61.1	0.93
$Li_{0.494}Mn_{0.506}O$	7.18	7.20	57.5	55.2	58.6	58.2	1.03

neglected. However, by assuming that the small loss in weight of the pellets upon sintering is exclusively due to Li_2O_2 and making appropriate corrections to the chemical formulas as shown in Table I, the analytical data are found to be in somewhat better agreement. To attribute the loss in weight to Li_2O_2 rather than Li_2O is somewhat arbitrary and is based solely on the analytical data which indicate that the ratio (atomic % Li^+/atomic % Mn^{+3}) in the final product is essentially unity. It should be emphasized that this correction is a small one and does not affect the results presented.

The analytical data are given in Table V. Lithium was analyzed as the sulfate after removing manganese by use of the mercury cathode. Total manganese was found by the sodium bismuthate method as in the case of MnO. Oxidizing power was measured by dissolving the sample in a standard ferrous ammonium sulfate solution and then titrating with standard $KMnO_4$. The entire operation was performed under argon. The results are recorded as % Mn^{+3}. It should be noted, however, that this analysis does not preclude the possibility of a manganese oxygen covalence or even O^-.

X-Ray Studies.—Most X-ray studies were performed using North American Phillips 11.54 cm. diameter Debye cameras. The radiation used in all cases was iron with the wave length taken as 1.93597 Å. for $K\alpha_1$ and 1.93991 Å. for $K\alpha_2$. For the study of the $LiMnO_2$ structure powder photographs were obtained with the use of a 19 cm. Unicam camera.

Samples were prepared by grinding under mineral oil and then drawing up the resulting mull in a 0.2 mm. Pyrex capillary. This procedure minimized the possibility of oxidation or hydrolysis of the specimens. It was, in fact, found that if this procedure was not followed, faint lines of Mn_3O_4 were occasionally noted on the X-ray patterns. In order to obtain accurate lattice parameters the extrapolation function of Taylor and Sinclair[16] was used. In the case of $LiMnO_2$ the absorption correction curve of Taylor and Floyd[17] was employed. It is estimated that the lattice parameter for the single phase NaCl structure materials are accurate to within ±0.0003 Å. The accuracy obtained from the two-phase pattern is somewhat less, but fortunately in this case high accuracy is not needed.

The $LiMnO_2$ powder pattern was indexed by noting the repeated appearance of certain values of $\sin^2\theta$ according to the method described by Klug and Alexander.[18] The density of this compound was determined pycnometrically using toluene.

Composition values for the phase diagram were obtained by measuring the lattice parameter of the NaCl phase in the two-phase pattern. Then by using the graph of lattice parameter *vs.* composition the composition of that phase could be determined.

Magnetic Studies.—All magnetic measurements were carried out by a field gradient method using fields of 9,500 to 13,000 oersteds, the gradient being 900–1000 oersteds/cm. The apparatus was standardized with $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$. Samples were sealed in small evacuated Pyrex bulbs for measurement in order to prevent oxidation or hydrolysis. These measurements subsequently were standardized by measuring a second portion of the same materials at room temperature in a copper container in order to take into account any non-uniformity in the Pyrex. The values of C_m and θ are the averages of two least square solutions of the experimental data. The probable error for C is 2% and for θ is 3.5%.

Acknowledgments.—The authors take pleasure in acknowledging the work of Mrs. J. Stanley and Mr. Donald Sestrich who assisted in this program. Dr. A. Taylor gave considerable help in the crystal structure determination. The spectroscopic analyses and some of the chemical analyses were performed under the direction of Dr. Frank Byrne.

PITTSBURGH, PENNSYLVANIA

---

(16) A. Taylor and H. Sinclair, *Proc. Phys. Soc.* (*London*), **57**, 126 (1945).

(17) A. Taylor and R. W. Floyd, *Acta Cryst.*, **3**, 285 (1950).

(18) H. P. Klug and L. E. Alexander, "X-Ray Diffraction Procedures," John Wiley and Sons, Inc., New York, N. Y., 1954.