

The Structure and Magnetic Properties of La_2MIrO_6 with $M = \text{Mg}, \text{Co}, \text{Ni}, \text{and Zn}$

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The structure of the compounds La_2MIrO_6 is a monoclinic deformation of the perovskite-like GdFeO_3 -type (space group $P2_1/n$) with complete ordering between iridium and M for $M = \text{Mg}, \text{Co}, \text{Ni}, \text{and Zn}$. These compounds are isomorphous with $\text{La}_2\text{NiRuO}_6$. The unit cell dimensions compare to those of the cubic perovskite as $a_m \approx b_m \approx a_c\sqrt{2}$, $c_m \approx 2a_c$, $\beta \approx 90^\circ$. The structure has been determined by Rietveld refinement on X-ray and neutron powder diffraction data. The magnetic susceptibility measurements show magnetic ordering for the compounds with $M = \text{Co}$ and Ni at 130 and 110 K respectively. © 1995 Academic Press, Inc.

ordering of Ni and Ru in $\text{La}_2\text{NiRuO}_6$ prompted further investigation into related La_2MIrO_6 .

In order to study the magnetic properties of La_2MIrO_6 for $M = \text{Mg}, \text{Co}, \text{Ni}, \text{and Zn}$, the magnetic susceptibilities of these compounds were measured between 4 and 300 K. The structure has been determined from X-ray powder diffraction data at 293 K. For a more accurate structure determination (based on neutron diffraction data at 293 K and at 4 K) $\text{La}_2\text{CoIrO}_6$ was chosen, because the preliminary measurements gave the most interesting results.

INTRODUCTION

The properties of IrO_2 as an anode material include high electrocatalytic activity (e.g., low polarization for oxygen evolution), high electron conductivity, and high stability in various environments. Therefore, the study of the structures of iridium oxide compounds is of interest. In this paper the synthesis, the structures, and the magnetic properties of some iridium oxide perovskites containing lanthanum and a transition element are discussed.

Galasso and Darby (1) reported the existence of the compounds La_2MIrO_6 for $M = \text{Mg}, \text{Mn}, \text{and Ni}$ in 1965. The X-ray patterns were indexed using a cubic perovskite unit cell with doubled axis ($a \approx 7.9 \text{ \AA}$). Single crystals were prepared out of a flux of PbO-PbF_2 . In the same year Blasse (2) reported the occurrence of the isostructural compounds for $M = \text{Mg}, \text{Co}, \text{Ni}, \text{and Cu}$. The unit cell of $\text{La}_2\text{CuIrO}_6$ was reported to be monoclinic with the unit cell parameters $a = 5.80$, $b = 5.60$, $c = 7.72 \text{ \AA}$, $\beta = 86^\circ 56'$. The other compounds were claimed to have the orthorhombic distorted perovskite structure (GdFeO_3) with unit cell dimensions $a \approx b \approx 5.6 \text{ \AA}$, $c \approx 7.9 \text{ \AA}$. Blasse prepared his samples by solid-state reactions starting from mixtures of oxides and carbonates at 1000–1300°C in air. No detailed structural characterization of the compounds has been published as yet. The discussion between Seinen *et al.* (3) and Battle and Jones (4) on the

EXPERIMENTAL

The samples were prepared from stoichiometric mixtures of A.R. La_2O_3 , IrO_2 , and MgO ; MnO , Fe , and Fe_2O_3 ; and CoCO_3 , NiO , CuO and ZnO , respectively. La_2O_3 was dried in air at 800°C. MnO was prepared by reduction of MnO_2 with H_2 at 900°C. IrO_2 was prepared as described by Vente and IJdo (5). All La_2MIrO_6 phases were prepared by heating at 650°C for one day, then at 800°C for two days, and finally at 975°C in air for two weeks in gold crucibles. As the Mg compound still showed some impurities, a last firing at 1100°C in alumina was performed. The synthesis was interrupted several times for grinding. Attempts to prepare pure La_2MIrO_6 for $M = \text{Mn}, \text{Fe}, \text{and Cu}$ in the same way failed. Two alternative syntheses of $\text{La}_2\text{CuIrO}_6$ were tried, in a flux of NaCl and in a high pressure solid media piston cylinder set up. For this last preparation method about 100 mg of the stoichiometric mixture was sealed in gold and heated at 975°C at 15 kbar for one week. The synthesis of La_2MIrO_6 for $M = \text{Mn}$ and Fe was also attempted by firing of stoichiometric mixtures in alumina in an evacuated quartz tube, to ensure the continued presence of the divalent oxidation state of M . No method of preparation of La_2MIrO_6 for $M = \text{Mn}, \text{Fe}, \text{and Cu}$ led to one single phase.

The electron diffraction patterns of all reaction products were examined with a Siemens Elmiskop 102, fitted

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with a 40° double tilt and lift cartridge, operating at 100 kV. The compounds were also examined at 293 K with a Philips PW 1050 X-ray diffractometer using monochromated $\text{CuK}\alpha$ radiation. At the Petten High Flux Reactor, the neutron powder diffraction patterns of $\text{La}_2\text{CoIrO}_6$ were collected at 293 K and at 4 K. Because of the high neutron absorption of Co and Ir, Al was added to the sample. The experimental details are as reported earlier (6). All diffraction patterns were analyzed using the Rietveld method (7). For this purpose the GSAS (version 6.2) computer program was used (Larson and Von Dreele (8)). In the Rietveld refinements, the first part of the diffraction patterns was excluded (up to $28^\circ 2\theta$). This was done to obtain a better fit of the background function as no Bragg reflections are present in this region. The instrumental parameters refined are listed in Table 1. In the X-ray refinements, the fractional coordinates of O were not refined, due to correlation effects and the low scattering factor of O. The neutron diffraction data were corrected for absorption ($\mu R = 0.52$ (9)). No precautions were taken to prevent preferred orientation. The coherent scattering lengths used were: La, 8.27; Co, 2.53; Ir, 10.6; O, 5.805; Al, 3.449 fm (8). In the initial cycles, only Al parameters were refined: cell axis, four profile parameters (Gaussian function with peak asymmetry), one U_{iso} , and the phase fraction. These parameters, except the phase fraction, were kept constant once convergence was achieved. For the structure of $\text{La}_2\text{MgIrO}_6$, derived from the GdFeO_3 structure-type, two models were available: (a) monoclinic with ordered *M* and Ir with space

group $P2_1/n$ as given by Seinen *et al.* (1) and López *et al.* (10); (b) orthorhombic with disordered *M* and Ir with space group $Pbnm$ as proposed by Battle and Jones (4). The refinements were started with the structural parameters provided by these authors.

The magnetic behavior of all pure compounds has been investigated on a SQUID magnetometer with a field strength of 0.01 T between 4 and 300 K. The field dependence was investigated between 80 and 300 K on a Faraday balance calibrated with A.R. Gd_2O_3 . All data were corrected for empty vessel effects and for diamagnetism using Selwood's table (11). In the paramagnetic region no field dependence was observed between 0.3 and 1.5 T. The results of the SQUID measurements were fitted above the ordering temperature against the Van Vleck relation for a paramagnetic compound with a T.I.P. for the orbital magnetism,

$$\chi = \frac{C}{(T - \theta)} + \alpha, \quad [1]$$

where

- χ the magnetic susceptibility (emu/mol $\text{La}_2\text{MgIrO}_6$)
- C the Curie constant (emu · K/mol $\text{La}_2\text{MgIrO}_6$)
- T the temperature (K)
- θ the Weiss temperature (K)
- α the temperature independent susceptibility (emu/mol $\text{La}_2\text{MgIrO}_6$).

TABLE 1
Parameters Present in the Refinements and the Fit Results

Compound	$\text{La}_2\text{MgIrO}_6$	$\text{La}_2\text{ZnIrO}_6$	$\text{La}_2\text{NiIrO}_6$	$\text{La}_2\text{CoIrO}_6$	$\text{La}_2\text{CoIrO}_6$
Type of measurement	X-ray at 293 K	X-ray at 293 K	X-ray at 293 K	Neutron 293 K	Neutron 4 K
Wavelength (Å)	1.54056 1.54439	1.54056 1.54439	1.54056 1.54439	2.57176	2.57176
2θ range (°)	10–80	15–90	10–80	28–155	18–155
Stepsize (°)	0.1	0.05	0.05	0.1	0.1
Background	2 ^a	3 ^a	2 ^a	6 ^b	4 ^a
Profile	4 ^c	4 ^c	4 ^c	4 ^d	4 ^d
Structure	9	9	9	18	18
R_{wp} (%)	17.47	17.06	18.16	2.85	3.72
R_p (%)	11.60	12.63	12.87	2.13	2.90
DW-d	0.851	0.464	0.537	0.560	0.893
DW-d limits	1.811	1.862	1.857	1.875	1.874
χ^2_{red}	2.189	2.138	2.143	2.125	2.126
Variables	3.846	5.588	4.561	4.847	3.417
	17	18	17	31	29

Note. For every diffraction pattern: zero point correction, one (X-ray) or two (neutron) phase fraction(s).

^a Shifted Chebyshev function.

^b Cosinus Fourier series.

^c Pseudo Voigt shape.

^d Gauss (with asymmetry) profile function.

RESULTS AND DISCUSSION

Crystal Structure

Iridium oxide compounds with the formula $\text{La}_2\text{M}\text{IrO}_6$ with $M = \text{Mg}, \text{Co}, \text{Ni},$ and Zn could be prepared as pure phases. These samples were deep black. All attempts to prepare pure $\text{La}_2\text{M}\text{IrO}_6$ with $M = \text{Mn}, \text{Fe},$ and Cu failed. The X-ray diffraction patterns of the first two compounds clearly show the presence of the target compound. In addition, in the electron diffraction experiments one crystal of $\text{La}_2\text{Cu}\text{IrO}_6$ prepared under high pressure was found to have the proper symmetry and unit cell axis. The compounds $\text{La}_2\text{M}\text{IrO}_6$ do exist for $M = \text{Mn}, \text{Fe},$ and Cu but could not be prepared as pure phases in the ways described above.

Systematic absent reflections in the electron microscopy diffraction patterns of $\text{La}_2\text{M}\text{IrO}_6$ with $M = \text{Mg}, \text{Co}, \text{Ni},$ and Zn ruled out the space group $Pbnm$ and indicated $P2_1/n$. However, it was possible to index the X-ray diffraction pattern fully by applying space group $Pbnm$, because $\beta \approx 90^\circ$, as was reported by Blasse (2). The width of the first maximum in the X-ray diffraction pattern at $\approx 19^\circ 2\theta$ indicates that this peak consists of more than one Bragg reflection, i.e., (011) and (101). The space group $Pbnm$ does not allow the (011) reflection. Refinement of the structure in $Pbnm$ led to a serious misfit for this peak and an increase of R_{wp} compared to $P2_1/n$ (with 13% for $\text{La}_2\text{Mg}\text{IrO}_6$). Therefore, it was concluded that the compounds are ordered perovskites. The monoclinic distortion is merely a result of ordering in the GdFeO_3 structure type. GdFeO_3 is orthorhombic with space group $Pbnm$. No orthorhombic space group exists which allows for cation ordering on the iron position and is a subgroup of $Pbnm$. Hayashi *et al.* (12) suggested space group $Pmm2$

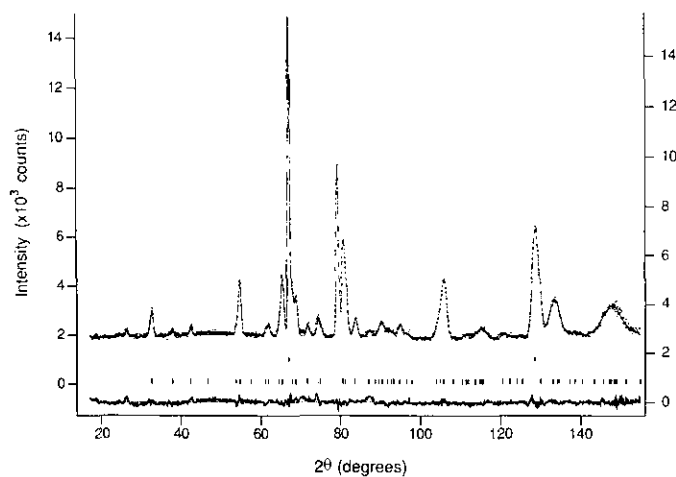


FIG. 1. Observed (dots) and calculated (full line) neutron diffraction pattern of $\text{La}_2\text{Co}\text{IrO}_6$ at 4 K; the difference ($I_{\text{obs}} - I_{\text{calc}}$) curves appear at the bottom of the figures.

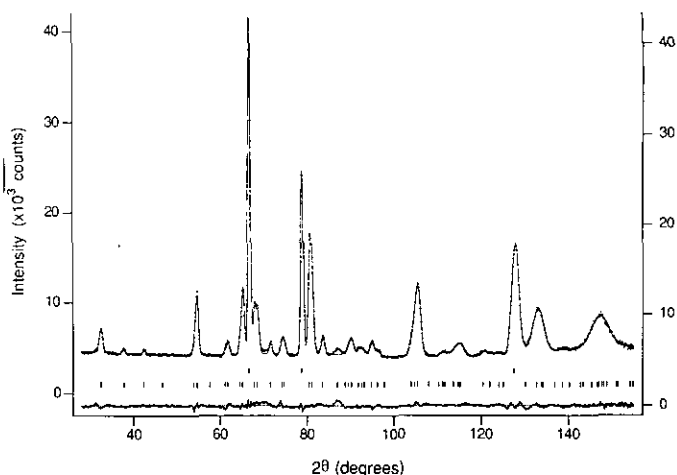


FIG. 2. Neutron diffraction pattern of $\text{La}_2\text{Co}\text{IrO}_6$ at 293 K.

for the comparable compound $\text{La}_2\text{Li}\text{IrO}_6$ to describe the total ordering between Li and Ir. However, this space group is very unlikely because it is not a subgroup of $Pbnm$.

Figures 1, 2, and 3 show the X-ray diffraction pattern of $\text{La}_2\text{Mg}\text{IrO}_6$ and the neutron diffraction patterns at 293 and 4 K of $\text{La}_2\text{Co}\text{IrO}_6$. Tables 1 and 2 give the results of the Rietveld refinements of the compounds studied. Selected atomic distances and angles are given in Table 3. The DW-d values of all refinements were smaller than the lower extreme of the 90% confidence interval; the estimated standard deviations are thus underestimated due to serial correlation (Hill and Flack (13)). The R_{wp} has a value of about 17%. The disagreements are predominantly due to a misfit in the peak shape. Attempts to improve the fit by applying more profile coefficients were

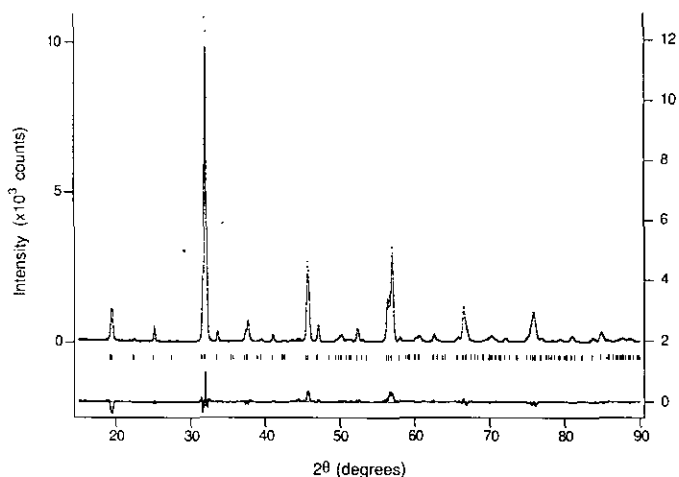


FIG. 3. X-ray diffraction pattern of $\text{La}_2\text{Co}\text{IrO}_6$.

TABLE 2
Refined Lattice and Atomic Parameters

Compound	La ₂ MgIrO ₆ (a)	La ₂ ZnIrO ₆ (a)	La ₂ NiIrO ₆ (a)	La ₂ CoIrO ₆	La ₂ CoIrO ₆
Type of measurement	X-ray at 293 K	X-ray at 293 K	X-ray at 293 K	Neutron 293 K	Neutron 4 K
Volume (Å ³)	248.42 (6)	252.82 (4)	247.73 (5)	251.16 (2)	250.16 (3)
Calculated density g/cm ³	3.934 (1)	4.2074 (7)	4.1636 (8)	4.1062 (3)	4.1226 (5)
Lattice parameters					
<i>a</i> (Å)	5.5856 (7)	5.5986 (4)	5.5752 (6)	5.5907 (4)	5.5765 (6)
<i>b</i> (Å)	5.6246 (6)	5.6869 (4)	5.6260 (6)	5.6720 (4)	5.6749 (7)
<i>c</i> (Å)	7.907 (1)	7.9405 (6)	7.898 (1)	7.9189 (5)	7.9250 (9)
β (°)	90.03 (5)	89.99 (5)	90.02 (7)	89.99 (3)	90.04 (5)
Atomic La parameters ^b					
<i>x</i>	0.504 (3)	0.505 (1)	0.500 (4)	0.505 (1)	0.510 (2)
<i>y</i>	0.5385 (5)	0.5467 (4)	0.5439 (5)	0.5443 (6)	0.551 (1)
<i>z</i>	0.247 (1)	0.2504 (6)	0.2498 (8)	0.256 (1)	0.254 (2)
<i>U</i> _{iso} ^c (Å ²)	0.013 (1)	0.0046 (7)	0.0114 (8)	0.0045 (9)	0.010 (1)
O(1)					
<i>x</i>		0.220		0.210 (2)	0.209 (3)
<i>y</i>		0.195		0.202 (2)	0.206 (2)
<i>z</i>		0.960		0.949 (1)	0.952 (3)
O(2)					
<i>x</i>		0.300		0.293 (2)	0.297 (3)
<i>y</i>		0.716		0.701 (1)	0.690 (2)
<i>z</i>		0.960		0.964 (1)	0.961 (3)
O(3)					
<i>x</i>		0.420		0.419 (1)	0.418 (2)
<i>y</i>		0.980		0.981 (1)	0.985 (1)
<i>z</i>		0.240		0.244 (1)	0.244 (2)
<i>U</i> _{iso} ^b (Å ²)	0.03 (1)	0.004 (5)	0.046 (9)	0.002 (1)	0.002 (1)

^a Oxygen positions not refined taken from (3).

^b La at 4e (*x*, *y*, *z*); M at 2c (0, ½, 0); Ir at 2d (½, 0, 0); O(1), O(2), O(3) at 4e (*x*, *y*, *z*).

^c One *U*_{iso} for La, M, and Ir and one *U*_{iso} for all O.

not fruitful. The refinement of La₂CoIrO₆ on the 293 K neutron data leads to an *R*_{wp} value of 2.85%. The oxygen positions are consistent with those of ordered La₂NiRuO₆ (3) and La₂LiSbO₆ (10). The results clearly indicate that the compounds studied are isomorphous with these compounds. Refinement of the amount of disorder between Co and Ir did not lead to a better fit, the system of equations was numerically unstable and the *R*_{wp} value in-

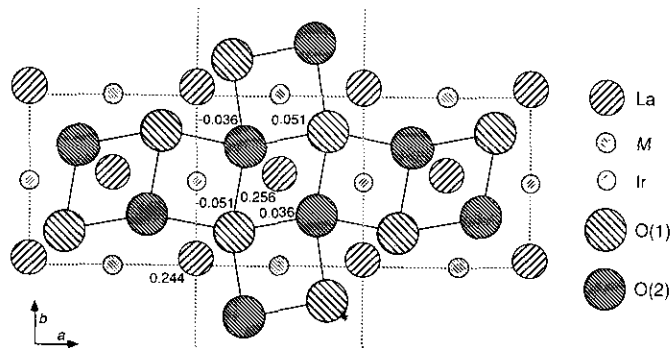


FIG. 4. Projection of the structure of La₂MgIrO₆, showing the rotation of the MO₆ and IrO₆ octahedra. For simplicity the atoms between *z* = -0.06 and 0.3 are given.

TABLE 3
Selected Atomic Distances (Å) and Angles (°) for La₂CoIrO₆

Atoms		293 K	4 K
Distances			
CoO ₆ octahedron	Co-O(1) (2×)	2.096 (9)	2.069 (14)
	Co-O(2) (2×)	2.022 (11)	2.005 (18)
	Co-O(3) (2×)	2.078 (14)	2.072 (21)
IrO ₆ octahedron	Ir-O(1) (2×)	2.027 (10)	2.035 (16)
	Ir-O(2) (2×)	2.069 (9)	2.112 (14)
	Ir-O(3) (2×)	1.987 (13)	1.987 (20)
LaO ₈ polyhedron	La-O(1) (1×)	2.778 (19)	2.767 (28)
	La-O(1) (1×)	2.687 (18)	2.646 (24)
	La-O(1) (1×)	2.366 (17)	2.407 (29)
	La-O(2) (1×)	2.753 (15)	2.729 (24)
	La-O(2) (1×)	2.494 (20)	2.434 (35)
	La-O(2) (1×)	2.714 (16)	2.711 (22)
	La-O(3) (1×)	2.527 (6)	2.519 (10)
	La-O(3) (1×)	2.402 (13)	2.422 (19)
	La-O(3) (1×)	2.402 (13)	2.422 (19)
Angles			
Co-O(1)-Ir	150.7 (7)	151.5 (14)	
Co-O(2)-Ir	153.5 (8)	150.1 (14)	
Co-O(3)-Ir	153.6 (4)	153.7 (7)	

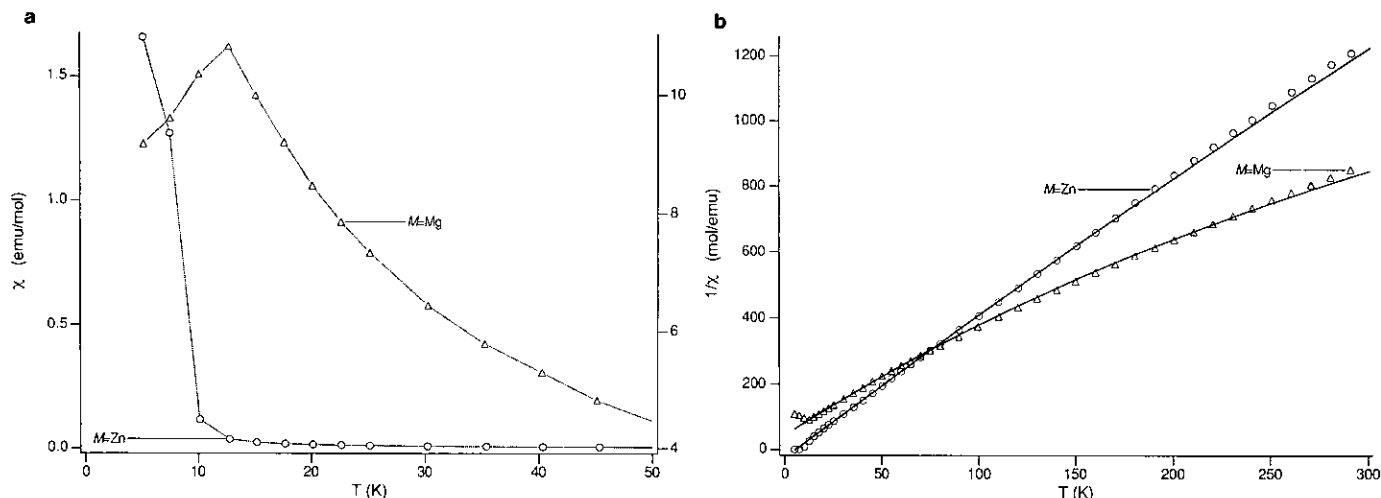


FIG. 5. (a) Magnetic susceptibility of $\text{La}_2\text{MgIrO}_6$ and $\text{La}_2\text{ZnIrO}_6$. (b) Reciprocal susceptibility of $\text{La}_2\text{MgIrO}_6$ and $\text{La}_2\text{ZnIrO}_6$.

creased with 2%. This confirms that compounds $\text{La}_2\text{MM}'\text{O}_6$, where M is a divalent transition metal and M' is Ru or Ir, are ordered. The refinement on the 4 K measurement led to an R_{wp} value of 3.72%. The reflections generated by the magnetic ordering were not strong enough to allow a detailed determination of the spin structure.

In Fig. 4 the structure of $\text{La}_2\text{M}\text{IrO}_6$ is shown. Each MO_6 octahedron shares corners with six IrO_6 octahedra, and vice versa. In the network thus formed, La occupies a void of about the same size as O. The deformation from the aristotype perovskite is caused by La with a too small radius. The size of the void is reduced by tilting the octahedra around the fourfold and twofold axes of the octahedra.

Magnetic Susceptibility

In Figs. 5 and 6 the magnetic measurements of the compounds are presented. The fit results are given in Table 4. In the paramagnetic region, the magnetic susceptibility is described by the Van Vleck relation. Superexchange interactions are possible through a 180° Ir–O–M, through a 90° M–O–O–M, and through a 90° Ir–O–O–Ir pathway. Ir–O–M interactions, over 180° , of Ir^{4+} ($t_{2g}^5 e_g^0$) with both Co^{2+} ($3d^7$) and Ni^{2+} ($3d^8$) are predicted to be ferromagnetic of moderate strength. The strength of the cation–anion–anion–cation interactions is reduced, probably by an order of magnitude (Goodenough (14)).

In Figs. 5a and 5b the magnetic measurements of

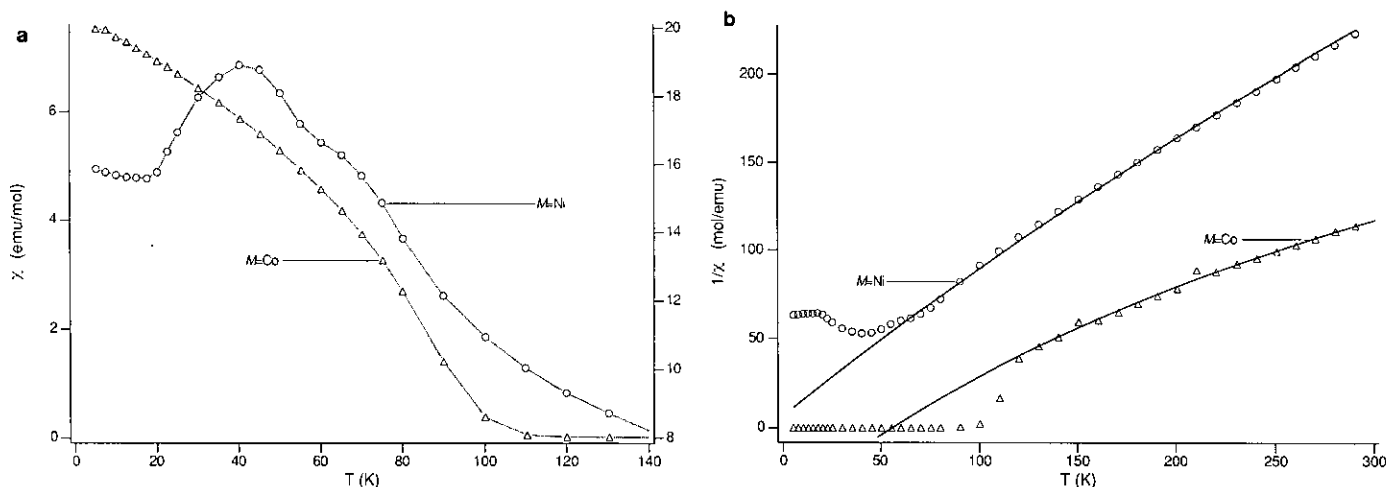


FIG. 6. (a) Magnetic susceptibility of $\text{La}_2\text{NiIrO}_6$ and $\text{La}_2\text{CoIrO}_6$. (b) Reciprocal susceptibility of $\text{La}_2\text{NiIrO}_6$ and $\text{La}_2\text{CoIrO}_6$.

TABLE 4
The Results of the Magnetic Susceptibility Measurements

Compound	Fit region (K)	Ordering traject (K)	C (emu/mol)	θ (K)	T.I.P. ($\times 10^{-4}$ emu/mol)
La ₂ MgIrO ₆	17–300	4–10	0.252 (2)	–11.0 (0)	5.1 (1)
La ₂ ZnIrO ₆	15–300	—	0.231 (9)	5.5 (2)	1.4 (3)
La ₂ NiIrO ₆	110–300	20–110	1.18 (1)	–15.7 (9)	7.8 (3)
La ₂ CoIrO ₆	130–300	100–145	1.4 (2)	55.3 (8)	28 (8)

La₂MgIrO₆ and La₂ZnIrO₆ are given. The magnetic behavior of La₂MgIrO₆ can be described with an antiferromagnetic model; a transition point is observed at 10 K. Below this temperature the compound shows spin ordering, through an Ir–O–O–Ir pathway, resulting in a decrease of χ . The nature of this superexchange interaction causes the antiferromagnetic ordering. The weakness of the interaction is caused by the relatively large distance between the Ir⁴⁺ ions and the difficulty in coupling between the adjacent oxygen ions. This results in a low transition temperature. La₂ZnIrO₆ might show spin ordering at an even lower temperature. However, the deviation from the Van Vleck relation can also be attributed to the fact that the term $(T - \theta)$ becomes very small as θ becomes large. As a result, χ increases. The octahedral position of Zn²⁺ ($3d^{10}$) is not favored. This may introduce strain in the structure, the reason for the positive θ .

In Figs. 6a and 6b the magnetic measurements of La₂NiIrO₆ are presented. The complex behavior may be the result of several interactions. The possibilities are Ir–O–Ni, Ir–O–O–Ir, and Ni–O–O–Ni ordering. The Ni–O–O–Ni exchange is predicted to be antiferromagnetic (14). With decreasing temperature, first an increase of χ^{-1} (possibly due to ferromagnetic ordering of Ir⁴⁺ and Ni²⁺) occurs, followed by a decrease (due to antiferromagnetic ordering of Ni²⁺ or Ir⁴⁺).

The measurement of La₂CoIrO₆ (Figs. 6a and 6b) shows spin ordering between Co²⁺ and Ir⁴⁺. Since the ordering in La₂CoIrO₆ occurs instantaneously, it is likely that the spin ordering is the result of one dominant interaction. The combination of the magnetic measurement and the refinement of the structure on the neutron data lead to the following conclusion: the compound shows magnetic ordering. The small peak in the neutron diffraction pattern at $26.2^\circ 2\theta$ could be explained by the magnetic reflection (010). This implies that the spins have an antiparallel component along the *b*-axis. It was not possible to determine the exact type and direction of the ordering.

CONCLUSIONS

The structure of La₂MIrO₆ with *M* = Mg, Co, Ni, and Zn is a monoclinic distortion of the orthorhombic

perovskite GdFeO₃. From specific absences in both X-ray and electron diffraction experiments and a better fit it was concluded that the compounds studied were ordered for *M* and Ir. This is in agreement with the results for ordered La₂NiRuO₆ (3). Attempts to prepare pure compounds La₂MIrO₆ for *M* = Mn, Fe, and Cu failed. The measurements of the magnetic susceptibility show magnetic ordering at 130 and 110 K for the compounds with *M* = Co and Ni.

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