The magnetic behavior of Li$_2$MO$_3$ (M=Mn, Ru and Ir) and Li$_2$(Mn$_{1-x}$Ru$_x$)O$_3$

I. Felner$^a$ $^*$ and I. M. Bradarić$^b$

$^a$The Racah Institute of Physics, The Hebrew University of Jerusalem, Jerusalem 91904, Israel
$^b$The "Vinča" Institute of Nuclear Sciences, Laboratory for Theoretical and Condensed Matter Physics, P.O. Box 522, Belgrade 11001, Yugoslavia.

The present study summerizes magnetic and Mossbauer measurements on ceramic Li$_2$MO$_3$ M=Mn, Ru and Ir and the mixed Li$_2$(Mn$_{1-x}$Ru$_x$)O$_3$ materials, which show many of the features reflecting to antiferromagnetic ordering or to existence of paramagnetic states. Li$_2$IrO$_3$ and Li$_2$RuO$_3$ are paramagnetic down to 5 K. Li$_2$(Mn$_{1-x}$Ru$_x$)O$_3$ compounds are antiferromagnetically ordered at $T_N=48$ K for $x=0$. $T_N$ decreases as the Ru content increases and, for $x=0.8$, $T_N=34$ K.

Keywords: Crystal structure, antiferromagnetism

$^*$Corresponding author Tel: 972-2-6585752; fax: 972-2-6586347.

E-mail address: israela@vms.huji.ac.il (I.Felner)
Introduction

Numerous studies carried out in recent years on ternary ruthenates and ternary manganites have revealed a wide range of electronic and magnetic properties, ranging from superconductivity to ferromagnetism. One class of oxides that has attracted renewed interest, due to their unusual magnetic properties, are the orthorhombic perovskite CaRuO$_3$ compounds [1-2]. The magnetic ground state of CaRuO$_3$ Ru(IV) was established to be paramagnetic down to 30 mK[3]. In recent studies we have shown that in ceramic and single-crystalline Ca(Ru$_{1-x}$Cu$_x$)O$_3$ samples, irreversibility appears in the zero-field-cooled (ZFC) and field-cooled (FC) curves when measured at low applied magnetic fields [4-5]. A small hysteresis loop opens at low temperatures and Mossbauer studies of 1% $^{57}$Fe doped in CaRuO$_3$ show a magnetic sextet at 4.1 K which disappears at 90 K. It is proposed that CaRuO$_3$ is not paramagnetic, but rather shows the characteristics of short-range magnetic interactions down to 90 K, possibly as spin-glass like behavior. On the other hand, CaMnO$_3$ is a G-type antiferromagnet (AFM) with $T_N$ around 120 K. The study of the Ca(Mn$_{1-x}$Ru$_x$)O$_3$ system shows [6] that ferromagnetism is induced over a large compositional range reaching a maximum value of $T_C$=210 K for $x=0.4$.

X-ray diffraction studies have shown that metallic Li$_2$RuO$_3$ Ru (IV) has a monoclinic unit cell [7] (space group C2/c (15) with lattice parameters: $a= 5.057$ Å, $b=8.759$ Å, $c=9.854$ Å and $\beta=100.08$. Magnetic measurements performed down to 80 K, indicate a paramagnetic behavior which obeys the Curie-Weiss (CW) law, with an effective moment $P_{eff}$ =1.83 $\mu_B$ and $\theta =-167$ K.

On the other hand the isostructural monoclinic compound Li$_2$MnO$_3$ ($a= 4.928$ A, $b=8.533$ A, $c=9.604$ A and $\beta=99.5$ ) is antiferromagnetically ordered with $T_N$ around 50 K [8]. The slight decrease in the unit cell volume of Li$_2$MnO$_3$ is a result of the smaller ionic radius of the Mn (IV) (0.54 Å), as compared to 0.63 Å for Ru (IV) in Li$_2$RuO$_3$ [7]. The stark contrast between the two compounds is surprising, because Li$_2$MnO$_3$ and Li$_2$RuO$_3$ are closely related, both chemically and structurally. The association of manganese and ruthenium therefore, is of great interest and the investigation of the magnetic behavior of the mixed system Li$_2$(Mn$_{1-x}$Ru$_x$)O$_3$ is the main goal of the present paper.

We present here a comprehensive study of the magnetic properties of ceramic Li$_2$(Mn$_{1-x}$Ru$_x$)O$_3$ measured at various applied fields. Our magnetic studies on Li$_2$RuO$_3$ measured down to 5 K, as well as Mossbauer studies of 1% $^{57}$Fe doped in Li$_2$RuO$_3$ demonstrate the paramagnetic nature of this compound. In addition, we show that Li$_2$IrO$_3$ is also paramagnetic down to 5 K. On the other hand, Li$_2$(Mn$_{1-x}$Ru$_x$)O$_3$ compounds are AFM ordered and the magnetic ordering temperature


decreases continuously (up to $x=0.8$) with increasing Ru content. This means that the paramagnetic Li$_2$RuO$_3$ is on the verge of magnetic ordering and readily evolves into a magnetically ordered phase.

**Experimental Details**

Ceramic Li$_2$MO$_3$ ($M = \text{Mn, Ru and Ir}$) and mixed Li$_2$(Mn$_{1-x}$Ru$_x$)O$_3$ samples were prepared by mixing Li$_2$CO$_3$ (10% excess) and $M$ metal powders and preheating at 800°C for 24 h. The materials were then pulverized, pelletized and fired again at 800°C for 12 h. The pellets were pulverized and washed in hot distilled water to remove the excess Li$_2$CO$_3$ and then sintered at 800°C (1000°C for Li$_2$RuO$_3$) 24h in air. Powder X-ray diffraction (XRD) measurements confirmed the purity of the compounds. Magnetic dc measurements were performed in a Quantum Design superconducting quantum interference device magnetometer (SQUID). A Mossbauer study of Li$_2$RuO$_3$ sample containing 1% $^{57}$Fe (doped for Ru) was performed at 4.1 K, using a conventional constant acceleration drive and a 100 mCi $^{57}$Co:Rh source.

**Experimental Results**

XRD studies confirm the monoclinic structure (space-group C2/c), with no secondary phases detected. The XRD patterns and the lattice parameters for all ceramic Li$_2$MO$_3$ ($M = \text{Mn, Ru and Ir}$) samples are in excellent agreement with Refs. 7,8 and 9. The XRD patterns of the mixed Li$_2$(Mn$_{1-x}$Ru$_x$)O$_3$ samples are similar to their parent compounds and the peaks indexed as 002 reflection ($18 < 2\theta < 19$) are shown in Fig. 1. As $x$ increases, the peak position shifts toward smaller angles, consistent with the larger unit cell volume of Li$_2$MnO$_3$ discussed above. For the $x=0.4$ and $x=0.6$ samples, the XRD patterns confirm the monoclinic structure but they do not allow to determine the lattice parameters (the number of peaks is not sufficient).

**Li$_2$MO$_3$ ($M=\text{Ru and Ir}$)**

Temperature dependent zero-field-cooled (ZFC) and field cooled (FC) magnetization curves $M(T)$ for both Li$_2$RuO$_3$ and Li$_2$IrO$_3$ samples have been measured at various applied fields and the data obtained at 10 kOe are shown in Fig. 2. No difference between the two ZFC and FC branches was observed even when measured at low applied fields (10 Oe). Li$_2$IrO$_3$ is paramagnetic down to 5 K and no anomaly is observed in the $M(T)$ curve. The magnetic properties of Li$_2$RuO$_3$ are more complex. Fig 2 shows a small cusp around 63 K, which may originate from magnetic ordering.
This cusp appears also in M(T) curves measured at low applied fields. The isothermal magnetization M(H) at 5 K measured up to 50 kOe is linear. Mossbauer spectroscopy (MS) on Fe-doped materials, has proven to be a powerful tool in the determination of the magnetic nature of the Fe site location. When the ions at this site (Ru) become magnetically ordered, they produce an exchange field at the Fe ions residing in this site. The Fe nuclei experience a magnetic hyperfine field leading to a sextet in the MS spectra. This method has been applied previously to prove the magnetic ordering of CaRuO$_3$ and several other ruthenate-based compounds [4]. The MS spectrum of 1% $^{57}$Fe diluted in Li$_2$RuO$_3$ measured at 4.1 K is shown in Fig. 3, and displays a single line with an isomer shift I.S.= 0.45(1) mm/s and a small quadrupole splitting of 0.18(1) mm/s. The presence of a singlet and the absence of a magnetic sextet at 4.1 K are a clear indication of non-magnetically ordered Fe$^{3+}$ ions at the Ru site, and serves as supporting evidence that Li$_2$RuO$_3$ is paramagnetic at 4.1 K. The origin of the cusp in Fig 2 is now under investigation.

The two curves (even at low fields) have the typical paramagnetic shape and follow closely the Curie-Weiss (CW) law: $\chi = \chi_0 + C/(T-\theta)$, where $\chi_0$ is the temperature independent part of $\chi$, C is the Curie constant, and $\theta$ is the CW temperature. For Li$_2$RuO$_3$, the fit of the CW law in the range of 75<T<275 K yields: $\chi_0 =-1 \times 10^{-4}$ emu/mol Oe, $\theta = -184(1)$ K, and C= 0.9 emu/mol Oe (Table 1). This corresponds to an effective moment $P_{eff} =2.68 \mu_B$, which is close to the expected 2.83 $\mu_B$ according to Hund’s rule for Ru$^{4+}$ (4d$^4$) in the low spin (S=1) state. Assuming $\chi_0=0$, we obtain $\theta = -171$ K and C=0.83 emu/mol Oe, in excellent agreement with Ref.7. The fit for Li$_2$IrO$_3$ (see the solid line in Fig. 2) yields: $\chi_0 =-3 \times 10^{-4}$ emu/mol Oe, $\theta = -84(1)$ K, and a Curie constant C= 0.45 emu/mol Oe which corresponds to an effective moment $P_{eff} =1.9 \mu_B$.

**Li$_2$(Mn$_{1-x}$Ru$_x$)O$_3$**

The M(T) curves measured at 10 kOe for all Li$_2$(Mn$_{1-x}$Ru$_x$)O$_3$ compounds are shown in Fig. 4. Here too, the field dependent M(H) plots at 5 K are linear and the ZFC and FC curves (measured at 20 Oe) are identical and no irreversibility is observed. The peaks in Fig. 4 are consistent with an AFM ordering. $T_N$ (determined as the peak position) decreases with increasing the Ru content (Table 1). $T_N =48$ K obtained for Li$_2$MnO$_3$, agrees well with Ref. 8, and the peak in Li$_2$RuO$_3$ (Fig. 2) is much higher than $T_N = 34$ K for x=0.8. Fitting the M/H(T) data in the paramagnetic range to the modified CW law yields the paramagnetic values given in Table1. The Curie constant obtained for Li$_2$MnO$_3$ corresponds to an effective moment $P_{eff} =3.79 \mu_B$, which is close to the
expected 3.87 $\mu_B$ according to Hund’s rule for Mn$^{4+}$ (3d$^5$, S=3/2). The C values decrease with increasing Ru content up to x=0.6, and in the limit of uncertainty the x=0.8 and x=1 samples have the same C value (Table 1). Note that all $\theta$ values obtained are negative, consistent with the AFM nature of the system.

The nature of the magnetic properties of oxide-ruthenates with narrow 4 d-bands strongly depends on the degree of band filling and bandwidth. Li$_2$RuO$_3$ is believed to have a narrow itinerant 4 d-band width, composed of Ru t$_{2g}$ and oxygen 2p orbitals, which is too narrow for magnetic ordering. It means that Li$_2$RuO$_3$ is on the verge of magnetic ordering and readily evolves into a magnetically ordered phase. Indeed, 20% of Mn substitution for Ru induces AFM ordering at $T=34$ K.

**Acknowledgment:** We are grateful to Dr. U. Asaf for assistance in the XRD experiments. I. Felner gratefully acknowledges support from the BSF (1999). I. M. Bradarić gratefully

**References.**

1) G. Cao, S. McCall, M. Shepard, J.E. Crow and R. P. Guertin, Phys. Rev. B 56 (1997) 321.
   M. Shepard, S. McCall, G. Cao, and J.E. Crow, J. Appl. Phys 81 (1997) 4978.
2) T. He, Q. Haung and R.J. Cava, Phys. Rev. B 63 (2001) 024402.
3) H. Kobayashi, M. Nagata, R. Kanno and Y. Kawamoto, Mater. Reserch. Bull. 29 (1994) 1271.
4) I. Felner et al Phys. Rev. B 62 (2000) 11332.
5) I. M. Bradarić, I. Felner, M. Gospodinov, Submitted to Phys. Rev. B
6) A. Maignan, C. Martin, M. Hervieux and B. Raveau, Solid State Commun. 117 (2001) 377.
7) H. Kobayashi et al, Solid State Ionics 82 (1995) 25; ibid 86-88 (1996) 859.
8) V.M. Jansen and R. Hoppe, Z. Anorg. Allg. Chem. 397 (1973) 279.
9) H. Kobayashi et al., J. Power Sources 68 (1997) 658.
Figure Captions

Fig. 1 The (002) XRD peak position for Li$_2$(Mn$_{1-x}$Ru$_x$)O$_3$.
Fig. 2 The magnetization curves of the paramagnetic Li$_2$MO$_3$ (M=Ru and Ir). Fig. 3 Mössbauer spectrum at 4.1 K for 1% Fe doped in Li$_2$RuO$_3$.
Fig. 4 The temperature dependence of the magnetization of Li$_2$(Mn$_{1-x}$Ru$_x$)O$_3$ indicating the AFM nature of the system. The solid line is the fit to Curie-Weiss law.

Table 1

| Compound                  | $T_N$ (K) | $C$ (emu/mol Oe) | $\theta$ (K) | $\chi_0$ ($10^{-4}$emu/mol Oe) |
|---------------------------|-----------|------------------|--------------|---------------------------------|
| Li$_2$MnO$_3$             | 48 (1)    | 1.79             | -44(1)       | -4(0.4)                         |
| Li$_2$Mn$_{0.8}$Ru$_{0.2}$O$_3$ | 43 (1)    | 1.66             | -54(1)       | -2.7(0.3)                       |
| Li$_2$Mn$_{0.6}$Ru$_{0.4}$O$_3$ | 41 (1)    | 1.46             | -64(1)       | -3.2(0.4)                       |
| Li$_2$Mn$_{0.4}$Ru$_{0.6}$O$_3$ | 37 (1)    | 0.87             | -83(1)       | -2(0.5)                         |
| Li$_2$Mn$_{0.2}$Ru$_{0.8}$O$_3$ | 34 (1)    | 0.92             | -84(1)       | -2(0.5)                         |
| Li$_2$RuO$_3$             | 0.90      | -183(1)          | -1 (0.1)     |                                 |
|                           | 0.83      | -171             | -            |                                 |
Fig. 1 The (002) XRD peak position for Li$_2$(Mn$_{1-x}$Ru$_x$)O$_3$. 
Fig. 2 The magnetization curves of the paramagnetic Li$_2$MO$_3$ (M=Ru and Ir).
Fig. 3  Mossbauer spectrum at 4.1 K for 1% Fe doped in Li$_2$RuO$_3$. 

1%Fe in Li$_2$RuO$_3$

4.1 K
Fig. 4. The temperature dependence of the magnetization of Li$_2$(Mn$_{1-x}$Ru$_x$)O$_3$ indicating the AFM nature of the system.